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Sorption and diffusion of supercritical carbon dioxide in polycarbonate

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Abstract

Sorption and diffusion of supercritical carbon dioxide ($SCCO_2$) in polycarbonate (PC) at temperatures ranged from 40 to 60 °C and pressures ranged from 10 to 40 MPa are presented in this study. The equilibrium CO_2 sorption in PC specimen with 0.5 mm thickness has been observed at 2 h, and the experimental data were analyzed by a mass-loss analysis. The linear relationship between mass gain and square root of time indicates that $SCCO_2$ conducted Fickian sorption and desorption in the PC specimen within the experimental conditions. The equilibrium CO_2 sorption amount in PC specimen varies from 7.6 wt.% (at 60 °C and 10 MPa) to 14.7 wt.% (at 40 °C and 40 MPa). Upon plotting the equilibrium sorption amounts against $SCCO_2$ density, crossover of the sorption isotherms is observed and the change of mass transfer mechanism is suggested. The sorption diffusivities under supercritical conditions as well as the desorption diffusivities under ambient temperature and pressure were determined. The sorption diffusivities increased with temperature and decreased with pressure of $SCCO_2$, unless the glass transition state of polymer was exceeded. The desorption diffusivities were also observed to increase with CO_2 concentration inside the PC specimen. At lower temperature and pressure, the desorption diffusivity may become larger than that of sorption due to the plasticizing effect.

Keywords: Diffusivity; Supercritical carbon dioxide; Polycarbonate

1. Introduction

The applications of supercritical carbon dioxide ($SCCO_2$) as a solvent or swelling agent in polymer chemistry are developing in recent years [1–10]. This fluid has conventional advantages for applications in green processes. It is also provided with plasticizing and swelling effects that can accelerate the infusion of additives into a polymer substrate [3–10]. Operation of the supercritical fluid process is easily managed by adjusting the temperature and pressure. In our previous investigation, we used $SCCO_2$ as an impregnation solvent to synthesize conducting polymer composites of polypyrrole (PPy) with polymer substrates of polystyrene (PS) and polycarbonate (PC) [3–5]. It was indicated that the interactions of $SCCO_2$ with polymer substrates are important factors to the resulting conductivities. Different CO_2 sorption rates and hence the PPy contents in the composites

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were observed with different polymer substrates. These results suggest that the diffusion and sorption of $SCCO_2$ in polymers have to be investigated for further applications of $SCCO_2$ in polymer processing.

Various apparatus and methods have been employed to measure the diffusion coefficient and sorption amount of CO_2 in polymers [11–15]. Precise equipments such as the quartz spring or crystal microbalance were used [11,12] to measure the sorption amount, without experimental report at higher temperatures. Although a magnetic suspension balance was applied in high temperature measurements [15], only the equilibrium sorption amounts were generated. To provide explanation on the molecular interactions in polymer processing, further kinetic data and the sorption amounts at various time periods are also required.

Schnitzler et al. [10] studied the mass transfer of dispersed dyes in polyethyleneterephthalate (PET) using supercritical CO_2. Both the equilibrium and kinetic data were measured at temperatures up to 120 °C and pressures up to 35 MPa by a magnetic coupled balance. The gravimetric method was also applied to generate kinetic data by various authors [3,16–18]. The sorption amount was estimated by extrapolating the residual weight in the desorption process within a short time period. Applying reasonable assumption of Fickian diffusion, the experimentally measured desorption data were fitted by a linear equation to yield the sorption amount and the diffusion coefficients. In this method, the pressure vessel should be small to avoid venting a large volume of CO_2 under high pressure operation conditions. Otherwise, significant error is introduced in extrapolating the desorption data owing to a larger time period needed to transfer the sample to a balance. In this study, a small pressure vessel of 10 ml was employed in the measurement with a precise and dynamically controlled syringe pump. The desired pressure in the experiment was reached in a short period of 10 s. No problem of pressure drop was concerned, and the sample was easily taken out of the pressure vessel by hand screwing.

New data on the kinetic sorption amount and diffusion coefficient of $SCCO_2$ in PC, under pressures up to 40 MPa and temperatures up to 60 °C, were measured in this study. The sorption and desorption data of $SCCO_2$ at the experimental conditions were analyzed by the Fickian diffusion equation. The sorption isotherm, sorption and desorption diffusivities are presented. Tensile tests were also performed to verify the plasticizing effect of $SCCO_2$ in PC.

2. Experimental

2.1. Materials

Pellets of PC (molecular weight 64 000, Acros) were hot pressed at 200 °C to obtain PC sheet with 0.5 mm thickness. The sheet was cut into the experimental specimen with dimensions of 40×12 mm. Carbon dioxide was purchased from San-Fu Chemical (Taiwan) with purity better than 99.5 mol%.

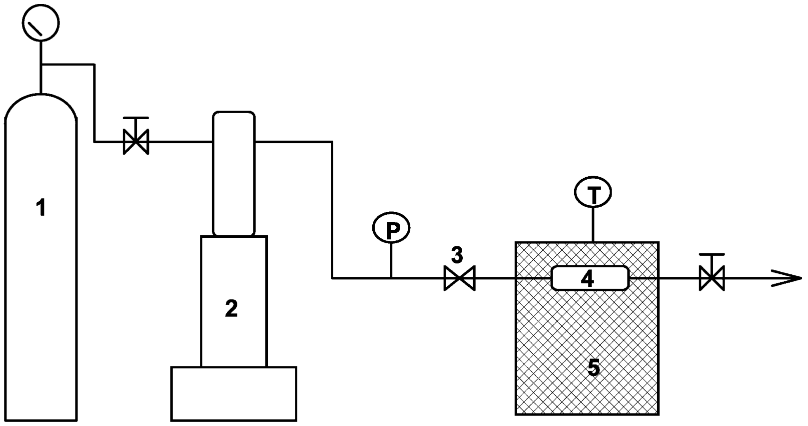
2.2. Experimental apparatus and procedures

The experimental apparatus is shown in Fig. 1. The high-quality CO_2 was compressed to the operating pressure by a syringe pump (ISCO, model 100DX). The compressed CO_2 flew into a column of 10 cm^3, which was placed in a constant temperature bath (ISCO, SFX 2-10). The experimental temperature and pressure were dynamically controlled within the desired values.

The weighted polymer specimen was put into the high pressure column in the thermal bath at a controlled temperature. The pre-pressurized CO_2 in the syringe pump was flowing into the column within 10 s. The pressure in the column was dynamically controlled throughout the sorption process. After a period of sorption time, the column was rapidly vented and the specimen was transferred to a digital balance (Mettler AE200, sensitivity 0.1 mg) under room temperature at atmospheric pressure for desorption measurements. Generally, it took 30 s during the venting and weighting processes before the first data was recorded. The weight of specimen was recorded within 100 s at an interval of 10 s. As a consequence, eight data points have been reported for each experiment at a fixed temperature and pressure. These data points were used to determine the diffusivity for the sorption or desorption of CO_2 into or from the PC specimen.

2.3. Data analysis

The methods in analyzing the sorption and desorption data were described by previous investigators



1: CO_2 tank
2: high pressure syringe pump (ISCO 100DX)
3: non-return valve
4: high pressure column
5: thermostatted vessel (ISCO SFX 2-10)

Fig. 1. Schematic illustration of the experimental apparatus.

[16,18]. The governing equation was the basic mass transfer equation for a plane sheet system [19]:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial X^2} \tag{1}$$

where C is the concentration and D is the diffusivity. One-dimensional diffusion along the thickness ℓ of the planar polymer and constant diffusivity were assumed in this study. Since the ratio of thickness to length of specimen is small, edge effect is also negligible [19]. With proper initial and boundary conditions [19] and the application of Laplace transform method, the following analytical solution was obtained:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2}\exp\left(\frac{-D(2n+1)^2\pi^2 t}{\ell^2}\right) \tag{2}$$

where M_t is the amount of sorption into the planar specimen at time t, M_∞ is equilibrium sorption amount and ℓ is the thickness of the specimen. Simplification of Eq. (2) by truncating at the first term in the summation yields the following form for the longer time sorption process:

$$\frac{M_s}{M_\infty} = 1 - \frac{8}{\pi^2}\exp\left(\frac{-D_s\pi^2 t_s}{\ell^2}\right) \tag{3}$$

where M_s is the sorption amount at time t_s, expressed as the weight percentage of CO_2 per unit weight of polymer. M_∞ is the saturated sorption amount at a larger sorption time. A schematic illustration of the mass-loss analysis to evaluate the M_s and M_∞ values is demonstrated in Fig. 2. M_s was obtained by extrapolating the desorption amount M_d to the zero desorption time. M_d is the measured percentage weight loss during the desorption process. For a Fickian diffusion, M_d is a linear function of the square root of the desorption time t_d, and a linear fit gives M_s at zero t_d. Eq. (3) was then used to determine the sorption diffusivity D_s by plotting ln $(1-M_s/M_\infty)$ against (t_s/ℓ^2).

The solution of Eq. (1) can also be expressed by a series expansion of error functions. This alternative solution has been directly introduced to analyze the desorption process after simplifying the equation at a

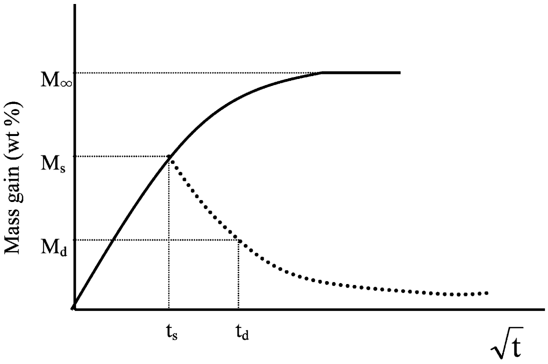


Fig. 2. Schematic illustration of the desorption measurement and mass-loss analysis.

small desorption time period [16,18]:

$$\frac{M_d}{M_\infty} = -\frac{4}{\ell}\sqrt{\frac{D_d t_d}{\pi}} \tag{4}$$

The desorption diffusivity D_d was thus determined by plotting (M_d/M_∞) against $(\sqrt{t_d}/(\ell)$.

2.4. Characterization

The apparent changes of the specimen were examined directly using digital photograph. The yielding stress of the polymer specimen was measured using the tensile meter (RTM-1T) for verifying the plasticizing effect of CO_2 on polymer.

3. Results and discussion

3.1. Sorption of CO_2 into PC

The amount of sorption of CO_2 into PC specimen, M_s, was estimated by extrapolating the measured desorption weight fraction, M_d, to the zero desorption time. An example is shown in Fig. 3 for the desorption

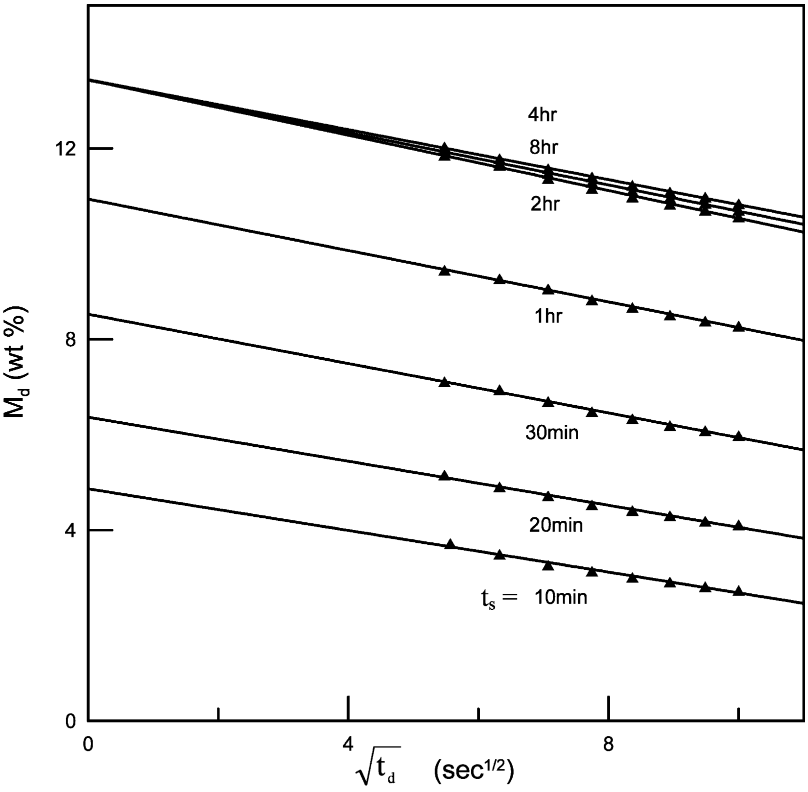


Fig. 3. Plot of the measured desorption weight fraction (M_d) against the square root of desorption time (t_d). PC specimen has been sorbed at 40 °C and 30 MPa with various sorption times (t_s).

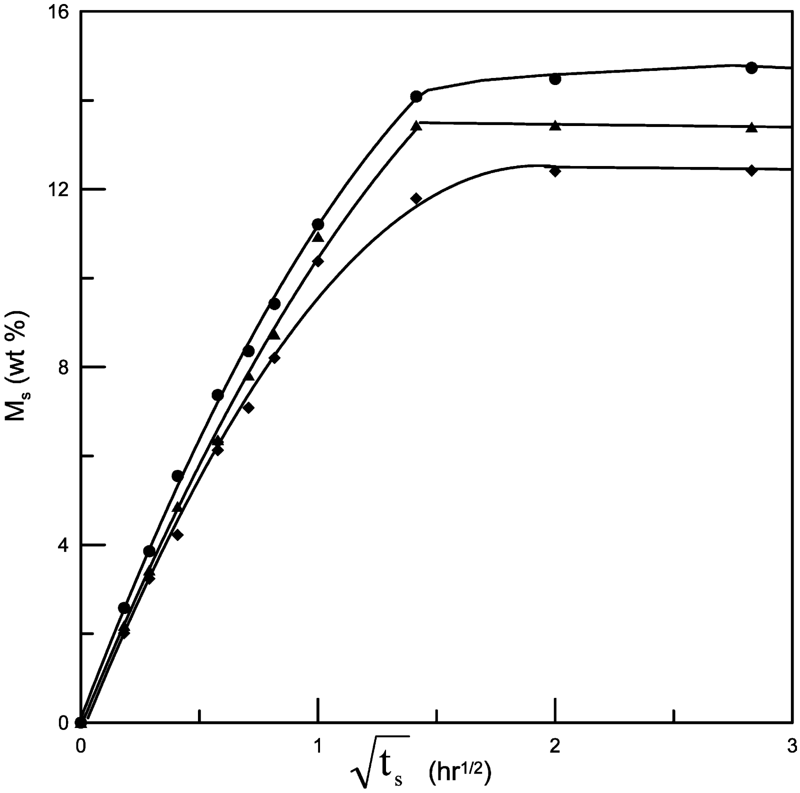


Fig. 4. Plot of the CO_2 sorption amount (M_s) against the sorption time (t_s) at 40 °C and various pressures: ◆, 20 MPa; ▲, 30 MPa; and ●, 40 MPa.

experiments at 40 °C and 30 MPa. The linear relationship between M_d and $\sqrt{t_d}$ at small desorption time period indicates that the assumption of Fickian diffusion is acceptable. The M_s values at various sorption times, t_s, are determined from the intercepts, and a sorption curve is then generated. Fig. 4 shows an example of the sorption curve at 40 °C where M_s values are plotted against $\sqrt{t_s}$ at various pressures. Initially, the M_s value increases linearly with $\sqrt{t_s}$, indicating that $SCCO_2$ conducted Fickian sorption into the PC specimen. The $SCCO_2$ sorption amount levels off after equilibrium is reached. In this study, equilibrium was reached around 2 h sorption time for PC specimen with 0.5 mm thickness at all experimental conditions. The equilibrium state sorption isotherms are shown in Fig. 5. The equilibrium sorption amounts, M_∞, in Fig. 5 were obtained from the average leveling off values of M_s shown in Fig. 4 at each temperature and pressure. The M_∞ values shown in Fig. 5 increase with increasing pressure for each isotherm. They also decrease with increasing temperature at a fixed pressure. The largest M_∞ value reaches 14.7 wt.% at 40 °C and 40 MPa. The easier capillary condensation and trapping of $SCCO_2$ inside a polymeric matrix at a lower temperature and a higher pressure lead to this result. The same trend has been observed in the investigation of the sorption and diffusion of $SCCO_2$ in poly (vinyl chloride) [18]. Furthermore, the M_∞ values are plotted against the density of $SCCO_2$, as shown in Fig. 6. The crossover of isotherms is observed. At lower densities, the $SCCO_2$ solubility in PC decreases with increasing temperature. At higher densities, however, the CO_2 solubility increases with increasing temperature. The same relation is also found for the mass transfer in poly (ethylene terephthalate) [10]. It has been suggested that a change in the mass transfer mechanism occurred. At lower densities, dual mode sorption dominates where $SCCO_2$ was absorbed

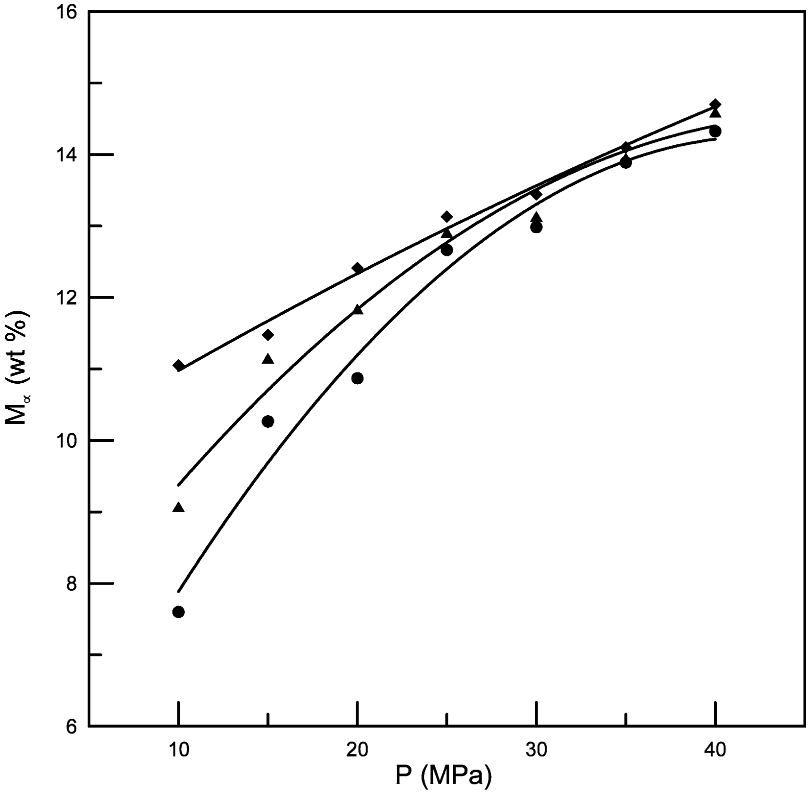


Fig. 5. Plot of the CO_2 equilibrium sorption amount (M_∞) against the pressure at various temperatures: ◆, 40 °C; ▲, 50 °C; ●, 60 °C.

up to the second layer of a polymer site. This model is used to explain the solubility of gas in a glassy state polymer. At a higher temperature, the kinetic motion of $SCCO_2$ increases, and hence results in a decrease in sorption amount. At a higher density region, more $SCCO_2$ has been absorbed into the polymer. The sorption amount increases with temperature owing to the increase in polymer chain mobility to accommodate more CO_2 molecules [10]. The M_∞ data from this study at 50 °C under various densities of $SCCO_2$ are also compared with literature values [10], as shown in Fig. 6.

3.2. Desorption kinetics and diffusivities

The desorption diffusivity D_d of CO_2 from PC specimen at ambient temperature and pressure was evaluated by the negative slope from plot of (M_d/M_∞) against ($\sqrt{t_d}/\ell$) at small desorption time. An example based on the experimental sorption at 40 °C and 30 MPa is shown in Fig. 7. Similar method is employed to determine the D_d values based on other sorption conditions and a plot of D_d against M_∞ is presented in Fig. 8. The maximum value of D_d is 2.55×10^{-11} m^2/s with the highest M_∞ obtained at 40 °C and 40 MPa. The minimum D_d is 4.6×10^{-12} m^2/s with the lowest M_∞ at 60 °C and 10 MPa. These data are in the similar range with those obtained by Muth et al. [18] for the desorption of CO_2 from PVC. It is indicated in Fig. 8 that D_d increases with the CO_2 concentration inside the PC specimen. Similar effect has also been presented in literature [16,18] for other polymers.

3.3. Sorption kinetics and sorption diffusivities

The sorption diffusivities D_s are determined from the sorption curves shown in Fig. 4. The sorption amount data ln ($1-M_s/M_\infty$) are plotted against (t_s/ℓ^2) and an example is shown in Fig. 9 based on the experiment data at 40 °C and 30 MPa. According to Eq. (3),

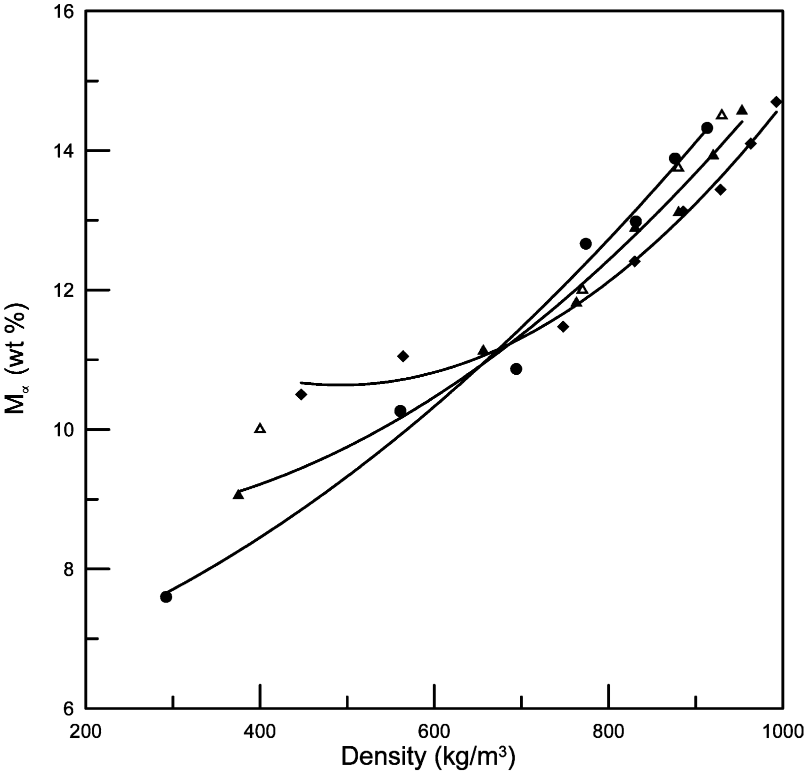


Fig. 6. Plot of the CO_2 equilibrium sorption amount (M_∞) against $SCCO_2$ density at various temperatures: ◆, 40 °C; ▲, 50 °C; ●, 60 °C (△: literature data at 50 °C [10]).

the slope of the linear plot yields D_s. The calculated D_s values at various temperatures and pressures are presented in Fig. 10. At each fixed pressure, D_s increases with increasing temperature and reaches a maximum value of 3.4×10^{-11} m²/s at 60 °C and 20 MPa. It is believed that the driving force of mass transfer increases and the resistance decreases due to higher polymer chain mobility at higher temperature. At a lower temperature like 40 °C, D_s is smaller at a higher pressure. The $SCCO_2$ would be more liquid-like at a lower temperature and a higher pressure, and hence leads to a lower diffusivity. Catchpole et al. [20] presented the similar viewpoint as they suggested an equation in estimating the diffusion coefficient for near critical fluids. They proposed that within the reduced density range of $1<\rho_r<2.5$, the diffusivity is related with $SCCO_2$ density by (−2/3) power. The decreasing of diffusivity by increasing density or pressure may also be due to the increasing viscosity in $SCCO_2$ phase. The crossover phenomenon of D_s at 40 MPa is observed in Fig. 10. This observation suggests a significant physical change in the polymer phase. It is known that glass transition temperature T_g of a polymer will be lowered at a higher pressure [10]. Schnitzler and Eggers [10] have presented that T_g of PC decreases to 70 °C under $SCCO_2$ at 30 MPa. In our sorption experiment at 40 MPa, the T_g of PC could be lower than 60 °C. The polymer changed from its glassy state to rubbery state as temperature increased from 40 to 60 °C at 40 MPa. The mobility of the polymer chain was enhanced during this transition, and this resulted in a significant increase in diffusivity as shown in Fig. 10. Visible changes of PC specimen were observed at 60 °C and 40 MPa as shown in Fig. 11. The specimen was initially transparent, as shown in Fig. 11(a). It became opaque after the sorption process, which had not been found at other temperatures and pressures.

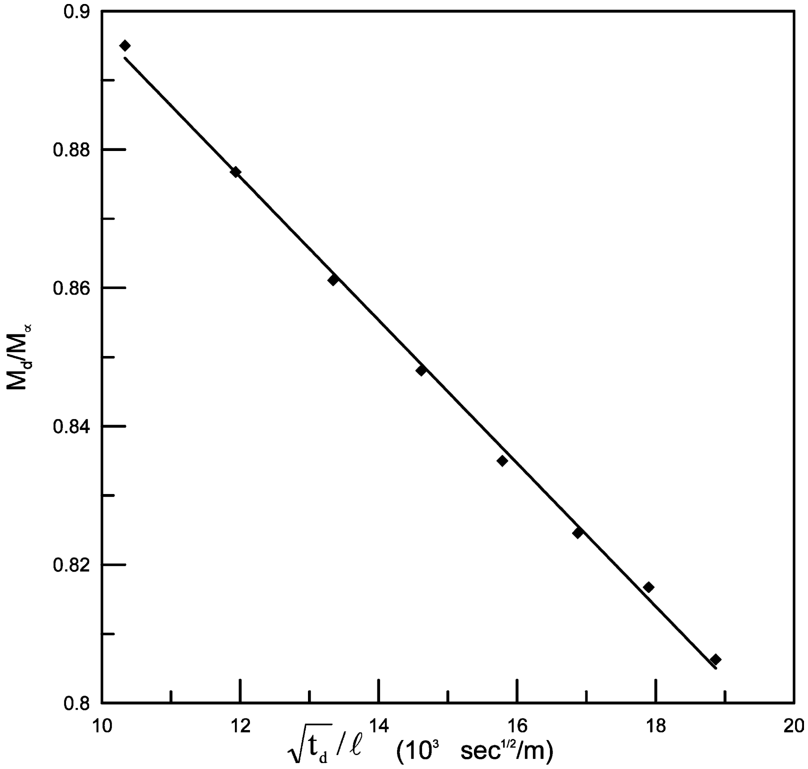


Fig. 7. Plot of M_d/M_∞ against $\sqrt{t_d}/\ell$ of 4 h sorbed specimen at 40 °C and 30 MPa.

3.4. Plasticizing effect on polymer

The experimental data of the density of $SCCO_2$, M_∞, D_d and D_s in this study are summarized in Table 1. Numerical value of D_d is usually larger than that of D_s at 40 and 50 °C, while the tendency is reversed at 60 °C. Muth et al. [18] investigated the $SCCO_2$ diffusion into PVC and they reported that the D_d is 3–25 times smaller than D_s. They explained that the sorption process of carbon dioxide was under supercritical condition but the desorption proceeded at ambient temperature and pressure. The higher temperature and pressure of $SCCO_2$ in the sorption process attributed a larger diffusivity. In this study, we explain

Table 1
Comparison of equilibrium sorption amount, desorption diffusivity and sorption diffusivity at various temperatures and pressures

T (°C)	P (MPa)	Density of $SCCO_2$[a] (kg/m^3)	M_∞ (wt.%)	D_d (10^{-11} m^2/s)	D_s (10^{-11} m^2/s)
40	20	830.04	12.41	2.01	1.22
40	30	928.42	13.44	2.16	1.07
40	40	992.50	14.70	2.55	0.91
50	20	763.12	11.71	1.61	1.68
50	30	880.24	13.13	1.85	1.19
50	40	953.02	14.59	2.07	1.63
60	20	694.03	10.87	1.67	3.36
60	30	831.24	12.98	1.70	1.59
60	40	913.09	14.32	2.07	2.74

[a] Evaluated using the Peng–Robinson equation of state.

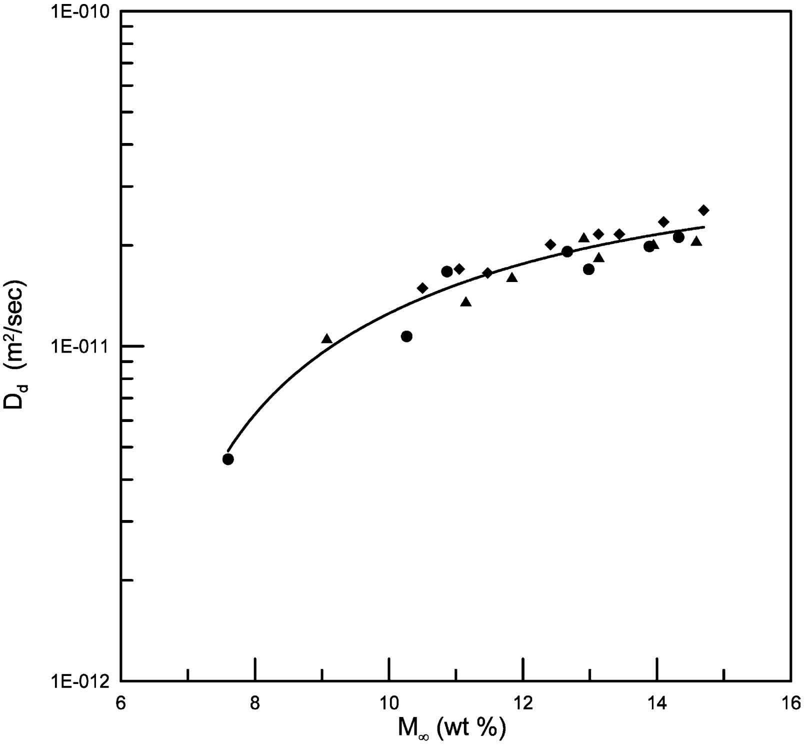


Fig. 8. Plot of the CO_2 desorption diffusivity (D_d) against the equilibrium sorption amount at various sorption temperatures: ◆, 40 °C; ▲, 50 °C; ●, 60 °C.

the difference between D_d and D_s for the diffusion of $SCCO_2$ in PC by the different states of the polymer phase during sorption and desorption. During the sorption process, the polymer substrate was rigid. The infusion of carbon dioxide has to overcome larger resistance due to lower chain mobility of neat polymer substrate. During the desorption process, however, the polymer substrate has been swollen and plasticized, the exudation of carbon dioxide suffered less resistance due to higher chain mobility of the polymer substrate. Previous authors [6,7] have proposed the acceleration of penetrant diffusion in CO_2 plasticized polymer substrate. About one to four orders of magnitude increase of diffusivity for gas penetrant upon plasticizing has been suggested [6]. In this study, the penetrated CO_2 diffused in the self-plasticized polymer substrate during the desorption process and demonstrated larger D_d than D_s values at 40 and 50 °C At higher temperature and pressure, larger D_s values are observed due to the change of polymer states.

The plasticizing effect has been verified by tensile testing in this study. The tested specimens have been ground into “I” shape by grinding wheel as shown in Fig. 12(a). Testing has been conducted with 50 mm/min pulling speed and 20 kg maximum loading. The CO_2-swollen PC polymer substrates were prepared by soaking the “I” shape specimen into high pressure vessel under 40 °C and 40 MPa for 4 h. After venting, neither visible deformation nor opaque phenomena were observed as shown in Fig. 12(c). The tensile stresses were measured at 160 s after venting. The first 100 s were spent for transferring the sample from the experimental equipment to the tensile machine location. The other 60 s were used to unload and bind the sample onto the tensile meter. After binding the sample, the tensile test was accomplished within 10 s. The CO_2 amount remained in the sample after the test was measured about 11.3 wt.%, while an initial saturated state had a concentration of 14.7 wt.%. Each of specimens was tested twice to verify

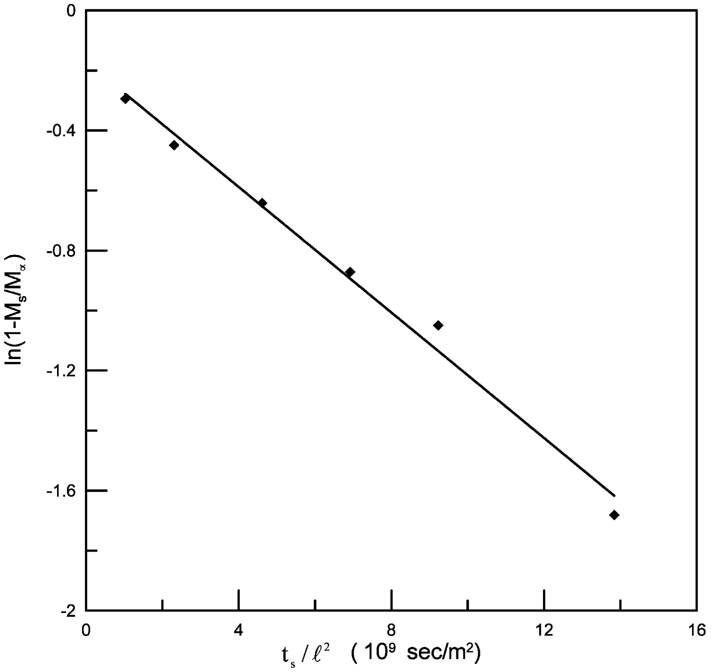


Fig. 9. Plot of ln $(1-M_s/M_\infty)$ against t_s/ℓ^2 based on the experimental data at 40 °C and 30 MPa.

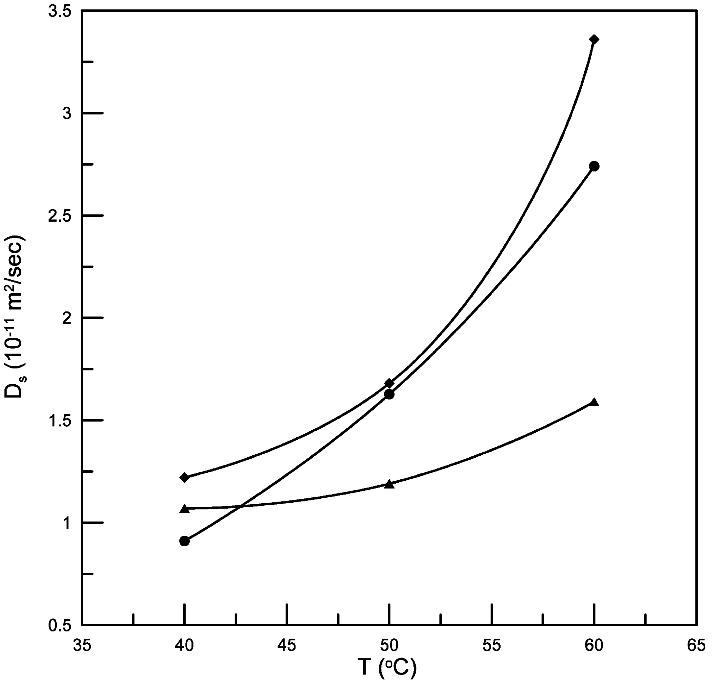


Fig. 10. Variation of sorption diffusivity (D_s) against $SCCO_2$ temperatures at various pressures: ◆, 20 MPa; ▲, 30 MPa; ●, 40 MPa.

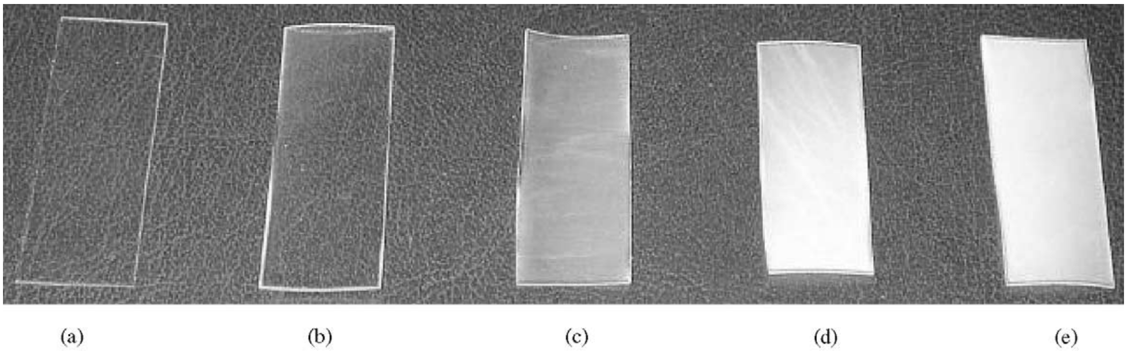


Fig. 11. Photographs of specimens after sorption at 60 °C and 40 MPa SCCO$_2$ at various sorption times: (a) zero, (b) 40 min, (c) 60 min, (d) 120 min, (e) 240 min.

the reproducibility. The results of tensile testing are shown in Fig. 12. As shown in Fig. 12(b and d), the elongation of CO$_2$-swollen specimen is much longer than that of the neat PC specimen. It is due to the increase of PC polymer chain mobility by plasticizing of the small CO$_2$ molecules. The yielding stress of the CO$_2$-swollen specimen is 32.4 MPa. This is about half with respect to the yielding stress of 68.1 MPa for the neat PC specimen. The plasticizing effect of increasing chain mobility is known to accelerate the diffusion of CO$_2$ in polymer substrate [6]. We conclude that there are two factors, the state of penetrant CO$_2$ and the state of polymer substrate, have to be considered during the diffusion process. At higher temperature

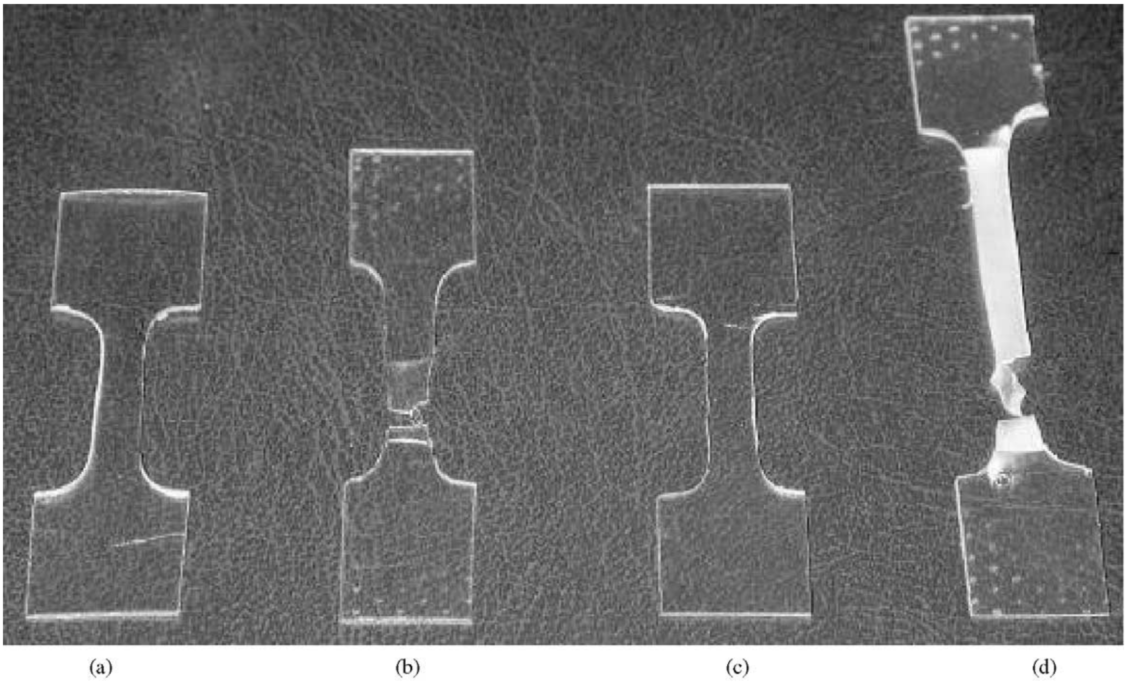


Fig. 12. Photographs of specimens used in tensile testing (a) neat PC, (b) neat PC after testing, (c) CO$_2$-swollen PC, (d) CO$_2$-swollen PC after testing under sorption at 40 °C, 40 MPa for 4 h.

and pressure, these competing factors lead to $D_s > D_d$. On the other conditions, the CO_2 plasticizing effect on polymer phase attributes to $D_d > D_s$.

4. Conclusions

In this study, sorption and diffusion of CO_2 into PC specimen at temperatures ranged from 40 to 60 °C and pressures ranged from 10 to 40 MPa are presented. The CO_2 sorption amount into PC increases with pressure and reach a highest value of 14.7 wt.% at 40 °C and 40 MPa. The crossover of sorption isotherm against $SCCO_2$ density was observed and the change of mass transfer mechanism is suggested. The desorption diffusivity isotherms increase with CO_2 concentration in the PC specimen and reach a higher value of 2.55×10^{-11} m^2/s at 40 °C and 40 MPa. The sorption diffusivities increase with temperature and reach a higher value of 3.36×10^{-11} m^2/s at highest temperature and lowest pressure. The opaque PC specimen was observed at 60 °C and 40 MPa. The glass transition state was reached and this leads to a large increase of the sorption diffusivities. It is suggested that plasticizing effect of CO_2 on PC is the dominating factor for $D_d > D_s$ in this study. The plasticizing effect on PC specimen has also been verified by tensile testing.

Acknowledgements

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