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Solubility of Carbon Dioxide in Polyethylene/Titanium Dioxide Composite Under High Pressure and Temperature

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ABSTRACT: Solubility of carbon dioxide (CO₂) in a low-density polyethylene (LDPE)/titanium dioxide (TiO₂) composite was measured using a magnetic suspension balance (MSB) at a temperature from 423 to 473 K and pressures up to 15 MPa. The effect of the TiO₂ concentration on the solubility is investigated by varying TiO₂ content in the range of 0–20 wt %. Extending the Sanchez–Lacombe equation of state and its mixing rule for binary mixture, a scheme of calculating CO₂ solubility in composite from MSB data is developed. The solubility of CO₂ in the composites increases in proportion to pressure and exponentially decreases with

temperature. The apparent solubility, which is defined by the weight of dissolved CO₂ per unit weight of the composite, decreases as the TiO₂ content increases. However, the true solubility, which can be defined by the weight of dissolved CO₂ per unit weight of polymer, is constant, although the TiO₂ content is changed. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 282–288, 2002

Key words: adsorption; polyethylene (PE); composites; swelling

INTRODUCTION

Utilization of supercritical carbon dioxide (scCO₂) in polymer processing has received a great deal of attention because the polymer/gas solutions show interesting rheological and thermal properties, and provide a variety of applications in the polymer field. Polymeric foaming with scCO₂ is one of the applications, where scCO₂ is used as a physical foaming agent. Since thermal instability, i.e., supersaturated condition, induced by pressure or temperature changes creates bubbles in the foaming process, the concentration of CO₂ dissolved in the polymer is one of the key factors determining bubble size and density of the polymer foams. Therefore, the solubility of CO₂ in the polymer is fundamental data to design the foaming die and operating conditions of the processes.

Several authors have published the solubility of CO₂ into polymers. Wang et al measured the solubility in poly(vinyl acetate) (PVAc) and poly(butyl methacrylate)¹; Durill and Griskey measured the solubility of CO₂ and nitrogen (N₂) gas in several polymers such as polypropylene (PP), low-density polyethylene (LDPE), high-density polyethylene (HDPE), and polystyrene (PS)^{2,3}; Sato et al. studied the solubility of CO₂ and N₂ in PS, PP, and HDPE.⁴ Wang used a piezoelectric quartz sorption method and others employed a

pressure decay method to measure the solubility. The pressure decay method, where the pressure change owing to the sorption is measured, was popular, but was difficult to apply to molten polymers because no high-resolution sensor of pressure was available at the high temperature condition, which was high enough to melt the sample polymer.

Kleirahm and Wanger developed a new gravimetric method that allows us to measure the solubility of CO₂ in a polymer at high pressure and temperatures.^{5,6} Their apparatus, called magnetic suspension balance (MSB), can isolate a sample from the balance and weigh the sample while keeping the sample in a high-temperature and high-pressure chamber. Recently, using the MSB, Sato and co-workers measured the solubility of CO₂ in PS, PP, and HDPE at temperatures ranging from 373 to 473 K and pressures up to 20 MPa.⁷

Most of the polymers for which solubility of CO₂ has been reported were homogeneous.^{2–8} There are few data available for polymer composites and blends. In this paper, using the MSB, the solubility of CO₂ in the polyethylene/titanium dioxide composites is measured at temperature in the range from 423 to 473 K and pressure up to 15 MPa.

THEORY

Operating mechanism of magnetic suspension balance

When CO₂ dissolves in a polymer, the weight of the polymer increases owing to the weight of dissolved CO₂. Thus, weighing the polymer in pressurized CO₂ can

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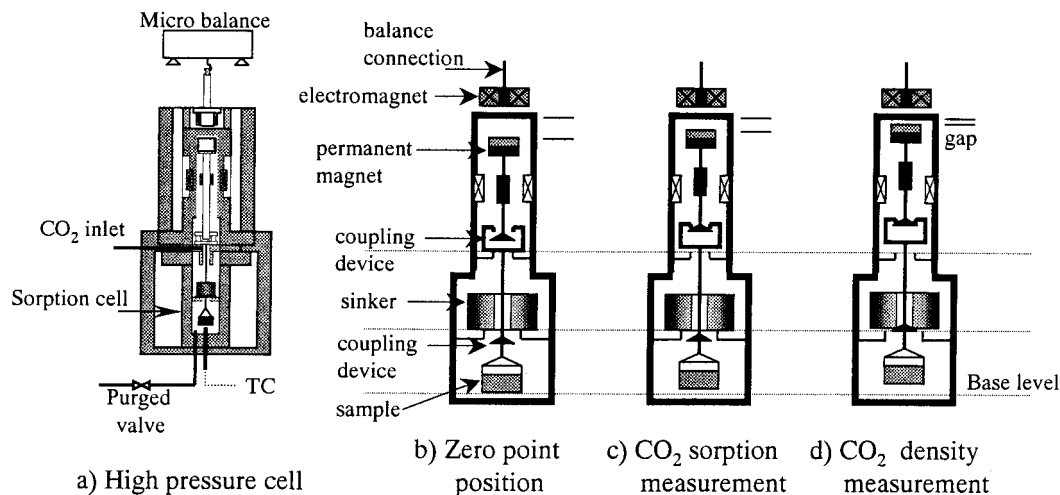


Figure 1 A schematic diagram of MSB and its three measuring modes.

allow us to calculate the solubility and diffusion coefficient of CO_2 . The MSB makes it possible to weigh samples under the high pressure and temperature environments without holding the balance in the environments. Figure 1(a) shows a schematic diagram of the MSB (Rubotherm and BEL Japan, Inc.), which consists of a measuring chamber and a balance (Mettler AT261, Switzerland). The balance is located outside the chamber under ambient atmospheric conditions.

In the measuring chamber where a high pressure and temperature condition is realized, the sample is hooked up to a so-called suspension magnet, which consists of a permanent magnet, a position sensor, and a device for coupling/decoupling the measurement load (sample). An electromagnet is attached to the under-floor weighing hook of the balance and situated outside the chamber so as to have the suspension magnet in a freely suspended state controlled by an electronic control unit. Using this magnetic suspension, the weight of the sample in the chamber can be transmitted to the balance without direct contact. A more detailed description can be found in the literature.^{5-7,9}

Principle of measurement

When CO_2 dissolves in polymer, it swells the polymer. Because the degree of swelling is affected by the amount of dissolved CO_2 , the buoyancy caused by the swelling will change in the course of the solubility measurement. To perform accurate measurements, the weight of dissolved CO_2 has to be measured with consideration of the buoyancy effect:

$$w_{\text{CO}_2}(T, P) = W_F(T, P) - W_O(T, P \approx 0) + \rho_{\text{CO}_2}(T, P) \times [V_{\text{comp}}(T, P, w_f, w_{\text{CO}_2}) + V_B] \quad (1)$$

where $W_F(T, P)$ and $W_O(T, P \approx 0)$ are readouts of the balance at temperature, T , and pressure, P , and that at a pressure close to zero, i.e., under vacuum. The ρ_{CO_2} is CO_2 gas density, which is also a function of temperature and pressure. V_B is a total volume of a sample basket and devices for coupling/decoupling. The V_{comp} is the volume of composite, which is a function of temperature, pressure and weight of dissolved CO_2 , w_{CO_2} . The w_f denotes the mass of TiO_2 in the sample composite.

The third term of the right hand side of eq. (1) shows the buoyancy effect. To estimate the mass of dissolved CO_2 from readouts of the balance, one has to calculate the value of the third term at any temperature and pressures condition. Therefore, either experimental data or mathematical equations are needed to calculate CO_2 gas density, ρ_{CO_2} , and volume of composite, V_{comp} , for any temperature, pressure, and the weight of dissolved CO_2 .

Density of CO_2

The MSB used in this study can measure the mass of two samples with only one suspension magnet by using the device for coupling/decoupling measuring load. As illustrated in Figure 1(b-d), by changing the position of the suspension magnet, three different measuring modes can be realized; zero position, the first sample measuring (gas sorption measurement) and the second sample measuring (fluid density measurement). At the zero position mode, the permanent magnet alone is suspended and then the balance is tarred and calibrated. At the first sample-measuring mode, the first sample (composite) is lifted up and weighed by connecting the coupling device, and at the second sampling mode, both samples are lifted together and weighed by connecting two coupling devices. Subtraction of the first measurement from the

second measurement provides the weight of the second sample. By weighing a titanium sinker as the second sample, whose weight and volume are known at any temperature and pressure level, the density of pressurized CO₂, ρ_{CO_2} , can be determined from the second measurement by following the Archimedes' principle.⁹

$$\rho_{\text{CO}_2}(T, P) = \frac{|\Delta W|}{V_{\text{sinker}}(T, P)} = \frac{|W_{\text{sinker}}(T, P \approx 0) - W_{\text{second}}(T, P)|}{V_{\text{sinker}}(T, P)} \quad (2)$$

where $V_{\text{sinker}}(T, P)$ is the volume of the sinker at temperature, T , and pressure, P . $W_{\text{sinker}}(T, P = 0)$ denotes the weight of the sinker at temperature T under vacuum, and $W_{\text{second}}(T, P)$ denotes the measurement of the second sample, which is the weight of sinker in the pressurized CO₂ at temperature, T , and pressure, P .

Correction of buoyancy effect

Calculation of the swollen volume of the composite, V_{comp} , is performed using an equation of state and a mixing rule. The Sanchez–Lacombe (SL) equation of state is employed in this study. It is derived from the lattice model and its equation is given by^{10,11}

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T} \left[\ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r}\right) \tilde{\rho} \right] = 0 \quad (3)$$

where \tilde{P} , \tilde{T} and $\tilde{\rho}$, are the reduced pressure, temperature, and density, respectively. The r is the size parameter, which represents the number of lattice sites occupied by a polymer molecule.

The reduced parameters and the size parameter are respectively defined by

$$\tilde{P} = \frac{P}{P^*}, \quad \tilde{T} = \frac{T}{T^*}, \quad \tilde{\rho} = \frac{\rho}{\rho^*}, \quad \rho^* \equiv \frac{\bar{M}_w}{\nu^*}, \quad r = \frac{P^* \nu^*}{RT^*} \quad (4)$$

where R is gas constant and \bar{M}_w is the average molecular weight. P^* , T^* , ν^* , and ρ^* are characteristic parameters.

For the polymer alone, these characteristic parameters are easily determined by fitting eq. (3) to a pressure-volume-temperature (PVT) data of the polymer. However, in this study, the volume of mixture of LDPE/TiO₂ composite with CO₂ has to be calculated at any temperature, pressure, CO₂, and TiO₂ concentration levels.

A preliminary experiment clarified that CO₂ did not dissolve into the TiO₂ filler. Thus, assuming that TiO₂ is physically blended—i.e., no chemical interaction is involved between polymer and TiO₂, the swelling occurs in the polymer phase not in the TiO₂ phase, the swollen volume of composite— $V_{\text{comp}}(T, P, w_f, w_{\text{CO}_2})$, can be represented by

$$V_{\text{comp}}(T, P, w_f, w_{\text{CO}_2}) = V_{\text{comp}}(T, P, w_f) + \Delta V_{\text{swell}}(T, P, w_g) = V_{\text{comp}}(T, P, w_f) + V_{\text{LDPE}+\text{CO}_2}(T, P, w_g) - V_{\text{LDPE}}(T, P) \quad (5)$$

Then, the specific volume of the composite with non-CO₂ dissolution is given by

$$V_{\text{comp}}^{\text{sp}}(T, P, w_f) = (1 - w_f) V_{\text{LDPE}}^{\text{sp}}(T, P) + w_f V_{\text{TiO}_2}^{\text{sp}}(T, P) \quad (6)$$

where $V_{\text{comp}}(T, P, w_f)$ is the volume of composite whose TiO₂ content is w_f and CO₂ concentration is zero. $\Delta V_{\text{swell}}(T, P, w_g)$ is the swelling of the polymer due to CO₂ dissolution only, $V_{\text{LDPE}+\text{CO}_2}(T, P, w_g)$ is the volume of single-phase mixture of the polymer with CO₂, whose CO₂ content is w_g , and $V_{\text{LDPE}}(T, P)$ is the volume of the polymer alone at temperature, T , and pressure, P . $V_{\text{comp}}^{\text{sp}}$, $V_{\text{LDPE}}^{\text{sp}}$, and $V_{\text{TiO}_2}^{\text{sp}}$ are the specific volumes of the composite, LDPE, and TiO₂, respectively.

The specific volume of TiO₂ can be described by a function of T and P .¹²

$$V_{\text{TiO}_2}^{\text{sp}}(T, P) = V_{\text{ref}}^{\text{sp}} + \alpha_f(T - T_{\text{ref}}) - \beta_f(P - P_{\text{ref}}) \quad (7)$$

where $V_{\text{ref}}^{\text{sp}}$ is the specific volume of TiO₂ at a reference temperature, T_{ref} , and pressure, P_{ref} . The α_f and β_f are thermal expansion and compressibility coefficients of TiO₂, respectively.

$V_{\text{LDPE}}(T, P)$, $V_{\text{LDPE}}^{\text{sp}}$, and $V_{\text{TiO}_2}^{\text{sp}}$ can be obtained by normal PVT measurements. Therefore, to calculate the swelling due to CO₂ dissolution, $\Delta V_{\text{swell}}(T, P, w_g)$, the volume of polymer/CO₂ mixture, $V_{\text{LDPE}+\text{CO}_2}(T, P, w_g)$, should be estimated. The mixing rule of the SL equation of state is used to estimate the density of the polymer/CO₂ mixture, $\rho_{\text{LDPE}+\text{CO}_2}$, and $V_{\text{LDPE}+\text{CO}_2}(T, P, w_g)$ is calculated by inverting the density. By the mixing rule, the characteristic parameters of LDPE/CO₂ single-phase mixture are derived from the characteristic parameters of both LDPE and CO₂.

The characteristic molar volume, ν^* , pressure, P^* , temperature, T^* , of a binary mixture and the size parameter are respectively given by the following mixing rules.¹³ In the equations, the superscript asterisk indicates the property of binary mixture, the subscript 1 stands for CO₂, and 2 for LDPE. The ρ^* denotes the characteristic parameter of the LDPE/CO₂ mixture and thus the density of the mixture, $\rho_{\text{LDPE}+\text{CO}_2}$, is given by $\rho^* \tilde{\rho}$.

$$\nu^* = \phi_1^0 \nu_1^* + \phi_2^0 \nu_2^* \quad (8a)$$

$$\phi_i^0 = \frac{\phi_i}{\phi_1 + \left(\frac{\nu_1^*}{\nu_2^*}\right) \phi_2} \quad \text{for } i = 1 \text{ and } 2 \quad (8b)$$

$$\phi_i = \frac{\frac{m_i}{\rho_i^*}}{\left[\frac{m_1}{\rho_1^*} + \frac{m_2}{\rho_2^*}\right]} \quad \text{for } i = 1 \text{ and } 2 \quad (8c)$$

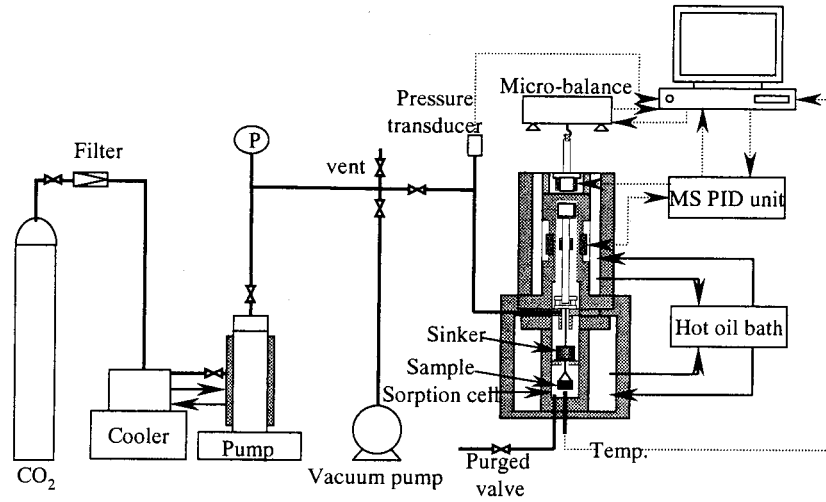


Figure 2 Experimental setup for gas solubility measurement.

$$\phi_1 + \phi_2 = 1 \quad (8d)$$

$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - \frac{RT}{v^*} \phi_1 \phi_2 \chi_{12} \quad (8e)$$

$$\chi_{12} = \frac{(P_1^* + P_2^* - 2(P_1^* P_2^*)^{1/2} (1 - k_{12})) v^*}{RT} \quad (8f)$$

$$T^* = \frac{P^* v^*}{R} \quad (8g)$$

$$r = x_1 r_1 + x_2 r_2; \quad x_1 + x_2 = 1 \quad (8h)$$

$$\frac{1}{\rho^*} = \frac{m_1}{\rho_1^*} + \frac{m_2}{\rho_2^*} \quad (8i)$$

where k_{12} is a binary interaction parameter. The x_1 and x_2 are mole fractions and m_1 and m_2 are weight fractions of CO_2 and LDPE relative to the polymer/ CO_2 mixture.

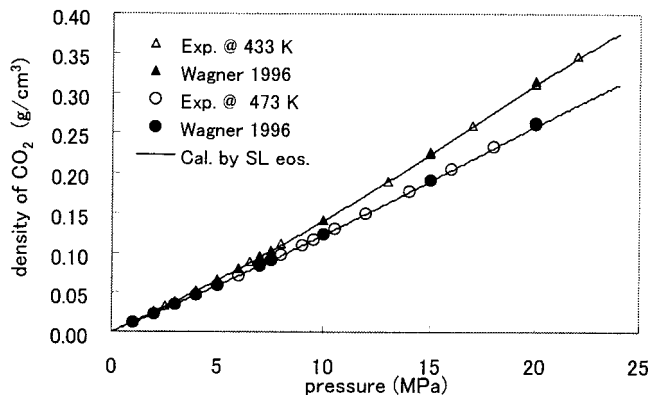


Figure 3 Comparison of measured density of CO_2 with the estimates of the Sanchez-Lacombe model. The solid lines represent values calculated by the SL model. The open symbols represent measured values and the filled symbols represent literature values by Wagner (1996).¹⁶

Solubility calculations

Assume that all the characteristic parameters and size parameter of the neat polymer as well as those of CO_2 are known, and that V_{LDPE} , $V_{\text{LDPE}}^{\text{sp}}$, $V_{\text{TiO}_2}^{\text{sp}}$, and ρ_{CO_2} are available at any temperature and pressure conditions. When W_F and W_o are obtained by performing the MSB measurements at a given temperature and pressure condition, unknown parameters in eqs. (1)–(8) are the mass fraction of CO_2 , m_1 , the volume fraction of CO_2 , ϕ_1 , and density of polymer/ CO_2 mixture, $\rho_{\text{LDPE}+\text{CO}_2}$. Namely, we have three unknown parameters and two process equations, which are eq. (1) and equation of state for the polymer/ CO_2 mixture, eq.(3). Therefore, in order to determine m_1 from the MSB readouts at the given temperature and pressure condition, which is equivalent to determine the solubility, one extra process equation is required.

When the polymer/gas mixture reaches at an equilibrium state at temperature, T , and pressure, P , the chemical potentials of CO_2 should be the same at the interface between the gas phase and the polymer/gas mixture. That is, the last equation required for solubility calculation is the equation of phase equilibrium, which equates the chemical potentials of gas in the two phases^{7,8,14}:

$$\mu_1^G(T, P) = \mu_1^P(T, P, m_1) \quad (9)$$

where the superscripts G and P represent the gas and the polymer/ CO_2 mixture, respectively.

TABLE I
Characteristic Parameters of CO_2 and LDPE.

| Characteristic parameter | ρ^* (g/cm ³) | P^* (MPa) | T^* (K) | Pressure range |
|--------------------------|----------------------------------|----------------|--------------|----------------|
| CO_2 | 1.253 | 369.1 | 341.2 | 0–20MPa |
| LDPE | 0.9054 | 420.8 | 628.2 | 0–50MPa |

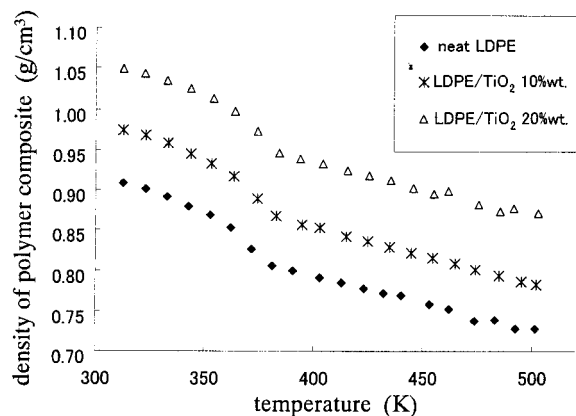


Figure 4 Effect of TiO_2 content on density of LDPE composites observed at PVT data (0.1 MPa).

The gas phase is assumed to be a pure gas, because of the low volatility of high molecular weight of polymer. The SL equation of state leads eq. (9) to the following equation of chemical potential of CO_2 .¹³

$$\begin{aligned} \frac{\mu_1^P}{RT} &= \ln \phi_1 + \left(1 - \frac{r_1}{r_2}\right) \phi_2 + r_1 \tilde{\rho} \chi_{12} \phi_2^2 \frac{\nu^*}{\nu} \\ &+ r_1 \left[\frac{-\tilde{\rho} + \tilde{P}_1 \tilde{\nu}}{\tilde{T}_1} + \tilde{\nu} \left((1 - \tilde{\rho}) \ln(1 - \tilde{\rho}) + \frac{\tilde{\rho} \ln \tilde{\rho}}{r_1} \right) \right] \\ &= r_1 \left[\frac{-\tilde{\rho}_1 + \tilde{P}_1 \tilde{\nu}_1}{\tilde{T}_1} + \tilde{\nu}_1 \left((1 - \tilde{\rho}_1) \ln(1 - \tilde{\rho}_1) + \frac{\tilde{\rho}_1 \ln \tilde{\rho}_1}{r_1} \right) \right] \\ &= \frac{\mu_1^G}{RT} \end{aligned} \quad (10)$$

Solving eqs. (1), (3), and (10) with the MSB measurements at an equilibrium state can give the three unknown parameters and determine the solubility of CO_2 in the composite at the equilibrium condition.

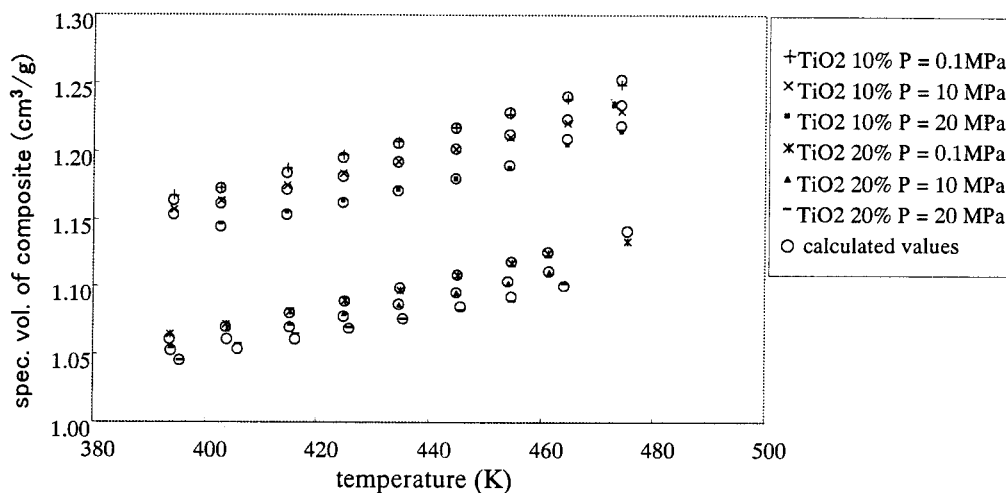


Figure 5 Comparison of measured specific volume of LDPE/ TiO_2 composites with the values predicted by the SL model. The symbols represent measured PVT data. The open circles represent the estimates of the SL model.

EXPERIMENTAL

Materials

A commercially available LDPE sample was used whose density is 0.919 g/cm^3 , the melt flow rate, $\text{MFR} = 8.0 \text{ g/10 min}$, the average molecular weight, $\overline{M}_w = 105,942$, and the polydispersity, $\overline{M}_w/\overline{M}_n$ is 6.94. The melting point measured by differential scanning calorimetry (DSC) (Perkin Elmer, Pyris 1) scanning at 10 K/min is 378.7 K . In this study, the TiO_2 , so-called titanium white, whose density is 3.9 g/cm^3 and primary particle size is about $0.2\text{--}0.3 \text{ }\mu\text{m}$, is used. The TiO_2 is often used as a white pigment in polymer processing. Three different composites whose TiO_2 contents are 0, 10, and 20 wt % are prepared for investigating the effect of TiO_2 content on the solubility of CO_2 .

Experimental setup and procedure

Figure 2 shows the experimental setup used in this study. CO_2 was pressurized and introduced to the MSB measuring chamber using a plunger pump (Isco 260D). At the chamber, pressure can be built up to 35 MPa and temperature can be increased up to 523 K. Resolution and accuracy of the microbalance are $10 \text{ }\mu\text{g}$ and $\pm 0.002\%$, respectively.

A polymer sample was set in a stainless steel basket and the basket was hung on a hook of the magnetic suspension. The chamber was heated to keep the sample molten state and vacuumed about 30 min at the specified temperature. Then CO_2 is introduced into the chamber. The data of the microbalance readouts, temperature, and pressure were acquired by a computer. The measurements were performed at 423, 448, and 473 K by changing CO_2 pressure stepwise from 2.0 to 15.0 MPa.

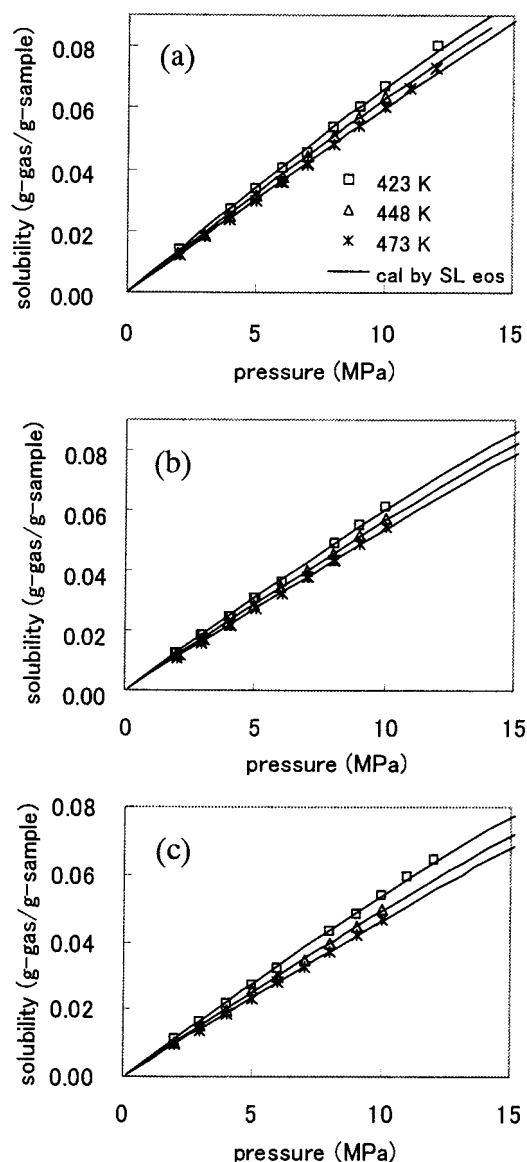


Figure 6 (a) Solubility of CO₂ in LDPE at temperatures 423, 448, and 473 K. The symbols represent experimental results. The solid lines represent the estimate of the SL model. (b) Solubility of CO₂ in LDPE/TiO₂ (10 wt %). (c) Solubility of CO₂ in LDPE/TiO₂ (20 wt %).

PVT measurement

The PVT data of all three composites were obtained by a high-pressure GNOMIX PVT apparatus¹⁵ (GNOMIX, Inc., USA) with an isothermal cooling procedure for the range of temperature from 313 to 503 K and pressure from 0.1 to 100 MPa.

RESULTS AND DISCUSSION

Figure 3 shows the density of CO₂ measured by the MSB at 433 and 473 K in the range of pressure 0.1–20 MPa together with the literature values.¹⁶ The characteristic parameters of equation of state for CO₂ were also obtained by fitting eq. (3) to the PVT experimental

data. The resulting parameter values are listed in Table I. To ensure the reliability of obtained equation of state, the density of CO₂ is calculated by the equation of state at 433 and 473 K and compared with literature as well as experimental values. The solid line represents the estimated by the resulting SL equation of state.

Since the PVT measurement of TiO₂ alone was not available, PVT measurements of the composite were carried out to determine the characteristic parameters and thermal expansion coefficients of composite. Figure 4 shows a PVT data of the composite. Because the density of TiO₂ is larger than that of polymer, the overall density of the composite becomes larger as TiO₂ content increases. The characteristic and size parameters of polymer alone could be determined by fitting eq. (3) to the PVT data of the sample with 0 wt % TiO₂ content. The resulting parameter values for neat LDPE alone are also listed in the Table I. The thermal expansion, α_f , and compressibility coefficients β_f of TiO₂ in eq. (7) were determined by fitting eqs. (6) and (7) to the PVT data of the neat LDPE and those composites. The resulting values are $V_{ref}^{sp} = 0.2564 \text{ cm}^3/\text{g}$, $\alpha_f = 2.38 \times 10^{-4} \text{ K}^{-1}$, $\beta_f = 2.40 \times 10^{-7} \text{ MPa}^{-1}$ at the reference temperature 298.2 K. Figure 5 shows the fitting results of PVT data of the composite for the case of no CO₂ dissolution. The opened circles represent the estimated by eqs. (6) and (7).

Figure 6 presents the MSB solubility data of LDPE

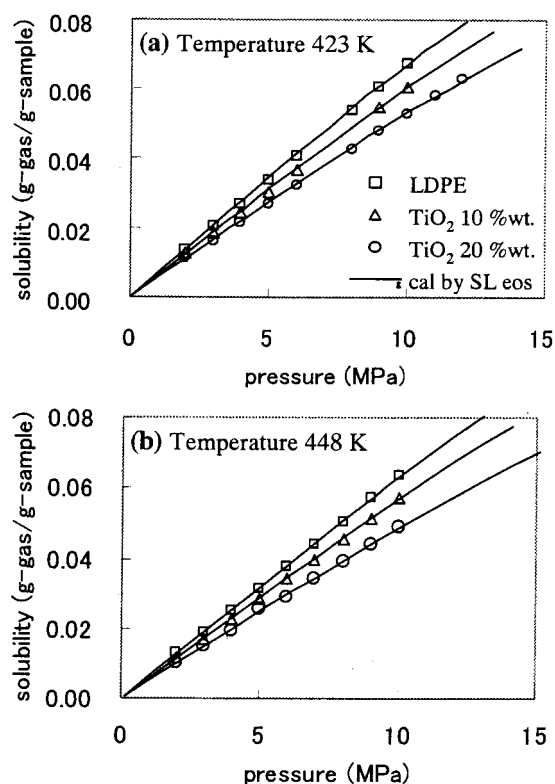


Figure 7 Solubility of CO₂ in LDPE and TiO₂ composites at temperatures (a) 423 and (b) 448 K. The symbols represent experimental results. The solid lines represent the values calculated by the SL model.

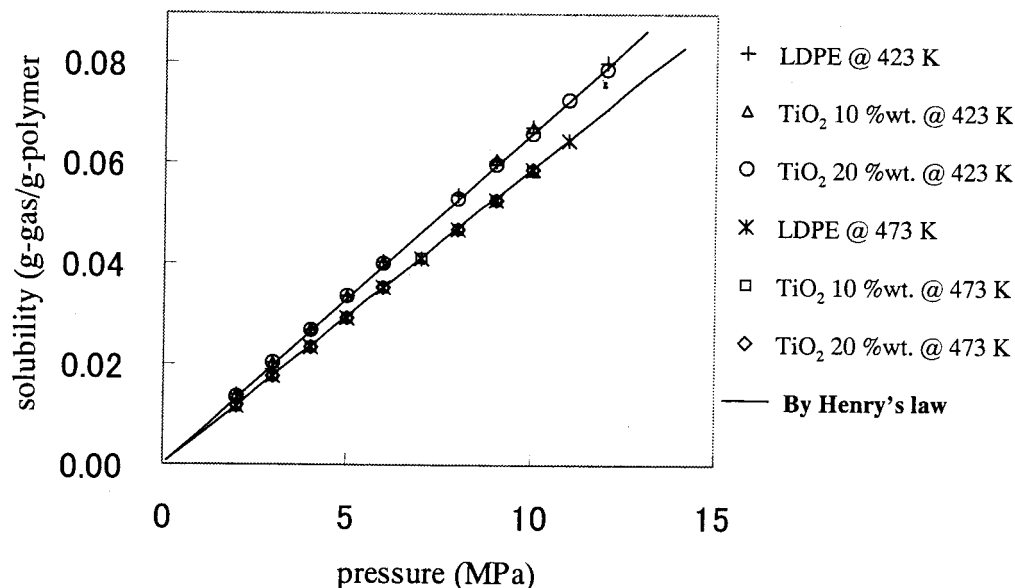


Figure 8 Solubility (g-gas per g-polymer) of CO₂ in LDPE and TiO₂ composites at temperatures 423 and 473 K. The solid lines represent the solubility predicted by Henry's law.

and LDPE/TiO₂ composites at three temperature conditions. The apparent solubility, which is defined by the mass of dissolved CO₂ per unit mass of the composite, increases in proportional to pressure level of CO₂ in all three samples. The solid line in Figure 6 represents the solubility estimated by the obtained SL equation of state of the polymer/gas mixture, eq. (3) with eq. (5). Figure 7 shows the effect of TiO₂ contents on the apparent solubility at three different temperatures. As can be seen, the apparent solubility decreases as TiO₂ content increases. However, the true solubility, which is defined by the mass of dissolved CO₂ per unit mass of the polymer, is not affected by the TiO₂ content, as shown in Figure 8. Figure 8 clearly supports the assumption we made for the SL equation of state solubility calculation, which was that the dissolution of CO₂ can occur only in the polymer phase and swelling due to the dissolution can occur only in the polymer phase.

Based on these results, the CO₂ solubility in LDPE/TiO₂ composites can be carried out in the following way: Identify the Henry's constant for the base polymer (LDPE) alone, which in this case is given by

$$H_p(T) = H_o \exp\left(-\frac{E_a}{RT}\right) \quad (11)$$

where $H_o = 1.16 \times 10^3$ cm³(STP)/kg-polymer MPa; E_a is heat of solution and is given by -3.76 kJ/mol.

Then, multiplying the constant by $(1 - w_f)$ provides the apparent Henry's constant for the composite whose TiO₂ content is w_f , i.e., $H_p^{app} = (1 - w_f)H_p(T)$.

CONCLUSION

This study shows that the Sanchez-Lacombe equation of state can be successfully extended to estimate the

solubility of CO₂ in LDPE/TiO₂ composites from the MSB data. The solubility of CO₂ decreases as temperature increases and increases as pressure increases. The TiO₂ has no effect on the solubility of CO₂ relative to polymer matrix. Therefore, estimation of CO₂ solubility for LDPE/TiO₂ composites can be carried out using the solubility data of matrix polymer with TiO₂ contents. This scheme can be extended to any composites whose fillers do not absorb CO₂.

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