A NEW GAS DIFFUSIVITY MEASUREMENT TECHNIQUE FOR CO₂ INFUSED POLYMER SYSTEM DURING GAS DESORPTION

Selina X. Yao and Patrick C. Lee*, University of Vermont, Burlington, VT

Abstract

In this study, theoretical CO₂ diffusivity coefficients in amorphous polymers were calculated from dielectric constant changes during CO₂ desorption. Compared with experimental diffusivity coefficients from a gravimetric method, these values agree well with each other. Three amorphous polymer films made from Polystyrene (PS), Polycarbonate (PC), and Cyclic Olefin Polymer (COP) resins were saturated with supercritical CO₂ under high pressure in a pressure chamber. Then, the CO₂ infused films were removed from the chamber for gas desorption experiments. Both capacitance and weight changes of the samples were recorded by an Inductance, Capacitance and Resistance (LCR) meter and a scale simultaneously. The dielectric constant changes of the polymer/CO₂ systems were calculated from the capacitance change measurements during gas desorption experiments. The trend of dielectric constant changes is found to be similar to that of the CO₂ weight percentage changes during gas desorption. A mathematical model was built to predict the CO₂ weight percentages at any given time during a desorption process from the measured dielectric constants. The theoretical diffusivity coefficients were obtained from the predicted CO₂ weight percentage changes and these theoretical diffusivity coefficients agree well with the experimental data.

Introduction

Supercritical fluids (SCFs) and gases are widely used in polymer processing. For example, plastic foam products used for light-weight structural components, thermal insulation panels, and food packaging containers can be fabricated by nano-/micro-cellular foaming processes with gases/SCFs. A SCF is also used as a carrier in a polymer impregnation process, a process of depositing a solute into a polymer. Many properties such as rheological properties, plasticization behaviors, glass transition temperatures, and crystallization of polymers can be affected by the dissolved SCFs and gases. Gas/SCF solubility and diffusivity are two critical parameters to understand the aforementioned property changes in foaming processes. Therefore, these properties are essential to characterize in order to better understand the various processes, but they are not trivial to measure.

There are several methods to obtain gas/SCF diffusivity and solubility such as gravimetric, manometric, spectroscopic, and chromatographic methods. The gravimetric method measures solubility of a gas/SCF dissolved in a polymer by acquiring the changes of the sample weight by a gas/SCF. However, the measurement instruments based on the gravimetric methods are either expensive, complex, and/or sensitive to an electromagnetic field [1]. A manometric method determines the solubility of gases/SCFs in a polymer by measuring the pressure or volume of the gas absorbed in or desorbed from the sample in equilibrium [2]. The instruments based on the manometric methods provide relatively simple experimental setups but these devices measure the sample volume indirectly by monitoring gas pressures and volumes, which may affect the measurement accuracy. A spectroscopic method gives a characteristic pattern of absorption bands for the sample and a change in the characteristic pattern can clearly indicate the change in the composition of the material. Gas/SCF solubility and volume swelling behavior can be measured from this method by analyzing the characteristic pattern [3]. But it only works for short time gas diffusion cases and can not record the background spectra. In chromatography, a thin polymer film is fixed in the column (i.e., stationary phase or solid phase) and the gas is injected to the column (i.e., mobile phase or gas/vapour phase). Because gas sorption is related with the retention time and retention volume of the solute in the chromatographic column, a chromatography technique measures retention time and retention volume to acquire the gas sorption data. Chromatographic methods are fast and effective in acquiring solubility and diffusivity, but have limitations on the types of polymers [2]. In order to overcome these disadvantages in the measurement techniques, a new solubility and diffusivity measurement method for gas/SCF in polymers using a dielectric property was investigated in this study. If this technique which relates a gas/SCF transport property with dielectric constants performs well, then a cost effective, simple, and portable gas/SCF diffusivity/solubility measurement method may be possible, opening up many potential applications.

For example, foam aging is a common problem for many polymer foam products due to significant product dimension changes and long storage times. Gas/SCF diffusivity significantly affects foam aging behaviors. Once a foaming process finishes, blowing agents leave the polymer foam matrix and the bubble volumes are replaced by air. This gas exchange rate strongly depends on gas/SCF diffusivity. Some volatile gases, such as CO₂ and N₂ leave the structure quickly, while other long-chain molecule gases, such as fluorocarbons and hydrocarbons escape slowly. In order to manufacture dimensionally stable foam products and shorten a storage time, it is essential to investigate gas desorption behavior after a foaming process. Furthermore, gas diffusion is also
critical to the initial foam expansion control in a foam extrusion process. The study performed by H. E. Naguib, C. B. Park, and P. C. Lee [4] demonstrated that an initial foam expansion behavior at the die exit determines the final foam volume expansion ratio and there is an optimum temperature range to achieve the maximum volume expansion ratios. Blowing agent diffusivity plays a key role in this process. At high temperatures, the gas diffusivity is high and gas escapes from the polymer matrix quickly. This yields low foam expansion ratios. On the other hand, at low temperatures, the polymer matrix is too stiff to expand and thus yields low expansion ratios. For better foam expansion control during a foam process, in-situ gas diffusivity measurement would be beneficial.

Dielectric properties refer to storage and dissipation of electric and magnetic energy in materials. According to the Clausius-Mossotti relation, dielectric constant can be described as a function of a polymer’s free volume fraction, which can significantly affect the polymer transport properties such as permeability, solubility, and diffusivity. Several groups investigated the relationship between a gas transport property and dielectric constants for various polymer and gas combinations at steady state conditions for membrane filter applications. K. Matsumoto, P. Xu, and T. Nishikimi reported the relationship between CO$_2$, CH$_4$, H$_2$, O$_2$, N$_2$ gas permeability and dielectric constant values of several aromatic polyimides films [5]. Dielectric constants were calculated from the capacitance values from a parallel plate measurement method. CO$_2$ and CH$_4$ permeability coefficients with various polyimide films were measured for membrane separation applications at a steady state condition (i.e., 53.33 MPa at the upstream and vacuum at the downstream of the membrane). They observed that gas permeability coefficients decreased with increasing dielectric constants of the membrane films. S. Miyata’s research team studied the gas transport properties and dielectric properties of four hexafluorosopropylidene polyimides with CO$_2$, CH$_4$, H$_2$, O$_2$ and N$_2$ [6]. They also tested the gas permeability at a steady state condition and claimed that gas permeability coefficients were higher with films with lower dielectric constants as K. Matsumost et al.’s study.

These previous studies confirmed the relationship between gas diffusivity and dielectric constants under steady state conditions for gas membrane applications. However, in these studies, dielectric constants were measured at steady state conditions (i.e., high pressures at the upstream and low pressures at the downstream of the membranes). In this paper, capacitance values were measured during a gas desorption process (i.e., unsteady conditions) and demonstrated that these values change significantly with a CO$_2$ amount in the polymer matrix. In this study, three amorphous polymers (e.g. PS, COP and PC) were used to investigate CO$_2$ desorption behaviors by measuring weight and capacitance changes over time. CO$_2$ diffusivity coefficients by both methods were calculated and compared.

Diffusivity, Solubility and Dielectric Property

Two different diffusion coefficients for different periods of the diffusion process are given as $D_{\text{short}}$ and $D_{\text{long}}$. $D_{\text{short}}$ describes the initial part of desorption, and $D_{\text{long}}$ describes the later stage of the desorption process.

At time $t_{1/2}$, $\frac{M_t}{M_{\text{max}}}$ = 0.5. The approximation of $D_{\text{short}}$ can be expressed as [7]:

$$D_{\text{short}} = \frac{0.04919}{(t/\ell)^2}$$

When the gas concentration in the polymer film approaches zero (i.e., $r$ has a large value), a more precise description of diffusion is given as [8].

$$D_{\text{long}} = \frac{\theta L^2}{\pi^2}$$

where $D_{\text{long}}$ is the diffusion coefficient as the gas concentration approaches zero. $\theta$ is the average value of $\frac{\ln(M_{\text{max}}-M_t)}{t}$, and $L$ is the film thickness.

A dielectric constant can be calculated from capacitance, which is the ability of a body to store an electrical charge. The capacitance values of the samples can be measured using two parallel plates with surface area, $A$, and gap distance, $d$. Then, the dielectric constant, $\varepsilon_r$, can be expressed as:

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A L}$$

where $\varepsilon_0$ is the vacuum permittivity, $8.85 \times 10^{-12}$ farad.

Experimental

Commercial grade pellets of Polycarbonate (PC, Caliber 201 TRP, Styron), Polystyrene (PS, MB3150, AmSty), Cyclo Olefin Polymers (COP, 1020R, ZEON Chemicals) and CO$_2$ (USP Grade Medical Carbon Dioxide, Airgas) with purity over 99.9% were used in this study. PC, PS and COP pellets were heated to 200 °C, 160 °C, and 150 °C, respectively, and pressed. After pressing, the films were then quenched in cold water. The PC, PS and COP films were 0.20 mm, 0.18 mm and 0.34 mm thick, respectively.

The films for capacitance and weight measurements were saturated in a pressure chamber (4720 high pressure cell, Parr) pressurized by a positive displacement pump (500D Syringe pump, Teledyne) at 5.5 MPa for 24 hours before weight and capacitance measurements.

After releasing the CO$_2$ pressure in the chamber, the CO$_2$ infused samples were immediately moved to the weight and capacitance measurement devices. The
capacitance of samples during a CO₂ desorption process was measured by a parallel plate method with an LCR meter (SR715, Stanford Research Systems) at 1 kHz, 25 °C, and a relative humidity of 45%. The dielectric constants were calculated from the capacitance values measured by the LCR meter. The films with 50 mm × 50 mm areas were inserted into a parallel plate capacitor with the plate area of 38.2 mm × 38.2 mm. The capacitance change was recorded for 90 minutes.

The 50 mm × 100 mm films were put on the Ohaus Precision Standard scale, with 3 decimal place accuracy, once the samples were taken out of the pressure chamber. The weight change of the film was recorded for 90 minutes simultaneously as the capacitance measurements.

Results and Discussion

1. Diffusivity of CO₂ in Polymer Films

Diffusivity can be measured by a gas desorption gravimetric experiments [2]. Figure 1 shows the CO₂ weight percentage changes in the polymer samples during desorption processes. The corresponding weight percentage changes of polymers in the CO₂ filled polymer systems are also drawn in Figure 1. Each measurements were repeated for three times and the average values as well as the standard deviations were shown in Figure 1.

![Desorption curves of CO₂ saturated polymer films](image)

Figure 1. Desorption curves of CO₂ saturated polymer films: a) PC, b) PS, and c) COP films

The CO₂ weight decreases dramatically in the beginning of the desorption process and then slows down for all cases. This trend can be explained by the diffusion dependence on gas contents. As the gas amount decreases in the polymer, the gas transporting rate slows down leading to a slower weight change. Based on the desorption curves, the diffusion coefficients can be calculated for each case from the theories introduced in Section 2. The results are tabulated in Table 1. The films reached an equilibrium after 24 hours of CO₂ saturation at 5.5 MPa. Assuming the gas loss is minimum during the sample removal process from the chamber, the first data in the CO₂ desorption curves equal to the CO₂ weight at the equilibrium. Thus, approximate CO₂ solubility values in these systems under 5.5 MPa and 25 °C can be estimated by the first data points in Figure 1.

Table 1. Experimental CO₂ diffusivity coefficients and approximate solubility data at 25 °C and 5.5 MPa

<table>
<thead>
<tr>
<th></th>
<th>$D_{\text{short}}$ (m²/s)</th>
<th>$D_{\text{long}}$ (m²/s)</th>
<th>Approx. Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>2.41E-12</td>
<td>3.47E-11</td>
<td>~ 6.9 wt%</td>
</tr>
<tr>
<td>PS</td>
<td>3.30E-12</td>
<td>2.82E-11</td>
<td>~ 5.0 wt%</td>
</tr>
<tr>
<td>COP</td>
<td>3.49E-12</td>
<td>1.51E-11</td>
<td>~ 4.2 wt%</td>
</tr>
</tbody>
</table>

The experimental data from this study was compared with the literature data. CO₂ diffusivity in PC was studied by W. J. Koros, D. R. Paul and A. A. Rocha [9]. Permeation experiments were conducted to obtain sorption curves. A time lag method was used to calculate the CO₂ diffusivity at 35 °C with pressures changing from 0.1 to 2.3 MPa. The diffusivity coefficient was reported as 4.67×10⁻¹² m²/s. For a PS/CO₂ system, Y. Sato and his colleagues reported that the CO₂ diffusivity coefficients, at temperatures in the range of 100 to 200 °C and pressures changing from 0 to 20 MPa, ranged from 0.81×10⁻¹⁰ m²/s to 10.5×10⁻¹⁰ m²/s [10]. A precise measuring equipment such as magnetic suspension balance was used in their research to measure the polymer weight changes during sorption. Within our knowledge, no diffusion experiments were
performed for the COP/CO₂ system. For better comparison, experiments conditions and results of literature and this study are tabulated in Table 2. W. J. Koros’ result agrees well with the diffusivity coefficient from this study since the experimental conditions are similar (i.e., 25 °C, 5.5 MPa vs. 35 °C, 2.3 MPa).

Table 2. Comparison of experimental vs. literature diffusivity coefficient data

<table>
<thead>
<tr>
<th>Polymers</th>
<th>PC</th>
<th>PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusivity coefficient from this study (m²/s)</td>
<td>2.41E-12</td>
<td>3.30E-12</td>
</tr>
<tr>
<td>Experimental conditions</td>
<td>25 °C, 5.5 MPa</td>
<td>25 °C, 5.5 MPa</td>
</tr>
<tr>
<td>Diffusivity coefficients from literatures</td>
<td>4.67E-12</td>
<td>1.14E-10</td>
</tr>
<tr>
<td>Experimental Conditions</td>
<td>35 °C, 2.3 MPa</td>
<td>100 °C, 4.6 MPa</td>
</tr>
<tr>
<td>Reference</td>
<td>[9]</td>
<td>[10]</td>
</tr>
</tbody>
</table>

2. Dielectric Property of Polymer/CO₂ Systems

The dielectric constants of polymer/CO₂ systems were calculated by their capacitance value changes during the desorption process. The dielectric constants shown in Figure 2 are the average values from 3 experiments. The polymer weight percentage changes in the polymer/gas systems, reported in Figure 1, were normalized and used in the comparison between dielectric constant change and the weight change experiments during CO₂ desorption. Two sets of data are normalized in the range of 0 to 1 using a max-min normalization scaling method.

The normalized polymer weight % changes with the dielectric constant changes of the 3 polymer/gas systems over time were compared and plotted in Figure 2. Since the dielectric constants and CO₂ weight percentages are changing in opposite ways with time, corresponding polymer weight percentage changes (polymer weight % = 1 - CO₂ weight %) were used to compare with the dielectric constant changes of the test samples.

As shown in Figure 2, the changes of dielectric constants with respect to time are well overlapped with the corresponding polymer weight percentage changes for all cases. Both values agree well with each other and the trends show significant changes in the beginning of the desorption process and then the changes slow down. These trends for the weight changes are explained in Section 1. The dielectric constant changes of the polymer/CO₂ systems can be directly related to the CO₂ content in the system at time 𝑡. The dielectric constant of CO₂ is significantly smaller than those of pure polymers used in this study [11]. Therefore, the polymer/CO₂ systems have lower dielectric constants than the pure polymers. During CO₂ desorption, CO₂ escaped from the polymer/CO₂ systems and the dielectric constants of the system increase up to the dielectric constants of corresponding pure polymers. Therefore, the exact amount of CO₂ at any time 𝑡 in the CO₂ infused polymer systems during a desorption process can be measured by a relatively simple and inexpensive dielectric property measurement technique.

Based on the relationship between experimental dielectric constant and polymer weight % data, a model
was built to predict a CO₂ amount in the polymer at time \( t \). From this model, both solubility and diffusivity with respect to time can be calculated during gas desorption.

Theoretical normalized polymer weight percentages can be predicted at any time \( t \) by:

\[
w_t = d_t
\]

(4)

where \( d_t \) is the normalized dielectric constant at time \( t \), and \( w_t \) is the normalized polymer weight percentage of a polymer/gas system at time \( t \). According to Equations (Error! Reference source not found.), the polymer weight percentage of a polymer/gas system can be calculated as below:

\[
W_t = d_t \times (W_{\text{max}} - W_{\text{min}}) + W_{\text{min}}
\]

(5)

where \( W_t \) is the predicted polymer weight percentage at time \( t \), and \( W_{\text{min}} \) and \( W_{\text{max}} \) are the polymer weight percentages measured at the beginning and end of the desorption experiment, respectively. A gas weight percentage can be defined as:

\[
M_t = 1 - W_t
\]

(6)

Thus, theoretical diffusivity coefficients can be calculated from the change of \( M_t \) with time. Theoretical diffusivity coefficients, \( D^*_{\text{short}} \) and \( D^*_{\text{long}} \), and experimental diffusivity coefficients, \( D_{\text{short}} \) and \( D_{\text{long}} \), are tabulated in Table 3. The differences between theoretical and experimental diffusivity coefficients are small for all cases.

Table 3. Theoretical and experimental diffusivity coefficients at 25 °C and 5.5 MPa

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Theoretical</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( D^*_{\text{short}} ) (m²/s)</td>
<td>( D^*_{\text{long}} ) (m²/s)</td>
</tr>
<tr>
<td>PC</td>
<td>3.43E-12</td>
<td>3.33E-11</td>
</tr>
<tr>
<td>PS</td>
<td>3.43E-12</td>
<td>3.28E-11</td>
</tr>
<tr>
<td>COP</td>
<td>3.49E-12</td>
<td>1.54E-11</td>
</tr>
</tbody>
</table>

Conclusion

This research investigated the relationship between a dielectric property and gas diffusivity/solubility of polymer/CO₂ systems during gas desorption. Three amorphous polymer films prepared from PC, PS and COP resins were saturated in pressure chamber with supercritical CO₂ at 25 °C and 5.5 MPa for 24 hours and then removed from the pressure chamber for gas desorption experiments. CO₂ weight percentage changes and capacitance changes during CO₂ desorption were recorded using a scale and LCR meter for CO₂ diffusivity coefficients calculation, respectively. The trends of the CO₂ weight percentage changes and the dielectric constant changes over time during desorption experiments agree well with each other. A mathematical model was built to describe the relationship between CO₂ weight percentage and dielectric constants. It can be used to predict CO₂ weight percentages at any time during a gas desorption process based on the dielectric constant data. Theoretical diffusivity coefficients are also calculated from the predicted CO₂ weight percentages and agree well with the experimental diffusivity coefficients.

Acknowledgements

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References

7. Park, G.S.; Cran, J.: Diffusion in polymers. (1968)