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Experimental Determination of Composition-Dependent Diffusivity of Carbon Dioxide in Polypropylene

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This work provides the experimentally determined composition-dependent diffusivity of environmentally benign plasticizer such as carbon dioxide in polypropylene. For this purpose, a pressure decay system is employed to determine composition-dependent diffusivity of carbon dioxide in polypropylene at isothermal conditions. On the basis of a detailed mass transfer model, variational calculus is used to establish the conditions necessary to yield the composition-dependent diffusivity that enables the model-predicted mass of absorbed gas in polymer to match with the experimental counterpart. The experimental solubility and composition-dependent diffusivity of carbon dioxide in polypropylene are obtained at (170, 180, and 190) °C for pressures up to 7.32 MPa.

Introduction

Ever since the invention of polymers, different types of organic plasticizers have been extensively used in polymer processing. Since almost all of them are harmful to some degree to the environment, the use of carbon dioxide as a plasticizer is preferred. The reason is that carbon dioxide on account of being noncorrosive, low-cost, and being environmentally benign eliminates the disadvantages associated with organic plasticizers.

As carbon dioxide is a gas under atmospheric conditions, it can be used as a plasticizer and is then easily removed from the polymer to obtain the original physical properties of the polymer matrix.[1] Further, it has been shown that the incorporation of a small mass fraction of carbon dioxide, (3 to 5) %, in a polymer decreases its viscosity by 2 to 3 orders of magnitude.[1] This phenomenon not only reduces energy cost but also improves the efficiency of polymer processing. The softening effect of plasticizers is the same as that of an increase in temperature; thus, there is a smaller danger of thermal degradation. In this respect plasticizers are indirectly thermal stabilizers.[2] While carbon dioxide is known to be an effective plasticizer for polymers, little is known about the diffusion mechanism and the resulting change in rheology.

The diffusion of a gas in a polymer is a complex phenomenon. Diffusivity is a coefficient in Fick's first law, which results from the statistical modeling of a large nonequilibrium system.[3] That coefficient is a product of Maxwell−Stefan diffusivity[4] and a thermodynamic nonideality factor related to the composition of a chemical species in the medium. Hence, diffusivity is a function of the species composition at a given temperature and pressure. Depending upon the nonideality, the diffusivity of a species varies with its composition in the medium, the effect being significant at finite compositions, and notably present in gas−polymer systems. Tendulkar et al.[5] have recently determined the composition-dependent diffusivity of carbon dioxide in polyethylene. Prior to this work, only a few related experimental studies on polymers are reported in the literature,[6–11] all of which used simplified mass transfer models and (or) assumed negligible effects of the nonideality. It is therefore desirable to increase our knowledge of composition-dependent diffusivities, which can improve our ability to describe and predict diffusion and associated phenomena in polymer processing.

The objective of this work is to experimentally determine the composition-dependent diffusivity of carbon dioxide in polypropylene at elevated temperatures and pressures. For this purpose a pressure decay system[5] was employed to measure the pressure drop with time due to gas absorption by the polymer in a closed carbon dioxide−polypropylene system of known volume at constant temperature. The generated pressure data were used for the determination of the gas diffusivity as well as solubility subject to the mathematical model of the experimental mass transfer process. The composition-dependent diffusivity and solubility were determined for carbon dioxide in polypropylene for (170, 180, and 190) °C at different pressures in the range of (0.45 to 7.32) MPa.

Experimental Section

Since the last century, numerous efforts have been made to investigate the diffusion coefficient and solubility of a gas in polymer simultaneously from a single sorption experiment.[5–17] There are various direct and indirect experimental methods for diffusion coefficient and solubility calculations. The methods in which we directly measure the mass gain of polymer (i.e., the absorbed gas mass) exposed to the gas are known as direct methods. The indirect methods are those in which a system property is measured and then related to the mass of absorbed gas.

While the mass of gas absorbed in the polymer with time enables the determination of the diffusion coefficient, the total mass of gas absorbed over an extended time period helps determine the gas solubility in the polymer at the final temperature and pressure. An indirect pressure decay method was employed in this work and followed the approach we took in our recent study.[5]

Materials. Polypropylene of melting points of (160 to 165) °C and respective number and weight average molecular weights of (50 000 and 190 000) kg·kmol^{-1} was supplied by Sigma-Aldrich Company. Carbon dioxide (more than 99.5 % pure) was obtained from British Oxygen Company, Canada.

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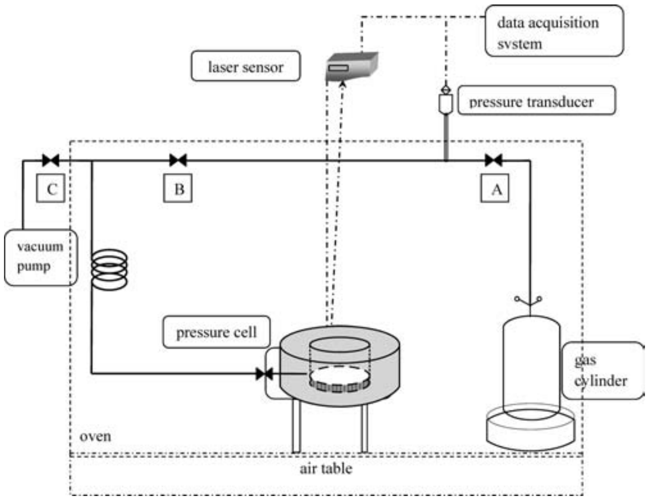

Figure 1. Schematic diagram of the experimental setup.

Equipment and Method. The diffusivity and solubility of carbon dioxide in polypropylene were determined by employing a pressure decay system. Figure 1 shows a schematic diagram of the experimental setup used to measure the decaying pressure as the gas gradually diffused into the polymer layer inside a closed pressure cell at a constant temperature. The primary component of the setup was a pressure cell with a concentric 4 cm diameter cylindrical slot at the bottom to hold a polymer sample. The lid of the pressure cell had a glass window allowing a complete view of the polymer surface to an external online Keyence LKG displacement laser sensor, which tracked the polymer surface movement with 10 μm accuracy. A Teflon core composite Viton O-ring was used between the lid and the lower part of the pressure cell, and threaded screws were used to seal pressure cell. As shown in the figure, the pressure cell was connected to a gas cylinder through a preheating coil. The gas cylinder was used for storing and preconditioning gas obtained from an external tank.

In addition to the above-mentioned pressure cell, the heart of the apparatus was a Paroscientific Digiquartz intelligent pressure transmitter, which was connected to the tube between valves A and B to record pressure inside the pressure cell. To maintain a constant temperature conditions for isothermal diffusion, the whole setup was placed inside a forced convective oven. The oven was placed over an air table to prevent any kind of convective mass transfer by vibrations from the surroundings.

Prior to each experiment, the experimental setup was leak tested for 12 h at the experimental temperature by pressurizing it to 1.25 times the experimental pressure. After pressurizing the system, valves A and C were closed, while valve B was open during the testing. After the test was successful, valve C was opened to depressurize the system, and polypropylene granules were placed in the sample slot. The whole system was again pressure-tested again. After the successful completion of the second test, the polypropylene granules were melted under reduced pressure at the experimental temperature to form a cylindrical layer of uniform thickness. The temperature was controlled within ± 0.5 °C of the desired value. Valve C was then closed, and the laser sensor was positioned and calibrated to track the movement of the polymer surface.

The experiment was started by quickly introducing the gas above the polymer surface inside the pressure cell. This was accomplished by simultaneously opening valve B and closing valve A to isolate the pressure cell from the gas holder. As the gas gradually diffused into the polymer layer, the decaying pressure inside the cell was recorded every 1.2 s. The pressure sensor had a resolution of ± 6 Pa. To determine gas solubility, the experiment was carried out until the pressure reduction could not be discerned. That was the time when the mass fraction of the gas in the polymer sample tended to a uniform equilibrium value. On the other hand, for diffusivity determination, the experiment was carried out for a short duration, and pressure decay data over a sufficiently short time period were used to ensure that pressure decay was less than 2 % of the initial pressure. The experiment was terminated by gradually opening valve C to release the gas. After the completion of each run, the polymer slot was cleaned up for the next run.

Theory

Because the polymer is not volatile, the recorded pressure versus time data, the pressure−volume−temperature relationship of the gas, and the volume change data for the gas−polymer mixture yield the experimental mass of gas absorbed in the polymer at any time. The primary objective is to determine the diffusivity (D) of a gas as a function of its mass concentration (ω) in a polymer phase. The criterion for the determination is the agreement of the experimental mass of the gas absorbed in the polymer with that predicted by the mass transfer model, which has the composition-dependent diffusivity as an optimization parameter.[5]

Mass-Transfer Model. In the aforementioned experiments, the laser sensor did not detect any swelling of polymer samples. This fact implies that in the experimental mass transfer process, the volume change of mixing is negligible, and the amount of the gas absorbed in the polymer has virtually no effect on its density (ρ). Hence, under the isothermal and vibration-free conditions, the convection currents in the polymer phase are absent. They would set up only if the polymer density increases with the gas composition, which being maximum at the top of polymer decreases with depth. Thus, the transfer of gas to the polymer is solely due to molecular diffusion along the z-direction perpendicular to the top polymer surface exposed to the gas. Furthermore, the transfer is a pure physical phenomenon since carbon dioxide is nonreactive with polypropylene under the experimental temperature and pressure conditions. With these considerations, the mass balance of the gas in the polymer is given by[5]

$$\frac{\partial c}{\partial t} = D\left[1 + \frac{\omega}{\rho}\right]\frac{\partial^2 c}{\partial z^2} + \left[\left(1 + \frac{c}{\rho}\right)\frac{\partial D}{\partial c} + \frac{D}{\rho}\right]\left(\frac{\partial c}{\partial z}\right)^2 \quad (1)$$

where $c = c(z,t)$ is the mass concentration of the gas in the polymer at a depth z and a time t. Depending on c, the diffusivity D is a composite function, $D = D[c(z,t)]$. Since there is no gas in the polymer at $t = 0$,

$$c(z, 0) = 0 \qquad 0 < z \leq L \quad (2)$$

where L is the depth of the polymer layer. The interfacial gas concentration is known at all times, that is,

$$c(0, t) = c_{\text{sat}}(t) \qquad 0 \leq t \leq T \quad (3)$$

where T is the final time. Because there is no mass transfer at the bottom of the cell,

$$\left.\frac{\partial c}{\partial z}\right|_{z=L} = 0 \qquad 0 \le t \le T \tag{4}$$

Equations 2 to 4 are the initial and boundary conditions for eq 1.

The Objective. Mathematically, the objective can be written as

$$\underset{\min}{I} = \int_0^T [m_{\mathrm{gp,m}}(t) - m_{\mathrm{gp,e}}(t)]^2 \, \mathrm{d}t \tag{5}$$

In the above equation, $m_{\mathrm{gp,e}}(t)$ is the experimental mass of gas absorbed in the polymer, while $m_{\mathrm{gp,m}}(t)$ is the model-predicted gas mass absorbed in polymer given by

$$m_{\mathrm{gp,m}}(t) = \int_0^L \omega(z,t) A \, \mathrm{d}z \tag{6}$$

where A is the cross-sectional area of the polymer layer. Note that $c(z,t)$ is given by highly nonlinear partial differential equation, eq 1, having $D(c)$ as the control function. The necessary condition for the constrained minimum of I is

$$\lambda \frac{\partial f}{\partial D} = 0 \qquad 0 \le z \le L \qquad 0 \le t \le T \tag{7}$$

subject to the satisfaction of eq 6 as well as the equation for the adjoint variable, $\lambda(z,t)$, given by[5]

$$\frac{\partial \lambda}{\partial t} = 2A(m_{\mathrm{gp,m}} - m_{\mathrm{gp,e}}) + \frac{\lambda}{\rho}\frac{\partial D}{\partial c}\left(\frac{\partial c}{\partial z}\right)^2 + \left(1 + \frac{c}{\rho}\right)\left[\lambda \frac{\partial D}{\partial c}\frac{\partial^2 c}{\partial z^2} + \lambda \frac{\partial^2 D}{\partial c^2}\left(\frac{\partial c}{\partial z}\right)^2 - D\frac{\partial^2 \lambda}{\partial z^2}\right] \tag{8}$$

The above equation has the final condition,

$$\lambda(z,T) = 0 \qquad 0 < z \le L \tag{9}$$

and the two boundary conditions,

$$\lambda(L,t) = 0 \qquad 0 \le t \le T \tag{10}$$

$$\lambda(0,t) = 0 \qquad 0 \le t \le T \tag{11}$$

The detailed derivation of eqs 7 to 11 is provided by Tendulkar et al.[5] In summary, these equations are obtained after adjoining the mass transfer model (eq 1) with the objective (eq 5) to obtain an augmented objective functional. Its variation must vanish at the optimum, which corresponds to the desired (optimal) diffusivity versus concentration function. It is in eliminating the variation we obtain eqs 7 to 11. Hence, the optimal diffusivity function must be such that these equations are satisfied along with eq 1 and the associated initial and boundary conditions. The left-hand side of eq 7 is the variational derivative of the augmented functional with respect to diffusivity. At each value of gas concentration, this derivative provides the correction in diffusivity needed to decrease the objective given by eq 5. The following describes the iterative procedure for diffusivity calculations.

Table 2. Parameters Used in the Diffusivity Calculations

parameter	value
mass of polymer	$5 \cdot 10^{-3}$ kg
density of polymer	763.417 $\mathrm{kg \cdot m^{-3}}$
diameter of polymer sample holder	$4 \cdot 10^{-2}$ m
initial guess for D	$6 \cdot 10^{-10}$ $\mathrm{m^2 \cdot s^{-1}}$
no. of D vs c points	75
no. of grid points along the sample depth	60

Diffusivity Calculations. The diffusivity was calculated by integrating eq 1 with an initial guessed diffusivity and storing the results for use in the backward integration of eq 8 using the final condition given by eq 9. This exercise enabled the calculation of the left-hand side of eq 7, which was used to apply gradient corrections to the diffusivity. This functional optimization procedure was repeated until there was no further reduction in the objective functional, I. Note that the calculation of I requires $m_{\mathrm{gp,e}}(t)$, which was obtained from the experimental pressure versus time data in conjunction with the PVT relationship of the gas.[18]

The value of $m_{\mathrm{gp,e}}(t)$ at the final pressure corresponding to an infinite time yields the solubility or saturation mass composition of the gas, that is, $c_{\mathrm{sat}}[P(t)]$, which furnishes the boundary condition expressed by eq 3. $c_{\mathrm{sat}}(P)$ was determined at the three experimental temperatures by performing 19 experiments for extended time durations. The solubility data are provided in Table 1. It is observed that the solubility of carbon dioxide in the polypropylene resin at a given temperature increases with pressure, while it decreases with the increase in temperature.

Equations 1 and 8 were numerically integrated after applying second-order finite difference formulas along the z direction. The time period for the integrations was carefully selected to restrict pressure decay to less than 2 % of the initial pressure. The fifth-order adaptive step method of Runge–Kutta–Fehlberg was employed with Cash–Karp parameters.[19] The diffusivity was considered to be a discrete function, $D(c)$, at specified gas mass compositions between zero and the maximum, at time $t = 0$, for an experiment. For best results, as several numerical experiments had indicated, $D(c)$ was initialized to a uniform value as high as possible without causing $m_{\mathrm{gp,m}}(t)$ to cross $m_{\mathrm{gp,e}}(t)$.

During the computations, cubic splines were used to interpolate the following: $D(c)$ as well as its first and second derivatives with respect to c, $m_{\mathrm{gp,e}}(t)$, $c_{\mathrm{sat}}[P(t)]$, and $c(t)$ at a given z and the variational derivative $J(c)$ derived elsewhere.[5] The values of $J(c)$ were time-averaged before their usage for the gradient correction in $D(c)$ by the Broyden–Fletcher–Goldfarb–Shanno algorithm.[19] The maximum correction in diffusivity was limited to 1 % of its value to allow a slow but

Table 1. Solubility c_{sat} of Carbon Dioxide in Polypropylene at (170, 180, and 190) °C and Different Pressures

$t = 170$ °C	P/MPa	0.43	1.34	2.19	3.48	6.45				
	$c_{\mathrm{sat}}/\mathrm{kg \cdot m^{-3}}$	1.13	5.59	10.05	15.55	22.73				
$t = 180$ °C	P/MPa	0.28	0.93	1.74	2.42	2.62	2.85	3.87	5.17	6.49
	$c_{\mathrm{sat}}/\mathrm{kg \cdot m^{-3}}$	0.71	3.20	6.42	9.35	10.17	10.83	14.09	17.46	20.18
$t = 190$ °C	P/MPa	1.34	2.54	3.92	5.23	7.03				
	$c_{\mathrm{sat}}/\mathrm{kg \cdot m^{-3}}$	4.31	7.66	11.38	14.01	18.97				

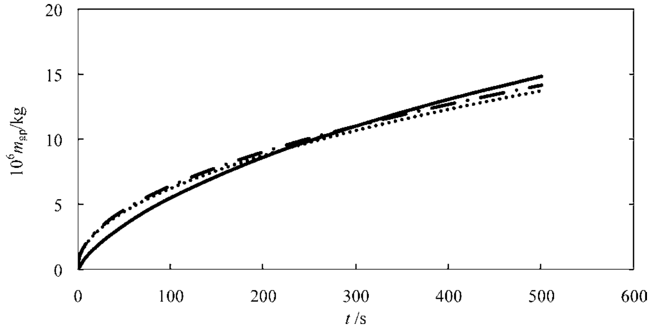

Figure 2. Experimental versus calculated gas mass of carbon dioxide absorbed in polypropylene (m_{gp}) as a function of time (—, experimental; •—•, from optimal diffusivity; and ••••, from diffusivity correlated using eq 12) at 180 °C and 1.86 MPa.

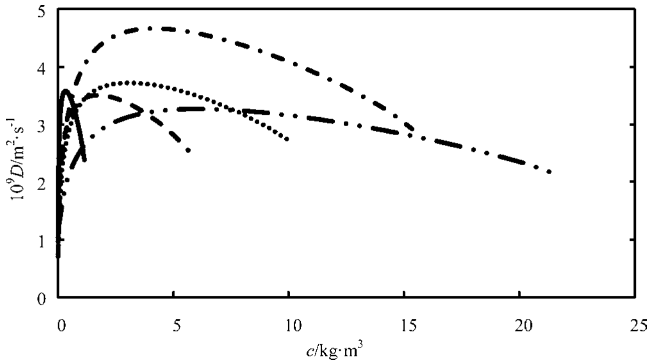

Figure 3. Diffusivity D of carbon dioxide as a function of its concentration c at 170 °C and different pressures (—, 0.45 MPa; — — —, 1.44 MPa; ••••, 2.35 MPa; —•—•, 3.71 MPa; —••—, 6.77 MPa).

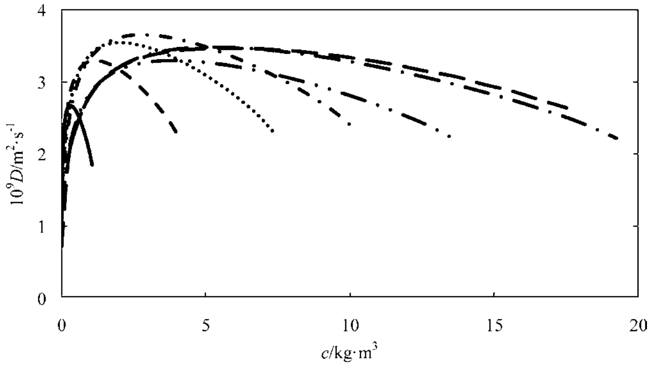

Figure 4. Diffusivity D of carbon dioxide as a function of its concentration c at 180 °C and different pressures (—, 0.29 MPa; — — —, 0.99 MPa; ••••, 1.86 MPa; —•—•, 2.79 MPa; —••—, 4.09 MPa; — —, 5.43 MPa; —•—, 6.78 MPa).

steady approach to the minimum. Table 2 provides the parameters used in the calculations. The number of grid points and diffusivity values and the accuracy of integrations were determined after varying those parameters to the point when the changes in the solution became insignificant. The experimental and the optimally calculated values of gas mass absorbed in the polymer agree well, as shown in Figure 2.

Results and Discussion

By using the pressure decay method, the composition-dependent diffusivity and solubility of carbon dioxide in polypropylene were determined at (170, 180, and 190) °C and pressures up to 7.32 MPa. Figures 3 to 6 present the experimentally determined diffusivities. Sensitivity analyses showed that there were insignificant changes in these diffusivities due to ± 2 % variation (uncertainty) in the gas phase volume or pressure sensor readings.

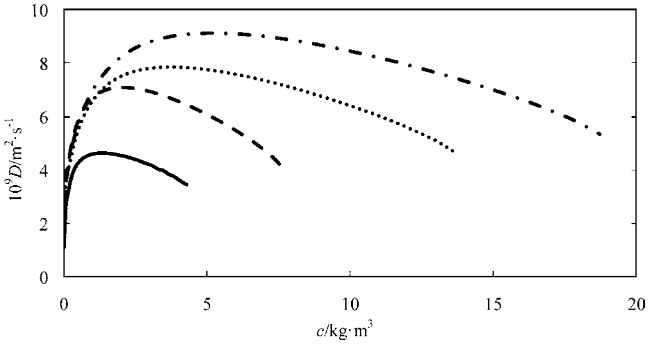

Figure 5. Diffusivity D of carbon dioxide as a function of its concentration c at 190 °C and different pressures (—, 1.42 MPa; — — —, 2.67 MPa; ••••, 5.45 MPa; —•—•, 7.32 MPa).

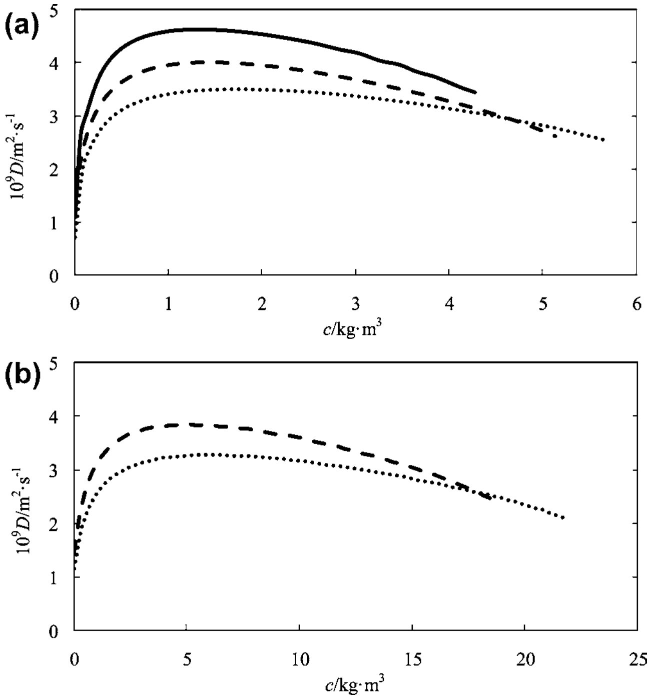

Figure 6. (a) Carbon dioxide diffusivity D versus its concentration c at different temperatures (—, 1.42 MPa and 190 °C; — — —, 1.44 MPa and 180 °C; ••••, 1.44 MPa and 170 °C). (b) Carbon dioxide diffusivity D versus its concentration c at different temperatures (— — —, 6.78 MPa and 180 °C; ••••, 6.77 MPa and 170 °C).

Since the equilibrium concentration increases with pressure, the diffusivity versus concentration graphs span longer intervals on the concentration axis for higher pressures (Figures 3 to 5), or lower temperatures (Figure 6). It is evident from these results that diffusivity is a unimodal function of composition. Such composition-dependent behavior of diffusivity has been observed in a solvent−polymer system.[5,20,21]

Effect of Pressure on Diffusivity. Figures 3 to 5 show the diffusivity versus concentration graphs for different pressures, respectively, at (170, 180, and 190) °C. No general trends are observed except for the fact that the maximal concentration (corresponding to the maximum diffusivity) increases with pressure at a given temperature. In other words, the diffusivity maxima shift toward right with increase in pressure. Thus, at a given temperature, a higher concentration is needed at higher pressures to achieve maximum possible flux per unit concentration gradient (i.e., maximum diffusivity). However, neither the maxima nor the diffusivities at a given concentration indicate any clear-cut trend with pressure changes, which appears to be nonlinear in nature.

At 170 °C (Figure 3), except at the intermediate pressure of 3.71 MPa for which the peak diffusivity is about 4.8 $\text{m}^2\cdot\text{s}^{-1}$, the peak diffusivities are found to be in the neighborhood of $3.5\cdot10^{-9}$ $\text{m}^2\cdot\text{s}^{-1}$. This value is also in close proximity to the peak diffusivities at 180 °C (Figure 4) except the one at 0.29 MPa, which is about 2.7 $\text{m}^2\cdot\text{s}^{-1}$. In Figure 3 as well as 4, the graphs intersect with each other, implying same diffusivity at a given concentration but at different pressures. The diffusivity versus pressure trend at 190 °C (Figure 5) is however more conceivable. At a given concentration above a threshold value, the diffusivity at 190 °C is observed to increase with pressure. Thus, the diffusivity graphs never intersect with each other at concentrations greater than the maximal concentration. This behavior is in contrast with the intersections occurring even at concentrations greater than the maximal concentration at the two lower temperatures.

An explanation for the nonlinear effect of pressure on diffusivity may be given as follows. An increase in pressure increases the frequency of intermolecular collision but reduces the intermolecular distances. While increased molecular collisions facilitate gas diffusion, the reduced intermolecular distances impede diffusion. Thus, at given temperature and concentration, depending on the dominance of a first or second effect, the diffusivity either increases or decreases with pressure. In addition to these effects, the pressure change could engender some significant changes in the structure of the polymer matrix and influence mass transfer. For example, this phenomenon might be responsible for mostly higher diffusivity values at 3.71 MPa relative to other pressures at 170 °C. More experiments coupled with in situ and nonintrusive examinations of the polymer layer are needed to gain a better understanding of this phenomenon.

Effect of Temperature on Diffusivity. A broad comparison of diffusivities in Figure 6 shows the effect of temperature on the diffusivity of carbon dioxide in the vicinity of (1.44 and 6.77) MPa. In both cases, the diffusivity is observed to increase with temperature except close to the terminal equilibrium concentrations. At lower gas concentrations, the increase in diffusivity with temperature may be attributed to a decrease in polymer viscosity, reduction in the activation energy, and increase in molecular motion. These phenomena are expected to facilitate the penetration of gas in the polymer matrix. The reversal in this trend is observed at gas concentrations greater than (4.5 and 17.7) $\text{kg}\cdot\text{m}^{-3}$, respectively, for pressures close to (1.44 and 6.77) MPa. A possible reason may be the overcrowding of gas molecules in the polymer matrix hampering their movement as a consequence.

Table 3. Composition-Averaged Diffusivity D of Carbon Dioxide in Polypropylene at (170, 180, and 190) °C and Different Pressures

t / °C	P / MPa	$10^9\,D$ / $\text{m}^2\cdot\text{s}^{-1}$
170	0.45	3.15
	1.44	3.13
	2.35	3.32
	3.71	4.03
	6.77	2.85
180	0.29	2.36
	0.99	2.89
	1.86	3.09
	2.79	3.18
	4.09	2.89
	5.43	3.13
	6.78	3.02
190	1.42	4.14
	2.67	6.06
	5.45	6.67
	7.32	7.77

Table 4. Parameters for the Diffusivity Correlation (eq 12)[a]

parameter	t = 170 °C	t = 180 °C	t = 190 °C
$a_o/\text{m}^2\cdot\text{s}^{-1}$	1.598	2.145	−0.983
$a_1/\text{m}^2\cdot\text{s}^{-1}\cdot[\ln(\text{MPa})]^{-1}$	−0.582	−0.528	12.650
$a_2/\text{m}^2\cdot\text{s}^{-1}\cdot[\ln(\text{kg}\cdot\text{m}^{-3})]^{-1}$	3.302	3.348	5.013
$a_3/\text{m}^2\cdot\text{s}^{-1}\cdot[\ln(\text{MPa})]^{-2}$	1.200	−0.197	−10.434
$a_4/\text{m}^2\cdot\text{s}^{-1}\cdot[\ln(\text{kg}\cdot\text{m}^{-3})]^{-2}$	−1.977	−2.055	−2.655
$a_5/\text{m}^2\cdot\text{s}^{-1}\cdot[\ln(\text{MPa})]^{-1}\cdot\ln(\text{kg}\cdot\text{m}^{-3})]^{-1}$	1.367	0.661	0.089
$a_6/\text{m}^2\cdot\text{s}^{-1}\cdot\ln[(\text{MPa})]^{-3}$	−0.510	0.124	2.622
$a_7/\text{m}^2\cdot\text{s}^{-1}\cdot[\ln(\text{kg}\cdot\text{m}^{-3})]^{-3}$	−0.013	0.055	−0.205
$a_8/\ \text{m}^2\cdot\text{s}^{-1}\cdot[\ln(\text{MPa})]^{-1}\cdot[\ln(\text{kg}\cdot\text{m}^{-3})]^{-2}$	0.682	0.631	0.802
$a_9/\text{m}^2\cdot\text{s}^{-1}\cdot[\ln(\text{MPa})]^{-2}\cdot[\ln(\text{kg}\cdot\text{m}^{-3})]^{-1}$	−0.988	−0.573	0.136
goodness of fit			
r^2 coefficient of determination	0.836	0.854	0.991
fit standard error	0.258	0.201	0.164
F-statistic	193	359	3191

[a] D is in 10^9 $\text{m}^2\cdot\text{s}^{-1}$; P is in MPa, and c is in $\text{kg}\cdot\text{m}^{-3}$.

The composition-averaged diffusivity values at experimental temperatures and pressures are provided in Table 3. The temperature dependence of diffusivity for this system is the same as typically observed for other polymer systems.[5,20–23]

The experimentally determined solubility data are listed in Table 1. The solubility is found to increase, almost linearly, with pressure and decrease with temperature. This pressure and temperature dependence of solubility is usually observed in gas−polymer systems.

Diffusivity Correlations. To develop a mathematical correlation for diffusivity as a function of gas concentration and pressure at a given temperature, we utilized Table Curve 3D (Systat Software, Inc., Chicago, IL). The best function with as few parameters as possible was found to be:

$$\begin{aligned} D = {} & a_0 + a_1 \ln P + a_2 \ln(1 + c) + a_3(\ln P)^2 + \\ & a_4[\ln(1 + c)]^2 + a_5 \ln P \ln(1 + c) + a_6(\ln P)^3 + \\ & a_7[\ln(1 + c)]^3 + a_8 \ln P[\ln(1 + c)]^2 + a_9(\ln P)^2 \ln(1 + c) \end{aligned} \tag{12}$$

In the above equation, D is in 10^9 $\text{m}^2\cdot\text{s}^{-1}$, P is in MPa, and c is in $\text{kg}\cdot\text{m}^{-3}$. Table 4 lists the fitting parameters and details for eq 12 at (170, 180, and 190) °C. The absorbed gas mass predicted by eq 12 agrees well with that based on the optimally determined diffusivity as well as the experimental data. Figure 2 shows one such comparison.

Conclusion

This paper experimentally determined the composition-dependent diffusivity and solubility of carbon dioxide in polypropylene at (170, 180, and 190) °C. The applied pressure ranged up to 7.32 MPa. A pressure decay method was used to obtain pressure versus time data, which were used in detailed mass transfer model to calculate the diffusivity as a function of composition, and saturated pressure was used to determine the solubility of gas in polymer. Effects of temperatures and pressures were examined. The experimental results indicate that the solubility of carbon dioxide in polypropylene increased almost linearly with increasing pressure and decreased with an increase in temperature. Generally of the order of 10^{-9} $\text{m}^2\cdot\text{s}^{-1}$, the diffusivities of carbon dioxide in polypropylene were found to be strongly unimodal functions of gas concentration in polypropylene. Mathematical correlations of the diffusivity as a function of the gas concentration and pressure were developed at (170, 180, and 190) °C. The effect of pressure on diffusivity was found to be highly nonlinear at the two lower temperatures.

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