Residual Porosity in Polymeric Latex Films

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Synopsis

Solubility and diffusivity measurements of a probe gas (CO_2), which has an inherently low solubility in the polymer, have been used to characterize residual porosity in polymeric latex films. Sorption isotherms resembling those of a glassy polymer were obtained, even though the glass transition temperature of the polymer was 1°C, about 30°C below the experimental temperature. Solvent cast films of the same polymer exhibited much lower solubilities, and followed the expected Henry's law behavior. CO_2 solubility and diffusivity were found to decrease with aging time for the latex films, but did not quite reach the values of the solvent cast films, even after 75 days at room temperature. The sorption data could be described by the dual-mode sorption model, which is commonly employed in the analysis of glassy polymer sorption isotherms. Estimates of the amount of porosity were made from the sorption data, and values ranging from 0.6–0.03% were obtained for latex films aged from 62 h to 75 days, respectively. Our results suggest that permeability differences noted by others for latex and solvent cast films of the same polymer are due to the substantial solubility differences for low-solubility penetrants in these two types of films.

INTRODUCTION

Water-based latex paints now comprise more than 85% of all coatings currently used to protect residential housing structures.[1] A continuing problem with latex-based coatings is their high permeability (compared with solvent-based coatings) toward water vapor and other potentially harmful pollutant gases. Some studies have shown that substrates protected with latex coatings are more susceptible to deterioration than those protected with solvent-based coatings, when exposed to corrosive gases and vapors.[2] Chainey et al.[3] have measured permeabilities of helium in films cast from homopolymer latex suspensions, and in solvent-cast films of the same polymers. The permeability of the latex films decreased with time, but never reached the values found for the solvent-cast films, even for polymers that were well above their glass transition temperatures (T_g) and were aged for as long as 30 days.

Vanderhoff and others[4-8] have studied the process of film formation from a precursor latex dispersion. Several stages of drying have been identified, and the importance of surface tension forces and capillary forces during water removal have been cited. These investigations have dealt primarily with film formation up to the point where the film is dry, continuous, and transparent. However, Voyutskii[9] points out that film properties continue to change with time after drying to the transparent stage. This further gradual coalescence is attributed to autohesion; the mutual interdiffusion of polymer chain ends across the latex particle interfaces.

The above observations are highly suggestive of the presence of residual porosity in latex-cast films. A pore network could account for increased permeability and gradual aging effects noted for latex films that are already dry and transparent. The pores or voids must be smaller than the wavelength of light, and could be as small as several nanometers. The pores may be uniformly distributed, or may exist in clusters or channels. The nature of this porosity must be dependent on various film-forming conditions such as temperature, drying time, humidity, presence and type of coalescing solvents, and initial latex particle size.

Elementary sintering theory provides another way to model the evolution of such porosity, and was used to a certain extent in early attempts to explain latex film formation.[7] The particles first move toward one another, and the pore network (initially filled with water) normally changes from a continuous topology to discrete voids. In some cases, the pore network may remain continuous. The pore fraction decreases at a rate which is dependent on the pore size, topology, and physical characteristics of the polymer such as viscosity and surface energy. Factors favoring complete removal of the pores are small pore size, low polymer viscosity, and high polymer surface energy. Without the correct balance between these variables, pore removal may slow to an imperceptible rate before completion. Since most latex polymers have a T_g that is very close to ambient, polymer viscosity is relatively high. Conversely, polymer surface energies are quite low, compared to ceramics or metals used in sintering processes. Based on the predictions of sintering theory, therefore, it is not unusual to expect incomplete pore removal in polymer-based latex films.

The purpose of the present paper is to report additional evidence for the existence of this porosity, using sorption and diffusion measurements of a probe gas. A convenient framework for discussing the sorption behavior of amorphous polymers is the "dual-mode" model originally suggested by Barrer.[10] Below T_g, the gas is assumed to exist in two distinct sorbed sites. The Henry's law mode involves dissolution of the gas between polymer chains, analogous to dissolution of a gas in a liquid. The second mode involves sorption into pre-existing microvoids, or regions of essentially frozen-in free volume (Langmuir mode). The total concentration of gas in the polymer (C) is given by the sum of the Henry's law (C_D) and Langmuir mode (C_H) concentrations:

$$C = C_D + C_H = k_D P + \frac{C_H' bP}{1 + bP} \tag{1}$$

where k_D is the Henry's law constant, C_H' the Langmuir capacity, b the affinity of the gas for the Langmuir sites, and P is the gas pressure. C_H', b, and k_D are the dual-mode sorption parameters characteristic of each polymer/gas system at a given temperature. They are obtained by fitting eq. (1) to the experimental isotherms of C vs. P, which for glassy polymers are concave to the pressure axis. It has been demonstrated that there is a quantitative connection between C_H' and the excess volume associated with the glassy state.[11,12] As the temperature rises toward T_g, C_H' approaches zero. Above T_g, the Langmuir mode disappears, and the sorption isotherms become straight

lines having a slope equal to k_D. The shape of the sorption isotherm is therefore quite sensitive to the presence of microvoids or excess volume in the polymer.

We have used this aspect of gas sorption to characterize residual porosity in polymer latex films above T_g. There is a morphological similarity between a homogeneous glassy polymer containing excess volume, and a polymer latex film above T_g containing some residual porosity. Both represent non-equilibrium states and should exhibit "dual-mode" sorption behavior. The Langmuir capacity constant C_H' can be associated with the amount of porosity in latex films. If the latex film is above T_g, the porosity should disappear with time. All of these features have been observed and are discussed herein. CO_2 was chosen as the probe gas for these experiments, since its solubility in the polymers being investigated is small, and therefore sorption is dominated by the pores [C_H in eq. (1)]. As will be seen, total sorption levels are quite low, indicating a very small amount of porosity exists. A more soluble gas (high C_D) would make it difficult to extract the pore contribution from the experimental isotherms.

EXPERIMENTAL

Latex Film Preparation

The polymer latex suspension was generously provided by UCAR Coatings and Emulsions, Cary, NC. It contains 49.5% solids with both anionic and nonionic surfactants. The polymer is a terpolymer of vinyl chloride, butyl acrylate, and vinyl acetate, but the exact composition was unspecified. The T_g was reported to be 1°C, and the average particle size was 0.10 μm.

Latex films were prepared by casting on a clean glass plate with a conventional casting knife and drying in air until transparent (about 6 h) before removing them from the glass. Films were aged in a desiccator for various times until needed. For latex films, the film age refers to the amount of time between removal of the film from the glass plate and initiation of a sorption run. Solvent cast films were prepared by dissolving the latex films in chloroform, recasting using a similar procedure, then annealing at 55° for 4 days followed by slow cooling in the oven. Typical film thickness for all samples was about 250 μm.

Apparatus

Sorption and diffusion measurements were made with a Cahn electrobalance, model RG-2000, enclosed in a glass vacuum system with service lines to a CO_2 tank, MKS pressure gauge, thermocouple vacuum gauge, and mechanical vacuum pump. An 8 L reservoir was included to maintain constant pressure in the system as the polymer sorbed the penetrant. Polymer films were suspended directly from the balance by custom made thinly drawn glass fibers. Static charges were minimized with a Zero-stat gun. The electrobalance was housed in a plywood box equipped with a fan and heating tape, and was thermostatted to maintain the temperature at 30 ± 0.5°C. The sample weight was continuously monitored with a chart recorder. Similar systems have been described by others.[13,14]

To begin a run, the polymer film was attached to one arm of the electrobalance, a counterweight to the other arm, and the system was evacuated to 1 mtorr and maintained until a constant sample weight was achieved. A fixed degassing time of 38 h was used for all samples. The system, excluding the electrobalance chamber, was then backfilled with CO_2 to some pressure slightly above the desired pressure. Sorption was initiated by opening a stopcock to admit gas to the electrobalance chamber. The sample mass increased linearly with the square-root of time before leveling off, indicating a Fickian diffusion mechanism. Diffusion coefficients were obtained from the initial slope of this curve, and the equilibrium sorption levels from the plateau value. After sorbing to the equilibrium level, desorption measurements were also made by re-evacuating the system and monitoring weight loss.

RESULTS

Sorption

Sorption isotherms at 30°C for CO_2 in latex films aged from 62 to 1800 h (75 days) are shown in Figure 1, along with the isotherm for the solvent cast film. Two different sets of runs were made with two different sets of samples. All of
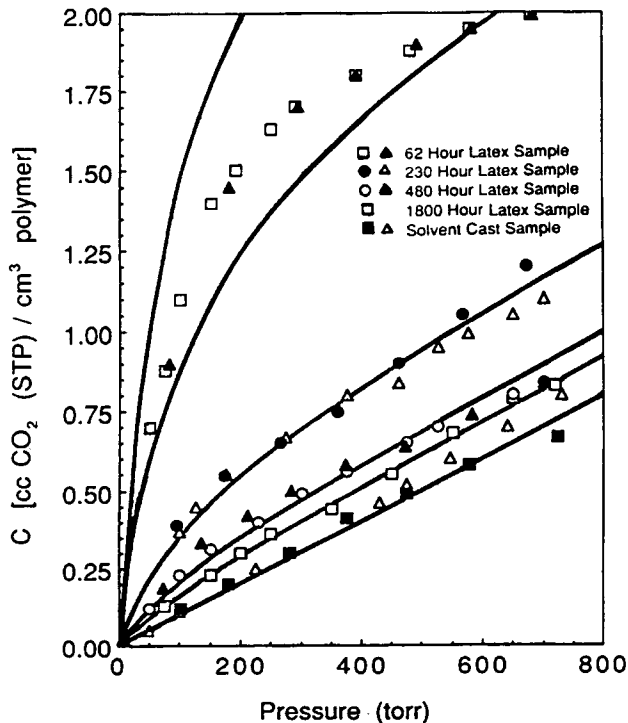

Fig. 1. Sorption isotherms for latex and solvent cast films. Data from two different runs on separate samples aged for the same period are shown, except for the 1800 h sample, for which only one run was made. The solid lines are calculated isotherms using the parameters from Table II. They represent, from top to bottom, 62 h, 74 h, 230 h, 480 h, 1800 h, and solvent cast samples, respectively.

this data is plotted in Figure 1 and shows excellent reproducibility, except for a few data points at higher pressures for the 230 h and solvent cast films. The solvent cast film exhibits the expected Henry's law behavior, described by the first term in eq. (1). The latex films show a much larger sorptive capacity than the solvent cast films. These isotherms exhibit the downward curvature normally expected for a glassy polymer. The curvature in this case is attributed to residual porosity in the latex films. The decrease in sorptive capacity of the latex films with aging time is attributed to the further gradual coalescence of these samples, and consequent removal of residual porosity. As can be seen, not all of the porosity is removed, even for the 1800 h sample.

A number of factors must be considered when fitting these data to the dual-mode model. Each sample is prepared from the same polymer, therefore the solubility of CO_2 in the polymer itself, i.e., k_D should be the same for all samples. The excess solubility in the latex samples is treated simply as sorption into the pores. This is accounted for in the model by the Langmuir capacity parameter C_H'. The Langmuir affinity b, is the ratio of the rate of condensation of gas onto the internal surface of a pore to the rate of evaporation from this surface.[15] This parameter depends on the chemical structure of the polymer and the gas, and varies with temperature. Since these parameters do not change during these experiments, b should also be constant for all samples containing pores. Finally, in the case of the 62 h sample, the time required to obtain the isotherm (about 12 h) is a significant fraction of the age of the sample. Therefore, a significant amount of coalescence will occur during acquisition of the isotherm, which manifests itself in the dual-mode model as a time-varying, rather than a constant C_H'. As shown by the two sets of data in Figure 1 for the 62 h sample, the way in which the sorptive properties change during acquisition of the isotherm is reproducible. For the other samples, the time required to obtain the data is negligible compared to the age of the film, and no significant changes in the sorption parameters are expected during measurement of the isotherms.

The time dependence of C_H' that exists for the 62 h sample can be modeled using a modified form of eq. (1):

$$C = k_D P + C_H'(t_r) f(t) \frac{bP}{1 + bP} \tag{2}$$

where $C_H'(t_r)$ is the (instantaneous) Langmuir capacity constant at some arbitrary reference time t_r during acquisition of the sorption isotherm, and $f(t)$ is a function expressing the fractional change in C_H' with time. A second type of experiment was conceived to monitor coalescence continuously, and to determine $f(t)$. A sample aged for 62 h was exposed to a constant CO_2 pressure of 700 torr at 30°C for 530 h (22 days). Sample weight was monitored continuously. Results are plotted against $t^{0.5}$ as the data points in Figure 2. The initial uptake of CO_2 to an "equilibrium" level very close to that shown in Figure 1 is observed, and is followed by a slow loss of weight with time. The decrease in weight is attributed to a gradual loss of porosity, accompanied by a decrease in the amount of CO_2 contained in the pores. The dashed line indicates the equilibrium solubility at 700 torr for CO_2 in the solvent cast film, which presumably has zero pore volume. The open data points in Figure 2 will
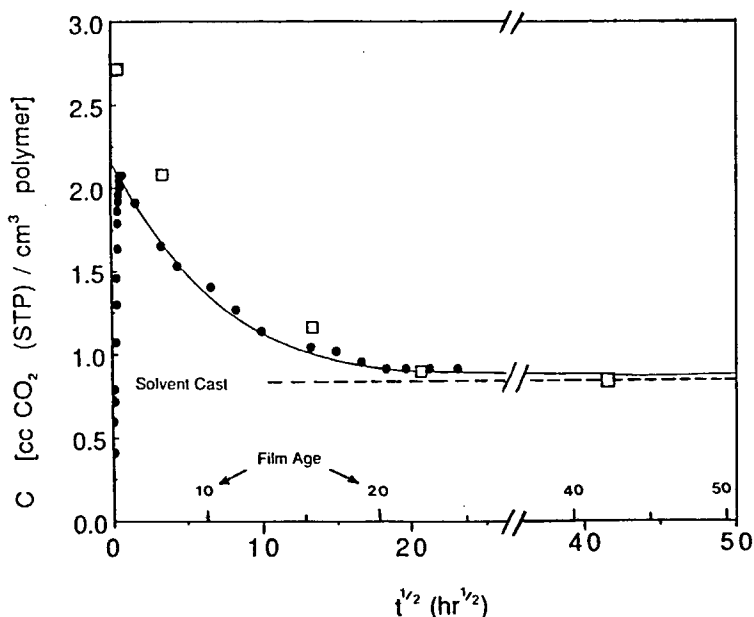
Fig. 2.   Change in CO_2 concentration with time in a 62 h latex film exposed to 700 torr CO_2 at 30°C. The solid points were obtained from continuous measurements of film mass with time. The open points represent the equilibrium concentration of CO_2 calculated at 700 torr from the fitted sorption isotherms in Figure 1. The solid line is the least-squares fit of eq. (2) to the solid points. The dashed line represents the sorption level for the least-squares fit of eq. (2) to the solid points. The dashed line represents the sorption level for the solvent cast film at 700 torr. The lower time scale begins at the start of this experiment, after the sample has aged for 62 h. The upper time scale indicates actual sample age.

be discussed later. The following empirical equation was used to describe the decaying region of this plot:

$$C(t) = 0.748 + 1.556 \exp(-0.197t^{0.409}) \tag{3}$$

where $C(t)$ is the concentration of CO_2 in the sample at time t in hours, where $t =$ aging time -62 (h). The solid line in Figure 2 is a plot of this equation, which provides an excellent fit to the data.

The time-dependent function $f(t)$ is now defined using eq. (3):

$$f(t) = \frac{C(t) - 700k_D}{C(t_r) - 700k_D} \tag{4}$$

The terms in k_D remove the Henry's law contribution from the total concentration of CO_2 in the sample at 700 torr. The numerator and denominator in eq. (4) represent instantaneous C_H' values that exist at times t and t_r, respectively, in a coalescing sample. The reference time t_r was chosen as 0 h, which corresponds to a film age of 62 h. During acqusition of the isotherm for

the 62 h sample, $f(t)$ varies from 1.00 at the beginning ($t = t_r$) to 0.59 ($t = 12$ h) at the end of the data collection process. The dual mode parameters that are obtained from a curve fit using eq. (2) with $t_r = 0$ h are indicative of a sample that has been aged for 62 h and does not coalesce during acquisition of the sorption isotherm.

Dual mode parameters were obtained using nonlinear regression techniques from the data in Figure 1, using eq. (2) for the 62 h sample, and eq. (1) for the other samples. Initially, each isotherm was individually fitted, making no assumptions concerning the constancy of any of the dual-mode parameters among the samples. Only the first term (Henry's law) of eq. (1) was used in the fit for the solvent cast sample. The parameter values are listed in Table I, along with their associated uncertainties (2σ; 95% confidence level). It can be seen that b is essentially constant among the latex samples, given the rather large uncertainties for this parameter. The k_D for the solvent cast film matches the k_D values for the 230 and 1800 h latex samples. The k_D values for the other two latex samples are somewhat lower, especially for the 62 h film, although the uncertainty in k_D for this sample is very large. This discrepancy is not surprising, given the correction that has been applied in this case. C_H' shows the expected monotonic decrease with aging time. A unique C_H' cannot be listed for the 62 h sample, since this parameter is effectively changing during the experiment. Instead, the values quoted represent the values that existed at the beginning (62 h) and at the end (74 h) of the acquisition of the isotherm data. The values obtained directly from the nonlinear regression are listed next to the 62 h sample, whereas the values listed next to the 74 h sample were obtained by multiplying the 62 h C_H' and its associated uncertainty by the appropriate value of $f(t)$ (= 0.59).

The tendency toward constant values of k_D and b for the latex samples in Table I is consistent with the ideas presented earlier, given the physical interpretation of these parameters. This prompted a second way of fitting the data, using a single value of b and k_D to describe the entire data set, and allowing only C_H' to vary for the latex sample. This amounts to a total of six parameters to fit all five isotherms. Equation (2) was still applied in fitting the 62 h data, and only the first term of eq. (1) was used for the solvent cast film.

TABLE I
Dual-Mode Parameters; Individual Isotherm Fits

Sample	$k_D \times 10^3$ [cc CO_2 (STP)/cc polymer torr]	C_H' [cc CO_2 (STP)/cc polymer]	$b \times 10^2$ (torr^{-1})
Latex, 62 h[a]	0.14 ± 0.54	4.12 ± 0.92	0.53 ± 0.17
Latex, 74 h[a]	0.14 ± 0.54	2.43 ± 0.54	0.53 ± 0.17
Latex, 230 h	0.96 ± 0.25	0.52 ± 0.21	1.01 ± 0.90
Latex, 480 h	0.64 ± 0.18	0.48 ± 0.18	0.57 ± 0.32
Latex, 1800 h	1.01 ± 0.16	0.13 ± 0.15	1.03 ± 2.38
Solvent cast	1.05 ± 0.02	—	—

[a] These parameters represent hypothetical samples that do not undergo any coalescence during acquisition of the sorption isotherm; see text for explanation.

TABLE II
Dual-Mode Parameters and Pore Fractions; Overall Regression
Assuming One Value of k_D and b for All Samples

Sample	$k_D \times 10^3$ [cc CO_2 (STP)/ cc polymer torr]	$b \times 10^2$ (torr^{-1})	C'_H [cc CO_2 (STP)/ cc polymer]	Pore fraction (%)
Latex, 62 h[a]			2.70 ± 0.10	0.59
Latex, 74 h[a]			1.60 ± 0.07	0.35
Latex, 230 h			0.53 ± 0.04	0.12
Latex, 480 h	1.00 ± 0.05	1.00 ± 0.13	0.22 ± 0.04	0.05
Latex, 1800 h			0.14 ± 0.05	0.03
Solvent cast			—	—

[a] These parameters represent hypothetical samples that do not undergo any coalescence during acquisition of the sorption isotherm; see text for explanation.

All of the data in Figure 1 were regressed simultaneously. The results are listed in Table II. Making this simplifying assumption does not degrade the regression appreciably. The overall root-mean-square deviation (RMSD) for this fit is 0.048, whereas the average RMSD for all of the individual fits is only slightly lower at 0.044. The k_D obtained agrees with that found for three of the samples in Table I, including the solvent cast sample. The uncertainty in the value of b is significantly reduced. The values of C'_H change slightly, but the decreasing trend with aging time remains, and the uncertainties are much smaller.

The solid lines in Figure 1 represent the calculated isotherms using the dual mode parameters from Table II. For the 62 h sample, two lines were plotted, representing 62 and 74 h time-invariant samples. These were computed using the instantaneous C'_H values from Table II, obtained as described above. As expected, these "constant-C'_H" lines bracket the actual data; the data points move from near the 62 h line at low pressures, toward the 74 h at higher pressures (aging time increasing), reflecting the change in porosity (and C'_H) with time during acquisition of the isotherm. The misfit that is observed between the data and the lines for the other samples is a result of carrying out the least-squares minimization on the *entire* set of curves using the minimum number of adjustable parameters. A careful examination of the residuals shows that the dual mode model does not completely account for the shape of the experimental data curves, particularly the 480 h sample, which showed a low k_D in the individual regression (Table I). This reflected in Figure 1 by the fact that the predicted values lie above the data points at high pressures and below at low pressures. Run-to-run variations mask this effect in some other curves. In the most extreme departure from agreement with the dual mode model, the data for the solvent cast and the 480 and 1800 h latex samples appear to converge at the highest pressure, whereas the calculated curves suggest that they should be slightly separated.

The total concentration of CO_2 in the latex samples at 700 torr was calculated from the fitted isotherms and plotted as the open data points in Figure 2. The open points therefore represent samples that aged in the desiccator, and the closed points represent a 62 h sample that aged in a CO_2
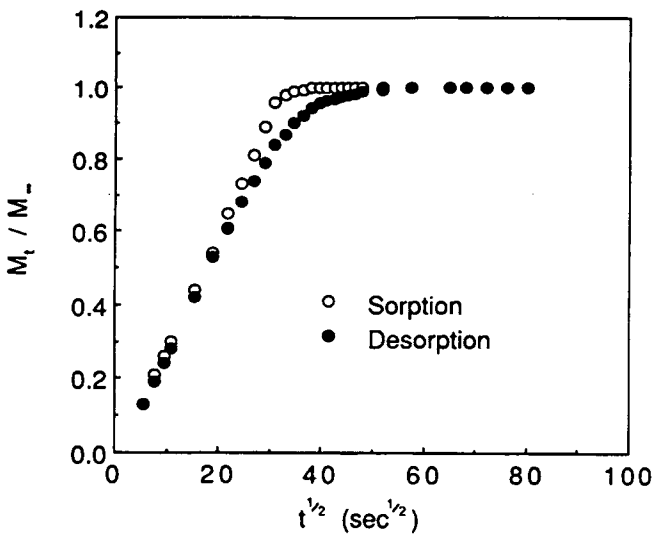
Fig. 3. Typical sorption/desorption kinetics plot obtained for a 62 h sample at 200 torr CO_2.

two sets of data indicates that the presence of CO_2 in the pores does not significantly alter the coalescing kinetics. The deviations between the two sets of data at shorter times can largely be explained by the deviations of the data points in Figure 1 from the fitted isotherms. Better agreement would result had the actual data points nearest to 700 torr from Figure 1 been plotted in Figure 2.

Diffusion

A typical sorption-desorption run is shown in Figure 3. M_t represents the mass of penetrant sorbed or desorbed at time t, and M_∞ represents the total mass sorbed or desorbed. For Fickian diffusion into or out of a thin slab at short times, M_t/M_∞ is given by:

$$\frac{M_t}{M_\infty} = \frac{4}{l}\left(\frac{Dt}{\pi}\right)^{0.5}$$ (5)

where D is the (concentration independent) diffusion coefficient and l is the film thickness. Diffusion coefficients are calculated from the slope of the initial linear region of plots of M_t/M_∞ vs. $t^{0.5}$ using eq. (5).

The initial portion of the sorption curve in Figure 3 shows a slight sigmoidal deviation from absolute linearity. This behavior has been observed previously for organic penetrants at relatively high activities in glassy polymers,[16] and for SO_2 in Kapton polyimide.[17] In these references, the sigmoidal shape was attributed to the simultaneous occurrence of diffusion and polymer relaxation resulting from plasticization by the penetrant. A slight amount of relaxation is probably occurring for the latex films as well, not because of penetrant plasticization, but because they undergo a slight amount of coalescence within
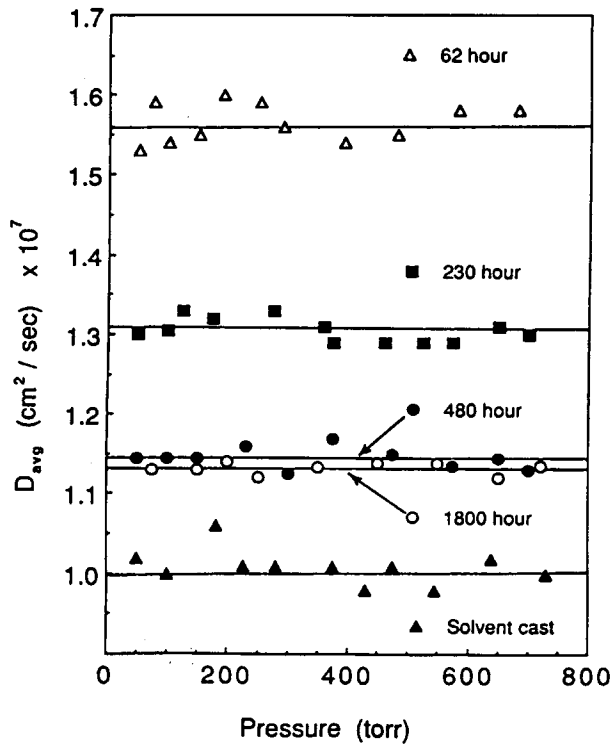
Fig. 4. Dependence of the average diffusion coefficient for latex and solvent cast samples on CO_2 pressure. The solid lines represent the average value of D_{avg} for each sample.

the time scale of the experiment. The effect is greatest for the samples aged for the least amount of time, and Figure 3, which represents the 62 h sample, might be considered the worst case. In any case, the deviations from linearity are generally minor, and analysis of the data using Fickian kinetics is quite acceptable.

In cases where D is concentration-dependent, an average diffusion coefficient D_{avg} is usually defined, which describes transport behavior over some small range of penetrant concentrations for intergral sorption, as performed here. A good approximation to D_{avg} is the arithmetic mean of the sorption and desorption diffusion coefficients,[17] obtained from eq. (5) and plots such as Figure 3. Very little difference was noted for sorption and desorption diffusion coefficients at a given pressure. Plots of D_{avg} against pressure for the four latex samples and the solvent cast sample are shown in Figure 4. While the data do show some scatter, there is essentially no concentration dependence over this (rather dilute) range of concentrations. The horizontal lines represent the average of the D_{avg} values for each sample over the experimental pressure range. The diffusion coefficient of CO_2 drops monotonically from 1.6×10^{-7} for the 62 h latex film to 1.0×10^{-7} cm^2/s for the solvent cast film. The trend in D is consistent with gradual pore removal and coalescence of the latex samples. Over the aging time period studied here, D for the latex samples does not quite reach the "infinite time" D represented by the solvent cast value. In

fact, the 480 and 1800 h samples have essentially the same D, suggesting that the coalescing process has either slowed to an imperceptible rate or stopped altogether. In contrast, the sorption behavior for these two samples continues to change, as shown in Figure 1.

DISCUSSION

The sorption isotherms for the latex films clearly indicate an excess sorptive capacity when compared with solvent cast films, irrespective of the applicability of any sorption model such as eq. (1). These data, in addition to the trend in D_{avg} with aging time in Figure 4, are strong evidence for the existence of residual porosity in the latex films. Furthermore, the changes in the sorptive and diffusive properties with film age are consistent with the gradual removal of this porosity as the films undergo further coalescence. The pore removal kinetics can be followed continuously, as illustrated by Figure 2 and eqs. (3) and (4), or can be obtained from the time dependence of C'_H (Table II).

Although there is some misfit at the higher pressures, the dual mode model does explain the general behavior of the data in Figure 1 quite well, despite the simplifying assumption of constant b and k_D for all of the samples. This lends some validity to the physical significance usually ascribed to the dual mode parameters. The Langmuir capacity constant C'_H can be associated with the amount of porosity in the latex films. A quantitative estimate of the pore volume can be made, using the known sorbed-state molar volume for CO_2 in the pores. This number has been determined for CO_2 in a number of different environments, including organic solvents and zeolites,[12] and has been found to be relatively constant at 49 cc/mol between 25 and 50°C. This is also near the saturated liquid state molar volume for CO_2 below the critical point. Assuming the same value can be applied here, the pore fractions listed in the last column of Table II were calculated from the C'_H values. The pore (volume) fraction is 0.6% or less for all of the samples. These pore fractions should be considered lower bounds, since the sorbed-state molar volume of CO_2 in the polymer could be larger, but is probably not much less than 49 cc/mol.

The diffusion coefficient for CO_2 is significantly higher (about 60%) in the 62 h latex sample than it is in the solvent cast sample, yet the pore fraction in the 62 h sample is only about 0.6%. A change in D of this magnitude cannot be accounted for by discrete voids which comprise only 0.6% of the sample, even if unrealistically large values are assumed for the pore diffusivity. These facts can only be reconciled by assuming that the pores are at least partially connected in some sort of a continuous network that allows relatively fast diffusion into the sample. The effect of such a pore network on the overall diffusivity of a gas in the polymer can be quite significant, even for pore fractions as small as 0.6%. The Knudsen (pore) diffusivity for CO_2 in a single, cylindrical pore having a diameter of 20 Å at 30°C is estimated to be 2.5×10^{-3} cm²/s.[18] This is four orders of magnitude higher than the diffusivity of CO_2 in the bulk polymer, as measured for the solvent cast sample with no porosity (see Fig. 4). A continuous network of cylindrical pores 20 Å in diameter (or larger) can easily be constructed under the constraint of a pore fraction of 0.6%. This suggests that changes in D of 60% resulting from the presence of such a pore network is not unrealistic. A more exact estimate of

the effect of this type of porosity on the overall diffusivity requires adoption of a model for the topology of the network; these calculations are beyond the scope of this paper. This type of pore morphology would be very difficult to detect and characterize by other direct methods such as microscopy.

The permeability of polymer to a penetrant is defined as the product of the diffusion coefficient and the solubility. The solubility of CO_2 in the 62 h latex film is much larger than the solvent cast film, especially at low pressures where they differ by almost an order of magnitude. In contrast, the diffusion coefficients for these samples differ only by 60%. Previous permeability measurements for helium in latex and solvent cast films of other acrylic latex polymers having similar T_gs shows differences of up to a factor of 5 between the two.[3] Our results indicate that it is the excess solubility associated with residual porosity in the latex films that accounts for this, and not diffusivity differences. The effect is most pronounced at low pressures and short aging times. A gas more soluble in the polymer than CO_2 or helium would probably exhibit a smaller permeability difference between latex and solvent cast films, since the pore contribution [C_H in eq. (1)] would be a smaller fraction of the total solubility. In the limit of high penetrant solubility, the pore contribution would be negligible, and the permeabilities of solvent cast and latex cast films should be essentially equal.

CONCLUSIONS

Sorption and diffusion measurements of CO_2 have been successfully used to characterize residual porosity in latex films of a vinyl chloride/vinyl acetate/butyl acrylate terpolymer having a T_g of 1°C. The low solubility of CO_2 in this polymer is the key to the sensitivity of this technique. The sorption isotherms obtained for the latex films resemble those of a glassy polymer, and the dual mode sorption model can be used successfully to describe the data. Pore removal and gradual film coalescence is accompanied by decreasing solubility and decreasing diffusion coefficient, with changes in the solubility being more pronounced. Pore removal kinetics can be followed by exposing latex films to CO_2 at constant pressure and monitoring weight loss as sorbed gas is "squeezed out" during film coalescence. The presence of CO_2 in the pores does not seem to alter the pore removal kinetics. The solubility and diffusivity remain above the values measured for CO_2 in solvent cast films of the same polymer, even after 75 days at room temperature (24°C above T_g). Estimates of the pore volume fraction from the condensed state molar volume of CO_2 result in values less than 0.6%. This small amount of porosity still has a measurable effect on the diffusion coefficient, which suggests that the pores are not discrete voids, and must therefore be connected into some kind of a network.

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