

Solubility and Diffusion Coefficient of Carbon Dioxide in Biodegradable Polymers

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The solubility and diffusion coefficient of carbon dioxide in the biodegradable polymers poly(butylene succinate) and poly(butylene succinate-*co*-adipate) were measured at temperatures from 323.15 to 453.15 K and pressures up to 20 MPa. The solubilities in the polymer's molten state increased linearly with pressure and decreased with temperature. Solubilities could be correlated to within 2.2% by the Sanchez–Lacombe equation of state in conjunction with a temperature-dependent interaction parameter. The Sanchez–Lacombe equation of state was also found to be applicable to the correlation of solubilities in the semicrystalline state. The interaction parameter determined from fitting the solubility was inversely proportional to temperature. The diffusion coefficients of carbon dioxide showed a weak concentration dependence and had an order of magnitude of 10^{-9} m²/s in the molten state. The diffusion coefficients were correlated with the free-volume model of Kulkarni and Stern.

Introduction

Biodegradable polymers have received much attention because they are seen as a solution to the environmental waste problems caused by conventional plastics. Production of these polymers is actively being studied, and their commercial applications are growing.¹ Bionolles [poly(butylene succinate) (PBS) and poly(butylene succinate-*co*-adipate) (PBSA)] are biodegradable aliphatic polyesters that have been developed jointly by Showa Highpolymer Co. Ltd. and Showa Denko K.K.^{2,3} Imaizumi et al.⁴ reported on the molecular structure, viscoelastic properties, and processability of PBS for direct extrusion gas foaming. Sato et al.⁵ reported *PVT* properties of three biodegradable polymers: branched PBS, linear PBSA, and polylactide. Bionolle is expected to be used as a foam material. However, the gas solubility and diffusivity of the gas in Bionolle have not been reported. The objective of this study was to measure the solubility and diffusion coefficients of carbon dioxide, which was expected as a new blowing agent, in the Bionolle.

Experimental Section

Materials. Branched PBS, which had been polymerized with a multifunctional monomer to give a branched structure,⁶ and a linear PBSA random copolymer were made on an experimental basis by Showa Highpolymer Co. Ltd. (Tokyo) and Showa Denko K.K. (Kawasaki). Monomer contents of PBSA determined by ¹H NMR spectroscopy (Bruker AMX-400) were 0.5, 0.4, and 0.1 mole fractions for 1,4-butanediol, succinic acid, and adipic acid, respectively. Properties of the polymers

Table 1. Polymer Properties

	PBS	PBSA
$\bar{M}_n \times 10^{-4}$	2.9	5.3
$\bar{M}_w \times 10^{-4}$	14	18
T_m (K)	388	365
T_g (K)	243	231
crystallinity (wt %)	35	25

studied are given in Table 1. The crystallinity was determined from diffracted intensity data (Rigaku Co. Ltd., model RINT-2200, $\lambda = 0.154$ nm) by comparing the relative area under the crystalline peaks with that from amorphous scatter, as described by Ruland.⁷ The determination method of the other properties and chemical structures of the polymers have been described in a previous publication.⁵ Carbon dioxide (>99.5% purity) was obtained from Iwatani Industrial Gases Corp. (Hiroshima). All chemicals were used as received.

Solubility and Diffusion Coefficient. The solubility and diffusivity of carbon dioxide in polymers were obtained with a magnetic suspension balance (MSB).⁸ The apparatus of the MSB is shown in Figure 1. Using the magnetic suspension coupling, the measuring force is transmitted contactlessly from the measuring chamber to the microbalance, which is located outside the chamber under ambient atmospheric conditions. The MSB can be used at pressures up to 35 MPa and temperatures up to 523 K. The resolution and accuracy of the microbalance (Mettler AT261, Greifensee, Switzerland) are 0.01 mg and 0.002%, respectively.

The amount of dissolved gas, W_g (g) was obtained by the following equation considering gas buoyancy:

$$W_g = W_F(P, T) - W_0(0, T) + \rho(P, T) [V_P(P, T)\{1 + S_w(P, T)\} + V_B] \quad (1)$$

where W_F and W_0 are readouts of the balance at temperature T and pressure P and at zero pressure,

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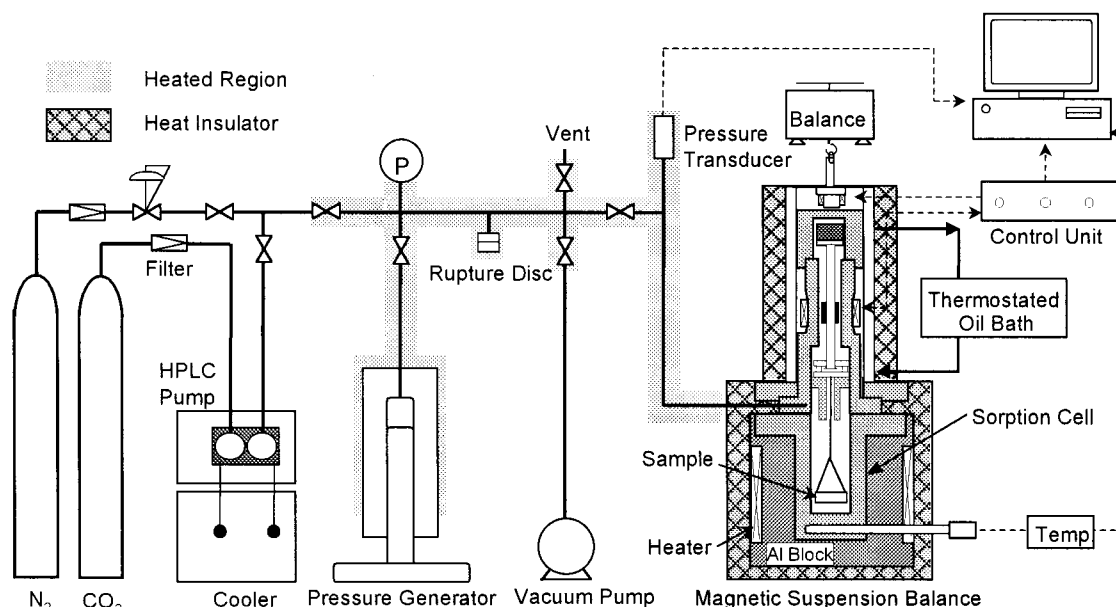


Figure 1. Schematic diagram of the solubility and diffusivity apparatus.

Table 2. Tait Parameters

polymer		a (cm ³ /g)	$\alpha \times 10^4$ (K ⁻¹)	B_0 (MPa)	$B_1 \times 10^3$ (K ⁻¹)	temp range (K)
PBS	$T > T_m$	0.6821	6.728	729.1	4.323	414–493
	$T < T_m$	0.6468	6.686	2194	6.290	314–374
	crystalline	0.5850	6.499			314–373
PBSA	$T > T_m$	0.6775	7.110	903.5	4.441	394–493
	$T < T_m$	0.6462	7.478	3340	7.819	314–354
	crystalline	0.5411	9.515			314–353

respectively, and ρ is the gas density obtained from the equation of state of Angus et al.⁹ V_P and the V_B (cm³) are volumes of the polymer sample and a sample basket (including a Petri dish, a sample holder, and the measuring load decoupling device, about 1 cm³), respectively. V_P was obtained from the specific volume of the pure polymer, ν_P , and the sample mass. ν_P was obtained from the Tait equation¹⁰ as follows:

$$\nu_P = \nu_0 \{1 - 0.0894 \ln[1 + P/B(T)]\} \quad (2)$$

where

$$\nu_0 = a \exp(\alpha T) \quad (3)$$

$$B(T) = B_0 \exp(-B_1 T) \quad (4)$$

The Tait parameters were determined in this work using experimental data of Sato et al.⁵ and are given in Table 2. The degree of swelling of the polymer, S_w , is caused by gas sorption. In this work, the swelling is defined as follows:

$$S_w = V_P(P, T, S)/V_{P0}(P, T, 0) - 1 \quad (5)$$

Because it is difficult to measure S_w of the molten polymer, we predicted its value by the Sanchez-Lacombe equation of state (S-L EOS).^{11,12} For the molten state, S_w is obtained as follows:

$$S_w = (1 + S)\nu(P, T, S)/\nu(P, T, 0) - 1 \quad (6)$$

For the rubbery state, S_w is obtained as

$$S_w = \frac{(1 - X_m)[(1 + S)\nu(P, T, S) - \nu(P, T, 0)]}{\nu_{\text{cry}}(P, T)X_m + (1 - X_m)\nu(P, T, 0)} \quad (7)$$

where S (g of gas/g of polymer) is the solubility, X_m is the mass fraction crystallinity of the polymer, and ν (cm³/g) is the specific volume of the polymer calculated by the S-L EOS. ν_{cry} is the specific volume of the crystalline fraction. ν_{cry} was determined from PVT data⁵ and crystallinity assuming volume additivity. Further details of the determination of ν_{cry} have been described in a previous publication.¹³ We assumed that the crystallinity was constant at the temperature of solubility measurements in the rubbery state. This was confirmed by the crystallinity observations of before and after the solubility experiments with X-ray diffraction. The ν_{cry} (cm³/g) was represented with eq 3 as a function of absolute temperature T . The parameters are listed in Table 2. Because S_w is a function of solubility, it is necessary to solve eqs 1 and 6 or 7 simultaneously. Predicted S_w could represent the experimental data to within an average relative deviation of 3.5% for the carbon dioxide + poly(vinyl acetate) system.¹⁴ The uncertainty of the solubility was estimated to be less than 4%. However, this uncertainty does not include the S_w error, because it is hard to estimate the uncertainty of the swelling predicted by S-L EOS. Hence, we assumed that S_w had a relative uncertainty of 5%. The uncertainty of the solubility including the S_w error was estimated to be less than 19%.

Mutual diffusion coefficients of gas in polymers were determined by measuring W_g vs time curves during gas dissolution. We used the following four assumptions to determine the diffusion coefficient. First, we assumed Fick's second law. Second, the diffusion coefficient D was treated as being independent of the gas concentration during each stepwise gas dissolution. Third, the diffusion was assumed to be one-dimensional in the polymer sample sheet, with all diffusing substances entering through a single face plane. Fourth, the thickness of the polymer L was assumed to be constant during the

Table 3. Solubility of CO₂ in PBS

temp (K)	pressure (MPa)	solubility without S_w correction (g of gas/ kg of polymer)	solubility with S_w correction (g of gas/ kg of polymer)	swelling S_w (S–L EOS)
323.15	1.025	9.70	9.84 (15.14) ^a	0.010
	2.209	19.90	20.63 (31.74)	0.023
	3.068	26.77	28.26 (43.48)	0.032
	4.245	35.72	38.79 (59.68)	0.045
	6.272	49.01	56.81 (87.40)	0.067
	8.008	58.02	73.00 (112.3)	0.085
	10.129	74.82	107.6 (165.6)	0.102
	1.148	8.63	8.76 (13.48)	0.009
353.15	2.103	14.75	15.23 (23.43)	0.017
	3.158	21.31	22.43 (34.51)	0.026
	4.218	27.53	29.61 (45.55)	0.035
	6.169	38.51	43.32 (66.65)	0.052
	8.050	47.16	56.01 (86.17)	0.067
	10.451	55.92	72.50 (111.5)	0.086
	2.351	21.00	21.74	0.025
	2.947	25.90	27.08	0.032
393.15	4.141	35.38	37.76	0.044
	4.725	39.94	43.08	0.050
	6.060	49.90	55.21	0.065
	6.599	53.77	60.14	0.071
	8.076	63.69	73.57	0.086
	8.928	69.00	81.30	0.095
	12.076	85.63	109.8	0.129
	12.606	87.95	114.6	0.135
423.15	16.035	98.42	144.0	0.169
	16.544	99.31	148.1	0.174
	19.987	103.1	176.1	0.207
	2.221	14.92	15.01	0.019
	2.935	19.60	19.93	0.025
	4.065	26.84	27.77	0.034
	4.705	30.76	32.16	0.040
	6.035	38.76	41.45	0.051
453.15	6.572	41.94	45.29	0.056
	8.242	51.26	57.10	0.071
	8.696	53.74	60.41	0.075
	12.036	68.89	83.09	0.103
	12.572	71.50	87.33	0.108
	16.038	83.10	110.7	0.137
	16.541	84.36	113.9	0.141
	20.095	90.86	135.5	0.167
453.15	2.133	11.55	11.92	0.016
	2.798	15.02	15.66	0.020
	4.132	21.73	23.15	0.030
	4.627	24.25	26.04	0.034
	6.039	31.01	34.11	0.045
	6.626	33.62	37.36	0.049
	8.037	39.75	45.34	0.059
	8.570	42.01	48.40	0.063
453.15	12.007	55.28	68.30	0.089
	12.592	57.16	71.53	0.093
	16.071	66.98	90.82	0.118
	16.574	68.25	93.67	0.122
	20.144	74.93	112.6	0.146

^a (): solubility (g of gas/kg of amorphous).

stepwise gas dissolution and used an average value between the initial and final solubility. The appropriate solution of the diffusion equation may be written¹⁵ as

$$\frac{W_g(t) - W_g(0)}{W_g(\infty) - W_g(0)} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[\frac{-(2n+1)^2 \pi^2 D t}{4L^2}\right] \quad (8)$$

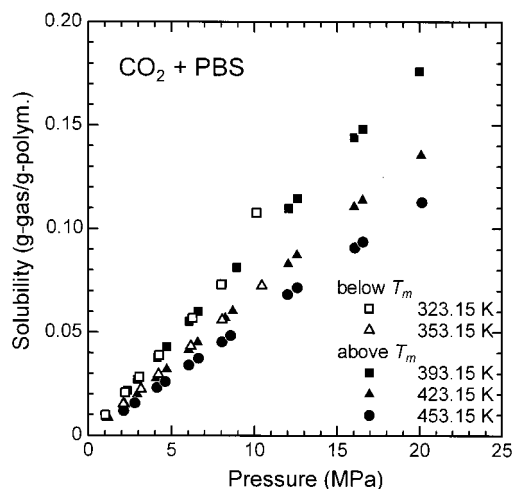
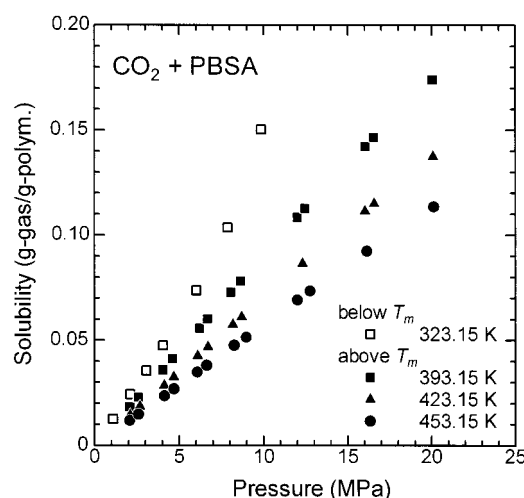
where $W_g(t)$ is the amount of gas in the polymer at time t . The polymer sample was mounted in a Petri dish (Ø

Table 4. Solubility of CO₂ in PBSA

temp (K)	pressure (MPa)	solubility without S_w correction (g of gas/ kg of polymer)	solubility with S_w correction (g of gas/ kg of polymer)	swelling S_w (S–L EOS)
323.15	1.098	12.37	12.59 (16.79) ^a	0.014
	2.097	23.33	24.18 (32.24)	0.027
	3.065	33.67	35.59 (47.45)	0.041
	4.053	43.91	47.49 (63.32)	0.054
	6.016	64.52	73.64 (98.19)	0.082
	7.870	85.02	103.6 (138.1)	0.106
	9.844	111.8	150.3 (200.4)	0.128
	2.082	17.84	18.39	0.021
393.15	2.581	21.99	22.85	0.026
	4.028	33.74	35.91	0.041
	4.610	38.33	41.22	0.047
	6.200	50.32	55.78	0.064
	6.681	53.79	60.20	0.069
	8.053	63.14	72.80	0.084
	8.630	66.88	78.14	0.090
	11.997	84.95	108.4	0.125
423.15	12.460	87.12	112.7	0.130
	16.024	97.68	142.3	0.164
	16.548	98.73	146.7	0.170
	20.036	102.3	174.1	0.201
	2.102	14.08	14.51	0.018
	2.676	17.80	18.51	0.024
	4.118	26.89	28.63	0.035
	4.684	30.36	32.63	0.040
453.15	6.098	38.70	42.64	0.052
	6.700	42.11	46.92	0.057
	8.177	50.14	57.49	0.070
	8.699	52.78	61.17	0.074
	12.314	68.83	86.49	0.105
	16.027	80.53	111.5	0.135
	16.572	81.82	115.0	0.139
	20.074	88.06	137.4	0.166
453.15	2.079	11.49	11.84	0.015
	2.600	14.27	14.83	0.019
	4.126	22.16	23.57	0.030
	4.698	25.03	26.89	0.034
	6.070	31.70	34.85	0.045
	6.628	34.32	38.09	0.049
	8.259	41.66	47.63	0.061
	8.973	44.43	51.50	0.066
453.15	12.009	56.15	69.20	0.088
	12.766	58.66	73.49	0.094
	16.139	68.24	92.35	0.118
	20.127	75.95	113.6	0.144

^a (): solubility (g of gas/kg of amorphous).

25 × 4 mm) by melt molding the sample in the Petri dish above the melting point temperature of the sample. In the rubbery state of the polymer, the powder sample was used in the Petri dish. Therefore, the diffusion coefficients in the rubbery state could not be obtained for this case. The amount of polymer used in the experiments was 0.4–0.7 g. The polymer sample in the rubbery state was renewed in each isothermal measurement so that the thermal history of the sample in the solubility measurements was the same as that of the crystallinity measurements. The diffusion coefficient was determined by fitting of a sorption curve with about 0.5 MPa stepwise pressure changes to minimize the effect of concentration dependence on the diffusion coefficient. The sample thickness was obtained by dividing the sample volume corrected with S_w at an average value between the initial and final solubility by the area of the Petri dish. The details of the experimental apparatus and procedures have been described elsewhere.¹⁶

Figure 2. Solubility of CO₂ in PBS.Figure 3. Solubility of CO₂ in PBSA.

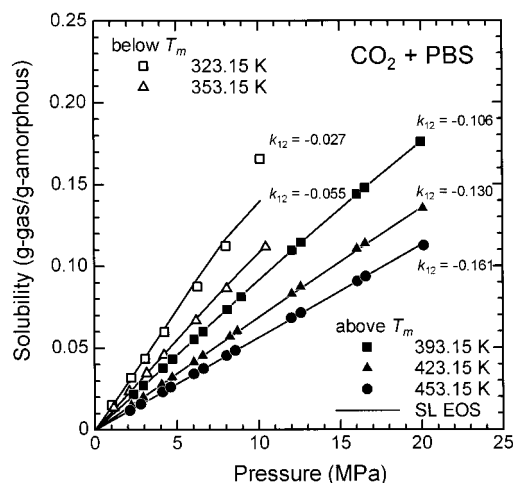
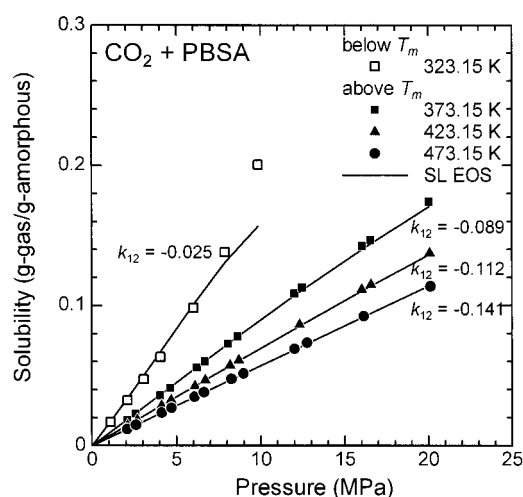
Results and Discussion

Solubility. The solubilities of carbon dioxide in PBS and PBSA are shown in Figures 2 and 3, respectively. For the PBSA system, the solubility at 353 K could not be measured, because the readout of the balance was not stable. This unstability might be caused by the crystallinity change of the polymer during the sorption, because the measurement temperature was close to the melting point temperature, T_m , of PBSA ($=365$ K). The solubilities decreased with increasing temperature except for the rubbery state. In the rubbery state, the solubilities were lower than those extrapolated based on the molten state. For this case, the gas was probably insoluble in the crystalline domain.¹⁷ The amounts of gas in the amorphous part of the polymers are shown in Figures 4 and 5. The solubilities in the amorphous region of the polymers were evaluated by considering the crystallinity described above. The solubilities in the amorphous region decreased with increasing temperature.

Experimental solubility data were correlated with the S-L EOS:^{11,12}

$$\tilde{P} = -\tilde{\rho}^2 - \tilde{T}[\ln(1 - \tilde{\rho}) + (1 - 1/r)\tilde{\rho}] \quad (9)$$

$$\tilde{P} = P/P^*, \quad \tilde{\rho} = \rho/\rho^*, \quad \tilde{T} = T/T^*, \quad r = MP^*/RT^*\rho^* \quad (10)$$

Figure 4. Solubility of CO₂ in the PBS amorphous region.Figure 5. Solubility of CO₂ in the PBSA amorphous region.

where characteristic parameters P^* , ρ^* , and T^* of the S-L EOS for the mixture were evaluated with the following mixing rules:

$$P^* = \sum_i \sum_j \phi_i \phi_j P_{ij}^* \quad (11)$$

$$P_{ij}^* = (1 - k_{ij})(P_i^* P_j^*)^{0.5} \quad (12)$$

$$T^* = P^* \sum_i (\phi_i^0 T_i^* / P_i^*) \quad (13)$$

$$1/r = \sum_i (\phi_i^0 / r_i^0) \quad (14)$$

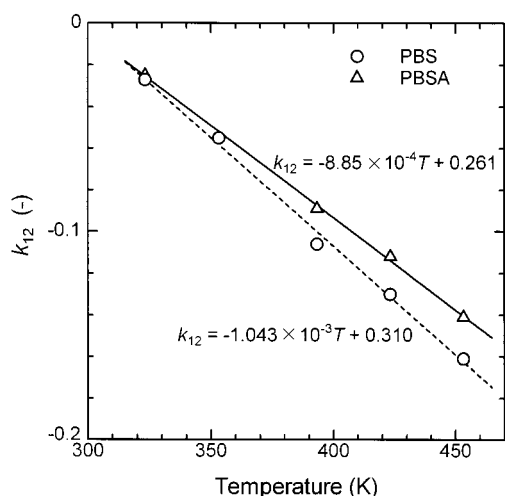
$$\phi_i^0 = (\phi_i P_i^* / T_i^*) / \sum_j (\phi_j P_j^* / T_j^*) \quad (15)$$

$$\phi_i = (w_i / \rho_i^*) / \sum_j (w_j / \rho_j^*) \quad (16)$$

In eqs 11–16, T_i^* , P_i^* , ρ_i^* , and r_i^0 refer to the characteristic parameters of component i in the pure state and k_{ij} is a binary interaction parameter determined by fitting the equation to the experimental data. The pure-component parameters used are given in Table 5. In the calculation of the solubilities, it was assumed that the

Table 5. Characteristic Parameters for S-L EOS

substance	P^* (MPa)	ρ^* (kg/m ³)	T^* (K)	ref
CO ₂	720.3	1580	$208.9 + 0.459T - 7.56 \times 10^{-4}T^2$	18
PBS	523.5	1233	717.8	this work
PBSA	570.1	1235	691.8	this work

**Figure 6.** Interaction parameter k_{12} for S-L EOS.

polymer was monodisperse and that it did not dissolve in the vapor phase.

The binary interaction parameter, k_{ij} , in eq 12 was determined so as to minimize the relative deviations between experimental and calculated solubilities at each temperature. Correlation results are shown as solid lines in Figures 4 and 5. The S-L EOS could correlate solubilities to within 1.9% for PBS and 2.2% for PBSA in an average relative deviation of the solubility. k_{12} varied almost linearly with temperature as shown in Figure 6. This result is useful to interpolate or possibly extrapolate the solubilities at a given temperature.

The temperature dependence of Henry's constants for carbon dioxide in the amorphous region of PBS and PBSA was determined. Henry's constant, K_P (kg·MPa/cm³(STP)), was defined as

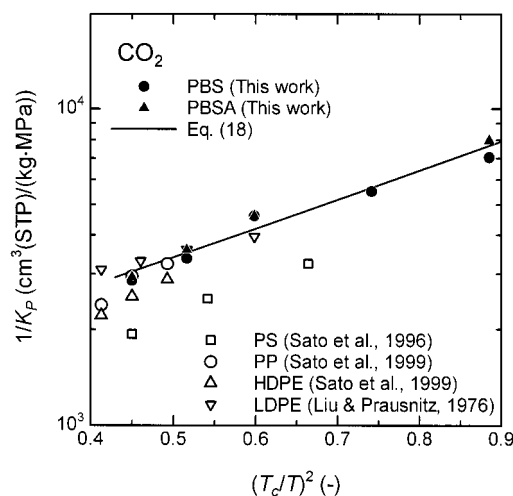
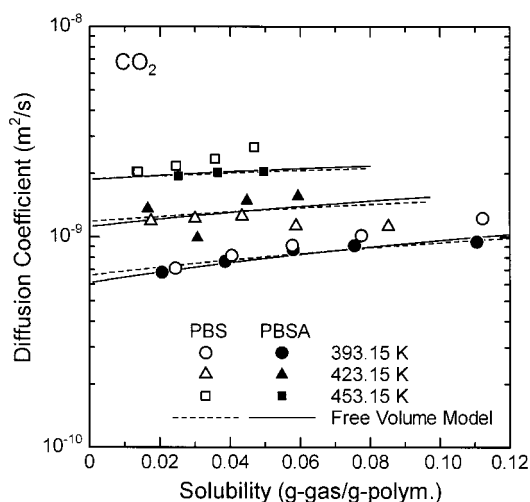
$$K_P = \lim_{s \rightarrow 0} (f_g/s) \quad (17)$$

where f_g is the fugacity of the gas and s is the solubility of the gas (cm³(STP)/kg of polymer). The reciprocal Henry's constants, $1/K_P$, for carbon dioxide in PBS and PBSA obtained in this work are shown in Figure 7. The difference in the Henry's constants between PBS and PBSA cannot be regarded as significant. $1/K_P$ of PBS and PBSA had almost the same order of magnitude in molten polyolefins^{19,20} and was 2 times larger than that of polystyrene (PS).²¹

Stiel and Harnish²² found a linear relationship between $\ln(1/K_P)$ and $(T_c/T)^2$ for the solubility of various solutes in molten PS. Here T_c is the critical temperature of the solute. We formulated an equation to represent Henry's constants for carbon dioxide in PBS and PBSA as follows:

$$\ln(1/K_P) = 7.073 + 2.114(T_c/T)^2 \quad (18)$$

Equation 18 could represent the Henry's constant to within an average relative deviation of 6.7%.

**Figure 7.** Henry's constants for CO₂ in PBS and PBSA.**Figure 8.** Diffusion coefficients of CO₂ in PBS and PBSA.

The crystallinity change induced by a dissolved gas was reported by several investigators.^{23,24} However, in the systems studied in this work, the crystallinity would not change, because the interaction parameter k_{12} exhibited a linear function of temperature, as was extrapolated based on the molten state. The solubilities were almost linear functions of pressure and the Henry's law could apply in these systems. If the crystallinity change was induced by CO₂ sorption, the Henry's law would not apply.

Diffusion Coefficient. Mutual-diffusion coefficients of carbon dioxide in PBS and PBSA as a function of the average solubility during sorption are shown in Figure 8. The diffusion coefficients are listed as functions of the initial and final pressures and the average solubilities of carbon dioxide in the polymers in Tables 6 and 7. These diffusion coefficients increased with increasing temperature and exhibited weak concentration dependence. The difference in the diffusion coefficient between PBS and PBSA cannot be regarded as significant. The diffusion coefficients of both the systems had an order of magnitude of 10⁻⁹ m²/s. It was found that those values were 5 times lower than those in high-density polyethylene (HDPE)²⁰ at 453.2 K and 3 times higher than those in PS¹⁶ at 423.2 K.

The mutual-diffusion coefficients of CO₂ in the polymers were correlated with the free-volume model of

Table 6. Diffusion Coefficients of CO₂ in PBS

temp (K)	pressure range (MPa)	average pressure (MPa)	average solubility of CO ₂ (g of gas/kg of polymer)	diffusion coefficient of CO ₂ × 10 ⁹ (m ² /s)
393.15	2.351–2.947	2.649	24.41	0.714
	4.141–4.725	4.433	40.42	0.820
	6.060–6.599	6.330	57.68	0.916
	8.076–8.928	8.502	77.44	1.02
423.15	12.076–12.606	12.341	112.2	1.23
	2.221–2.935	2.578	17.47	1.19
	4.065–4.705	4.385	29.97	1.22
	6.035–6.572	6.304	43.37	1.26
453.15	8.242–8.696	8.469	58.76	1.13
	12.036–12.572	12.304	85.21	1.13
	2.133–2.798	2.466	13.79	2.04
	4.132–4.627	4.380	24.60	2.18
	6.039–6.626	6.333	35.74	2.35
	8.037–8.570	8.304	46.87	2.68

Table 7. Diffusion Coefficients of CO₂ in PBSA

temp (K)	pressure range (MPa)	average pressure (MPa)	average solubility of CO ₂ (g of gas/kg of polymer)	diffusion coefficient of CO ₂ × 10 ⁹ (m ² /s)
393.15	2.082–2.581	2.332	20.62	0.681
	4.028–4.610	4.319	38.57	0.768
	6.200–6.681	6.441	57.99	0.872
	8.053–8.630	8.342	75.47	0.912
423.15	11.997–12.460	12.229	110.6	0.950
	2.102–2.676	2.389	16.51	1.37
	4.118–4.684	4.401	30.63	0.993
	6.098–6.700	6.399	44.78	1.49
453.15	8.177–8.699	8.438	59.33	1.57
	2.079–2.600	2.340	13.34	2.06
	4.126–4.698	4.412	25.23	1.95
	6.070–6.628	6.349	36.47	2.03
	8.259–8.973	8.616	49.57	2.05

Kulkarni and Stern.²⁵ The self-diffusion coefficient D_{self} is given by the expression:²⁶

$$D_{\text{self}} = RTA_d \exp[-B_d/\nu_f] \quad (19)$$

where R is the gas constant, T is the absolute temperature, and A_d and B_d are characteristic parameters. The volume fraction ν_f of the free volume of the system comprised of gas and polymer was defined as²⁵

$$\nu_f(T, P, \phi_1) = \nu_{fs}(T_g, P_s, 0) + \alpha(T - T_g) - \beta(P - P_s) + \gamma\phi_1 \quad (20)$$

where ν_{fs} is the free-volume fraction at the glass transition temperature and atmospheric pressure, α is the thermal expansion coefficient, β is the compressibility, γ is a concentration coefficient of the free volume, T_g is the glass transition temperature, P_s is the standard pressure (=0.1 MPa), and ϕ_1 is the volume fraction of the gas. The value for ν_{fs} was fixed at 0.025 for amorphous polymer. This value was investigated by Williams et al.²⁷ The compressibility was determined from the following equation:²⁵

$$\frac{\beta}{1 - \nu_f^*} = \beta' = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (21)$$

where β' is the isothermal compressibility of the pure polymer and was obtained from the Tait equation described above. The ν_f^* in eq 21 is the free volume of

Table 8. Characteristic Parameters of the Free-Volume Model

	PBS	PBSA
$A_d \times 10^{11}$ (m ² ·mol·s ⁻¹ ·J ⁻¹)	2.406	3.548
B_d	0.4230	0.5076
	0.2672	0.2827

the polymer at temperature T and pressure P_s and was obtained with following equation:

$$\nu_f^* = \nu_{fs} + \alpha(T - T_g) + \beta P_s = \frac{\nu_{fs} + \alpha(T - T_g) + \beta' P_s}{1 + \beta' P_s} \quad (22)$$

where $\alpha = 4.8 \times 10^{-4} \text{ K}^{-1}$ can apply in the temperature range of $T_g < T < T_g + 100 \text{ K}$.²⁷ Hence, the following equation was used in the temperature greater than $T_g + 100 \text{ K}$.²⁵

$$\nu_f^* = \frac{0.025 + \int_{T_g}^T (\alpha_r - 0.975\alpha_g) dT}{1 + \int_{T_g}^T \alpha_r dT} \quad (23)$$

where α_r and α_g are the thermal expansion coefficients of the rubbery and glassy states, respectively. Because α_g 's of PBS and PBSA were not available, we used the following empirical relationship proposed by Simha and Boyer.²⁸

$$(\alpha_r - \alpha_g) T_g = 0.113 \quad (24)$$

The relationship between the self-diffusion coefficient D_{self} and the mutual-diffusion coefficient D_{mtl} was obtained from²⁹

$$D_{\text{mtl}} = \frac{D_{\text{self}} x_2}{RT} \left(\frac{\partial \mu_1}{\partial \ln x_1} \right)_{T,P} \quad (25)$$

where x_i is the mole fraction of i and μ_1 is the chemical potential of the gas in the polymer. The chemical potential gradient of the gas in eq 25 was obtained from numerical calculation using the S–L EOS. To develop a correlation for the mutual-diffusion coefficients, the characteristic constants A_d and B_d in eq 19 and γ in eq 20 were used as fitting parameters to represent the experimental diffusion coefficients. The fitting parameters determined were given in Table 8. Correlation results of the mutual-diffusion coefficients are shown by the solid lines in Figure 8. The free-volume model could correlate the diffusion coefficients in PBS and PBSA to within 12% and 6.6% in average relative deviation, respectively.

Conclusions

The solubility and diffusion coefficient of carbon dioxide in PBS and PBSA were measured at temperatures from 323.15 to 453.15 K and pressures up to 20 MPa. The gas solubilities in the amorphous region of the polymers decreased with increasing temperature. The solubilities were correlated with the S–L EOS to within 1.9% and 2.2% in average relative deviations of the solubilities in PBS and PBSA, respectively. The interaction parameters determined from fitting the solubility exhibited were inversely proportional to temperature. Henry's constants for CO₂ in the polymers were obtained, and the equations to represent the

Henry's constant were developed. The difference in the Henry's constants between PBS and PBSA cannot be regarded as significant. The diffusion coefficients of carbon dioxide showed weak concentration dependence and had an order of magnitude of 10^{-9} m²/s in the molten state. The diffusion coefficients in PBS and PBSA were correlated with the free-volume model of Kulkarni and Stern to within 12% and 6.6% in average relative deviation, respectively.

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