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Drifts in penetrant partial molar volumes in glassy polymers due to physical aging

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Abstract

Sorption and dilation measurements on three different glassy polymer materials are reported to characterize the presence of unrelaxed volume and how it is affected by physical aging. Substantial changes in the sorption and dilation due to physical aging were observed for 25.4 μm thick films of Matrimid® and Lexan®, but not significantly for Ultem®. Such effects are more pronounced when the partial molar volume is considered, since the more aged samples showed less sorptive capacity yet more swelling as compared to their unaged counterparts. Experimentally observed trends in the partial molar volume due to physical aging are qualitatively consistent with trends expected based on the idealized dual mode sorption and dilation models. On the other hand, quantitative discrepancies between expected and observed dilation behaviors reveal some limitations associated with the conventional simple interpretation of the model parameters.

Keywords: Glassy state; Physical ageing; Gas sorption

1. Introduction

Fundamentally, physical aging causes a reduction of free volume in glassy polymers and thus a reduction in the mobility and solubility of penetrants. While many investigations have been reported on the effect on penetrant permeability coefficients, little prior work has been reported regarding the effects of physical aging on penetrant solubility; and essentially no studies of the effect of aging on sorption-induced dilation have been reported. Fleming was the first to study penetrant partial specific (or, alternately, molar) volumes in glassy polymers by combining polymer-gas sorption data along with dilation data [1]. The same approach is used here to study the effect of physical aging on the polymer environment as probed by penetrant sorption.

2. Background and theory

2.1. The glassy state

During the transformation from the rubbery to the glassy state, a snapshot of the rubbery state becomes temporarily frozen in, trapping 'pockets' of unrelaxed or excess free volume. Fig. 1 shows the transition in specific volume that occurs as the T_g is traversed. The shaded area represents the excess free volume trapped during the transition. The excess free volume should be distinguished from the standard free volume which results from volume 'swept out' by thermal oscillations of the polymer segments below T_g. Such segmental mobility below the T_g is hindered, but remains significant. A more in depth discussion, which further categorizes different types of free volume, may be found in Refs. [2,3]. The nomenclature of free volume in polymers is not standardized; however, in the remainder of this article, the phrase 'unrelaxed free volume' will be used to refer to the excess free volume (Fig. 2).

2.2. Sorption and swelling models in glassy polymers

This study considers the validity of various aspects of the well known 'dual-mode' model for sorption and dilation for

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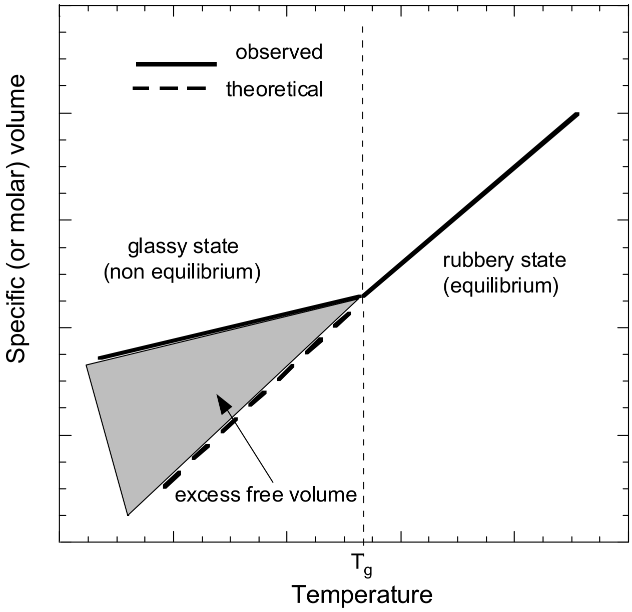

Fig. 1. Specific (or molar) volume vs temperature for a glassy polymer.

analysis of experimental data. As with all polymer sorption models, the dual mode model is a simplification of the complex interactions between polymer and penetrant. The applicability of other models such as the non-equilibrium lattice fluid equation of state [5] and the site-distribution model [4,6] were also considered as part of a larger study [7]. While the various models each had strengths and weaknesses, the simple dual mode model offered a useful balance between physically interpretable model parameters and computational simplicity. This paper, therefore, considers the application of this model for the description of penetrant-induced sorption and dilation of aged and essentially unaged glassy polymers.

For the dual mode model [8,9], the penetrant may sorb into the medium by dissolution or by a hole filling mechanism. The total concentration, c, is then the sum of the 'dissolved' concentration, C_D, and the 'hole-filling' concentration, C_H. This is expressed given as:

$$c = C_D + C_H = k_D p + \frac{C'_H b p}{1 + bp} \tag{1}$$

where p is the external pressure, k_D is the Henry's law constant, C'_H is the Langmuir capacity constant which is related to unrelaxed free volume, and b is the Langmuir affinity constant. The first term of the equation (C_D) represents dissolution of the penetrant into well-packed regions of the polymer matrix and thus uses a Henry's law expression. The second term (C_H) represents accommodation of penetrants into voids or holes and thus uses a Langmuir law expression.

In the simplest and most common physical interpretation of Eq. (1), only the Henry's law sorption population contributes to sample dilation, since sorption into Langmuir sites involves the filling of pre-existing voids [10]. The dilation, expressed as the ratio of the change in total volume to the original volume ($\Delta V/V_0$) then ideally may be calculated as:

$$\frac{\Delta V}{V_0} = (k_D p) v^* \tag{2a}$$

The constant, v^*, is the molar volume of the 'condensed' penetrant. Pope suggested that the value for v^* should correspond to the same as that measured for the gas sorbed in equilibrium fluids. With the assumption of a concentration independent penetrant molar volume, this simple model predicts linear dilation as a function of pressure. While this behavior was found by Fleming [1] to be adequate for the polycarbonate sample he studied, this does not appear to be generally observed. Indeed, as also found by Pope [11,24], in this study we found that Eq. (2) is too simplified to describe the data for the cases considered here.

Kamiya also found deviations from Eq. (2a) from experimental data in his dilation studies and suggested a modification to accommodate sample dilation caused by sorption of penetrants assigned to the Langmuir sorption population [12]. The dilation can then be described by:

$$\frac{\Delta V}{V_0} = \left(k_D p + f\frac{C'_H b p}{(1 + bp)}\right) v^* \tag{2b}$$

Eq. (2b) includes the Langmuir term weighted by a factor, f, ranging from 0 to 1. The physical significance of f may be interpreted as either the fraction of Langmuir sites that require matrix dilation to be accommodated, or as

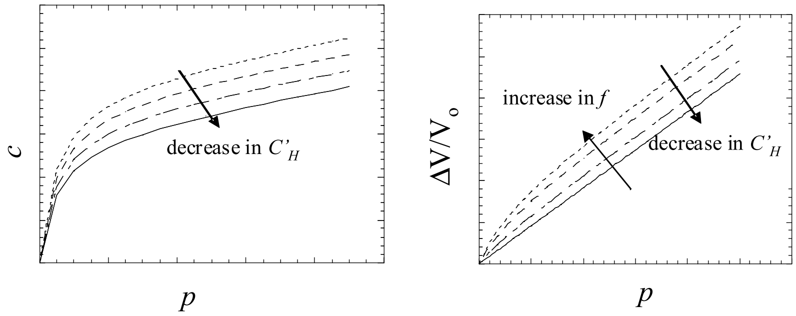

Fig. 2. Dual mode theory interpretation of physical aging on sorption and dilation isotherms.

the average fractional dilation induced in all Langmuir sites due to sorption.

The penetrant partial molar volume, v_2, is thermodynamically defined as [13]:

$$v_2 = \frac{\partial V}{\partial n_2}\Big|_{T,P,n_1} \tag{3}$$

where n is the mole fraction and the subscripts 1 and 2 refer to the polymer and penetrant, respectively. The physical significance of v_2 is the amount of induced dilation per mole of penetrant at a given concentration. Eq. (3) can be rearranged to yield the following working equation for determining v_2 [1]:

$$v_2 = v_T + (1 - w_2)\frac{\partial v_T}{\partial w_2}\Big|_T \tag{4}$$

where v_T is the total specific volume of the polymer-penetrant 'solution' (i.e. penetrant laden polymer) and w_2 is the weight fraction uptake of the penetrant. Eq. (4) yields the partial specific volume (cm^3/g) and can easily be converted to partial molar volume (cm^3/mol) by multiplying by the molecular weight of the penetrant. The derivative, $(\partial v_T/\partial w_2)|_T$, may be expressed as in the following equation:

$$\frac{\partial v_T}{\partial w_2}\Big|_T = \frac{\partial v_T}{\partial p}\Big|_T \frac{\partial p}{\partial w_2}\Big|_T \tag{5}$$

The first derivative on the right hand side is experimentally obtained from the dilation isotherm and the other derivative is obtained from the sorption isotherm. For ideal mixing (e.g. mixing in non-interacting, equilibrium fluids), v_2 is simply equal to the condensed molar volume of the penetrant and is independent of concentration. For penetrants in glassy polymers, however, there is typically concentration dependence. Adopting the formalism from vapor-liquid equilibrium for convenience, the value of v_2 in the limit of zero or low concentration is referred to here as the infinite dilution partial molar volume, v_2^∞; and the value of v_2 in the limit of higher concentration may be referred to as the 'saturated' partial molar volume, v_2^{SAT}. Note, however, that in this context, the term 'saturated' is not meant to indicate a true solubility limit. For 'ideal' mixing, $v_2^\infty = v_2^{\mathrm{SAT}}$.

As mentioned earlier, the concept of unrelaxed or excess free volume is reasonably widely accepted to exist in glassy polymers and it can be rationalized that the concentration dependence of the partial molar volume arises because of it. At low penetrant concentrations (or weight fractions) the regions of unrelaxed volume are vacant and available for penetrant accommodation, thus v_2^∞ is relatively low (i.e. the penetrant induces little swelling). At higher concentrations, however, all regions of excess free volume are occupied and the matrix must be dilated to accommodate sorption of penetrants, as would be the case for a simple liquid or a rubbery polymer.

Returning to the subject of physical aging and dual mode theory, it is reasonable to assume that the associated volumetric contractions would lead to an increase in the number of sorption sites requiring dilation and/or the requisite amount of dilation for each site (i.e. an increase in f). However, since physical aging should also cause a decrease in C'_H, it is unclear whether decreases in C'_H or increases in f will dominate the effect of physical aging on penetrant induced swelling. The figures below graphically illustrate the potential competing effects on sorption and dilation isotherms caused by changes in C'_H and f due to physical aging using the values of sorption parameters for tetramethyl polycarbonate reported by Pope [14].

To further illustrate expected fundamental trends, Fig. 3 was generated using hypothetical dual mode parameters, with a 15% decline in C'_H and 50% increase in f due to physical aging. The qualitative shape of the solid line for partial molar volume curves based on Eq. (2b) follows quite closely the trends experimentally observed by Fleming and Pope; starting at a relatively low value, gradually increasing and then leveling off at the higher concentration range. The dashed line in Fig. 3 also demonstrates the ability of the dual mode models for sorption and dilation to describe trends in penetrant partial molar volume as a result of physical aging. The actual trends observed in the present study for the various types of polymers studied here will be discussed later as well as a more detailed interpretation of the types of response shown in these graphs.

3. Experimental

3.1. Materials

The three polymers used in this study are Matrimid®, Ultem® and Lexan®, representing members of the important polyimide, polyetherimide and polycarbonate families, respectively. The table below lists densities and glass transition temperatures (T_g) for these materials. Matrimid®

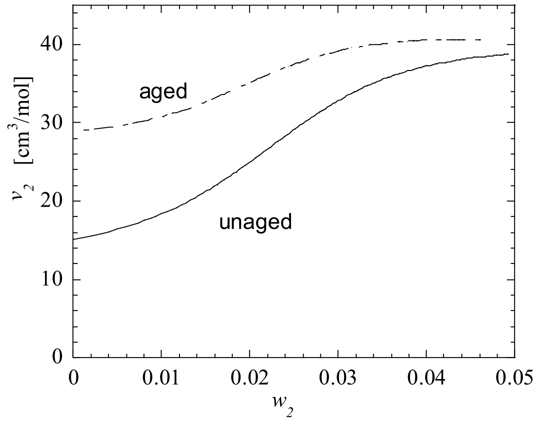

Fig. 3. Simulations on methane partial molar volume in tetramethyl polycarbonate due to physical aging based on dual mode models; assumes a 15% decline in C'_H and 50% increase in f due to physical aging.

and Ultem® are studied since they have attractive gas separation membrane properties; thus, an understanding of polymer-penetrant interactions in these materials is relevant for their practical use. Lexan® is studied since it is a fairly well understood glassy polymer and there are abundant data available in the literature for comparison [15,22].

All thick films are prepared by uniformly spreading a solution of the material over a flat, smooth mirror surface with a doctor blade. The films are made from the pure polymers with no additives. All polymers are completely amorphous as indicated by absence of first order transitions in differential scanning calorimetry measurements. The solvent used for this work was dichloromethane (CH_2Cl_2, $T_{boil}=39.8$ °C). An 8 wt% polymer solution gave a convenient fluid viscosity for casting of films of roughly 25.4 μm in thickness. The films were then placed in a vacuum oven and heated at 100 °C for 24 h. Films prepared this way are referred to 'as cast' for this work. Each sample was then heated 25 °C above T_g (Tables 1 and 2) in an inert environment to ensure removal of casting effects and to uniformly define a 'time zero' for all aging experiments. The cooling time is held to a minimum in order to reduce the effect of near or sub-T_g annealing. Ideally, a step change in temperature from T_g to the experimental temperature would be used. For the apparatus used in this experiment, the absolute minimum cooling time achieved was approximately 15 min.

Gas sorption is measured using the well known dual volume pressure decay apparatus which can determine penetrant concentration to within ±0.5%. An in depth discussion on this technique is given in Ref. [21]. Sample dilation measurements were conducted by exposing a long strip of the polymer of interest to various penetrants in a high pressure cell equipped with a see-through borosilicate viewing window. The dilation was measured with a Gaertner optical cathetometer (Model: M255C), which has a resolution 25 μm, allowing swelling to be tracked easily within ±2%. A sample holder was fabricated which allowed the polymer film to dilate freely. All sorption and dilation measurements made for this study are conducted slightly above room temperature at 35 °C to ensure thermal stability of the experimental apparatus. Unaged samples were tested immediately after reaching room temperature from the annealing procedure. The sorption process was typically started in less than 3 h after cooling from the annealing process above T_g. Identical, but separate, virgin samples were used for measurements on aged samples. The aged samples are stored at room temperature for 10 days prior to testing in the presence of a desiccant to ensure low relative humidity. Sorption and dilation measurements are conducted concurrently to ensure the same aging times for the different samples.

Table 1
Summary of materials [16–20]

Material	ρ (g/cm^3)	T_g (°C)
Matrimid® 5218 (BTDA-DAPI)	1.24	313
Ultem® (polyetherimide)	1.27	215
Lexan® (bisphenol-A poly-carbonate)	1.20	151

4. Discussion and results

The results for bisphenol-A polycarbonate (Lexan®) /CO_2 sorption and dilation measurements are given in Fig. 4. As expected, the sorption isotherm was suppressed for the physically aged sample compared to the unaged sample. Moreover, as suggested in Section 2, the aged sample did, in fact, show more swelling as illustrated by the elevated dilation isotherm of the aged sample. Such behavior was hypothesized as a result of a reduction in size and/or number of voids available for sorption. To the author's knowledge, this is the first known observation of such phenomena in which the more physically aged sample actually demonstrates more penetrant induced swelling.

As shown in Fig. 5 above, the trends in penetrant partial molar volume curves due to physical aging roughly mimic those were calculated as first shown in Fig. 3. Note that the partial molar volumes in the lower pressure regime are markedly different for the unaged and aged sample, but converge in the high penetrant uptake regime. This observation implies that, for this system, once CO_2 occupies some critical number of sorption sites, the polymer-penetrant environment is fairly independent of physical aging time in regards to sample swelling.

The differences in penetrant partial molar volume in the low and high pressure regime may be thought of as a consequence of the heterogeneous nature of the glassy state. Regions, which are closely packed are less affected by physical aging and require maximal dilation for penetrant accommodation during sorption. These regions contribute to higher penetrant partial molar volumes. On the other hand, regions, which are not well packed, require little dilation for sorption of penetrants, which contributes to lower penetrant partial molar volumes. Since these packing disruptions can be expected to diminish due to physical aging, it follows that the penetrant partial molar volume would increase. This phenomena, however, will only be significant when the hole-filling mechanism for sorption is significant, which is in the low pressure limit. At higher penetrant pressures, such sorption sites are saturated and sorption into the well packed regions dominates.

Note the surprisingly small value for v_2^∞ in the unaged sample, which is close to zero. When the sample is allowed to age for 240 h, however, the v_2^∞ greatly increases (~11 cm^3/mol), reflecting a more densified structure. Thus, while sorption measurements give the experimenter some sense of the densification, not until the corresponding dilation data is considered does it become apparent how strong the effect of physical aging can be. We find that the change in penetrant partial molar volume for glassy

Table 2
Extracted dual mode model parameters for sorption and dilation: Effect of physical aging

		k_D	C'_H	b	f	v^*
Lexan® CO_2	Unaged	0.47	0.74	0.29	0.30	27
	Aged	0.48	0.58	0.40	0.74	27
Matrimid® CO_2	Unaged	0.050	1.47	0.38	0.42	21
	Aged	0.052	1.29	0.40	0.78	21
Matrimid® CO_2	Unaged	0.008	0.82	0.09	0.24	22
	Aged	0.008	0.80	0.09	0.58	22

Units: k_D, mmol/(cm^3 polymer bar); C'_H, mmol/cm^3 polymer; b, bar^{-1}; v^*, cm^3/mol, used in Eq. (2b) for calculation of f.

polymers can be easily noticeable since physical aging may cause reductions in sorption capacity with concomitant increases in swelling.

For the Matrimid/CH_4 and CO_2 system we observe similar behavior, though with some differences. Plots of v_2 vs w_2 are given in Fig. 6. Again, model parameters to describe these data are listed in Table 2.

For Matrimid®/CH_4, similar to the Lexan®/CO_2 system, again we observe an independence of $v_{CH_4}^{SAT}$ with physical aging time, as well as strong drifts in $v_{CH_4}^{\infty}$, which increases from from ~2 to 9 cm^3/mol. When the Matrimid® sample is probed with CO_2, however, we observed highly unexpected results. While the $v_{CO_2}(w_2)$ curve is observed to shift upward for the aged sample, it does not converge in the higher concentration regime with the unaged sample (i.e. $v_{CO_2,\text{ unaged}}^{SAT} \neq v_{CO_2,\text{ aged}}^{SAT}$). This observation suggests that, for this system, even the most well packed regions of the matrix are affected by physical aging. Such a conclusion is actually not at all accounted for in the dual mode sorption model which idealizes the well packed regions of the glassy material behave as 'Henry's law' or equilibrium fluids. That the more aged sample undergoes dramatically more swelling is not yet currently well understood. It should be noted, however, that CO_2 induced plasticization of Matrimid® has been documented in the literature [16,23].

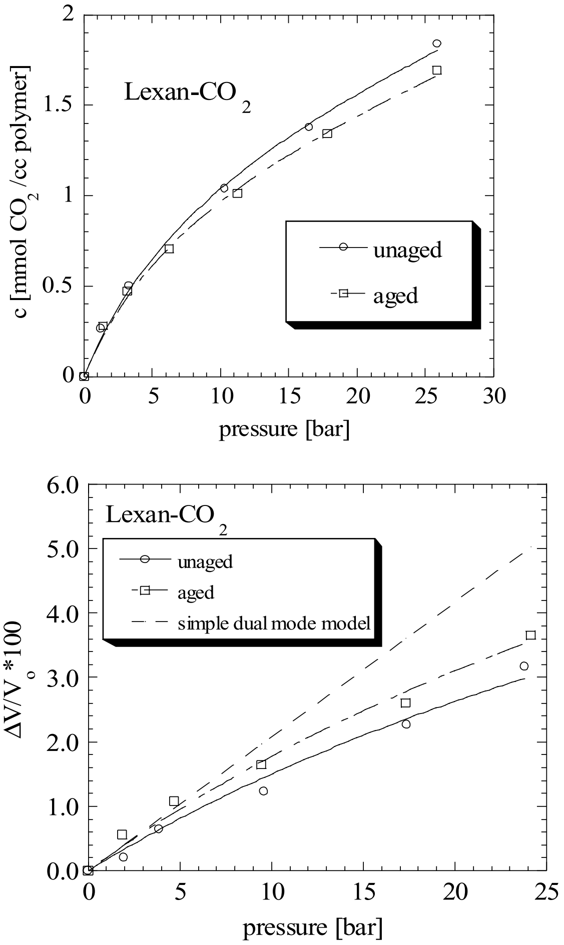

Fig. 4. (a) Effect of physical aging on Lexan® –CO_2 sorption and (b) dilation isotherms. The lines through the points were calculated by least squares fitting of sorption and dilation data to Eqs. (1) and (2b), and the associated parameters are summarized in Table 2.

Finally, for the Ultem®/CO_2 system, essentially no drifts in sorption or dilation isotherms were observed (Fig. 7), indicating the polymer penetrant environment is largely unaffected by physical aging. Of all the materials studied here, Ultem® has the highest density and it is not unexpected that such a densified structure is less susceptible to physical aging. Using Park's [22] method of calculating fractional free volume (FFV), indeed it is found that Ultem® has a remarkably lower computed FFV value of 0.07, compared to Matrimid® (0.17) and Lexan® (0.19). The fractional free volume is essentially the atomistic void fraction of a polymer material; thus the lower the FFV, the less amount of voids. With Ultem® possessing a significantly lower FFV, it is reasonable that dramatically less

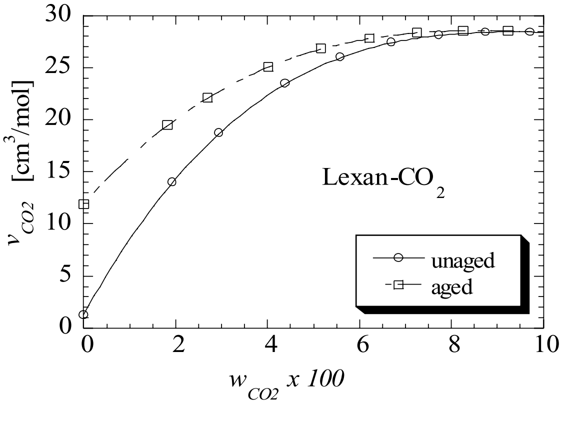

Fig. 5. CO_2 partial molar volume (computed from experimental sorption and dilation data) in aged and unaged samples of Lexan®.

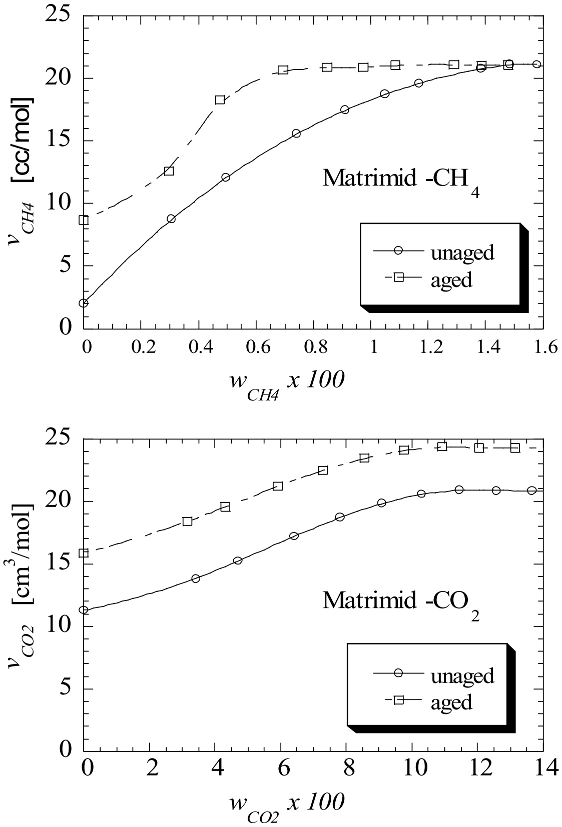

Fig. 6. Effect of physical aging on the partial molar volume of CH_4 and CO_2 in Matrimid®.

physical aging is observed compared to the other two materials. It is possible the small magnitude of physical aging as would be expected with a material with so little free volume precludes observation as tracked in this study with sorption and dilation measurements.

Alcoutlabi, et al. have conducted similar studies which elucidate the differences in aging of thermally-quenched vs swelling induced high free volume glasses [25]. The experiments discussed here involve only thermally quenched samples as probed by gas sorption, but based on Alcoutlabi's work, it is likely that different qualitative results would be obtained if the samples were quenched solely from the removal of a swelling agent or plasticizer. It is important to note also that the work discussed here considers only free volume based arguments to rationalize the observations from these experiments. Interpretations based on fictive temperature arguments could also be used. However, this discussion employs the free volume conceptual framework since it is well established for sorption and diffusion in glassy polymers [26].

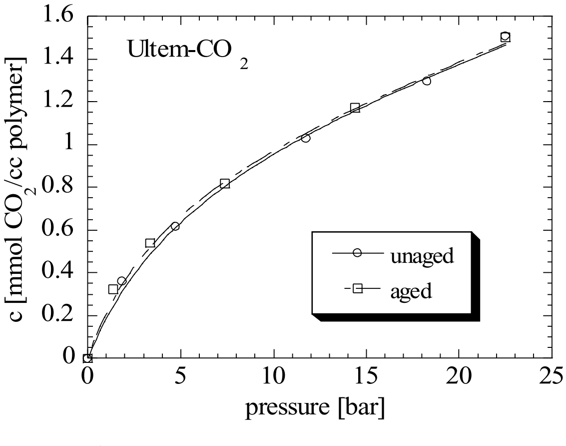

Fig. 7. Ultem® –CO_2 sorption isotherms for unaged and aged samples.

4.1. Evaluation of the dual mode models for sorption and dilation

The effect of physical aging on the dual mode parameters extracted from the sorption and dilation data are qualitatively reasonable and consistent with many of the aspects of this simple visualization of sorption of gases in glassy polymers. As mentioned earlier, the parameters were fit by non-linear least squares analysis of the respective experimental data. For the sorption data, trends of the extracted model parameters are consistent with their 'dual-mode' physical interpretation. In other words, the values of k_D remain essentially constant due to physical aging. Moreover, the extracted values for C'_H are lower for aged samples compared to unaged samples, declining from 0.74 to 0.58 mmol/cm^3 for Lexan®/CO_2 (a 21% decline), from 1.47 to 1.29 mmol/cm^3 for Matrimid®/CO_2 (a 12% decline) and from 0.82 to 0.80 mmol/cm^3 for Matrimid®/CH_4 (a 2.3% decline).

For the dilation data, as mentioned earlier, the simplest dual mode prediction (Eq. (2a)) yielded poor agreement with experimental data as can be seen in Fig. 4(b). It was found that Eq. (2a) actually over-predicts dilation in both the unaged and aged samples if the constant value of v^* characteristic for simple liquids is used, as suggested by Pope for the case of polycarbonate. Since polymer chain motion is more inhibited in glass polymers than in equilibrium materials, this approximation appears not to be valid, in general. In the glassy state, it is reasonable that even the well packed regions may contain some unrelaxed volume that effectively lowers the amount of penetrant induced dilation. We suggest that a more reasonable choice for v^* may be v^{SAT}, since at high concentrations, the penetrant must be accommodated in the most closely packed regions of the polymer matrix, which may vary somewhat from polymer glass to polymer glass. The following figure (Fig. 8) shows the improved model agreement with experimental data when v^{SAT} is used for v^*. The Kamiya *f* factors given in Table 2 were calculated using this method. All samples demonstrated increased swelling for physically aged samples as indicated by the uniform strong increases of *f* for all systems studied.

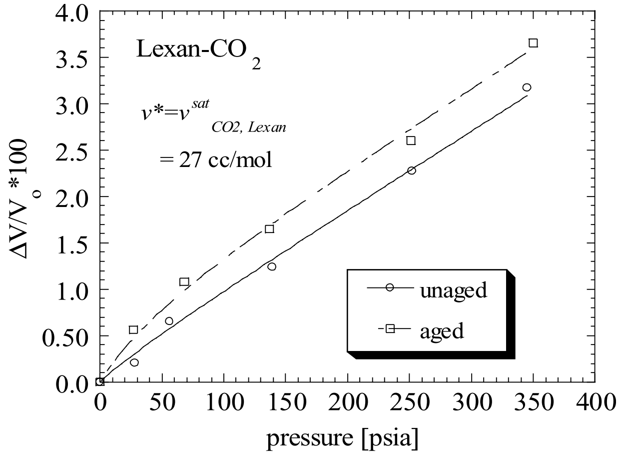

Fig. 8. Improved agreement of dual mode dilation model (lines) when $v^* = v_2^{\mathrm{SAT}}$.

5. Conclusions

We have experimentally observed reductions in sorptive capacity with concomitant increases in sorption-induced dilation of physically aged glassy polymer samples. This effect was observed in the polycarbonate (Lexan®) and polyimide (Matrimid®) sample, but not for the polyetherimide (Ultem®). The absence of observed effects of aging in the polyetherimide material is attributed to the exceptionally low fractional free volume. Physical aging effects are made more prominent when the partial molar volume is computed from the experimental sorption and dilation data. The trends in the partial molar volume due to physical aging based on empirical observations mimic those as predicted by hypothetical calculations from dual mode sorption and dilation models. These models reasonably describe the experimentally observed data; it should be noted, however, that the value for v^* required for the dilation model was taken from experimentally observed v_2^{SAT}, thus limiting the predictive ability of the model. Within the context of the dual mode understanding of the polymer-penetrant environment, however, we learn that the most well packed regions in these glassy polymers are much different from those in equilibrium fluids, as indicated by the strongly suppressed values of v_2^{SAT} compared to the gas molar volume in liquids and rubbery polymers.

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