Characterization of Physical Aging of Poly(methyl methacrylate) Powders by a Novel High Pressure Sorption Technique

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Synopsis

High pressure CO_2 sorption isotherms were measured at 35°C in previously dilated PMMA microspheres, which were subsequently aged in vacuum at 35°C. The dilation was induced by preswelling with high activity methanol vapor at 13°C, or alternatively with CO_2 at a pressure of 20 atm and a temperature of 5°C. The state of the samples during long-term aging was probed by rapid and intermittent determination of complete high pressure CO_2 isotherms. The dilation increased the sorption levels observed in the sorption experiments compared to those observed in untreated samples and, as the aging time increased, the sorption level progressively decreased. The isotherms under all conditions were well described by the dual mode sorption model. The observed time dependence of the isotherms was successfully described by confining all changes in sorption capacity to a systematic decay of the Langmuir capacity parameter. The equilibrium parameters of the model, however, were essentially unaffected by the preswelling and aging histories.

INTRODUCTION

Two recent papers[1,2] examined the effects of aging previously dilated glassy polymer powders in the presence and absence of various sorbed penetrants. Systematic drifts in the low-activity sorption behavior of preswollen poly(methyl methacrylate) (PMMA)[1] and preswollen polystyrene[2] were related to the type and amount of penetrant sorbed during the aging protocol.

These studies were motivated by the similar work of Berens[3–7] with PVC and Enscore et al.[8,9] with polystyrene. The studies constitute a systematic investigation of the low-pressure sorption aging behavior of several penetrant–preswollen polymer systems, including the following: CO_2, water, methanol, ethanol, and n-propanol in PMMA[1,10]; propane[2] and n-hexane[8,9] in polystyrene; and vinyl chloride monomer in PVC.[3–6] In all cases, preswelling the polymer, by exposure to a highly sorbing vapor followed by the rapid removal of the swelling penetrant, increased the apparent equilibrium sorption observed in subsequent low-activity sorption experiments. Moreover, cyclic sorption/desorption experiments, with alternating periods of exposure to penetrant and vacuum, demonstrated that the sorption levels of the

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preswollen polymers declined during vacuum aging. Presumably, the increased sorption levels in the preswollen glass are due to an increase in the excess volume of the polymer caused by the combined preswelling and subsequent rapid removal of the swelling penetrant. The dilated polymer slowly densifies during vacuum aging, and this protracted drift toward equilibrium, which is characteristic of the glassy state, also results in a systematic decrease in the sorption capacity.[1]

At long vacuum aging times, the sorption levels in the preswollen polymer appeared to approach the levels observed in the as-received polymer contacted for a long time with the probing penetrant. Even though the approach to equilibrium is extremely protracted, the preswollen samples and the as-received samples apparently relax toward the same, true equilibrium for the respective two-component two-phase system.[1-6,8,9]

The presence of penetrant within the polymer during aging has been shown to affect the sorption aging behavior.[1,2,8,9] In the large majority of cases, the presence of low concentrations of penetrant within the polymer during aging appears to arrest the relaxations in sorption capacity that occur over the same time scale in the absence of penetrant. Presumably, penetrant molecules sorbed in out-of-equilibrium, molecular scale gaps between segments of polymer molecules in the glassy state restrict or retard the chain motions which would otherwise lead to consolidative relaxation[1] and thereby significantly slow the kinetics of the approach to equilibrium.

The sorption behavior of preswollen polymers was analyzed in terms of the dual mode sorption model since the wealth of information to date indicates that all vapors at low activities and gases at pressures up to approximately 30 atm sorb into polymeric glasses by a mechanism which is well described the model. According to the dual mode model, the total sorption in a glassy polymer, C, is given by[11]

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

where k_D is the Henry's law constant, C_H' is the Langmuir capacity parameter, b is the Langmuir affinity parameter, and p is the penetrant pressure. The dual mode model assumes that the penetrant species exist within the glass in two subtly different populations that are in local equilibrium with each other throughout the polymer.[11] The Henry's law mode, which is represented by the first term in eq. (1), is assumed to reflect true dissolution. The sorption process in this mode is presumed to be identical in nature to the solution process for low concentrations of gases and vapors in both low molecular weight liquids and rubbery polymers. The second term in eq. (1) represents the Langmuir mode and is considered to be excess sorption arising from uptake into preexisting microvoids that constitute the nonequilibrium, excess volume of the glass.[11] The penetrant sorbed in the Langmuir mode is, therefore, assumed to be the amount by which the actual amount sorbed exceeds the amount of penetrant which would sorb into a densified, equilibrium glassy polymer at the same temperature and penetrant pressure.

The parameters b and k_D in the model are both equilibrium constants.[11] The equilibrium constant between penetrant sorbed in the Henry's law mode

and penetrant in the gas phase is given by k_D, and the equilibrium constant between penetrant sorbed in the Langmuir mode and penetrant in the gas phase is given by b. These equilibrium constants should, in principle, be minimally affected by the history of the polymer sample.

The parameter C'_H represents the total asymptotic capacity for sorption in the Langmuir mode, and is believed to depend upon the distribution and total amount of excess volume of the polymer and, in turn, the history of the polymer sample.[11] Thus, according to the dual mode model, the history dependence of the sorption behavior should reside primarily in the Langmuir capacity parameter. An explicit ralationship between the Langmuir capacity parameter and the excess volume of the glass which has been observed by Koros, Paul, and co-workers[11-14] is given by

$$C'_H = \frac{V_g - V_1}{V_g} \frac{1}{v^*} \qquad (2)$$

where V_g is the actual specific volume of the glass, V_1 is the specific volume of a hypothetical equilibrium glass at the temperature of interest ($V_g - V_1$ is, therefore, the excess volume of the glass), and v^* is the effective molar volume associated with penetrant molecules sorbed in the Langmuir mode. This relationship has been quantitatively verified for CO_2 at various temperatures in poly(ethylene terephthalate), poly(benzyl methacrylate), poly(phenyl methacrylate), polyacrylonitrile, polycarbonate, poly(ethyl methacrylate), and poly(methyl methacrylate).[15]

History-dependent, high-pressure sorption behavior was reported by Chan and Paul,[13] who measured time-dependent high-pressure CO_2 sorption isotherms in annealed polycarbonate. In their experiments, the time dependence was induced by sub-T_g annealing, rather than by a preswelling or conditioning treatment. Annealing near the T_g resulted in sorption levels which decreased as the annealing time increased. Consistent with the dual mode model, they were able to describe the relaxations observed by allowing C'_H to be a function of annealing time, but maintaining b and k_D constant.

In general, the extent of sorption and rate of transport of a penetrant also are affected by the previous sorption history of the sample,[14-19] and the sorption isotherm obtained for the first exposure of a penetrant to a glassy polymer is significantly different than those obtained for subsequent exposures.[14] As these phenomena were often not of interest in the previous studies, experimental procedures were developed to minimize these effects.[14,18-20] Recently, however, these "conditioning" effects have been examined by Wonders and Paul,[14] Stern and Kulkarni,[21] Sanders,[16] Fleming and Koros,[22] and Jordan et al.[23]

Wonders and Paul[14] studied CO_2 sorption in polycarbonate samples which had previously been exposed to 0, 20, 40, and 60 atm of CO_2. The isotherms were measured at 35°C and in the pressure range of 0–20 atm. Consistent with earlier observations, they found that the isotherms were stable and reproducible for the course of the experiment, as long as the sample was never exposed to a pressure greater than its conditioning pressure.[14] Furthermore,

they observed a substantial increase, with conditioning pressure, in CO_2 sorption level at a given pressure. They attributed the increase in sorption level to an increase in C_H' due to the conditioning step. They also obtained density data for the conditioned step. They also obtained density data for the conditioned samples, and found that the changes in C_H' were well described by eq. (2). In addition, Wonders and Paul demonstrated that their results were entirely consistent with an extension of ideas proposed by Chan and Paul[13] for CO_2 sorption in samples of polycarbonate densified by annealing.

Stern and Kulkarni[21] measured CO_2 and CH_4 sorption in a modified cellulose acetate reverse osmosis membrane. They found that preexposure to 35 atm of CO_2 increased the subsequent sorption of CO_2 and CH_4. In the case of CH_4 the increase was as large as 100%. Similar results were reported by Sanders,[16] who studied the pure and mixed gas sorption of CO_2 and CH_4 in PMMA over the pressure range from 0 to 20 atm. He found that the CH_4 sorption levels were as much as 40% higher for a sample that had been exposed to 20 atm of CO_2 immediately before the CH_4 sorption experiment.

Fleming and Koros[22] measured CO_2 sorption and desorption isotherms in polycarbonate over the pressure range from 0 to 900 psia and reported large hysteresis in the isotherms determined. Jordan et al.[23] have also reported conditioning effects on high pressure permeability. They measured the pure and mixed gas permeation of CO_2 and CH_4 through polycarbonate film, and found that conditioning the film by exposure to 900 psia of CO_2 increased the subsequent CO_2 and CH_4 permeabilities. In addition, they reported time-dependent permeabilities induced by the conditioning treatment.

These results indicate that a highly sorbing gas may affect the polymer in a manner entirely analogous to, though possibly to a lesser extent than, the preswelling treatment used in the low pressure vapor experiments described earlier, and that the increases and time dependence noted in the low pressure sorption capacity of preswollen polymers would also be evident in the high pressure sorption behavior. None of these studies, however, has dealt specifically with time dependence of high pressure sorption induced by a preswelling or conditioning treatment. The sorption aging results for preswollen polymer powders described above were all obtained in subatmospheric sorption experiments which were typically limited to observations of the drift of a single total concentration of sorbed penetrant with aging time. In these experiments, there was no means for explicit separation of the effects of dilation on each of the two sorption modes. Thus, to date there has been no direct experimental study designed to determine whether the consolidative relaxations in sorption capacity, which follow dilation, are confined to changes in the Langmuir capacity with no concomitant variation in the equilibrium parameters b and k_D. No systematic study of penetrant-induced time-dependent high-pressure sorption has been conducted.

The purpose of this work was to investigate the time dependence of rapidly determined high pressure CO_2 sorption isotherms in previously dilated PMMA. The aging resulting from penetrant-induced dilation of glassy polymers was studied by measuring high pressure CO_2 sorption in preswollen glassy PMMA powders as a function of vacuum aging time. The results were analyzed in terms of the dual model sorption model, and the behavior of the individual isotherm parameters as a function of aging time was determined.

Suspension-polymerized PMMA microspheres were used in this work. Microspheres were used because the extremely small characteristic dimension of the primary particle permits a rapid approach to diffusive equilibrium.[24] The preswelling penetrant can, therefore, be desorbed from microspheres in a time scale which is much shorter than the time scale of the consolidative relaxations initiated by the removal of the penetrant, which take place over a period of several days or weeks. In addition, the rapid approach to diffusive equilibrium also permits the determination of entire CO_2 sorption isotherms in a few hours. The sample is, therefore, exposed to the penetrant probe for a relatively small fraction of the total aging time.

EXPERIMENTAL

Polymer Samples

The PMMA powder used in this work was suspension polymerized at North Carolina State University using a recipe provided by The B.F. Goodrich Co., Brecksville, OH. PMMA from two different lots, arbitrarily designated as PMMAI and PMMAII, were used in this study. PMMAI was prepared for a previous study of enthalpy relaxations in PMMA[25] and was used in the first set of experiments with methanol-preswollen samples. The remaining experiments were performed with PMMAII, which was prepared especially for this study. The T_g's of both samples, as determined from differential scanning calorimetry, were approximately 124°C. A comparison of the particle sizes and number average molecular weights for the two samples is given in Table I. The molecular weights were determined from gel permeation chromatography and the particle diameters were determined from scanning electron microscopy. Scanning electron microscopy also revealed that the microspheres are grouped into secondary particles having an average dimension of approximately 20 μ. This clustering is consistent with earlier observations and Berens[7] has shown that the resistance to mass transfer in the vapor spaces between primary particles within a secondary particle is negligible.

Penetrants

Certified ACS grade methanol from the Fisher Scientific Co. was used as a preswelling agent. The methanol was subjected to two freeze–thaw cycles before use to remove dissolved gases. Coleman grade (99.99% pure) carbon dioxide from M. G. Scientific Gases was used as both a preswelling agent and a probe. CO_2 is a supercritical gas at 35°C and its sorption behavior in polymers has been extensively studied.[10,11,13-16,20-23,26-31]

TABLE I
Particle Size and Number Average Molecular Weight for Polymerization Lots I and II

	PMMAI	PMMAII
Weight average primary particle diameter (μ)	0.550	0.656
Number average MW	386,000	597,000

Sorption Measurements

Sorption measurements were obtained using the constant volume, or pressure decay method, which has been widely used for high pressure gas sorption measurements in glassy polymers.[11,13-16,20,26] The equipment constructed for this study and the related experimental technique are very similar to those used by others[26,32,33] and will not be described here, except for details which are unique to this work.

The sorption cell was designed with two sample-containing volumes attached to one metering reservoir. This allowed for two samples to be preswollen and aged simultaneously but probed at different times.

Polymer films have normally been used with the pressure decay method.[11,13-16,20,26,33] The PMMA used here, however, was in powder form and, to prevent dispersion of the powder, it was necessary to enclose it in a sample container before placing it in the sorption cell. The sample containers consisted of two Nupro 8F-P4-7 sintered metal filter elements, which were pressed into opposite sides of a lead washer, thereby creating a hollow cylinder. Polymer was loaded into the container through a 5/16 in. hole, which was drilled through the end of one of the filters before the container was assembled. Once the container was filled with polymer, a lead plug was pressed into the hole to seal it. The entire container was then placed in the sorption cell. The sintered metal filters contain the powder, but offer negligible resistance to the flow of gas.

In order to obtain accurate sorption measurements, precise knowledge of the gas phase volume above the sample is required. This value is usually obtained from a calibration procedure consisting of a series of expansions from the metering volume into the sample volume.[33] Since the sample containers exclude volume from the sample side gas phase, it was necessary to perform these calibrations with the empty sample containers in place in the sample volume of the sorption cell. Following the calibration, the sample containers were removed from the cell, filled with approximately 2 g of polymer, and then returned to the sample volumes of the cell.

Sorption measurements were performed at 35°C over the pressure range of 0–20 atm. Unless otherwise noted, the isotherms were determined with 30-minute intervals between pressure increases. This protocol will be referred to here as short-term measurements. These arbitrary experimental conditions were developed to ensure that the time required for the measurement of an isotherm was small compared to the time required for the polymer to relax, which was on the order of 10,000 min at 35°C.[29] Since the half-time for Fickian sorption in this system, based upon a CO_2 diffusivity of 1×10^{-8} cm^2/s, is well under 1 min,[24,29] the sorption levels measured in the short-term experiments are highly representative of the nonequilibrium state of the sample. In fact, kinetic data for the long-term CO_2 sorption in PMMAI indicate that the CO_2 sorption level achieved after 30 min of exposure was approximately 94–97% of the sorption level achieved after 2 days.

Preswelling and Aging Procedure

Preswollen samples were prepared by two methods. The first sample, PMMAI, was preswollen by exposure to 0.80 activity methanol at 13°C for 14

days followed by rapid removal of the methanol. Samples of PMMAII were preswollen by exposure to 20 atm of CO_2 at 5°C for 7 days followed by rapid removal of the penetrant. The sorption level achieved in the two preswelling procedures was approximately 20 wt% for methanol and 15 wt% [or 90 cc (STP)/(cc polymer)] for CO_2. In both cases, the preswelling was performed with the PMMA samples in the sorption cell and with the entire cell placed in a water bath thermostatted at the preswelling temperature. Following preswelling, the preswelling penetrant was rapidly desorbed from the polymer and the sorption cell was transferred to the sorption water bath. The samples were maintained under vacuum until the pressure transducer readings stabilized, which required approximately 2–3 h, and the sorption measurements were then begun.

Aging proceeded with the samples in place in the cell and the cell in the water bath. During aging, the samples were maintained under a vacuum of approximately 5×10^{-3} mm Hg.

RESULTS AND DISCUSSION

Sorption in Unconditioned Samples

The data for short- and long-term sorption of CO_2 in unconditioned PMMA at 35°C are presented in Figure 1. As noted above, the short-term data were measured with 30-min intervals between pressure increases, and the sorption levels reported are those calculated at the end of each interval. The long-term measurements represent apparent equilibrium values and, in general, several thousand minutes elapsed between pressure increases.

The short-term measurements were performed with samples of PMMAII and the long-term measurements were performed with samples of PMMAI. As expected the sorption levels obtained in the short-term experiments are
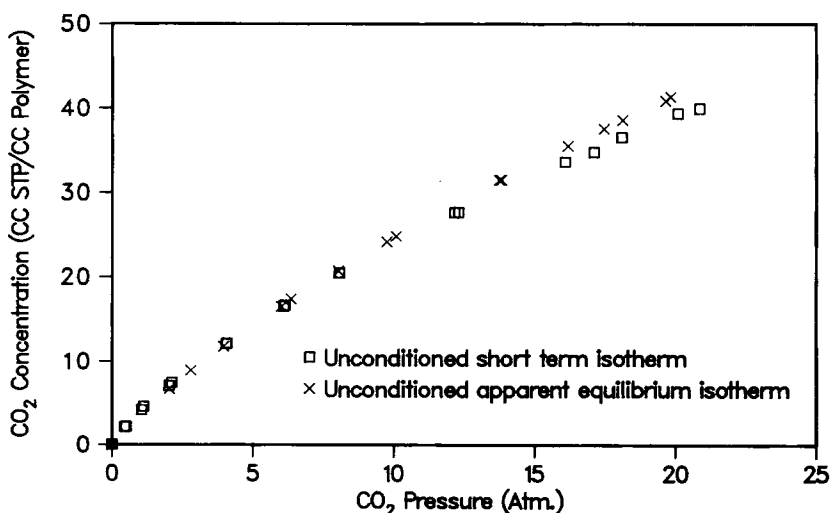

Fig. 1.   Unconditioned apparent equilibrium (×) and short term sorption (□) isotherms for the initial exposure of CO_2 to PMMA at 35°C.

slightly lower than the apparent equilibrium sorption levels. The optimal dual mode parameters for both isotherms were determined using a SAS, nonlinear, Marquardt regression subroutine that minimizes the sum of the squares of the residuals in the regression analysis.[34, 35] The resulting parameters for the apparent equilibrium isotherm are $k_D = 1.35$ cc (STP)/(cc polymer atm), $b = 0.109$ atm^{-1}, and C'_H-21.26 cc (STP)/(cc polymer), and the dual mode parameters for the short-term isotherm are $k_D = 1.27$ cc (STP)/(cc polymer atm), $b = 0.164$ atm^{-1}, and $C'_H = 17.96$ cc (STP)/(cc polymer). The differences in the isotherms and isotherm parameters reflect differences in both the original samples and the experimental protocol (e.g., short vs. long term measurements).

The sorption levels observed in the present study are noticeably greater than those reported by others.[22, 36, 37] The difference does not appear to be due to surface adsorption on the greater surface area of the microsphere samples. Assuming monolayer adsorption and an area of 30 Å^2 per CO_2 molecule, surface adsorption on the polymer powder would contribute only 1.4 cc (STP)/(cc polymer) to the total sorption observed. Moreover, apparent equilibrium CO_2 sorption data determined with film cast from the PMMA used in this work are practically identical to the data for sorption in microsphere samples. This indicates that adsorption of CO_2 on the surface of the powders is not large enough to account for the differences in the sorption level observed in the present study. Moreover, the results of preliminary measurements with Kapton polyimide using the same equipment and techniques were very similar to those reported previously.[38, 39] The discrepancy between the results of the previous studies and those of the present study is, therefore, most probably due to variations in both the PMMA samples used and the sample preparation techniques.

Sorption in PMMA Preswollen with Methanol

Samples of PMMAI were preswollen with methanol as described in the experimental section, and short-term CO_2 sorption measurements at 35°C were performed with the samples at various times after the preswelling treatment. The rapid removal of the preswelling penetrant results in relaxations in the polymer which persist long after the penetrant has been desorbed. Representative sorption isotherms for these methanol-preswollen samples, with aging times at the beginning of the sorption run of 170, 1190, and 28,920 min, are presented in Figure 2. As expected, the sorption level at a given pressure decreases as the time after preswelling increases. The decrement in sorption capacity with aging, however, is relatively small and the major portion of the decrease occurs early in the aging. These results are qualitatively consistent with the previous low-pressure experiments in preswollen polymers.[1-10] The optimal dual mode parameters for each isotherm were determined using the SAS regression technique, and the results for b and k_D are plotted against aging time in Figure 3.

As discussed in the introduction, k_D and b are equilibrium parameters and should be unaffected by the preswelling treatment and, therefore, should also be independent of aging time. The individual isotherm parameters presented in Figure 3 provide support for this a priori assumption. If a nonlinear fit is
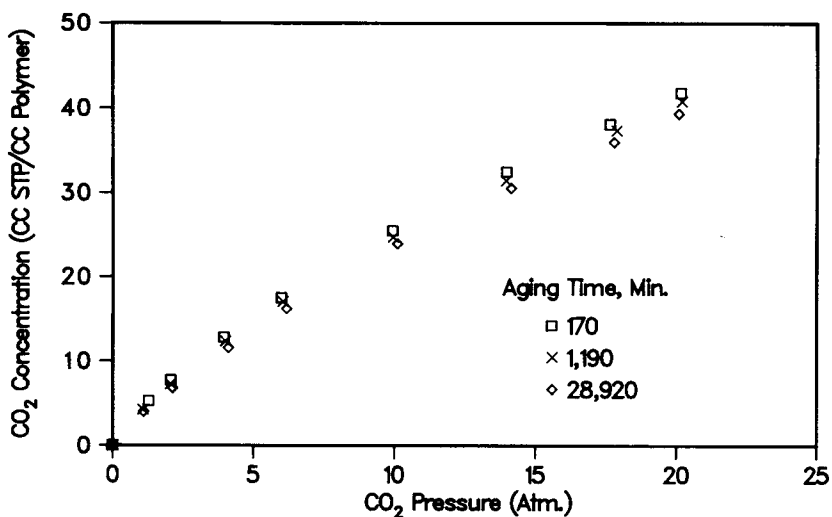
Fig. 2. Representative isotherms for short term CO_2 sorption in methanol-preswollen PMMA at 35°C. Aging time (min): (□) 170; (×) 1190; (◇) 28,920.
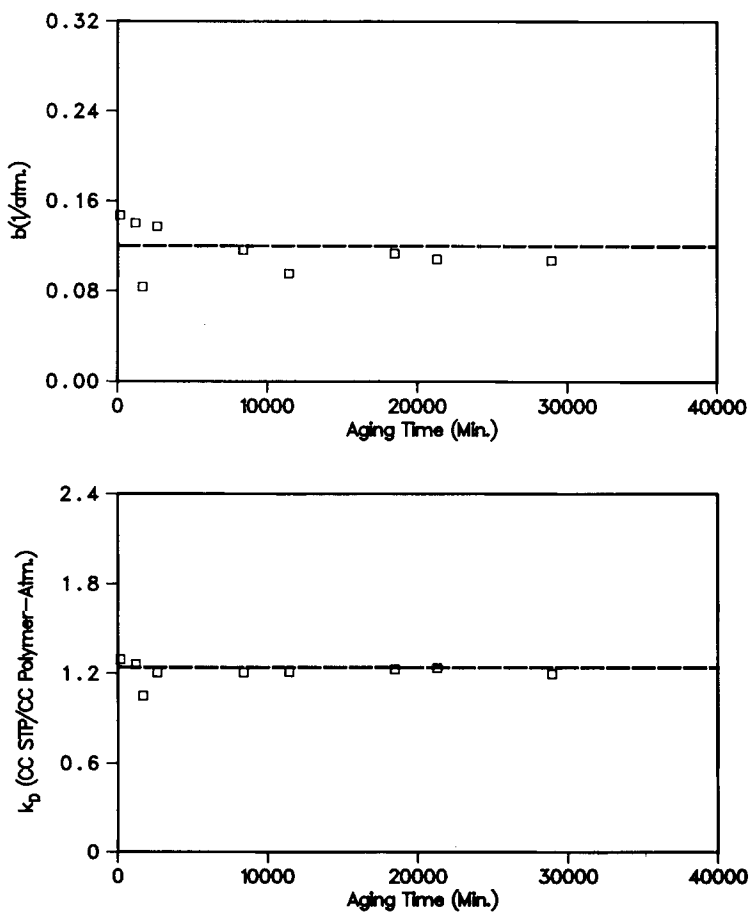

Fig. 3. Langmuir affinity parameters and Henry's law constants for CO_2 sorption in methanol-preswollen PMMA at 35°C.
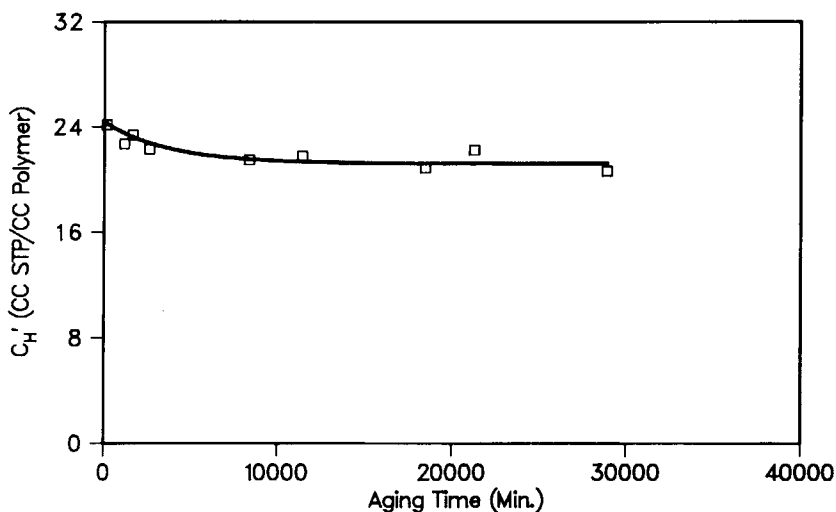
Fig. 4.   Langmuir capacity parameters for CO_2 sorption in methanol-preswollen PMMA at 35°C.

performed on all the data, allowing C_H' to vary between isotherms, but requiring k_D and b to be independent of aging time, then the values of k_D and b obtained are represented by the dashed lines in Figure 3. The values represented by the dashed lines are, therefore, the parameter values that best described all the data, assuming that the sorption behavior can be modeled by b and k_D values which are independent of aging time. This data analysis technique is very similar to the technique used by Chan and Paul.[13] The only difference is Chan and Paul fixed the values of b and k_D before performing the regression to determine C_H', while, in the analysis in this work, the optimal values of b and k_D were determined at the same time as the C_H' values.

The values obtained for k_D and b using this technique are 1.24 cc (STP)/ cc polymer atm) and 0.120 atm^{-1}, respectively. These quantities are very close to the arithmetic numerical averages of the estimates determined for the individual isotherms. Furthermore, in all cases except for the isotherm at 1670 min of aging, these results are within the approximate asymptotic 95% confidence intervals[34,35] for the individual isotherm parameters provided by the SAS regression routine. The a priori assumption that b and k_D are independent of aging time is, therefore, also substantiated by this analysis.

If k_D and b are in fact constant, then the time dependence of the isotherms must result in time dependence of C_H'. The results obtained for C_H' under these conditions are plotted against aging time in Figure 4. The Langmuir capacity parameter of the preswollen samples decreases monotonically with time from 24.11 to 20.62 cc (STP)/(cc polymer). The majority of the decrease occurs in the first 10,000 min (approximately 1 week), and the Langmuir capacity parameter appears to approach an asymptote at long times. The Langmuir capacity parameter is assumed to be directly related to the excess volume of the polymer as given by eq. (2).[11,12] This variation of the Langmuir capacity parameter with sample history is, therefore, consistent with Berens'

very early and cleverly intuitive hypothesis that the sorption measurements in preswollen polymers trace the relaxation of volume introduced into the polymer by the preswelling treatment.[5]

Relaxation phenomena in glassy polymers are generally not simple first-order exponential responses, and a significant portion of the decrease in sorption capacity probably occurs in the first few minutes following preswelling.[1,9,10,40,41] At relatively long aging times, however, Connelly et al.[1] and Enscore et al.[9] reported that the decrease in *total* sorption capacity of the preswollen samples at a given penetrant activity could be described by a first-order exponential decay. Similarly, the solid line in Figure 4 was drawn using an arbitrary first-order relaxation model for C_H'. The sorption data were used to fit eq. (1) with b and k_D replaced by the optimal values reported above, and C_H' given by

$$C_H' = C_{H\infty}' + (C_{H0}' - C_{H\infty}') \exp(-k_c t) \tag{3}$$

where C_H' is the Langmuir capacity parameter for the glass at apparent equilibrium, or very long times since preswelling, k_{H0}' is the Langmuir capacity parameter for the glass immediately following preswelling, k_c is a first-order relaxation constant, and t is the time since preswelling. The values of C_{H0}', $C_{H\infty}'$, and k_c determined from the regression are 24.32 cc (STP)/ (cc polymer), 21.18 cc (STP)/(cc polymer), and 2.69×10^{-4} min^{-1}, respectively. [If b and k_D were also optimized in the regression using eq. (3), the new values were found to be within 2% of those from the earlier fit, and the values of C_{H0}', $C_{H\infty}'$, and k_c were also relatively unchanged.] Equation (3) provides a fairly good fit to the data shown in Figure 4, and this implies the anticipated rapid, short-time relaxations in sorption capacity occur in a time scale which is too short to be observed by this technique.
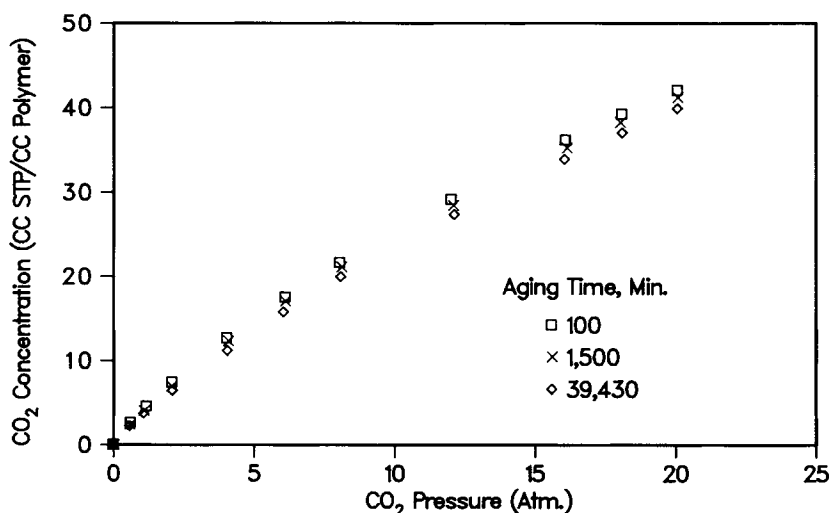

Fig. 5. Representative isotherms for short term CO_2 sorption in CO_2-preswollen PMMA at 35°C. Aging time (min): (□) 100; (×) 1500; (◇) 39,430.
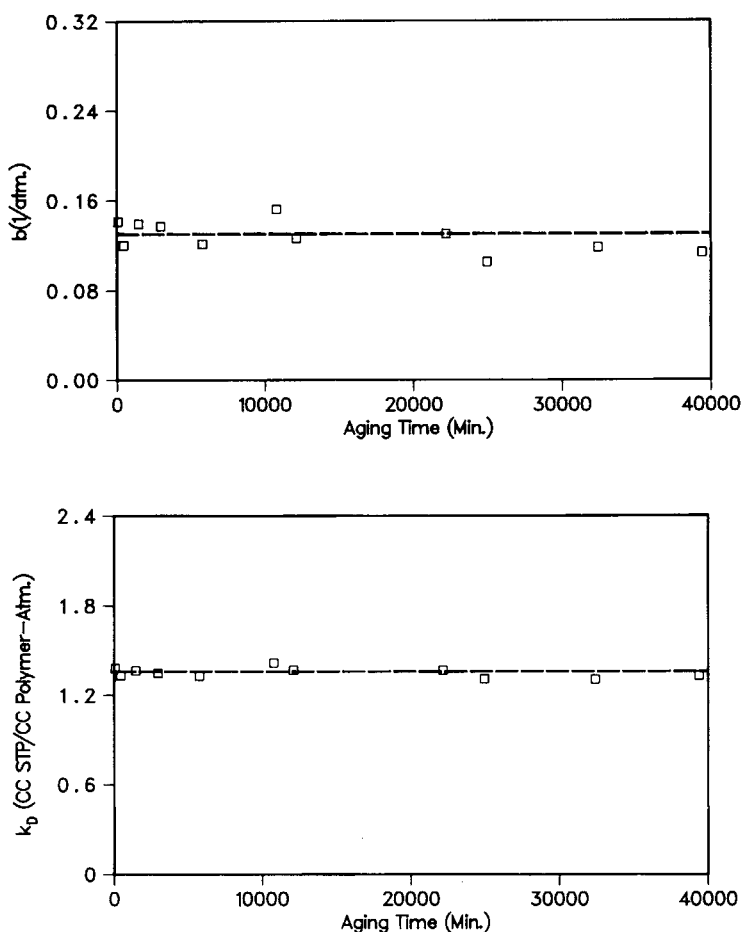
Fig. 6.   Langmuir affinity parameters and Henry's law constants for CO_2 sorption in CO_2-preswollen PMMA at 35°C.

CO_2 Sorption in PMMA Preswollen with CO_2

In an attempt to investigate the generality of the high pressure CO_2 sorption behavior of preswollen PMMA, samples of PMMAII were preswollen by exposure to 20 atm of CO_2 at 5°C. This particular treatment is termed preswelling instead of conditioning, because the sorption level reached in the polymer during the treatment is much greater than the sorption level achieved during the subsequent probing experiments. Moreover, the effect of the CO_2 preswelling on the subsequent sorption behavior of CO_2 at 35°C is almost identical to the effect of the methanol preswelling treatment. Representative sorption isotherms of the short-term sorption of CO_2 at 35°C in samples of CO_2-preswollen PMMAII are presented in Figure 5. The preswollen samples were aged in vacuum between sorption trials, and the isotherms presented in Figure 5 were determined at aging times of 100, 1500, and 39,430 min.

The values obtained for k_D and b for the individual isotherms are presented in Figure 6 and the dashed lines again represent the values obtained for these parameters corresponding to the single value associated with the best fit
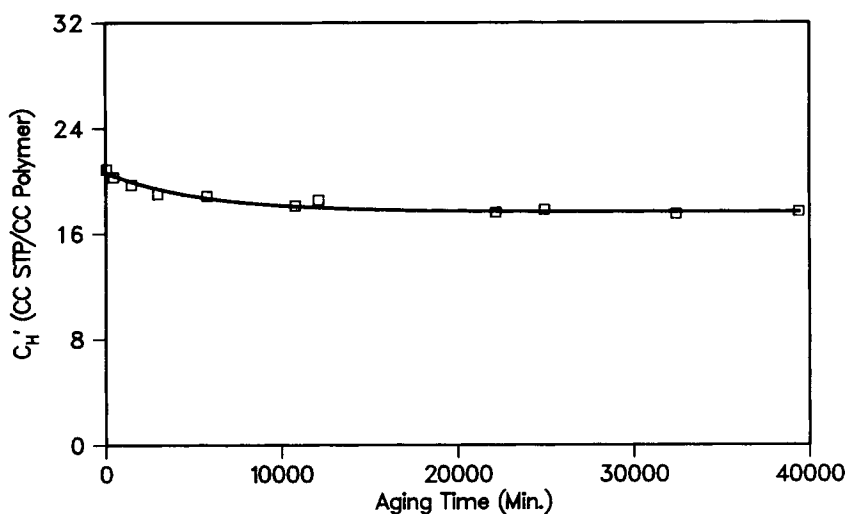
Fig. 7. Langmuir capacity parameters for CO_2 sorption in CO_2-preswollen PMMA at 35°C.

of all runs. The corresponding values of C_H' are presented in Figure 7. The optimal values determined from the fit to all the data for k_D and b are 1.36 cc (STP)/(cc polymer atm) and 0.130 atm^{-1}, respectively, and are in fair agreement with those for the methanol-preswollen samples. Once again, the values of k_D and b are very close to the arithmetic averages of the values determined for the individual isotherms. In addition, the results for k_D and b are within the approximate asymptotic 95% confidence intervals for all the individual isotherm parameters. The values determined for the C_H''s for these samples decrease from 20.89 to 17.49 cc (STP)/(cc polymer). The first-order relaxation model for these data is also shown as the solid line in Figure 7. The values of C_{H0}', $C_{H\infty}'$, and k_c determined for the CO_2-preswollen samples are 20.68 cc (STP)/(cc polymer), 17.64 cc (STP)/(cc polymer), and 1.80×10^{-4} min^{-1}, respectively. In this case, the optimal values of b and k_D determined by the two methods agree within 0.5%.

In the previous low-pressure sorption aging experiments, the apparent equilibrium sorption levels in the preswollen polymer at long aging times appeared to approach the apparent equlibrium sorption levels for as-received samples.[1-10] A comparison between the short-term isotherm for CO_2-preswollen PMMA determined at 39,430 min of aging time and the short-term, initial exposure isotherm of Figure 1 is presented in Figure 8. Even though the isotherms presented here are for short term rather than apparent equilibrium sorption, the two isotherms are very similar. This indicates that the preswollen samples are relaxing towards a state similar to the untreated samples, which is not surprising since the untreated samples were stored under air or vacuum at room temperature for several months prior to use. The untreated samples, therefore, were also asymptotically approaching equilibrium. The small difference in the isotherms is presumably due to subtle differences in the isotherms is presumably due to subtle differences in the distribution and amount of excess volume present in the two samples due to their quite different sorption histories.
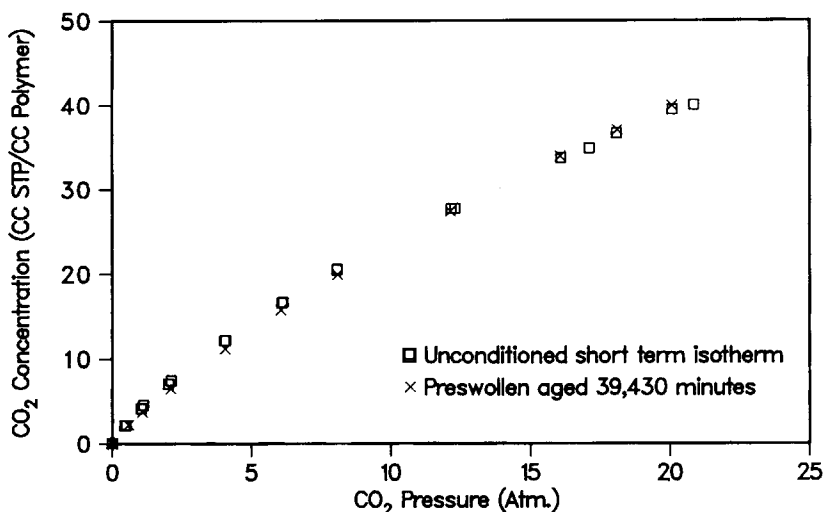
Fig. 8. Comparison of the unconditioned short term sorption isotherms ($\square$) for CO_2 in CO_2-preswollen PMMA at 39,430 min ($\times$) after preswelling and for the initial exposure of CO_2 in virgin PMMA at 35°C.

Comparison of the Results of the Two Preswelling Treatments

The effects of CO_2 preswelling and methanol preswelling are substantively and qualitatively similar. The differences in the magnitude of the sorption levels and dual mode parameters between the two samples is, at least in part, due to the differences in the original polymer samples and preswelling treatments. The dual mode parameters obtained for the CO_2-preswollen samples also show less scatter because there were 10 points per isotherm, compared to only eight points per isotherm in the methanol-preswollen samples.

The long-time aging constants of 2.69×10^{-4} and 1.8×10^{-4} min^{-1} for the two preswelling treatments are in fair agreement, and compare favorably with those reported by Connelly et al.[1] of approximately $1-2 \times 10^{-4}$ min^{-1} for the low pressure sorption of methanol, ethanol, n-propanol, and CO_2 in similar samples of preswollen PMMA. The difference in the aging constants determined for the two preswelling treatments appears to be due to variations in the length of the experiments and deviations of the response from a simple exponential decay, rather than a difference in the actual rate of consolidation of the two samples. If eq. (3) is used to fit the aging data of the CO_2-preswollen sample with aging times of less than 30,000 min (which was the duration of the experiments with the methanol-preswollen samples), the aging constant determined is 2.30×10^{-4} min^{-1} and the other parameters ($C'_{H0}, C'_{H\infty}$) are relatively unchanged. This aging constant is in good agreement with the value of 2.69×10^{-4} min^{-1} determined for the methanol-preswollen samples. Thus, it appears that the two preswelling treatments have approximately the same effect on the subsequent CO_2 sorption behavior.

The higher aging constant obtained for the initial portion of the response for the CO_2-preswollen samples indicates that, as expected, the data deviate from a simple first-order decay in the direction of more rapid relaxations at short times. This was also true in the data of Connelly et al.[1] and Fechter et al.[10]

SUMMARY

The time-dependent, high-pressure sorption of CO_2 in previously dilated PMMA powders can be phenomenologically separated into a true equilibrium contribution, which is essentially independent of the sample history, and excess sorption due to the nonequilibrium nature of the glass. Specifically, the entire time dependence of the isotherms following dilation can be accounted for by allowing only one of the dual mode model parameters, the Langmuir capacity parameter, to vary with time. The Langmuir capacity parameter is related to the excess volume of the glass, and, as such, reflects the effect of sample history on the nonequilibrium state of the polymer. The other model parameters, however, are equilibrium constants and are unaffected by the preswelling treatment or subsequent vacuum aging.

The results of this study are qualitatively consistent with previous low pressure sorption measurements in preswollen glasses, and with the data on history effects in high pressure gas sorption measurements. This study, therefore, offers further indirect evidence that the deviation from Henry's law behavior for low activity gases and vapors in glassy polymers arises due to sorption in excess volume of the glass. Moreover, the results are consistent with Berens' earlier hypothesis that the preswelling dilation increases the sorption level observed in subsequent sorption experiments by increasing the volume of the polymer, and that the decrease in sorption capacity which occurs during vacuum aging is due to consolidative relaxations in the volume of the glass.

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