Enormous CO_2 Sorption Capacity of PDMS Rubbers near Condensation Pressure and at Low Temperatures

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We report for the first time that PDMS rubber sorbs an extremely large amount of CO_2 (792 mg g^{-1}) at near the condensation pressure at a certain low temperature (−3 °C), giving the sorption enthalpy of 9.3–10.8 kJ mol^{-1}. The sorption isotherms were evaluated by means of the Flory–Huggins equation, and the resultant χ parameters (1.3–0.2) were used to estimate the solubility parameter (SP). The CO_2/CH_4 and CO_2/N_2 selectivities were 9.6–44 at 100–3000 kPa and were far larger than those of activated carbon.

Keywords: PDMS, Flory-Huggins theory, CO_2 sorption

The solubility of CO_2 in polymeric materials has been extensively studied in relation to membrane separation.[1–8] The miscibility of polymers with supercritical CO_2 has become another topic of interest in recent decades.[9–13] High-pressure CO_2 often plasticizes polymers, decreasing their glass-transition temperature. Rubbers such as polydimethylsiloxane (PDMS) sorb large amounts of CO_2; these amounts increase with increasing partial pressure in accordance with Henry's law. The dual-sorption model proposed by Barrer et al. has been used to estimate the Henry's and Langmuir's constants of CO_2 in membranes.[14] Although the latter constant is a measure of the adsorption capacity at a certain pressure, the dual-sorption model cannot predict the maximum amount of CO_2 that is sorbed near the condensation pressure.

A large sorption capacity of CO_2 is urgently required for systems for recovering greenhouse gases.[15,16] The sorption capacities of PDMS rubbers are generally far lower than those of porous adsorbents such as activated carbons, zeolites, or metal–organic frameworks. Merkel et al. reported that PDMS in membrane form sorbs 75 mg g^{-1} of CO_2 at 2500 kPa and 35 °C.[7] The solubility of CO_2 has in PDMS been reported to be in the range 70–120 mg g^{-1} at 2000–3000 kPa and 25 °C, as calculated by a first-principles calculation.[17] A study of the sorption of CO_2 in bulk PDMS rubber by Shah et al. gave a CO_2 solubility of 94 mg g^{-1} at 2000 kPa and 10 °C.[18] However, to the best of our knowledge there have been no detailed investigations of the maximum amount of CO_2 sorbed by PDMS rubbers. In this study, we evaluated CO_2 sorption behaviors of PDMS rubbers at low temperatures and we observed an extremely large sorption near the condensation pressure.

CO_2 separation at high pressure conditions is strongly demanded in oil & gas industry. For example, natural gas produced from deep underground has a pressure exceeding 120 MPa and often contains several tens of percent of CO_2. Most of the CO_2 can be separated by reducing pressure and subsequent cooling. However, partial pressure of CO_2 is still above 2.5 MPa even at −10 °C. Therefore, the sorbents that can selectively remove CO_2 from CH_4/CO_2 mixture at low temperature are required. Furthermore, if considered the efficient transportation, CO_2 separation process needs to be operated at high pressure. In this paper, we report PDMS powder has a high potential as the solution for this problem.

A sample of PDMS rubber was prepared from SYLGARD™ 184 (Dow Corning Co.). PDMS macromer (1.0 g) was mixed with a crosslinker (0.1 g) and the mixture was stirred for five minutes and then cured at room temperature for several days. To achieve a short equilibrium time in sorption measurements, submillimeter-sized PDMS particles were prepared by cryogenic grinding (Pulverisette 14, Fritsch) (Figure S1). CO_2 sorption isotherms were measured by using a BELSORP-HP (MicrotracBEL). The sorption temperature range was −30 to 25 °C, and the equilibrium criterion was set as a pressure deviation of less than 0.1% for 500 s.

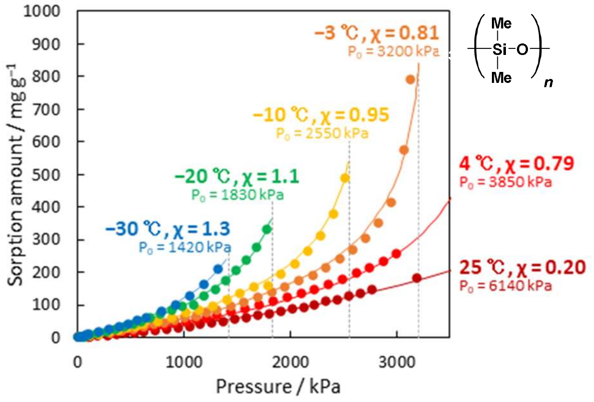

Figure 1. CO_2 sorption isotherms of PDMS rubber at −30 to 25 ℃. The upper limit of the sorption pressure in the system was 3200 kPa.

The condensation pressure of CO_2 at −30 °C is 1420 kPa, and it reaches a supercritical state at 31 °C and 7377 kPa. The sorption measurement equipment used in this study had an upper pressure limit of 3200 kPa. Figure 1 shows the CO_2 sorption isotherms for PDMS rubber at −30 to 25 °C. The dotted lines represent the condensation pressures at each temperature. Interestingly, the maximum sorption increased uniformly from 210 mg g^{-1} at −30 °C to 332 mg g^{-1} at −20 °C, 489 mg g^{-1} at −10 °C, and 792 mg g^{-1} at −3 °C. The final value was 4.4 times larger than that at −30 °C. At 3100 kPa, the amounts of CO_2 sorbed at 4 °C and at 25 °C were 260 mg g^{-1} and 180 mg g^{-1}, respectively.

Because of the high flexibility of the polymer chains, the sorption of CO_2 by PDMS rubber can be addressed in terms of solubility in a liquid polymer, and it can be quantitatively discussed by means of the Flory–Huggins equation (1):[19–22]

$$\ln P/P_0 = \ln(1-\varphi_2) + \left(1-\frac{1}{m}\right)\varphi_2 + \chi\varphi_2^2 \quad (1)$$

where, P is the vapor pressure (Pa) of the dissolving gas (CO_2), P_0 is its saturated vapor pressure (Pa), φ_2 is the volume fraction of the polymer in the liquid phase, m is the degree of polymerization, and χ is the interaction parameter. Note that this equation does not express the effect of elastic modulus. For the m value, we employed the degree of polymerization of the macromer ($m = 765$) from which the PDMS rubber was prepared. φ_2 was calculated directly from the amount of CO_2 sorbed. The solid lines in Figure 1 show the predicted isotherms calculated by using Equation (1), and the best-fit values of the χ parameter. The Flory–Huggins equation accurately traced the CO_2 sorption isotherms at all temperatures. The χ value was 1.3 at −30 °C, 0.81 at −3 °C, and 0.20 at 25 °C, decreasing with increasing temperature. In our experimental temperature range, the amount of CO_2 sorbed was predicted to be highest at 25 °C, near the saturated vapor pressure, because of the minimum χ value. However, the sorption pressure also becomes extremely high, to the point where it is unrealistic for practical separation processes. At a constant CO_2 pressure, the amount of CO_2 sorbed increased with decreasing temperature. For example, at a partial pressure of 1000 kPa, the amount of CO_2 sorbed was 124 mg g^{-1} at −30 °C and 33 mg g^{-1} at 25 °C. The former amount is 3.8 times larger than the latter.

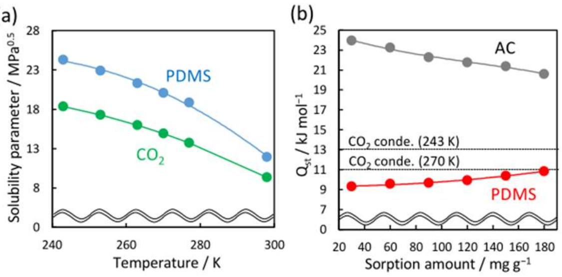

Figure 2. (a) Changes in the solubility parameters of CO_2 and PDMS rubber at 243–298 K. The values of CO_2 were obtained from literature.[23] (b) Sorption enthalpies of AC and PDMS rubber for various sorption amounts. The dashed lines are the CO_2 condensation heats at 243 K and 270 K.

The maximum amounts of CO_2 absorbed in PDMS are 210–792 mg g^{-1}, and we believe that CO_2 exists as a continuous body within the polymer chains at such high concentrations. Therefore, the CO_2 is in a condensed form. The miscibility of the polymer and solvent can be predicted from the values of the Hansen solubility parameter (SP), and its relation to the χ parameter can be described by the following equation:[24]

$$\chi = \frac{M_{poly}}{\rho m R T}\left(\delta_{poly} - \delta_{sol}\right)^2 \quad (2)$$

where, M_{poly} is the molecular weight of the polymer (PDMS macromer), ρ is the polymer density (kg m^{-3}), m is the degree of polymerization, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K), and δ_{poly} and δ_{sol} are the solubility parameters ($Pa^{0.5}$) of PDMS and CO_2, respectively. The PDMS rubber used here has M_{poly} = 57, ρ = 1030, and m = 765. The SP (δ_{poly}) for PDMS can be calculated from its χ value and the known SP of CO_2 (δ_{sol}), and the results are shown in Figure 2(a). The SP for CO_2 decreases with increasing temperature; it is 19 $MPa^{0.5}$ at −30 °C, 15 $MPa^{0.5}$ at −3 °C, and 9.4 $MPa^{0.5}$ at 25 °C.[23] On the other hand, the SP for PDMS was calculated to be 24 $MPa^{0.5}$ at −30 °C, 19 $MPa^{0.5}$ at −3 °C, and 10 $MPa^{0.5}$ at 25 °C.[25] The SP at −30 °C is therefore 80% larger than that at room temperature, and this is interesting new knowledge regarding PDMS rubber.

The sorption enthalpy change (ΔH_s) for CO_2 can be calculated by using the Clausius–Clapeyron equation:

$$\ln\frac{P_1}{P_2} = -\frac{\Delta H_s}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (3)$$

where, P_1 and P_2 are the gas partial pressures (Pa) at certain sorption amounts, ΔH_s is the heat of sorption (J mol^{-1}), R is the universal gas constant (J mol^{-1} K^{-1}) and T_1 and T_2 are the temperatures (K) used for the sorption measurements at P_1 and P_2, respectively. Figure 2(b) shows the change in the values of ΔH_s for PDMS rubber and for activated carbon (SORBONORIT 4) for sorptions of 30–180 mg g^{-1}. The ΔH_s values were calculated at $T_1 = 243$ K and $T_2 = 270$ K. The CO_2 condensation heats are 13 kJ mol^{-1} at 243 K and 11 kJ mol^{-1} at 270 K.[26] The ΔH_s values for activated carbon decreased with the sorption amount from 24 kJ mol^{-1} at 30 mg g^{-1} to 21 kJ mol^{-1} at 180 mg g^{-1}. These values are 9–12 kJ mol^{-1} larger than the average heat of condensation of CO_2. In contrast, the ΔH_s values for PDMS increased with increasing sorption, giving a value of 9.3 kJ mol^{-1} at 30 mg g^{-1} and 11 kJ mol^{-1} at 180 mg g^{-1}. These values were 39–52% of the corresponding values for activated carbon, and were slightly lower than the average values of the heat of condensation of CO_2. Interestingly, the ΔH_s values increase with increasing sorption amount. That is, CO_2 readily dissolved in the swollen PDMS rubber.

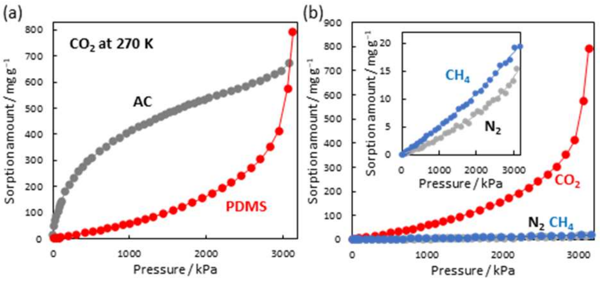

Figure 3. (a) Comparison of CO_2 sorption isotherms of PDMS rubber and activated carbon. (b) CO_2, CH_4, and N_2 sorption isotherms of PDMS rubber at 270 K.

Figure 3 (a) shows a comparison of the CO_2 isotherms for PDMS rubber and activated carbon. The amount sorbed by activated carbon was 644 mg g^{-1} at 3130 kPa, which is 19% less than that of PDMS rubber. In the CO_2 partial-pressure range 0–2000 kPa, activated carbon adsorbed a large amount of CO_2. However, complete desorption required the pressure to be reduced to below atmospheric pressure. In contrast, PDMS rubber desorbed 80% of CO_2 when the pressure was reduced from the saturation pressure to 2000 kPa.

A comparison of the CO_2, CH_4, and N_2 sorption isotherms at 270 K is shown in Figure 3(b). The inset contains magnified plots for CH_4 and N_2. The amounts of CH_4 and N_2 sorbed at 3100 kPa were 19 and 15 mg g^{-1}, respectively. At this pressure, the amount of CO_2 sorbed was about 37–53 times larger than these values. The ideal gas selectivities of CO_2/CH_4 and CO_2/N_2 were therefore 9.6–44 at 100–3000 kPa, and higher selectivities were observed at a higher pressure (Figure S2, Table S1). In contrast, these selectivities were 1.9–8.5 for activated carbon, and the values decreased at higher pressures.

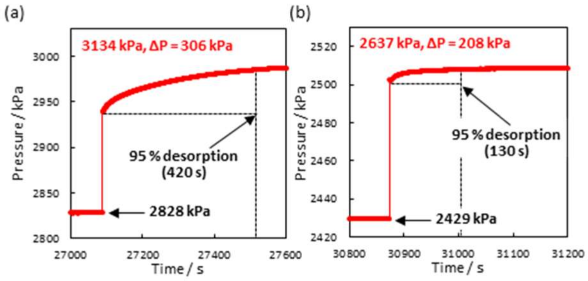

Figure 4. Comparison of desorption rates under (a) high-pressure and (b) low-pressure conditions.

In Figure 1, the amounts of CO_2 sorbed were measured by a volumetric method from the equilibrated pressure changes in a gas container of known volume (manifold) and a sample container. Figure 4(a) shows one of the desorption cycles, in which the pressure changes of the manifold at 2828 kPa were plotted after the sample container at 3134 kPa was opened. In this case, the initial manifold pressure was 306 kPa lower than that of the sample container. After 420 s, 95% of CO_2 was desorbed and the manifold reached an equilibrium pressure of 2988 kPa. Figure 4(b) shows the pressure changes of the manifold initially at 2429 kPa when the sample container at 2637 kPa was opened; in this case 95% desorption was reached after 130 s.

As mentioned before, a large amount of CO_2 (792 mg g^{-1}) was sorbed at 3134 kPa, and the desorption is an endothermic process. Presumably, when liquid CO_2 changes to the gas state, a longer desorption time is required. At a pressure of 2637 kPa, the amount sorbed was 290 mg g^{-1} and the CO_2 in PDMS rubber started to show a slightly gas-like behavior. The diffusion coefficient and the desorption rate of CO_2 then increased.

From the viewpoint of separation engineering, CO_2 recovery at a low temperature, that is, the amount sorbed at low partial pressures, is important. In Figure 5, the CO_2 sorption isotherms for PDMS rubber, acrylonitrile–1,3–butadiene rubber (NBR), and poly(vinylidene difluoride)–hexafluoro-propylene rubber (PVDF-HFP) are compared in the pressure range 0–900 kPa. At −30 °C and 900 kPa, the amounts of CO_2 sorbed by PDMS rubber, NBR, and PVDF-HFP were 100, 59, and 15 mg g^{-1}, respectively. It is clear that PDMS rubber is far superior sorbent to PVDF-HFP at low temperatures. The glass-transition temperatures (T_g) of PDMS rubber, NBR, and PVDF-HFP are −120 °C, −43 °C, and −35 °C, respectively.[27–29] At −30 °C, the elastic modulus of NBR is about 600 times larger than that of PDMS rubber and the elastic modulus of PVDF-HFP reaches 2 GPa.[30,31] The swelling of these two polymers by CO_2 must be strongly limited by their high elastic moduli.

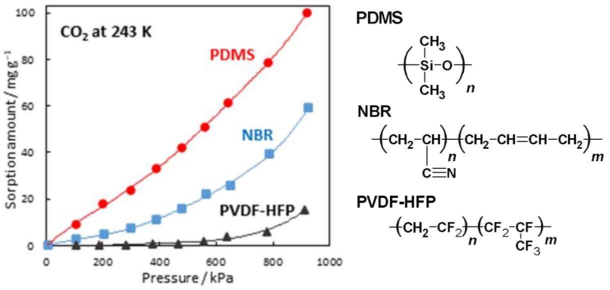

Figure 5. CO_2 sorption isotherms of PDMS rubber and other polymer rubbers at 243 K. NBR: PN20HA (JSR), PVDF-HFP: G701BP (DAIKIN).

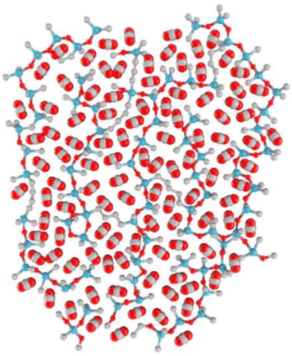

Figure 6. Schematic illustration of PDMS rubbers swollen with 792 mg g^{-1} of CO_2.

Figure 6 is a schematic illustration of PDMS rubber containing 792 mg g^{-1} of sorbed CO_2. The crosslinked rubber structure has 76 [$Si(CH_3)_2O$] units and 106 CO_2 molecules. By using a CO_2 density of 0.946 g cm^{-3} at −3 °C, the volume ratio of PDMS to CO_2 was calculated to be 54:46. The high CO_2 sorption capacity of nonporous PDMS rubber is surprisingly high, even in comparison to the corresponding values for porous sorbents.

The relationship between the CO_2 partial pressure and the amount of the gas sorbed was precisely analyzed by using the Flory–Huggins equation. From a mathematical viewpoint, this equation predicts that there is no particular upper limit to the amount sorbed when the χ parameter is less than ~0.7.

However, swelling of the PDMS rubber will stop when ΔH_s is balanced by the entropic elasticity of the polymer chains. This is quite different from the adsorption behavior of porous adsorbents such as activated carbon. Our results show that a lower elastic modulus at low temperatures favors the sorption of a large amount of CO_2. When choosing a polymer sorbent, the SP should be close to that of CO_2 at a low temperature. We also need to consider that the SP of CO_2 increases with decreasing temperature. The amounts of CO_2 sorbed by our PDMS rubber are an order of magnitude larger than those reported in the literature (Figure S3, Table S2). This is because previous studies used a dual-sorption model and examined only the range in which Henry's law is valid. In this study, by using a volumetric method, we have demonstrated that rubber powders can sorb large amounts of CO_2 at low temperatures and near the saturation pressure.

PDMS rubber is therefore a good sorbent for CO_2, even at low partial pressures, provided the temperature is low. This result opens up new applications for PDMS in CO_2 separation and recovery. In particular, because of the large selectivity between CO_2 and CH_4 sorption, we believe that PDMS rubber powders might be useful in the purification of CO_2-rich natural gas and biogas.

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