A new gas/supercritical fluid (SCF) diffusivity measurement method for CO₂ saturated polymer systems using a dielectric property

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Abstract. In this research, theoretical CO₂ diffusivity coefficients in amorphous polymers were calculated from dielectric constant changes during CO₂ desorption. These values showed agreement with experimental diffusivity coefficients from a gravimetric method. Three amorphous polymer films made from Polystyrene (PS), Polycarbonate (PC), and Cyclic Olefin Polymer (COP) resins were saturated with supercritical CO₂ at 5.5 MPa and 25 °C for 24 hours in a pressure chamber. The CO₂ infused films were removed from the chamber for gas desorption experiments. The capacitance of the samples were recorded with an Inductance, Capacitance and Resistance (LCR) meter. These values were used to calculate the change in dielectric constants. CO₂ weight percentages measured by a scale was used to calculate experimental diffusivity and solubility coefficients. It was found that the trend of dielectric constant changes was similar to that of the CO₂ weight percentage changes during gas desorption. A mathematical model was built to predict the CO₂ weight percentages during desorption from the measured dielectric constants. Theoretical diffusivity coefficients from this work agree well with literature data.

Keywords: polymer membranes, diffusivity, supercritical fluid (SCF), dielectric property, polymer/SCF system

1. 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 [1, 2]. A SCF is also used as a carrier in a polymer impregnation process, a process of depositing a solute into a polymer [3, 4]. 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 [5–9]. However, these measurements have their limitations. For example, Magnificent Suspension Balance, based on the gravimetric methods are either expensive, complex, and/or sensitive to an electromagnetic field [6]. 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 [8]. In order to overcome these disadvantages in the incumbent measurement techniques, a new solubility and diffusivity measurement method for a gas/SCF in polymers

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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, such as foaming aging and expansion control [10, 11].

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 [12], which can significantly affect the polymer transport properties such as permeability, solubility, and diffusivity [13]. 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 [14, 15]. Matsumoto *et al.* [14] reported the relationship between CO₂, CH₄, H₂, O₂, N₂ gas permeability and dielectric constant values of several aromatic polyimides films. Gas permeability is observed to decrease with increasing dielectric constants of the membrane films during steady diffusion. Miyata's research team studied the gas transport properties and dielectric properties of four hexafluoroisopropylidene polyimides with CO₂, CH₄, H₂, O₂ and N₂ [12]. 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 shown by Matsumoto *et al.*'s study [14].

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 CO₂ amount in the polymer matrix. In this study, three amorphous polymers (e.g. PS, COP and PC), which are widely used in foaming processes, were used to investigate CO₂ desorption behaviors by measuring weight and capacitance changes over time. CO₂ diffusivity coefficients by both methods were calculated and compared.

2. Diffusivity and solubility

By definition of the International Union of Pure and Applied Chemistry (IUPAC) [16], solubility is the proportional ratio of a solute in a solvent. In gas/SCF and polymer systems, solubility is determined by the weight of gas absorbed by a polymer after saturation over the polymer weight as shown by Equation (1):

$$S = \frac{W_{\text{gas}}}{W} \quad (1)$$

where W is the total weight of the sample (including the absorbed gas), and W_{gas} is the weight of gas absorbed by the polymer.

Diffusion can be described as a process where a material is transported by the thermal motion of the molecules in a fluid or a matrix. Unsteady diffusion is the most common type of diffusion which is described by Fick's Law; an analytical solution is available for this, see Equation (2):

$$\frac{\partial C}{\partial t} = \left(\frac{\partial(D\partial C)}{\partial x^2} \right) + \left(\frac{\partial(D\partial C)}{\partial y^2} \right) + \left(\frac{\partial(D\partial C)}{\partial z^2} \right) \quad (2)$$

where C is the gas concentration at time t , D is the gas diffusivity at a position (x, y, z) in the polymer. Frequently, diffusion occurs effectively in one direction when the thickness of the polymer sample is small enough to be ignored. In such cases, Equation (2) can be reduced to Equation (3):

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (3)$$

As a polymer film is immersed in CO₂, CO₂ concentration, C , can be solved, at time t , using Equation (3) [17]. The expression for an analytical solution is (Equation (4)):

$$\frac{M_t}{M_{\text{max}}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2} \exp\left(\frac{-D(2n+1)^2 \pi^2 t}{L^2}\right) \quad (4)$$

where M_{max} is the total amount of a diffusing substance absorbed by the polymer sheet at the onset of desorption, M_t is the corresponding quantity of the gas at time t and L is the film thickness. Based on Equation (4), two different diffusion coefficients corresponding to different periods of the diffusion process are given as D_{short} and D_{long} . D_{short} describes the initial part of desorption, and D_{long} describes the later stage of the desorption process [18].

At time $t_{1/2}$, $M_t/M_{\max} = 0.5$, and t/L^2 can be written as $t_{1/2}/L^2$. Based on Equation (4), $t_{1/2}/L^2$ can be expressed as shown by Equation (5) [19]:

$$\left(\frac{t_{1/2}}{L^2}\right) = -\left(\frac{1}{\pi^2 D}\right) \ln\left(\frac{\pi^2}{16} - \frac{1}{9}\left(\frac{\pi^2}{16}\right)^9\right) \quad (5)$$

The approximation of D_{short} can be expressed as shown by Equation (6) [19]:

$$D_{\text{shot}} = \frac{0.04919}{\left(\frac{t_{1/2}}{L^2}\right)} \quad (6)$$

When the gas concentration in the polymer film approaches zero (i.e., t has a large value), a more precise description of diffusivity coefficient is given by Park and Crank [19] (Equation (7)):

$$\bar{D} \approx \frac{1}{C_0} \int_0^{C_0} D(C) dC \quad (7)$$

where C_0 is the equilibrium gas concentration, and $\bar{D}$ is the integral diffusion coefficient. Equation (7) can be solved as Equation (8):

$$\ln(M_{\max} - M_t) = \ln\left(\frac{8M_{\max}}{\pi^2}\right) - \frac{D_{\text{long}} \pi^2 t}{L^2} \quad (8)$$

where D_{long} is the diffusion coefficient as the gas concentration approaches zero [20]. From Equation (8), it is observed that the graph of $\ln(M_{\max} - M_t)$ against t gives a straight line with a slope θ , and D_{long} can be simplified as Equation (9):

$$D_{\text{long}} = -\frac{\theta L^2}{\pi^2} \quad (9)$$

where θ is the slope of $\ln(M_{\max} - M_t)$ against t , and L is the film thickness [21].

3. Dielectric property

A dielectric constant is also called a relative permittivity. Typically, a relative permittivity is defined by Equation (10):

$$\epsilon_r(\omega) = \frac{\epsilon(\omega)}{\epsilon_0} \quad (10)$$

where $\epsilon(\omega)$ is the complex frequency-dependent absolute permittivity of a material, and ϵ_0 is the vacuum permittivity, $8.85 \cdot 10^{-12}$ Farad.

Capacitance 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 capacitance can be expressed as Equation (11):

$$C = \epsilon_r \epsilon_0 \frac{A}{d} \quad (11)$$

If the capacitance value and the geometry of the capacitor are known, a dielectric constant, ϵ_r (Equation (12)), can be calculated from Equation (11):

$$\epsilon_r = \frac{Cd}{A\epsilon_0} \quad (12)$$

4. Experimental

4.1. Materials and sample preparation

Commercial grade pellets of Polycarbonate (PC, Caliber 201 TRP, Styron), Polystyrene (PS, MB3150, AmSty), Cyclo Olefin Polymers (COP, 1020R, ZEON Chemicals) and CO₂ (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, 160, and 150 °C (around 50~60 °C higher than the glass transition temperatures), respectively, and pressed at 10.34 MPa for 5 minutes, then at 31.03 MPa for 15 minutes to make films. After pressing, the films were then quenched in cold water. The PC, PS and COP films were 0.20, 0.18 and 0.34 mm thick, respectively.

4.2. Experimental procedures

The films for capacitance and weight measurements were saturated in a pressure chamber (4720 high pressure cell, Parr Instrument Company) pressurized by a positive displacement pump (500D Syringe pump, Teledyne ISCO) at 5.5 MPa for 24 hours. For each experiment, two samples were saturated (i.e., one sample for the weight measurements and the other for the capacitance measurements). After releasing the CO₂ pressure in the chamber, the CO₂ infused samples were immediately moved to the weight and capacitance measurement devices. During desorption, the capacitance of samples were measured by a parallel plate method with an Inductance, Capacitance and Resistance meter (LCR meter, SR715, Stanford Research Systems) at 1 kHz, at a temperature of

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 clamped between two parallel plates. Area of both plates was 38.2 mm×38.2 mm. A minimal force was applied to hold the polymer film. The capacitance change of the sample was recorded for 90 minutes after depressurization. The 50 mm×100 mm films were put on the Ohaus Precision Standard scale, with 3 decimal place accuracy, as soon as 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.

5. Results and discussion

5.1. Diffusivity of CO₂ in polymer films

Diffusivity can be measured by a gas desorption gravimetric experiments [7, 22]. It can also be obtained by gas absorption experiments as well, but a gas desorption process is much easier since it does not need a high pressure condition during the measurements [23].

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 shown in Figure 1. Each measurement was repeated for three times for data consistency. The average values as well as the standard deviations are shown in Figure 1.

The CO₂ weight decreases dramatically in the beginning of the desorption process and then slows down over time for all cases. This trend can be explained by the diffusion dependence on gas concentration. 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. CO₂ in a COP matrix experiences the fastest diffusion (i.e., high D_{short}) in the beginning phase of the description process and the slowest diffusion (i.e., low D_{long}) toward the later desorption stage among 3 systems. Unlike the COP/CO₂ system, the diffusion of CO₂ in a PC matrix shows the opposite trend by yielding the lowest D_{short} and then the highest D_{long} among three systems. Approximate

Figure 1. Desorption curves of CO₂ saturated polymer films by a gravimetric method after CO₂ saturation under 5.5 MPa for 24 hours: a) PC, b) PS, and c) COP films

CO₂ solubility data in polymers under 5.5 MPa and 25 °C are also indicated in Figure 1 and tabulated in Table 1. The films reached an equilibrium after 24 hours of CO₂ saturation at 5.5 MPa and 25 °C. Assuming the gas loss is minimal during the sample

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

	D_{short} [m ² /s]	D_{long} [m ² /s]	Approximate solubility at 25 °C, 5.5 MPa [wt%]
PC	$2.41 \cdot 10^{-12}$	$3.47 \cdot 10^{-11}$	~6.9
PS	$3.30 \cdot 10^{-12}$	$2.82 \cdot 10^{-11}$	~5.0
COP	$3.49 \cdot 10^{-12}$	$1.51 \cdot 10^{-11}$	~4.2

removal process from the chamber, the first measurement of CO₂ weight percentage equals to the CO₂ weight at the equilibrium under 5.5 MPa and 25 °C. 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. The CO₂ solubility in polymers are in an order of PC > PS > COP. The experimental data from this study was compared with the literature data [24]. CO₂ diffusivity in PC was studied by Koros *et al.* [24]. 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 $4.67 \cdot 10^{-12}$ m²/s. In 2004, Tang, Du and Chen measured the weight changes of PC/CO₂ desorption experiments at temperatures in the range of 40 to 60 °C, and initial pressures in the range of 10 to 40 MPa. The diffusivity coefficients ranged from $1.61 \cdot 10^{-11}$ to $2.55 \cdot 10^{-11}$ m²/s [25]. For a PS/CO₂ system, 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 $0.81 \cdot 10^{-10}$ to $10.5 \cdot 10^{-10}$ m²/s [26]. 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. Compared to the diffusivity coefficients in this study, the diffusivity coefficients from Tang's and Sato's studies are higher. These differences are due to the different experimental conditions as shown in Table 2. 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).

5.2. Dielectric property of polymer/CO₂ systems

The dielectric constants shown in Figure 2 are the average values from three different experiments measured at 1 kHz, at a temperature of 25 °C, a relative humidity of 45% for data consistency. The difference in 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 percentage change experiments during CO₂ desorption. Two sets of data are normalized in the range of 0 to 1 using a min-max normalization scaling method as described in Equation (13):

$$x_i = \frac{X_i - X_{\min}}{X_{\max} - X_{\min}} \quad (13)$$

where X_i is i^{th} datum of the original series, $X_{\max}$ and $X_{\min}$ are the maximum and minimum data in the series respectively, and x_i is the i^{th} normalized datum.

The normalized polymer weight percentage changes with the dielectric constant changes of the 3 polymer/gas systems over time were compared and plotted in Figure 2. Due to the dielectric constants and CO₂ weight percentages are changing in opposite ways with time, corresponding polymer weight percentage changes (polymer weight percentage = 1 – CO₂ weight percentage) were used for a better comparison 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 their trends show significant increase in the beginning of the desorption process which plateaus over time. These trends for the weight changes are explained in Section 5.1. The dielectric constant changes of the polymer/CO₂ systems can be directly related to the CO₂ content in the system at time t .

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

Polymers	Diffusivity coefficient from this study [m ² /s]	Experimental conditions	Diffusivity coefficients from literatures [m ² /s]	Experimental conditions	Reference
PC	$2.41 \cdot 10^{-12}$	25 °C, 5.5 MPa	$4.67 \cdot 10^{-12}$	35 °C, 2.3 MPa	[24]
			$1.61 \cdot 10^{-11}$	40 °C, 20.0 MPa	[25]
PS	$3.30 \cdot 10^{-12}$	25 °C, 5.5 MPa	$1.14 \cdot 10^{-10}$	100 °C, 4.6 MPa	[26]

The dielectric constant of CO₂ is significantly smaller than those of pure polymers used in this study [27, 28]. 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. Additionally, an initial weight measurement of the sample at the onset of desorption can be used to estimate the solubility of CO₂ in the polymer.

Figure 3 shows the normalized dielectric constants as y axis and normalized polymer weight percentages as x axis to demonstrate the good agreement between two sets of data. As shown in Figure 3, the slopes of three experimental data are around 1 and the intercepts on the y axis are very close to 0, indicating good data agreement. Based on the relationship between experimental dielectric constant and polymer weight percentage data, a model was built to predict a CO₂ amount in the polymer at time t . From this model, both solubility and diffusivity values with respect to time can be calculated during desorption.

Theoretical normalized polymer weight percentages can be predicted at any time t by Equation (14):

$$w_i = d_i \quad (14)$$

where d_i is the normalized dielectric constant at time t_i , and w_i is the normalized polymer weight percentage of a polymer/gas system at time t_i . According to Equation (1) and (13), the polymer weight percentage of a polymer/gas system can be calculated by Equation (15):

$$W_i = d_i \cdot (W_{\max} - W_{\min}) + W_{\min} \quad (15)$$

where W_i is the predicted polymer weight percentage at time t_i , and $W_{\min}$ and $W_{\max}$ are the polymer weight percentages measured at the beginning and end of the desorption experiment, respectively. A gas weight percentage can be defined by Equation (16):

$$M_i = 1 - W_i \quad (16)$$

Thus, theoretical diffusivity coefficients can be calculated from the change of M_i with time. Theoretical

Figure 2. Normalized polymer wt% vs. dielectric constants during CO₂ desorption: a) PC, b) PS, and c) COP samples

diffusivity coefficients, D_{short}^* and D_{long}^* , and experimental diffusivity coefficients, D_{short} and D_{long} , are tabulated in Table 3. The differences between theoretical and experimental diffusivity coefficients are small for all cases.

Figure 3. Normalized dielectric constants vs. polymer [wt%] in polymer/CO₂ systems: a) PC, b) PS, and c) COP systems

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

Polymer	Theoretical		Experimental	
	D_{short}^* [m ² /s]	D_{long}^* [m ² /s]	D_{short} [m ² /s]	D_{long} [m ² /s]
PC	$3.43 \cdot 10^{-12}$	$3.33 \cdot 10^{-11}$	$2.41 \cdot 10^{-12}$	$3.47 \cdot 10^{-11}$
PS	$3.43 \cdot 10^{-12}$	$3.28 \cdot 10^{-11}$	$3.30 \cdot 10^{-12}$	$2.82 \cdot 10^{-11}$
COP	$3.49 \cdot 10^{-12}$	$1.54 \cdot 10^{-11}$	$3.49 \cdot 10^{-12}$	$1.51 \cdot 10^{-11}$

6. Conclusions

This study investigated the relationship between a dielectric property and gas diffusivity and solubility of polymer/CO₂ systems during a gas desorption process. Three amorphous polymer films prepared from PC, PS and COP resins were saturated with supercritical CO₂ at 25 °C and 5.5 MPa for 24 hours and removed from the pressure cell for gas desorption experiments. The change of CO₂ weight percentage was recorded for each polymer film using a high precision scale. The CO₂ weight percentage significantly decreases in the beginning with lower slow-down rates towards the end of the desorption process. By assuming that the equilibrium absorption is reached after 24 hours of saturation, solubility of the polymer films was calculated in the following order PC > PS > COP. Two diffusion coefficients, D_{short} and D_{long} , were also calculated. COP showed the highest D_{short} while PC presented the highest D_{long} among these three polymer systems. Capacitance increase during the CO₂ desorption was also recorded using an LCR meter. The dielectric constants of the polymer and CO₂ system were calculated from the capacitance values. It was found that trends of the polymer weight percentage and the dielectric constant during desorption overlap with each other. A model was successfully built to show the relationship between these two behaviors. Furthermore, the results demonstrated a good agreement between theoretical diffusivity coefficients obtained from the CO₂ weight percentage change and the experimental diffusivity coefficients.

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