Free-Volume Hole Properties of Gas-Exposed Polycarbonate Studied by Positron Annihilation Lifetime Spectroscopy

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ABSTRACT: Free-volume hole properties (free-volume size, fraction, and distribution) of polycarbonate (PC) exposed to CO_2 and N_2 gases are investigated using positron annihilation lifetime (PAL) spectroscopy. In PC/CO_2 systems, free-volume hole size and fraction significantly increase as a function of CO_2 pressure in the range 0−1000 psi. Hysteresis is observed during CO_2 sorption/desorption. In PC/N_2 systems, free-volume hole size and fraction reach maxima at a pressure of about 800 psi but no hysteresis is observed. Free-volume hole distribution in the CO_2-exposed polymers is found to be significantly broader than in unexposed samples. The observed variation in free-volume properties of PC exposed to gas is discussed in terms of penetrant plasticization, gas hydrostatic pressure effect, and molecular filling and creation of holes in the polymer matrix.

Introduction

The study of microstructural properties of glassy polymer−gas mixture has drawn considerable attention in recent years because of its important industrial applications, such as gas separation based on the glassy polymer membrane,[1] the extraction of monomer, solvent, and oligomer from the polymer by supercritical fluid;[2] and the production of polymer microcellular foam.[3] When a polymer is exposed to a gas vapor, the gas molecules may dissolve in the polymer matrix and subsequently change the microstructure of the polymer. Apparent effects include a decrease in T_g and an increase in specific volume. On the other hand, when the gas pressure is sufficiently high, the polymer matrix may be compressed. In this case, the effects may be diametrically opposite to those at low-pressure exposure: T_g increases while specific volume decreases. For example, these dual effects have been demonstrated by Assink using the NMR technique in elastomers exposed to He, Ar, and N_2 gases.[4]

Gas sorption and permeation in Bisphenol-A polycarbonate-based (PC-based) polymers have been extensively studied in the past two decades[5−16] because of their technological importance. The mechanisms of gas sorption and permeation in the glassy polymers have been described by various methods, including a dual-mode model,[5] a dual-mode partial-immobility model,[6,7] and a free-volume distribution model.[5,8] For highly interactive gases such as CO_2 and C_2H_4, large variations in thermal and volumetric properties have been observed. A typical behavior is the existence of hysteresis during sorption and desorption processes. The effect of temperature on gas sorption, permeativity, and selectivity has been studied in detail.[9,10] Other effects, such as those of chemical structure, thermal history, and exposure history on gas sorption and permeation, have also been reported.[11−13]

Gas sorption and transport in the glassy polymers are directly related to the gas−polymer interactions at the molecular level. Investigation of microstructural changes at the molecular (Å) level in polymers under gas exposure will shed light on the underlying reasons for gas transport properties. During the past few decades, the free-volume theory at the atomic scale has been developed to interpret gas−polymer interactions and penetrant transport phenomena.[14−18] In this work, we apply a novel technique, positron annihilation lifetime (PAL) spectroscopy, to measure free-volume properties of a PC exposed to two gases, a highly interactive CO_2 and a nearly inert N_2.

PAL has been employed to determine the free-volume hole size, fraction, and distribution in a variety of polymers.[19−23] The sensitivity of PAL in measuring free-volume hole properties is due to the unique localization of the positron and the positronium atom (Ps, a bound state consisting of an electron and a positron) in open spaces such as holes, free volumes, and voids. The observed lifetime of o-Ps (the triplet state of Ps) is found to be directly correlated to hole size, while the corresponding intensity is a measure of free-volume hole fraction.[23] In our most recent PAL results in a series of PC-based polymers, we found a correlation between gas permeability and the observed free-volume hole fraction.[24] Existing positron lifetime studies in sorption of CO_2 in a series of polyimides show correlations between hole volumes as obtained by PAL and diffusion properties of exposed gases.[25−27] In this paper, we report the PAL results in CO_2- and N_2-exposed PC systems as a function of exposed pressure.

Experimental Section

Materials and Sample Preparation. The polycarbonate was supplied by the General Electric Co. (Albany, NY). It has molecular weight $M_w = 79\,000$ and density = 1.200 g/cm^3. The sample thickness was 1 mm. The glass transition temperature (T_g) = 145 °C as measured by DSC at heating rate 10 °C/min. The sample was first heated above T_g under vacuum to remove any residual gases before the positron experiment.

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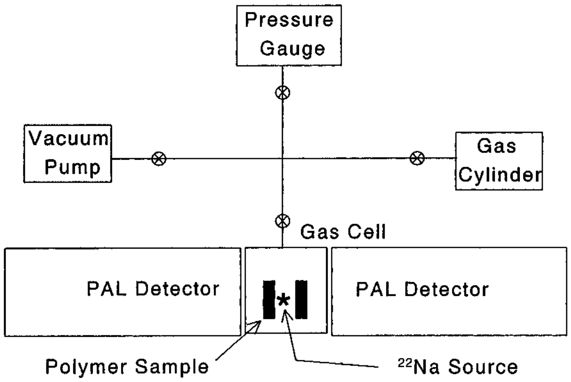

Figure 1. Schematic figure of the experimental setup for the polymer/gas system for PAL measurement.

The CO_2 gas has a purity of 99.99% (Matheson Gas, Montgomeryville, PA), and the N_2 gas is the ultrahigh grade (99.999%) (Matheson Gas). The gases were manipulated in a vacuum-sealed stainless-steel gas line. The pressure was monitored by an Omega transducer pressure gauge (Model 302−1KGY). The experimental setup is shown in Figure 1.

Positron Annihilation Lifetime (PAL) Spectroscopy. A 25−μCi positron source (^{22}NaCl from DuPont) was sealed in an aluminum coil (6 μm) and sandwiched in two identical polymer samples. All positron annihilation took place within a 1.0 mm radius of the source. The positron annihilation lifetimes were determined by detecting the prompt γ-ray (1.28 MeV) from the nuclear decay that accompanies the emission of a positron from the ^{22}Na radioisotope and the annihilation γ-ray (0.511 MeV). A fast−fast coincidence circuit was used to measure the positron lifetime. The time resolution of the PAL spectrometer was about 300 ps as monitored by using a ^{60}Co source at a coincident rate of 300 cps. Many spectra (1×10^6 and 20×10^6 counts) were collected for a complete data analysis. In the gas-exposed systems, the system is stabilized at constant pressure for several hours before the PAL experiment is performed. Procedural details of PAL measurements can be found elsewhere.[19,23]

Mean Free-Volume Hole Size and Fraction. The obtained PAL data were analyzed to finite term lifetimes using the PATFIT program.[28] The PATFIT program resolves a PAL spectrum into two to five functions of negative exponential. For the PC and PC/gas systems, we found that three lifetime results give the best χ^2 and most reasonable standard deviations. The shortest lifetime ($\tau_1 \approx 0.12$ ns) is the lifetime of p-Ps (the singlet state of Ps), and the intermediate lifetime ($\tau_2 \approx 0.40$ ns) is the lifetime of the positron. The longest lifetime ($\tau_3 \approx 1-3$ ns) is due to the pick-off annihilation of o-Ps (triplet Ps). In the current PAL method, τ_3 is directly correlated to the free-volume hole size by the following equation:[29]

$$\tau_3 = \frac{1}{\lambda_3} = \frac{1}{2}\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1} \tag{1}$$

where τ_3 is the o-Ps lifetime (ns), λ_3 is the o-Ps annihilation rate (ns^{-1}), R is the free-volume hole radius (Å), $R_0 = R + \Delta R$, and ΔR is the electron layer thickness, semiempirically determined to be 1.66 Å.

The relative intensity of o-Ps annihilation lifetime, I_3, is related to the free-volume hole fraction by the following empirical equation:[30]

$$F_v = CV_f I_3 \tag{2}$$

where F_v is the fraction (%) of the free volume and V_f is the volume (Å^3) of free-volume holes calculated from R from eq 1. For PC, C is an empirical constant (0.0018) determined from the specific volume data.

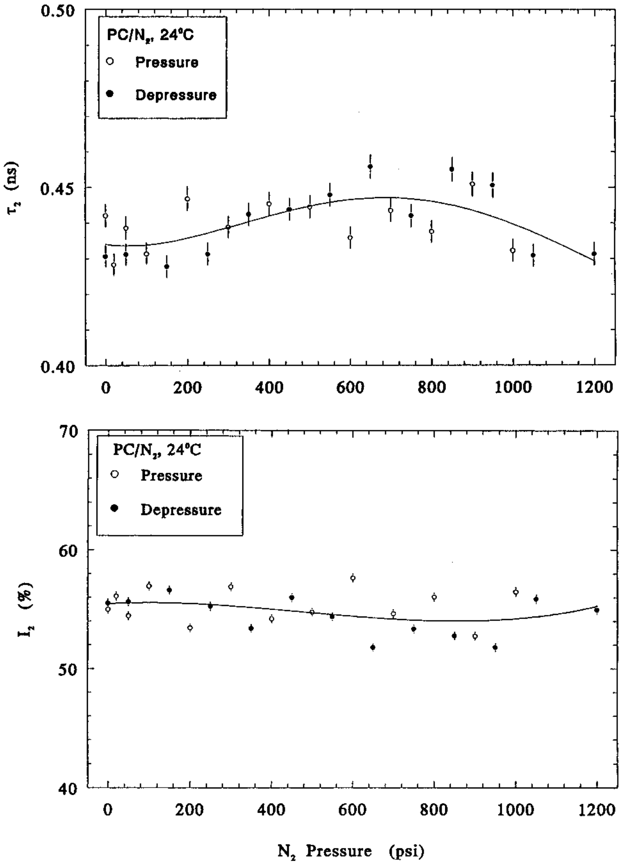

Figure 2. Positron lifetime τ_2 and relative intensity I_2 of PC vs N_2 pressure. (Lines drawn for visual clarification only.)

Free-Volume Hole Distributions. Since the free-volume holes in the polymer have a distribution, an annihilation lifetime spectrum can be expressed in a continuous form.[31]

$$Y(t) = R(t)\,[N(t)\int \lambda \alpha(\lambda)\exp(-\lambda t)\,d\lambda + B] \tag{3}$$

where λ is the annihilation rate (τ^{-1}), B is the background of the spectrum, and $\lambda\alpha(\lambda)$ is the annihilation probability density function. We employed the CONTIN program[32] to obtain the $\lambda\alpha(\lambda)$ vs λ. The reference spectrum is obtained from a radioisotope ^{207}Bi ($\tau = 0.183$ ns). Following the correlation between τ_3 and the hole radius R (eq 1) and considering the difference of o-Ps capture probability in different hole sizes with a linear correction $K(R)$ (=1 + 8R), the free-volume probability density function, V_f(pdf), is expressed as[33]

$$V_f(\mathrm{pdf}) = -3.32\frac{\left[\cos\left(\frac{2\pi R}{R + 1.66}\right) - 1\right]\alpha(\lambda)}{(R + 1.66)^2 K(R)(4\pi R^2)} \tag{4}$$

The fraction of the free-volume hole between V_f and dV_f is V_f(pdf) dV_f. Detailed descriptions in this regard can be found elsewhere.[23, 33−35]

Results and Discussion

A. Polycarbonate/N_2 System. We have performed PAL experiments for PC as a function of N_2 pressure at ambient temperature (24 °C). Since τ_1 does not vary with the pressure, we fixed $\tau_1 = 0.120$ ns in our three-lifetime analysis. The variations of τ_2, I_2, τ_3, and I_3 with the N_2 pressure are shown in Figures 2 and 3. From Figure 2, it is seen that τ_3 increases with the increase of N_2 pressure up to 600 psi. Above 600 psi, τ_3 starts to decrease with increasing N_2 pressure. When N_2 is depressurized, τ_3 decreases. I_3 increases monotonically with the N_2 pressure in the range of 0−1200 psi and without significant hysteresis. Figure 4 shows the results of the hole radius R and volume V_f changes with N_2 pressure as calculated using eq 1 and τ_3 data, and based on a spherical hole model. Figure 5 (upper part)

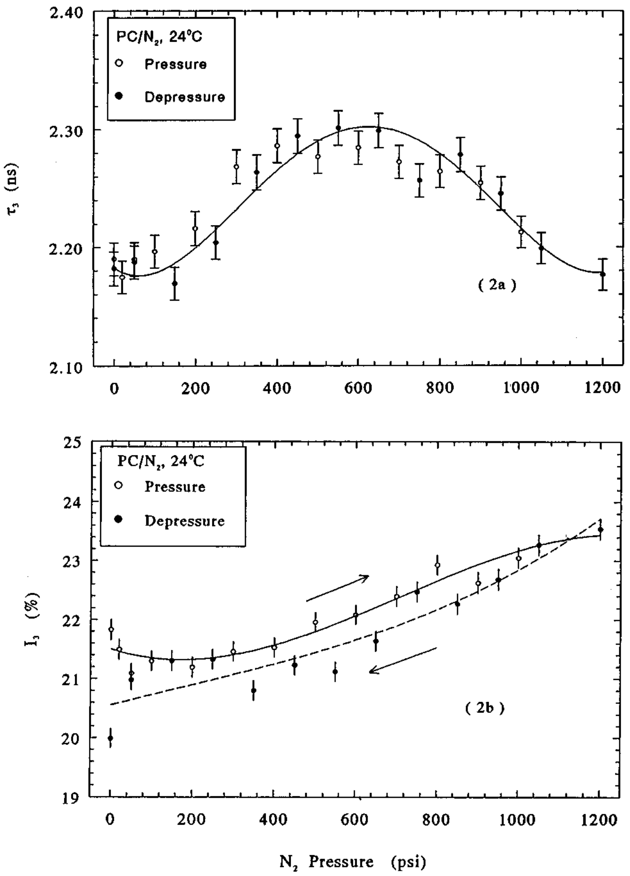

Figure 3. o-Ps lifetime τ_3 and the relative intensity I_3 of PC vs N_2 pressure. (Lines drawn for visual clarification only.)

shows the results of the fraction of free-volume hole vs the N_2 pressure as calculated using eq 1 and V_f results. It is seen in Figures 4 and 5 that R and V_f have their maxima at a pressure of about 600 psi and that the fraction of the free volume, F_v, has a maximum at about 800 psi.

These experimental results can be interpreted by the molecular interactions between the N_2 and the polycarbonate matrix, because Ps probes the local free-volume holes at the molecular level. Two effects may occur due to exposure of polymers to N_2 gas: (1) plasticization, *i.e.*, the gas dissolves into the polymer matrix and subsequently softens the polymer molecular packing and the polymer molecular segments; and (2) hydrostatic pressure, *i.e.*, the gas acts as a pressure medium, compressing the polymer matrices. Both effects may lead to a change in volume of the polymer. The plasticization leads to volume expansion while the hydrostatic pressure causes volume contraction. The first effect dominates at low pressure and the second effect becomes important at high pressure. Therefore, the free-volume results show an increase at low pressure due to plasticization and then a decrease at high pressure due to compression. An increase in macroscopic volume due to N_2 exposure in PC has also been reported, as plotted in Figure 5 (lower part).[8] It is interesting to observe the following differences between the microscopic free volume and macroscopic specific volume variations.

First, the specific volume is dilated monotonically up to a N_2 pressure of 1000 psi while the free volume shows a decrease at pressure >800 psi. Second, the percent of specific volume dilation is much smaller than the free-volume variation. The macroscopic volume was measured to increase 0.20% at 1000 psi, while the free volume increases to a much greater extent. For example, the relative fractional free volume (Figure 5) increases by 15%, *i.e.*, from 4.1 to 4.8% at 800 psi. This is interpreted as plasticization's increasing the relative free volume by 15%. The relative increase of free-volume fraction is nearly 2 orders of magnitude greater than the macroscopic volume dilation. At high pressure, the macroscopic volume measurement cannot detect the hydrostatic pressure effect, as current PAL does. This large variation of free-volume properties further supports the evidence that free-volume theory can be used to explain penetrant/polymer interactions in detail.[14-18] Since I_3 increases as the pressure increases (Figure 3), the number of holes is obviously increased. This means the sorption of N_2 creates new holes in addition to the preexisting free volume in PC. On the other hand, the sorption of N_2 molecules in the matrix also occupies some spaces in the free-volume holes. According to the sorption data,[8] the concentration of sorpted N_2 at 1000 psi is reported to be 3.5 cm^3 STP/cm^3 (9.4×10^{19} molecules/cm^3 of PC). The number of 5% holes in PC is calculated to be 4.4×10^{20}/cm^3. We then estimate the fraction of existing holes (5% of F_v) filled with N_2 to be about 20%, or 1 of every 5 holes. This filling of preexisting holes and creation of additional holes can be investigated via the free-volume hole distribution measured by PAL. A slightly broader distribution is observed due to the sorption of N_2 in PC. A larger broadening of hole distribution is observed in the PC/CO_2 system, which will be discussed below. It is worthwhile to mention that both o-Ps and positron are localized in free-volume holes of polymers.[36]

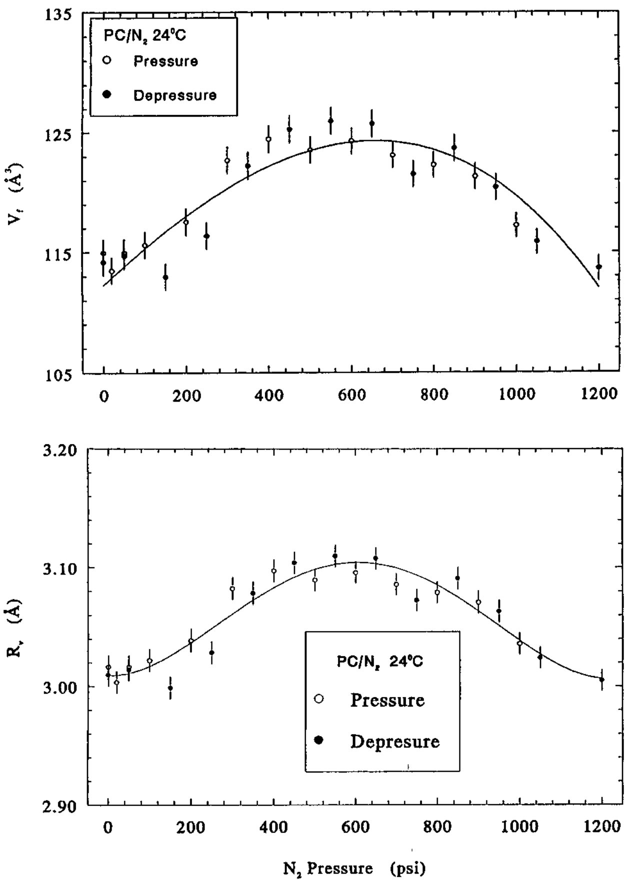

Figure 4. Hole radius (R) and volume (V_f) of the polycarbonate vs the N_2 pressure for the PC/N_2 system. (Lines drawn for visual clarification only.)

B. Polycarbonate/CO_2 System. CO_2 is known to be a high-sorbing penetrant for polymers and it has a critical temperature of 31 °C. We performed PAL

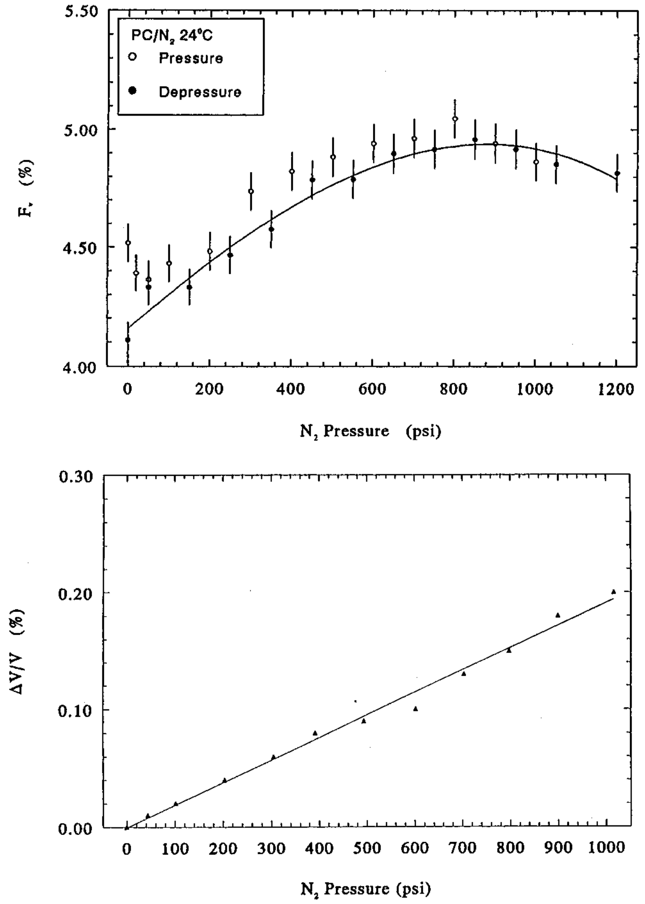

Figure 5. Fraction of the free volume hole (F_v) and specific volume dilation in PC vs N_2 pressure. Volume dilation data (lower figure) are taken from ref 8. (Lines drawn for visual clarification only.)

experiments in PC as a function of CO_2 pressure at 35 °C. Figures 6 and 7 show the results of the τ_2 (positron) and τ_3 (o-Ps) components as a function of CO_2 pressure for both pressurization and depressurization processes, with τ_1 fixed to 0.120 ns in the lifetime analysis. The hole radius (R) and volume (V_f) as calculated according to eq 1 are plotted in Figure 8. The result of fraction of free-volume hole (F_v) is plotted in Figure 9.

Similarly to the PC/N_2 system, during pressurization, τ_2 and τ_3 increase with increasing CO_2 pressure in the 0−1000 psi range, but to a greater extent, as shown in Figures 6 and 7. The enlargement of the average hole radius and volume with the gas pressure is clearly shown in Figure 8. In Figure 7, intensity I_3 increases with the CO_2 pressure during pressurization up to 700 psi and then tends to decrease slowly with the increase of CO_2 pressure. The fraction of the free-volume hole (F_v) as calculated according to eq 2 from τ_3 and I_3 data increases nearly linearly with increasing pressure, as shown in Figure 9.

These experimental results can be interpreted in terms of the molecular interactions between CO_2 and PC. Since CO_2 is a high-sorbing gas, the variation of free-volume results with respect to CO_2 pressure is much greater than that observed in PC/N_2 systems (Figures 4 and 5). During pressurization, free-volume hole size and fraction increase monotonically (Figures 8 and 9) and do not decrease at higher pressure up to 1000 psi, in contrast to the PC/N_2 system. We interpret this as due to the large PC/CO_2 molecular interaction and the fact that the resulting plasticization effect dominates over all the pressure range studied here. The softening of PC due to CO_2 sorption and the depression

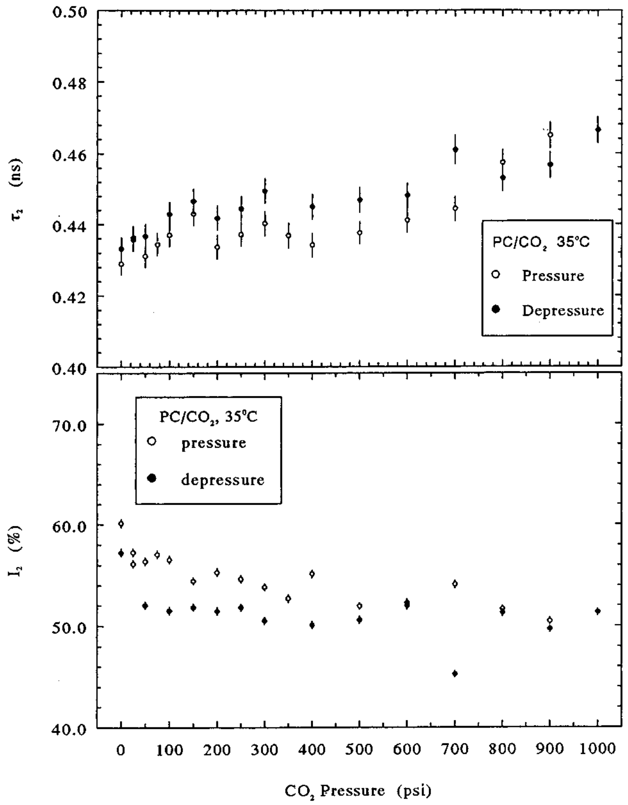

Figure 6. Positron lifetime τ_2 and relative intensity I_2 of PC vs CO_2 pressure. (Lines drawn for visual clarification only.)

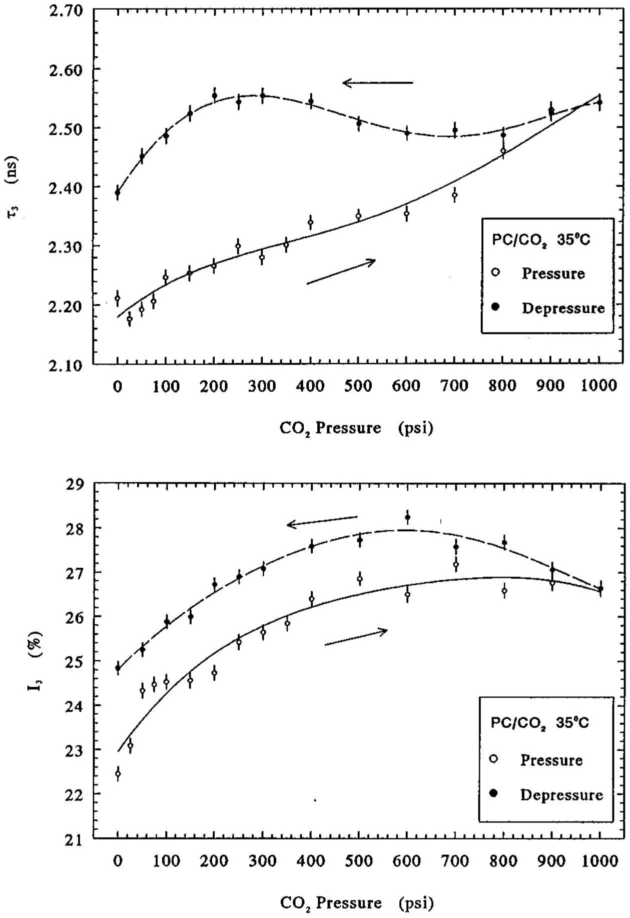

Figure 7. o-Ps lifetime τ_3 and the relative intensity I_3 of PC vs CO_2 pressure. (Lines drawn for visual clarification only.)

of T_g have recently been reported by the DSC method.[37] The hydrostatic pressure effect in the PC/N_2 system at

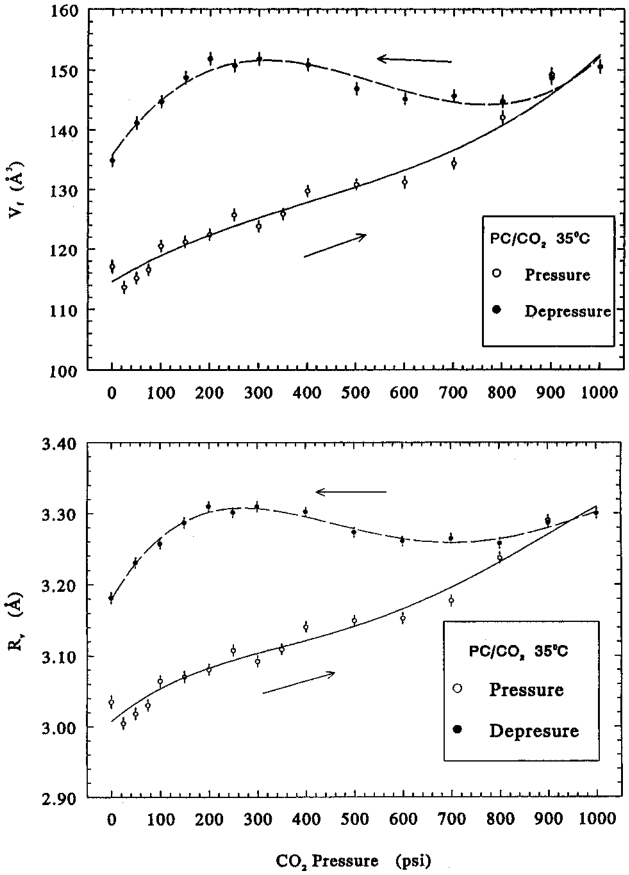

Figure 8. Radius (*R*) and volume (V_f) of PC vs the CO$_2$ pressure. (Lines drawn for visual clarification only.)

high pressure is insignificant compared to the plasticization effect in the PC/CO$_2$ system. This large effect is observed in the macroscopic volume dilation, which increases 7.5% at 900 psi.[13] But the relative magnitude of dilation in free-volume holes is even greater. For example, V_f increases from 116 to 150 Å^3 when CO$_2$ pressure changes from vacuum to 1000 psi. The relative free volume thus increases by 30%.

For the depressurization process, τ_3 and I_3 show a large hysteresis (Figure 7). Starting from 1000 psi, τ_3 first decreases with decreasing pressure, but always has a higher value than that during pressurization. Around 600 psi, τ_3 begins to increase with decreasing CO$_2$ pressure, and at 200 psi it reaches maximum. At lower pressure, τ_3 again decreases, but never returns to its original value, even under vacuum. The I_3 variation has a different pattern during depressurization, as shown in Figure 7. When gas pressure decreases from 1000 psi, the I_3 increases slightly, reaches maximum around 600 psi, and then decreases below 600 psi. As with τ_3, even under vacuum I_3 does not go back to the original value. Hole radius *R* and volume V_f follow a similar course with respect to pressure, as shown in Figure 8 for depressurization. The fraction of the free-volume hole, F_v (Figure 9), stays at nearly the same value as CO$_2$ pressure decreases from 1000 to 200 psi. Below 200 psi, F_v decreases with decreasing CO$_2$ pressure and does not return to its original value even when the sample is under vacuum. As shown in Figure 9, the F_v during depressurization is always higher than it is under pressurization, at every pressure.

It is obvious that the microstructures of PC are significantly changed when PC is exposed to CO$_2$. Free-volume hole size and fraction have been enlarged after CO$_2$ exposure. The hysteresis behavior of PAL results

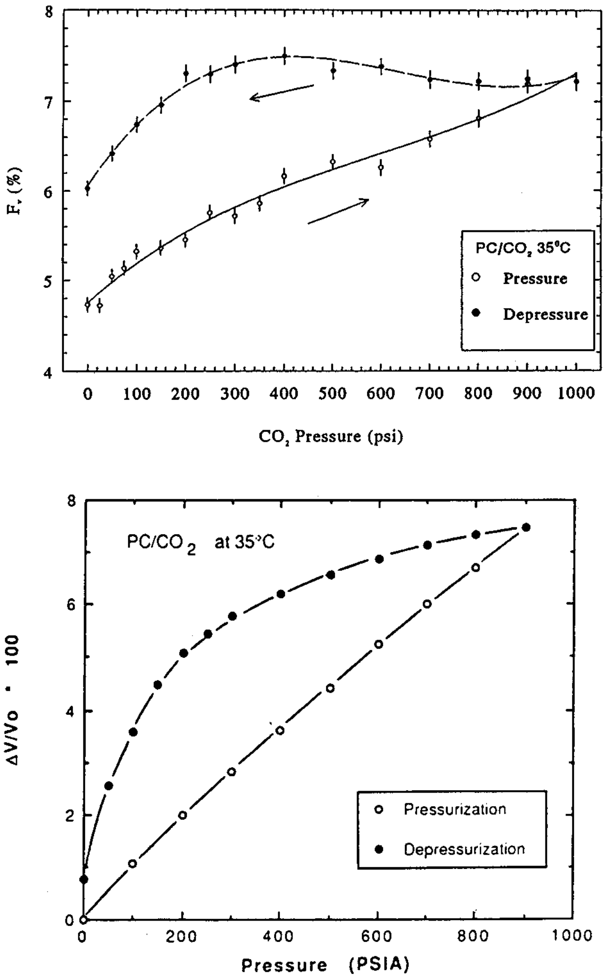

Figure 9. Fraction of the free volume hole (F_v) and specific volume dilation in PC vs the CO$_2$ pressure. Volume dilation data (lower figure) are taken from ref 13. (Lines drawn for visual clarification only.)

and free volume after depressurization is attributed to the strong molecular interaction between the CO$_2$ gas and the polycarbonate matrix. Similar results have been observed in macroscopic volume measurements, as shown in Figure 9 (lower part). Under 1000 psi of CO$_2$ pressure, the polycarbonate is highly sorbed by the CO$_2$ gas, and thus the free-volume hole size is greatly expanded and the number of holes increases. When the CO$_2$ pressure decreases, the gas escapes from the polymer matrix and free-volume hole size and fraction are expected to decrease. The observed slow decrease of *R* and F_v indicates a relatively long relaxation time (several days) of the excess free volume created by CO$_2$ pressurization.[5,36] This hysteresis is not seen in the PC/N$_2$ system, where N$_2$ is nearly inert in its interaction with PC.

The observed complicated variation of hole radius, volume, and fraction (Figures 8 and 9) resulting as a function of CO$_2$ exposure could be discussed in terms of the creation of new holes and the filling of preexisting holes in PC. According to the PC/CO$_2$ system data,[13] the concentration of sorpted CO$_2$ at 400 psi is reported to be 30 cm^3 STP/cm^3 (8.1 × 10^{20} molecules/cm^3 of PC). Then the number of CO$_2$ molecules per preexisting hole is estimated to be 2, based on 5% of F_v ($\equiv 4.4 \times 10^{20}$ holes/cm^3 of PC). The van der Waals volume of the CO$_2$ molecule (70.9 Å^3) is relatively large. For a hole of average radius 3 Å, two CO$_2$ molecules have effectively filled all available space at 400 psi, unless new holes are created. For a pressure larger than 400 psi, the

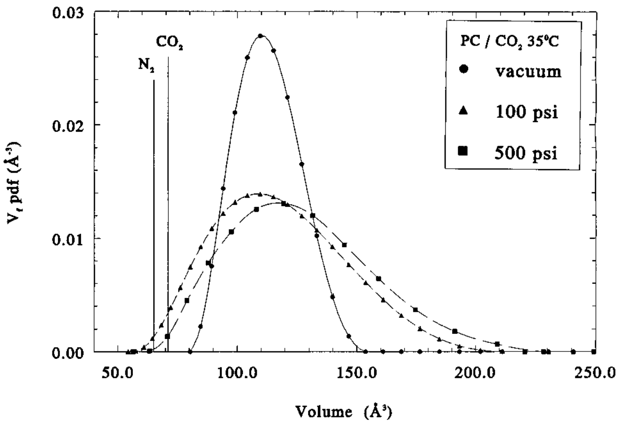

Figure 10. Distribution of the free-volume hole in the PC/CO_2 system at different gas pressures. The kinetic volumes of N_2 and CO_2 are indicated. (Lines drawn for visual clarification only.)

sorpted CO_2 concentration increases further. Therefore, we anticipate that the free-volume holes as observed by current PAL under CO_2 exposure are not the same preextant holes in PC, particularly when the pressure is greater than 200 psi (*i.e.*, about 1 CO_2 molecule per hole). It is observed in the results of V_f and F_v (Figures 8 and 9) that significant change occurs at pressure below 200 psi under depressurization. The newly created holes due to CO_2 sorption are expected to remain in the PC matrix with a relatively long molecular relaxation time. The total free-volume hole fraction is estimated from Figure 9 to increase about 1.2% at pressure = 0. It is about 4 times larger than $\Delta V/V_0$ as obtained from macroscopic measurements (Figure 9).

The distinct difference in the microstructures of free-volume holes in the PC/CO_2 system after CO_2 exposure can be clearly seen from the result of free-volume hole distribution in Figure 10. These results are measured at pressurization. As shown in Figure 10, the hole distributions are totally different from those in the original PC matrix. The distribution is largely broadened: smaller as well as larger holes emerge. The small holes are due to the filling of preexisting holes by CO_2, and the large holes are due to the creation of new holes after CO_2 sorption in the PC matrix. At low pressure (100 psi), the hole is distributed at a smaller size than at high pressure, due to filling. While at high pressure, the hole is distributed at a larger size than at low pressure, at which filling takes place. With these new free-volume distributions, we expect to see a distinct difference in the gas diffusion and permeability properties between the original and the CO_2-exposed PC polymers. In order to remove these newly created holes, we found that the PC needs to be heated well above T_g. A large variation of exposure history is expected in this system. Time dependence experiments are now in progress in our laboratory.

Conclusion

We have employed PAL to investigate the free-volume properties of polycarbonate exposed to the gases N_2 and CO_2. Large effects of pressure on free-volume properties have been observed in the PC/CO_2 system. These results show that CO_2-exposed PC has a very different microstructure from that of the original (unexposed) sample. Application of PAL to gas-exposed polymer systems appears to be very promising.

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