



Influence of previous history on physical aging in thin glassy polymer films as gas separation membranes

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ABSTRACT

The physical aging behavior of thin glassy polysulfone (PSF) films (~ 125 nm) with different previous histories was tracked using gas permeability measurements. The initial states of these materials were modulated by thermal annealing at fixed temperatures below the glass transition or by exposure to high pressure (800 psig (56.2 bara)) CO₂ for various times. Regardless of the previous history, the nature of the aging response in these samples was consistent with the aging behavior of an untreated film that was freshly quenched from above T_g , *i.e.*, permeability decreased and pure gas selectivity increased with aging time. However, the extent of aging-induced changes in transport properties of these materials depended strongly on previous history. The aging behavior was described using Struik's aging model by allowing the initial conditions to depend on each sample's previous history.

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1. Introduction

All non-equilibrium glasses, including glassy polymers, undergo physical aging, a process that causes property changes as the material spontaneously relaxes toward an equilibrium state, and the influence of these changes can be profound. Physical aging has been studied extensively for bulk materials to aid in understanding and predicting their long-term behavior [1,2]. More recently, attention has turned to thin glassy films where significant and unpredicted deviations from bulk behavior have been reported [3–5]. For example, the physical aging behavior of thin glassy polymer films has been shown to depend on film thickness, exhibiting greatly accelerated aging in films below ~ 1 micron in thickness [5]. Interest in thin glassy films is due to their growing applications in microelectronics, separation membranes, optical materials, lithography, *etc.* While studies show intriguing deviations from bulk behavior in thin films, the polymer physics underlying thin film phenomena, including aging, are not well understood [6–8].

The state of a glassy polymer and, correspondingly, its aging behavior, depend not only on the immediate environment, but also on the material's previous history (*i.e.*, thermal, stress, vapor exposure, *etc.*) [9–11]. This sensitivity to processing conditions and sample preparation is known to cause discrepancies in reported

properties of glassy polymers [12]. For instance, the rate at which a polymer is cooled from above the glass transition temperature, T_g , has profound effects on the material's physical properties [13]. These differences arise from the greater displacement from equilibrium in samples rapidly quenched from above T_g as compared to slowly cooled samples. As an example, Cangialosi *et al.* showed higher initial free volume and accelerated physical aging in polycarbonate with increasing cooling rates from above T_g [14]. The accelerated aging in these materials was attributed to the initially higher free volume state of the rapidly quenched samples as compared to the slowly cooled samples, which created a larger driving force to equilibrium and thus increased the rate of aging.

After a polymer vitrifies, various conditioning treatments are known to alter its thermodynamic state. For instance, in experiments with bulk glassy polymers, exposure to high pressure CO₂ causes the glassy polymer structure to swell, and upon removal of the CO₂, the system is unable to immediately return to its initial state, thus, it has a lower density than before the exposure [11,15–17]. While the effects of this conditioning treatment are not immediately reversible, the polymer may return to its original state by physical aging over time (*i.e.*, changes due to conditioning are only semi-permanent). This effect can also be caused by the uptake of vapors and liquids including hexane and water vapor [18–21]. Conversely, thermal annealing at elevated temperatures, yet below the glass transition, increases the density of glassy polymers [11,22]. Mechanical stresses can also alter the state of glassy polymers and affect aging behavior [23]. A study by Berens and Hodge illustrates the effects of applied stress and vapor exposure before

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aging of poly(vinyl chloride), as probed by differential scanning calorimetry (DSC) [9]. Enthalpy relaxation was enhanced similarly by the exposure to mechanical (tensile and compressive) and sorptive stresses [9]. While these effects have been demonstrated in bulk polymer samples, it is not well understood how thin films respond to the same conditioning treatments.

Since previous history has a strong influence on glassy polymer properties, it is important that aging studies employ samples with identified and reproducible histories. Typically, a controlled quench from above the glass transition temperature is used to define an experimental starting time. This technique was used in previous studies on physical aging in thin films; however, actual applications of these materials involve much more complex histories. For example, thin glassy polymer films used in gas separation membranes are created through an intricate phase inversion process, and they may undergo additional treatment steps before packaging and testing can begin. Additionally, a myriad of storage times and conditions exist before these materials reach their ultimate destination for use in the field. Because of the complex and ill-defined history of glassy polymers in various applications, it is critical to understand how aging behavior changes as a function of the material's previous history to accurately predict their long-term performance.

As an initial step toward understanding how previous history affects the physical aging behavior of thin glassy polymer films, a variety of heating and conditioning treatments were applied to thin polysulfone (PSF) membranes (~ 125 nm in thickness) before tracking their aging behavior. The influences of annealing at various temperatures below T_g and conditioning with high pressure CO_2 for various times on the physical aging behavior of thin PSF films were studied using gas permeability measurements. These treatments were applied after a well-defined quench from above the glass transition to ensure the histories were reproducible. The histories considered in this investigation were not chosen to mimic any particular application conditions, but rather to produce a range of starting points for the aging studies. The nature of the aging response was similar across the range of histories studied; however, the magnitude of aging-induced changes was sensitive to previous history. Additionally, exposure to high pressure CO_2 accelerated physical aging in comparison to unconditioned films. A previously developed model that illustrates aging behavior in thin glassy films, based on work by Struik, was used to describe the experimental results. To the best of our knowledge, this report contains the first systematic study on the influence of previous history on aging behavior in thin glassy films.

2. Experimental methods

Polysulfone (PSF), based on bisphenol-A, from Solvay Advanced Polymers (UDEL PSF-3500 NT LCD) was used as received in this study. PSF was chosen because it is a widely used gas separation membrane material, and its T_g (186°C) is well above the temperature of use, so the material is deep in the glassy state during use [5,24]. Thin polymer films (~ 125 nm) were prepared by spin casting 3 wt.% PSF solutions in cyclopentanone onto silicon wafers at 1000 rpm for 60 s. A variable angle spectroscopic ellipsometer manufactured by J.A. Woollam Co., Model 2000D, was used to measure film thickness.

The presence of microscopic pinhole defects, which form with increasing frequency as film thickness is reduced, can lead to difficulties in studying the gas transport properties of thin polymer films [25]. While a small fraction of trans-membrane defects may have little influence on studies using other techniques such as ellipsometry or fluorescence spectroscopy, these defects mask the native selectivity and permeability characteristics of a material under study

by allowing gas to pass through the defects in the membrane via convective transport rather than by the solution-diffusion mechanism that controls small molecule transport through dense polymeric membranes [26]. A defect fraction as small as 10^{-6} on an area basis is enough to prevent a membrane from performing a gas separation [27]. A previously developed coating technique was applied to circumvent this problem [28]. After spin-coating a thin glassy film of amorphous PSF, a layer of highly permeable, rubbery poly(dimethylsiloxane) (PDMS) was coated directly on top of the glassy film. The PDMS overcoat layer was created by spin casting a PDMS solution in cyclohexane directly onto the glassy film, which was supported on a silicon wafer. The PDMS solution consisted of Dehesive 940A with a proprietary crosslinker (V24) and catalyst (OL) system provided by Wacker Silicones Corporation, Adrian, MI; cyclohexane was added to create a 12 wt.% solution of polymer. The film was then annealed on a hot plate at 110°C for 15 min to crosslink the PDMS and remove residual solvent. The thickness of the PDMS layer (~ 3 μm) was measured using a Dektak 6 M stylus profilometer. The PDMS layer blocks convective flow through any pinhole defects of the glassy layer and, at the experimental conditions, PDMS is $\sim 160^\circ\text{C}$ above its T_g , so its properties do not change with time due to physical aging [4]. According to the series resistance model, the PDMS layer accounts for less than 4% of the total mass transfer resistance though the films in this study [29]. Additionally, the aging response of PSF was previously shown to be unaffected by the presence of the PDMS layer [28]. A similar coating technique was developed for hollow fiber membranes that initially enabled the industrial development of these materials for gas separation applications [27,30]. The two layer film was then lifted from the silicon support using a thin metal wire frame and heated 15°C above the bulk T_g of PSF for 20 min to erase the thermal history of the glassy film and define a starting point for the aging studies. More details regarding the sample preparation techniques were described by Huang and Paul [5].

After the quench from above T_g , samples were either tested immediately (*i.e.*, the base case), annealed for a prescribed period of time at a specific temperature under a nitrogen purge, or conditioned with CO_2 . All films used in this study were 125 nm thick PSF coated with PDMS. The annealing temperature ranged from 90°C to 170°C , and the annealing time ranged from 2 to 160 h. The samples conditioned with high pressure CO_2 (800 psig (56.2 bara)) at 35°C were aged for 500 h at 35°C in a dry environment prior to the conditioning treatment. After the CO_2 conditioning treatment, the CO_2 was removed slowly (over 40–50 min) through a fine control needle valve to prevent foaming or cooling in the sample and to prevent damage to the delicate thin film. This procedure minimized the changes due to physical aging over the time scale of the conditioning treatment. If the samples were conditioned with CO_2 immediately after the quench from above T_g , the influence of conditioning time on aging properties would be complicated by the rapid structural relaxation that occurs immediately following vitrification. Scholes et al. recently reported that the concentration of CO_2 in PSF was approximately 3 times higher at 15°C than at 75°C at 58.8 psig (5.1 bara) [31]. Although this pressure is considerably lower than the pressure used in the conditioning treatment, the results illustrate the influence of temperature on solubility. Because solubility is temperature dependent and influences the effects of conditioning, it is important to specify the temperature of the conditioning treatment, 35°C in this case [11].

Gas permeability coefficients for O_2 , N_2 , and CH_4 were determined using a standard constant volume, variable pressure method [32]. Measurements were conducted at 35°C , with an upstream pressure of 2 atm and a maximum downstream pressure of 10 torr. When not being tested, samples were aged in a dry environment (*i.e.*, $<10\%$ relative humidity) at 35°C .

3. Results and discussion

3.1. Influence of annealing time

Fig. 1a–c present the O_2 , N_2 , and CH_4 permeability coefficients as a function of aging time for thin PSF films that have been annealed at 170°C for up to 160 h following quenching from above T_g . After annealing, the films were stored at 35°C in a dry environment between measurements. All films display decreasing permeability with aging time, consistent with the loss of fractional free volume during physical aging. The initial permeability and aging behavior of the films annealed for 2 h at 170°C nearly matches that of the freshly quenched base case. Further annealing time at 170°C decreases the initial permeability and slows the aging process as compared to the base case, as expected due to the reduced free volume state of the annealed material, which lowers permeability and decreases the driving force to reach equilibrium. After ~ 1000 h of aging, the O_2 permeability of the films annealed at 170°C for 160 h prior to aging decreased by 24% while the O_2 permeability decreased nearly 40% in the base case.

The O_2/N_2 and N_2/CH_4 pure gas selectivities are shown as a function of aging time in Fig. 2a and b, respectively, for the films annealed at 170°C . Selectivity increases with physical aging due to the loss of excess free volume, which causes the material to become more size selective, primarily by reducing the diffusion coefficients

of larger molecules more than for smaller molecules. Consistent with the lower permeability in the annealed films as compared to the base case, the initial selectivities are higher in the annealed films.

3.2. Influence of annealing temperature

The influence of aging time on the O_2 , N_2 , and CH_4 permeability coefficients of thin PSF films after annealing for 160 h at 90°C , 150°C , and 170°C are presented in Fig. 3a–c. The aging behavior is similar in all films, showing decreasing permeability with aging time. As might be expected, the initial permeability and extent of permeability decline decreases with increasing annealing temperature prior to aging. The changes seen after annealing at 90°C and 150°C are similar to one another, while annealing at 170°C causes more significant changes in the permeability and aging response as compared to the base case.

Fig. 4 a and b show the O_2/N_2 and N_2/CH_4 pure gas selectivities of the annealed films as a function of aging time, respectively. Selectivity increases with physical aging in all cases, indicating the samples behave as defect free films. Again, consistent with the lower permeabilities of the films annealed at higher temperatures, the initial selectivities are higher than in the base case.

After long enough periods of time, the permeability data seem to be converging to a common permeability versus time behavior. These results show that the nature of the aging response is similar

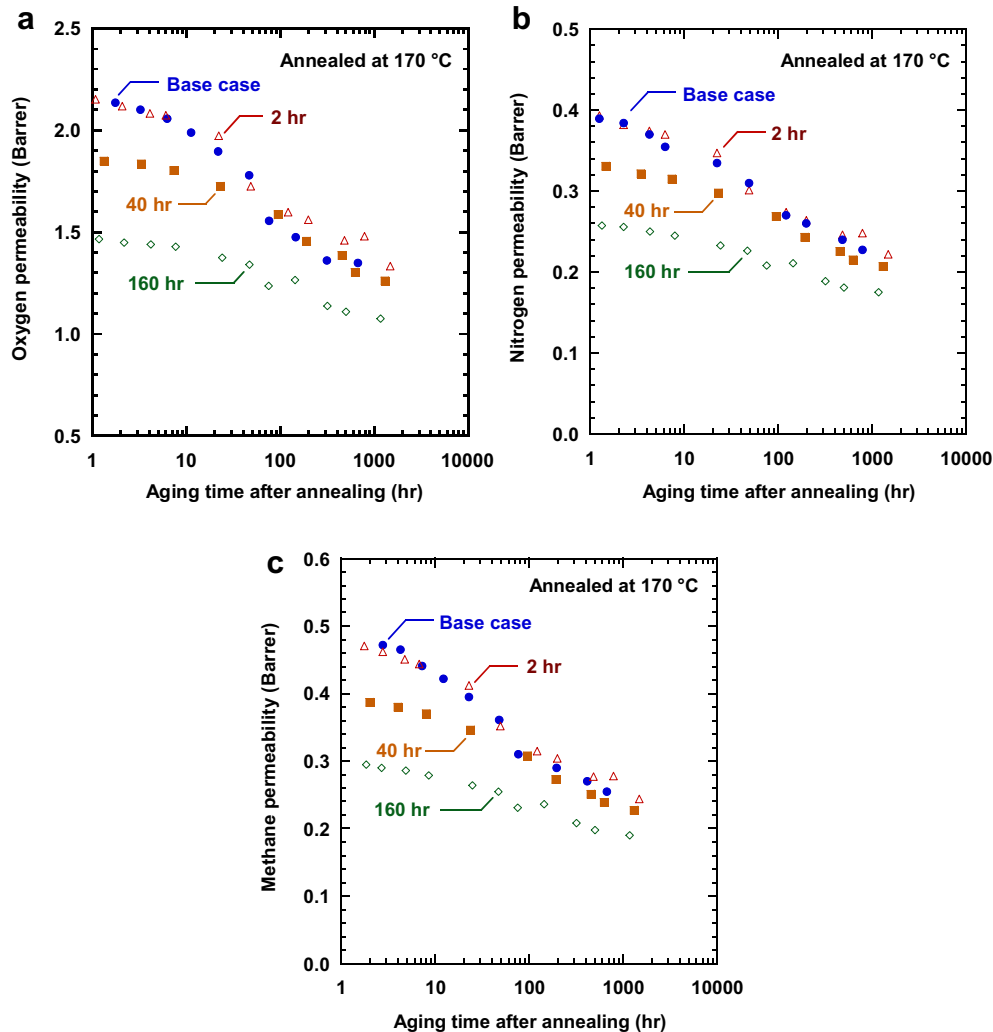


Fig. 1. Influence of aging time at 35°C on (a) O_2 , (b) N_2 , and (c) CH_4 permeability coefficients in thin PSF films annealed for specified time at 170°C after a quench from above T_g .

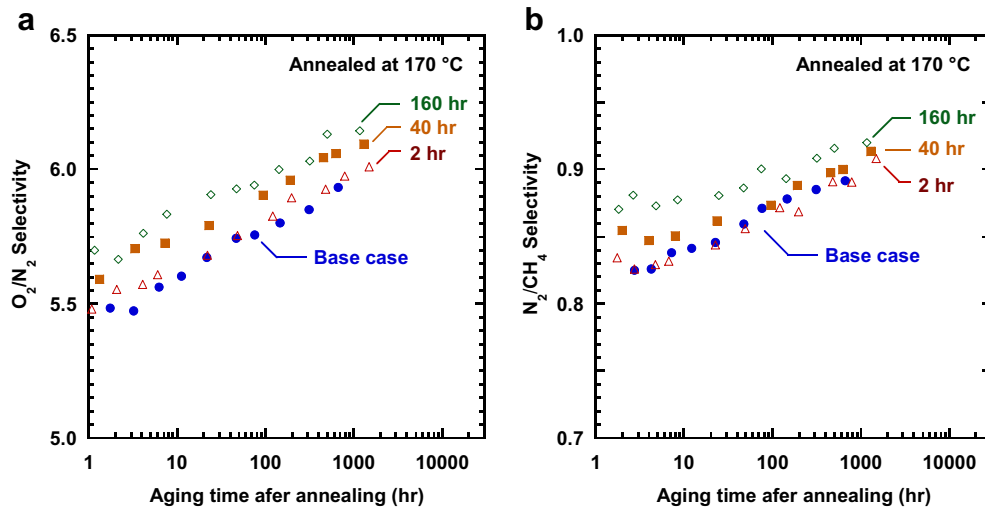


Fig. 2. Influence of aging time at 35 °C on (a) O_2/N_2 , and (b) N_2/CH_4 ideal selectivity in thin PSF films annealed for specified time at 170 °C after a quench from above T_g .

in all films considered; however, the extent of aging-induced changes depends on the annealing treatments applied prior to aging at 35 °C. The reduced aging rates at 35 °C for the annealed films, as compared to the base case, are likely related to the

decreased driving force for physical aging in these materials. These findings are consistent with Berens and Hodge's observation that while the development of endothermic peaks in DSC scans (*i.e.*, evidence of enthalpy relaxation) after aging was a completely

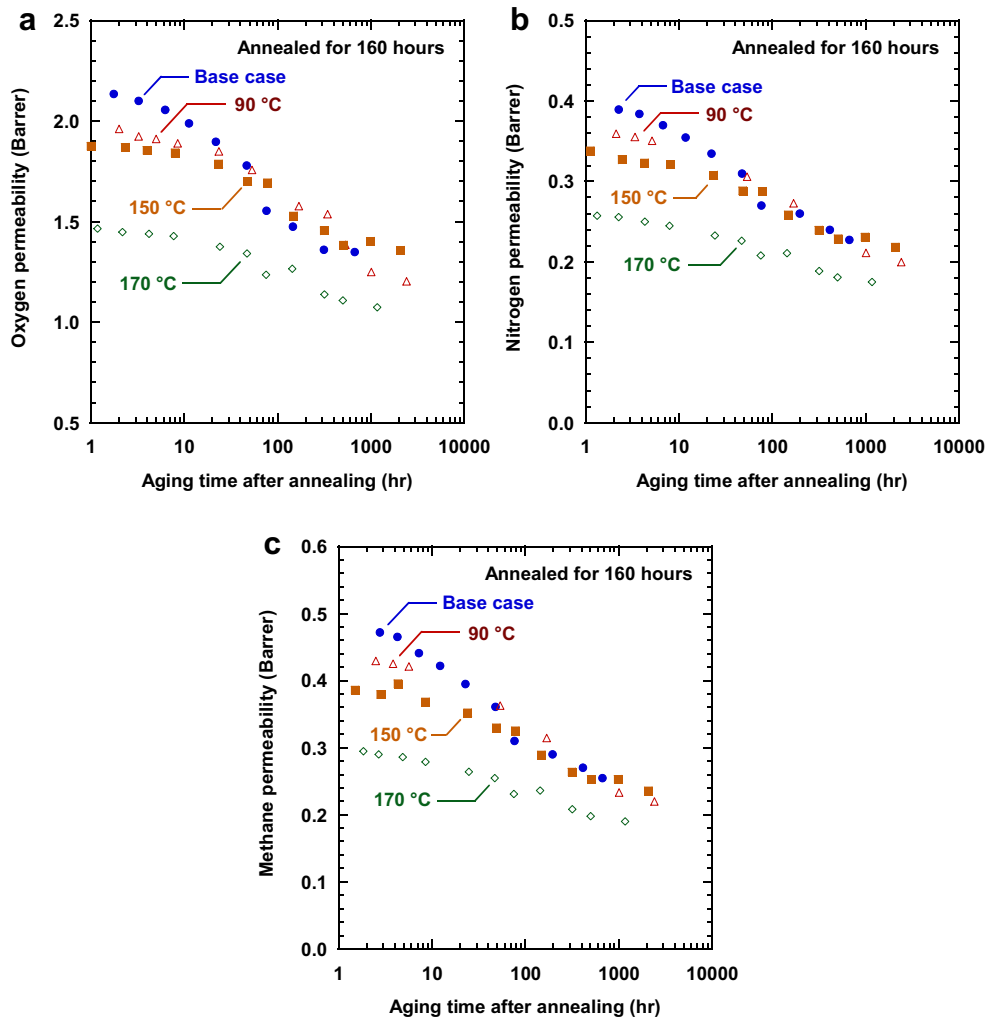


Fig. 3. Influence of aging time at 35 °C on (a) O_2 , (b) N_2 , and (c) CH_4 permeability coefficients in thin PSF films annealed for 160 h at specified temperature after a quench from above T_g .

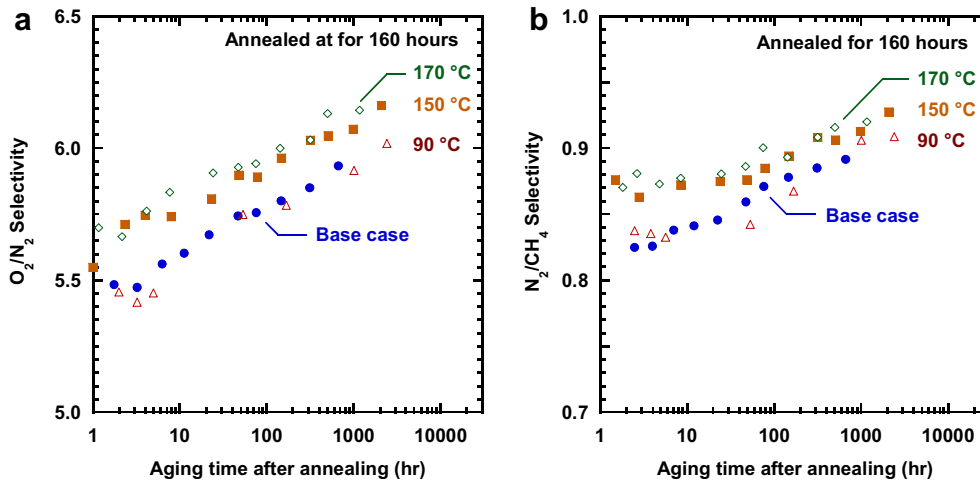


Fig. 4. Influence of aging time at 35 °C on (a) O_2/N_2 , and (b) N_2/CH_4 ideal selectivity in thin PSF films annealed for 160 h at specified temperature after a quench from above T_g .

general feature of the aging process, the magnitude of the observed peaks were strongly dependent on previous history [9].

3.3. Influence of conditioning with CO_2

In addition to thermal annealing below the glass transition, the state of a glassy polymer can be modified by conditioning with high pressure CO_2 . Fig. 5a–c present the impact of aging on O_2 , N_2 , and CH_4 permeability coefficients of thin PSF films after conditioning with 800 psig (56.2 bara) CO_2 for 2, 40, and 160 h at 35 °C; the unconditioned base case is included for comparison. Prior to the conditioning treatment, the films were aged for 500 h at 35 °C to minimize the influence of physical aging during the treatment process. As in all other films studied, permeability decreases with aging time. The lower permeability in the CO_2 conditioned films, as compared to the base case with no CO_2 exposure, results from the decrease in permeability that occurred during the 500 h of aging prior to the conditioning treatment. The initial permeability after conditioning for 2 or 40 h was similar to that of unconditioned films aged for 500 h; however, the initial permeability after conditioning for 160 h was slightly lower than the aged base case. Although the permeability decrease after 160 h of conditioning is not fully understood, it could be caused by physical aging during the conditioning treatment. Furthermore, this permeability decrease in thin films after long-term exposure to CO_2 is consistent with preliminary results from ongoing studies in our laboratories (data not shown). The behavior of these films following the conditioning treatment may not match predictions based on bulk behavior; however, it is not well documented how these processes affect thin film properties. While outside the immediate scope of this study, any deviations from bulk behavior indicate opportunities for additional investigations to better understanding thin film phenomena. The permeability coefficients were all calculated assuming a constant thickness during aging and conditioning. Although film thickness increases slightly upon exposure to high pressure CO_2 , the change is negligible in comparison to the permeability changes measured and experimental error. After exposure to 800 psig (56.2 bara) CO_2 for 40 h, film thickness increased by ~1% in thin PSF films, as measured using ellipsometry.

Fig. 6 a and b show the O_2/N_2 and N_2/CH_4 pure gas selectivities, respectively, of the conditioned films as a function of aging time. Selectivity increases with physical aging in all cases, as expected. The initial selectivities of the conditioned films are higher than in the base case, matching their initially lower permeability coefficients.

To illustrate the similarity in the aging response of the freshly quenched and conditioned films, Fig. 7 presents the relative O_2 permeability coefficients of these films over time, normalized by the permeability at 1 h of aging. Despite the initially lower absolute permeability coefficients of the conditioned films, the relative permeability decline is nearly identical to that of the base case. These results are consistent with a variable energy positron annihilation lifetime spectroscopy (PALS) study on the influence of aging and conditioning on the free volume properties of thin PSF films [33]. In the PALS study, aging of conditioned and unconditioned films was shown to proceed similarly, as indicated by decreasing free volume element size with aging. Additionally, the o-Ps intensity, which is related to the number of free volume elements in a material, was lower in the CO_2 conditioned films than in the base case. This result is likely related to the lower permeability of the conditioned films as compared to the unconditioned case.

While the relative aging behavior is similar in these films, the magnitude of aging induced permeability changes is greater after the conditioning treatment than in the unconditioned case. Fig. 8 shows the behavior of these films based on the total time elapsed after the quench from above T_g and illustrates the more rapid aging of the films after CO_2 conditioning as compared to the unconditioned base case. In the base case, the change in permeability measured after 500 h of aging is quite small for the next several hundred hours; however, after exposure to high pressure CO_2 for a time as short as 2 h, permeability declines more rapidly with aging time than would have occurred without this CO_2 treatment, e.g., the base case. After initially aging for 500 h, the O_2 permeability coefficient in the base case decreased by ~0.1 Barrer over then next 500 h; upon conditioning with CO_2 for 2 h, the O_2 permeability coefficient decreased by ~0.4 Barrer over the same 500 h period. Kim et al. have previously shown that permeability decreases more quickly with time in thin films after exposure to CO_2 than aged films not exposed to CO_2 [34]. The qualitative similarities and quantitative differences of the observed aging behaviors depending on previous history was also reported by Alcoutlabi et al for the aging response of epoxy resins with different previous histories [17].

3.4. Modeling considerations

A modified version of Struik's aging model was used to mathematically characterize the influence of previous history on

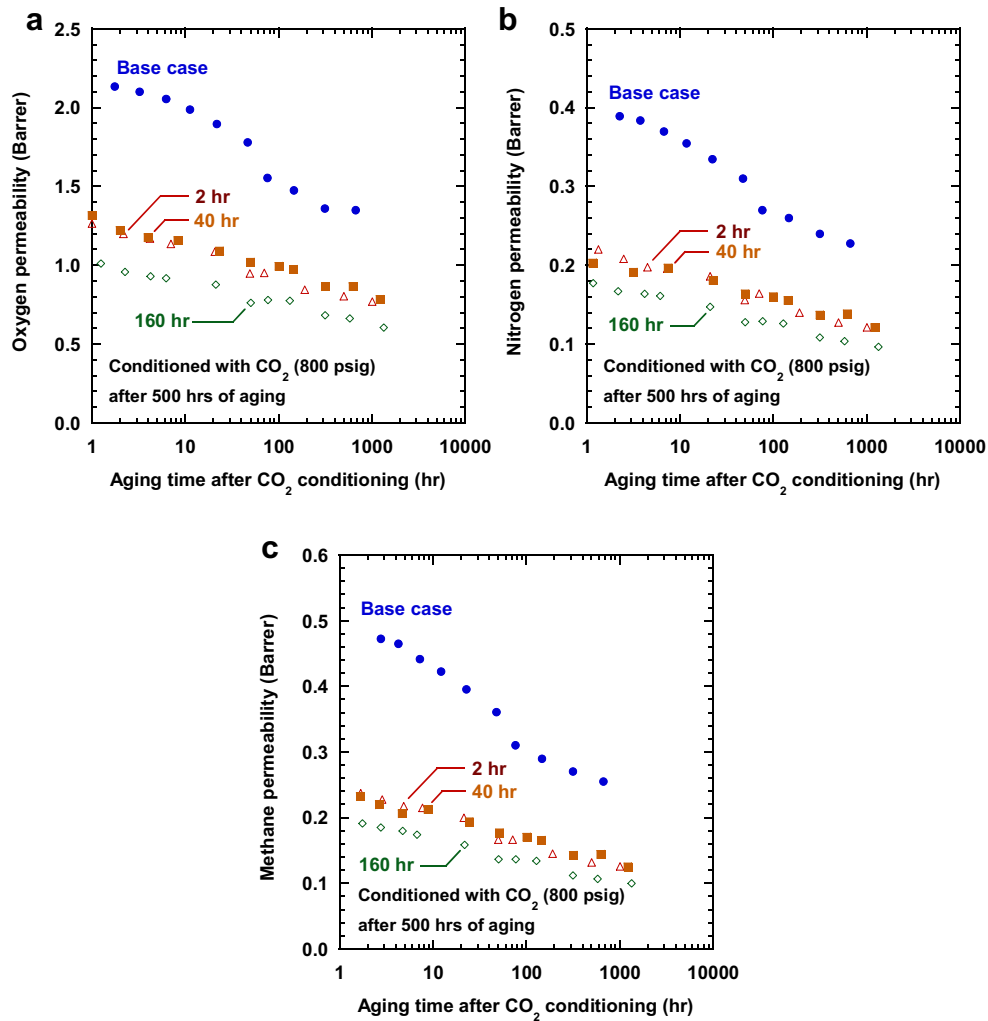


Fig. 5. Influence of aging time at 35 °C on (a) O₂, (b) N₂, and (c) CH₄ permeability coefficients in thin PSF films conditioned with 800 psig (56.2 bara) CO₂ after a quench from above *T_g* and 500 h aging at 35 °C.

physical aging in thin PSF films. The model describes the rate of physical aging as a function of the departure from equilibrium and a relaxation time, which depends on the system conditions and the current state of the material, given by:

$$\frac{d\Delta f}{dt} = \frac{-\Delta f}{\tau} = \frac{-\Delta f}{\tau_{\infty} \exp(-\gamma \Delta f)} \quad (1)$$

where Δf is the excess fractional free volume (*i.e.*, the difference between the fractional free volume in the polymer, f , at time t and

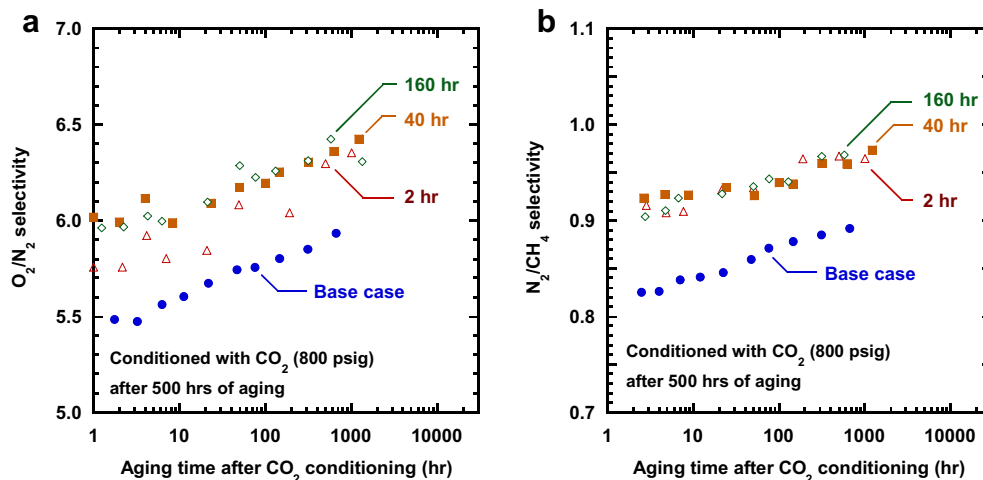


Fig. 6. Influence of aging time at 35 °C on (a) O₂/N₂, and (b) N₂/CH₄ ideal selectivity in thin PSF films conditioned with 800 psig (56.2 bara) CO₂ after a quench from above *T_g* and 500 h aging at 35 °C.

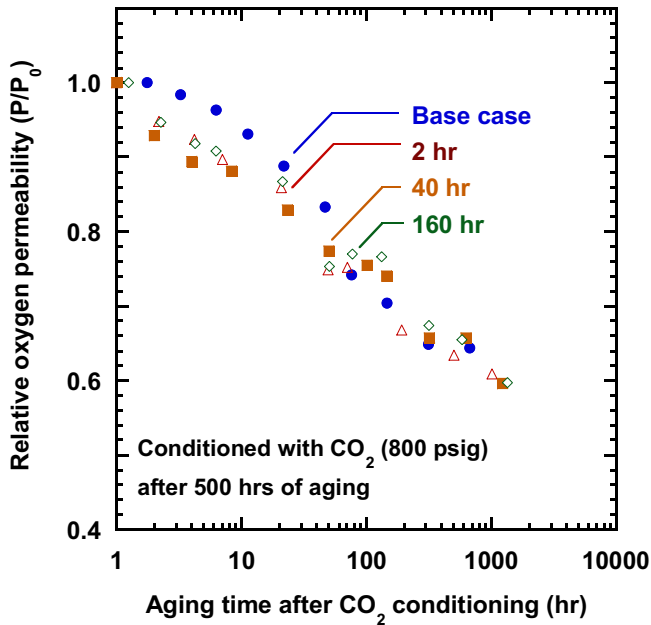


Fig. 7. Influence of aging time at 35 °C on relative O₂ permeability coefficients in thin PSF films conditioned with 800 psig (56.2 bara) CO₂ after a quench from the above T_g and 500 h aging at 35 °C. The relative oxygen permeability coefficients are based on the permeability at 1 h of aging time.

the fractional free volume in the fully relaxed, equilibrium state, f_e), $\Delta f = f - f_e$, τ is the relaxation time at time t , τ_∞ is the equilibrium relaxation time (i.e., at $t \rightarrow \infty$), and γ is a constant characterizing the sensitivity of relaxation time to excess fractional free volume. Fractional free volume, f , is related to the polymer's specific volume, v , by $f = (v - v_0)/v$, where v_0 is the occupied volume of the polymer and can be estimated by the Bondi method (i.e., $v_0 = 1.3v_w$), where v_w is the van der Waals volume calculated using group contribution methods [35]. The original Struik model was developed for bulk polymers, where physical aging is independent of sample dimensions, so in the modified model, τ_∞ was allowed to depend on film thickness to capture thickness-dependent aging behavior. The model was solved numerically using MATLAB software. Using the fractional free volume, f , given by the model, gas permeability was calculated as a function of time from the following correlation:

$$P = Ae^{-B/f} \quad (2)$$

where A and B are constants based upon oxygen permeability measurements in samples of bulk thickness from the literature, 397 Barrer and 0.839, respectively [36].

To capture the influence of sub- T_g annealing on aging behavior, model parameters reported for the aging of 125 nm PSF films at 35 °C were used, i.e., τ_∞ , γ , and f_e [28]. The initial fractional free volume, f_i , was allowed to vary with the films' annealing treatments to match their initial permeability coefficients. Thus, the value of f_i used in the model represents the material's state after the annealing treatment and is considered the apparent initial fractional free volume; differences in this value from the base case are not meant to suggest that the initial state immediately after the quench from above T_g is different in these samples. The model parameters, including the apparent initial fractional free volumes, used to describe the aging behavior of the annealed films are shown in Table 1. The equilibrium fractional free volume at 35 °C, f_e , was calculated based on extrapolation of the experimental pressure-volume-temperature data in the melt state to the aging temperature [37]. Fig. 9 compares the model predictions to the experimental data for films annealed at 170 °C for various times. Annealing at 170 °C for 2 h did not significantly influence the initial permeability coefficients or aging behavior of the thin PSF films, so this treatment is described using the base case parameters. After annealing at 170 °C for 40 h, the initial O₂ permeability coefficient decreased by 0.3 Barrer as compared to the base case and the consequent aging behavior matches the model predictions. Annealing for 160 h at 170 °C lowered the initial O₂ permeability coefficient by 0.7 Barrer as compared to the freshly quenched film. While subsequent aging behavior is similar to the model predictions, the model under-predicts permeability loss with time, suggesting that some free volume changes at the higher temperature does not influence permeability in the same way as aging at 35 °C. The material's free volume state at 170 °C, which is 16 °C below T_g , is very different than at 35 °C. Conceivably, relaxations far below T_g influence permeability and aging differently than high temperature relaxations. While beyond the scope of this study, understanding this behavior would require probing the free volume distribution as a function of annealing treatments. Films annealed for 160 h at 90 °C and 150 °C display similar behavior to the case of annealing for 40 h at 170 °C; therefore, these model predictions are not included for brevity.

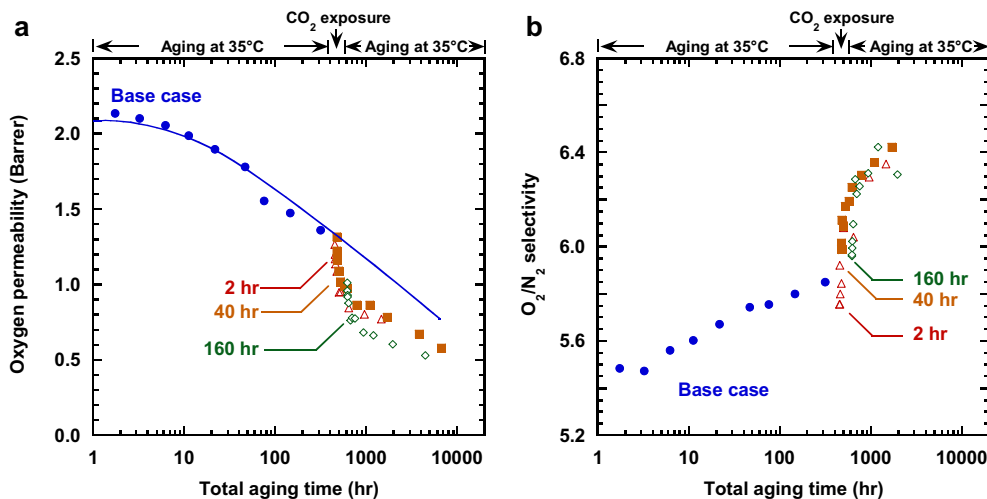


Fig. 8. Influence of total elapsed aging time after a quench from above T_g on (a) O₂ permeability coefficients and (b) O₂/N₂ pure gas selectivity in thin PSF films conditioned with 800 psig (56.2 bara) CO₂. Line drawn to guide the eye.

Table 1
Model parameters.

	τ_{∞} (s)	'Apparent' f_i	f_e	γ
Base case	5.4×10^{13}	0.1600	0.1069	350
40 h at 170 °C	↓	0.1562	↓	↓
160 h at 170 °C		0.1498		
2–40 h at 800 psig CO ₂	5.1×10^{11}	0.1459		
160 h at 800 psig CO ₂	6.8×10^{10}	0.1405		

To capture the aging behavior of the CO₂ conditioned films, the value of τ_{∞} was allowed to vary with the conditioning treatment. If the base case equilibrium relaxation time was used, as in the annealed films, the model would predict very little change in permeability with aging time after the conditioning treatment. To match the experimental data, the relaxation times were shortened after the CO₂ conditioning, consistent with the apparent 'restarting' of the aging process in the conditioned films. This 'restarting' of the aging process is consistent with the 'de-annealing' effect of CO₂ conditioning discussed by Chan and Paul [11]. The model parameters used are listed in Table 1. Good agreement between the model and the experimental aging data for the CO₂ conditioned films is shown in Fig. 10. Similar behavior is seen in the films conditioned for 2 and 40 h, and the same model parameters were used to describe their behavior. According to this modeling scheme, the equilibrium relaxation time decreases by 2–3 orders of magnitude after the CO₂ conditioning treatment. This enhanced mobility after exposure to CO₂ is consistent with an increase in the average free volume element size upon conditioning with CO₂, as suggested by the results of the PALS study. The applied model does not directly incorporate any information regarding the distribution of free volume element size; rather a value that represents the total free volume in the material is used. Thus, if the free volume distribution is altered, modification of other model parameters may be needed to account for the changed behavior. In comparison with small free volume elements, larger free volume elements will age more rapidly due to their greater deviation from equilibrium. If the free volume elements

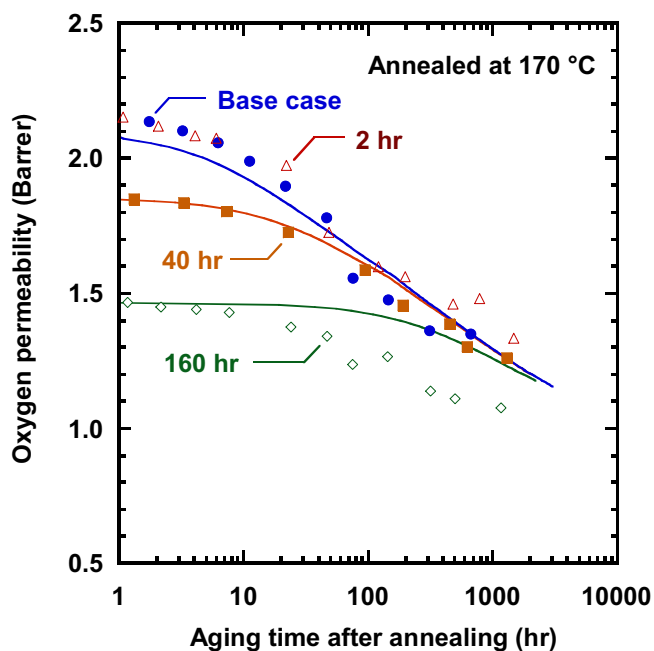


Fig. 9. Influence of aging time at 35 °C on O₂ permeability coefficients in thin PSF films annealed for specified time at 170 °C after a quench from above T_g . Lines generated from the model.

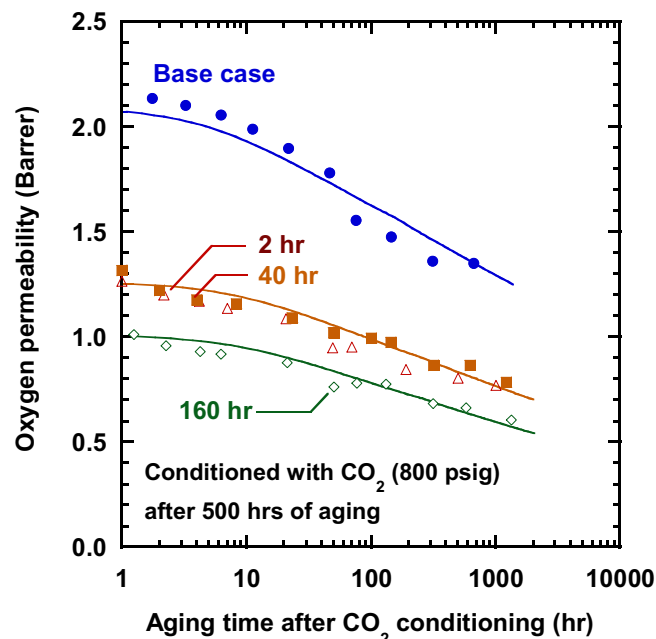


Fig. 10. Influence of aging time at 35 °C on O₂ permeability coefficients in thin PSF films conditioned with 800 psig (56.2 bara) CO₂ after a quench from above T_g and 500 h aging at 35 °C. Lines generated from the model.

sizes are increased by CO₂ conditioning, as suggested by the PALS results, the rate of aging is expected to increase. This accelerated aging, which is related to a shift in the free volume distribution, is captured by the current modeling treatment by a decrease in the equilibrium relaxation time, τ_{∞} . The ability of the model to describe the aging behavior of thin glassy films with a variety of previous histories illustrates the broad applicability of the model and the similarities in the aging responses of these samples.

4. Conclusions

The influence of previous history on the physical aging behavior of thin PSF films was tracked using gas permeability measurements. Similar aging behavior was seen in all films, regardless of previous history, *i.e.*, permeability decreased and selectivity increased with aging time. Annealing films below T_g reduces the initial permeability and slows the rate of physical aging by reducing the driving force to equilibrium, as compared to a film freshly quenched from above T_g . Exposure to high pressure CO₂ after aging for 500 h causes the aging process to accelerate in comparison to the base case, consistent with previous results from a variable energy PALS study. The aging behavior of these films with various previous histories is well described by a modified Struik model. The utility of this work is to shed light on the influence of initial properties on physical aging behavior, not to investigate the aging behavior under the treatment conditions considered, where more information is needed for full understanding. Deviations from expected aging behavior as a function of experimental conditions highlight the importance of further investigation regarding influences on departure from bulk behavior in these thin films.

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