

Simultaneous Measurement of Carbon Dioxide-Induced Swelling and Gas Sorption in Poly(methyl methacrylate) and Polystyrene

Feng He, Gui-Ping Cao*, Lei Li, Tao Liu, Ling Zhao

UNILAB, State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

Abstract: This paper deals with the swelling of Poly(methyl methacrylate) and Polystyrene samples in supercritical carbon dioxide in-situ at various temperatures and pressures by using directly optical observation. High pressure cell assembled with microscope and digital camera was used to record the volume change of the flat sheet sample. A good agreement of our results with the data in the literature demonstrates the validity of the method. Consequently, the effects of temperature and pressure over a wide range (from 7MPa to 25MPa) on the swelling kinetics were investigated. Increased pressure enhanced the swelling of the sample, while a decrease in the equilibrium swelling ratio was observed with increasing of temperature. Also, the pressure-decay technique was introduced to measure the solubility and diffusion of supercritical carbon dioxide in polymers. The pressure degradation in the vessel which involved the polymer sample and high-pressure CO₂ was monitored as a function of time, as the polymer absorbs the gas. It was found that there was a strong relationship between the CO₂ diffusion and the polymer swelling.

Keywords: swelling, polystyrene, poly(methyl methacrylate), supercritical carbon dioxide

Introduction

Supercritical fluid technology has made tremendous strides in the past decade in terms of polymer science and processing. Supercritical carbon dioxide, in particular, offers several advantages for its characteristics of readily availability, cheap and clean, and is considered to be a good plasticizer for many commercial polymers. Moreover, the gases state of CO₂ under ambient conditions makes its removal from the polymeric product very easy, avoiding, for example, the costly processes of drying or solvent removal, which is very important in the processing of polymer-based materials^[1-3].

When a polymer is exposed to supercritical CO₂, the absorption of CO₂ in polymer matrix results in increased mobility of the polymer phase, thus causes the matrix to swell. ScCO₂ induced swelling has occurred in most of polymers, especially the ones with large free volume, such as PDMS, PMMA, PS etc.

It is also important for accurate understanding of mass transfer of carbon dioxide in a polymer matrix. The transport mechanism of carbon dioxide in a polymer matrix under supercritical environments is very complicated because of the significant effects of CO₂ on the polymer, such as state transitions, chain mobility, plasticization, crystallization and swelling. Most of previous research on measurement of diffusion curve assumes that the volume of polymer sample does not change during the process. This assumption causes error in the measurement.

A variety of methods to measure polymer swelling extent, e.g., optical measurements^[4,5], waveguide spectroscopy^[6,7], and special techniques^[8,9] have been reported in the literatures. Maria Pantoula^[10] has summarized previous report of the swelling extent of glassy polymers (PMMA and PS) due to the sorption of scCO₂. Under a similar range of experimental condition, however by using different techniques, strong inconsistencies can be found. Moreover, few focuses on the kinetics of swelling which closely relates to the diffusion behavior of scCO₂ into polymers.

On this paper, the swelling behavior of glass polymer in contact with scCO₂ has been

* To whom correspondence should be addressed. E-mail: gpcao@ecust.edu.cn, Fax : 86-2164253528.

investigated which has been found the applications in foaming, extrusion and impregnation. The knowledge of proper degree of polymer swelling in scCO₂ is essential in these processes.

Experiment

Experiment material

Liquid carbon dioxide (CO₂) was supplied by Air Product Company with a purity of 99.9% and was used as received. Poly(methyl methacrylate) (PMMA) which was supplied by Altuglas (PMMA), with T_g of 118 °C. And polystyrene (PS) supplied by Shanghai Petrochemical Company with T_g of 108 °C were used for the experiment.

Preparation of plane sheet

Visualization method requires the assumption of isotropic volume expansion. The PS plane sheet in the high-pressure cell was prepared by solvent firstly. It was dissolved in 99.5% xylene (BDH) at room temperature onto a cellophane substrate and left for three days at room temperature before annealing at 80 °C for 24 h and then under vacuum at 60 °C for another three days, in order to completely remove the solvent. The T_g was measured before and after polymer dissolved in solvent, and was found to be the same for both sample. The preparation of PMMA was the same as that used for PS. The polymer was dissolved to 30% solids in chloroform, left at room temperature for three days before annealing at 80 °C for 24 h and then at 60 °C under vacuum for another three days. The T_g was measured before and after polymer dissolved in solvent, and was found to be the same for both sample. It indicates that the solvent have been removed.

Because one or two dimensional change was observed, for the convenience of calculation, polymers are shaped into a regular geometrical form. Secondly, by a hot press and stainless steel moulds producing samples in the form of sheet of 1mm×10mm×10mm. It was found that if polymers were not dissolved into solvents, when subjected to a CO₂ environment after hot press, the disks tended to deform in a particular direction rather than change isotropically.

Experiment Setup

High pressure view cell assembled with microscope and digital camera was used to record the volume change of the flat sheet sample. The schematic diagram in Figure 1 gives the details of the major components of high-pressure swelling apparatus. The cell was heated to the desired temperature, before the polymer plane sheet was placed. The cell was then sealed and evacuated by using a vacuum pump to remove any gas that could previously have been dissolved in the polymer. Then CO₂ was introduced into the view cell with the help of pump and pressure gauge which were used to control and monitor the CO₂ pressure. The images were continually captured with fixed time interval and analyzed the volume change by free software Image-Pro Plus 6.0. When the volume never changes, the polymer was considered as reaching swelling equilibrium.

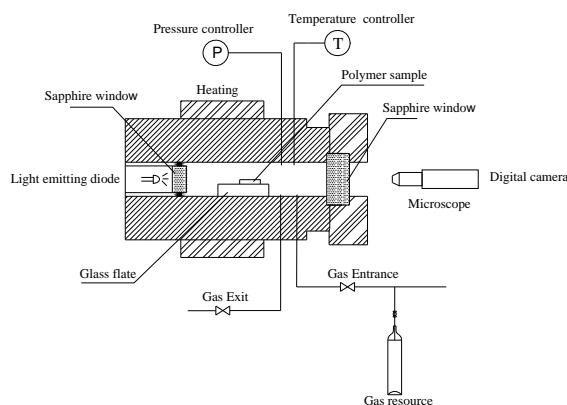


Fig. 1: Schematic image of the high-pressure swelling apparatus

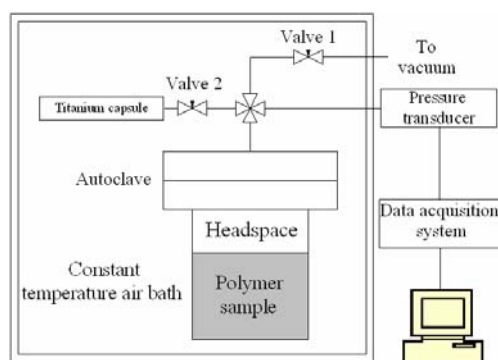


Fig. 2: Schematic diagram of pressure-decay method

Meanwhile, the pressure-decay method was utilized to measure the diffusion curve of CO₂ into polymers. Davis^[11] developed similar pressure-decay method which would easy determine the initial gas density gravimetrically, however it has few possibilities for leaks. The entire apparatus indicated in Figure 2 was placed in a temperature-controlled air bath. An experiment was conducted by filling the titanium capsule with CO₂. Then apparatus was placed inside the oven. After reaching the desired temperature of the experiment, valve 2 was opened. Pressure is acquired automatically by a data acquisition system. The obtained pressure drop curve directly indicates the diffusion behavior of scCO₂ into polymers.

Results and Discussion

Figure 3 show a set of images during the swelling of PS sheet exposed to CO₂ at 50 °C and 21.3 MPa. It is clear that the thickness of the polymer sample increases with time going up. To obtain quantitative information of volume from the images, an imaging software was used to correlate the number of pixels to the thickness and length of the polymer sample for each individual picture.

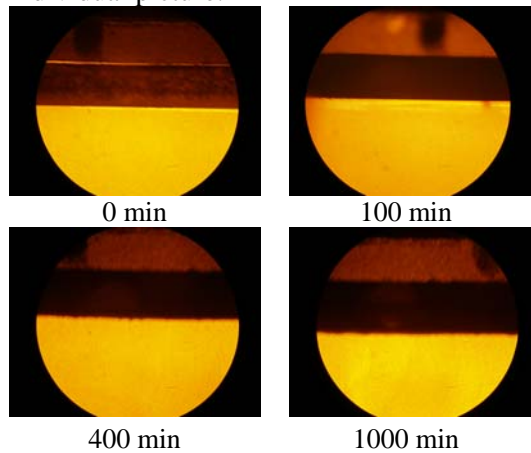


Fig. 3: Optical monitoring of PS sheet exposed to CO₂ at 50 °C and 21.3 MPa

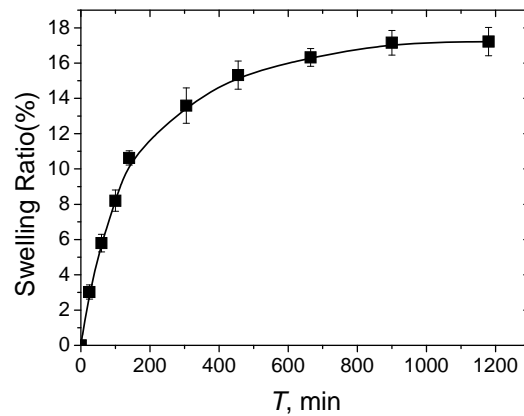


Fig. 4: Swelling kinetics of polymer sheet exposed to CO₂ at 50 °C and 21.3 MPa

The polymer plane sheet with the size of 1mm×10mm×10mm is shown in the figure 5. Because of the same size if length and width, it is assumed that the same percentage of change takes place in both direction of length and width. Therefore, based on the observation on the change of length and thickness, the swelling degree of polymer can be obtained.

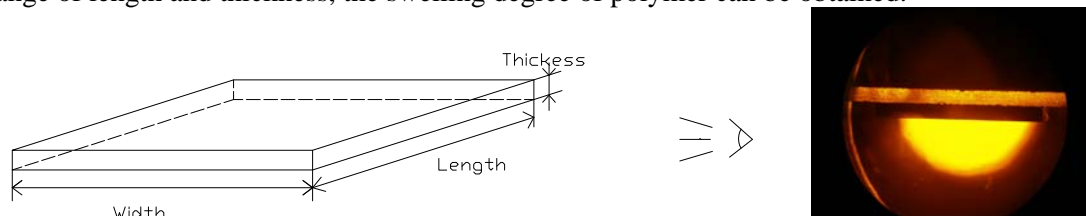


Fig. 5: Schematic image of polymer sample

In this paper, a new technique is applied for the visualization method, by using a glass sheet as substrate of polymer sample. It has two major functions: 1. The glass sheet is helpful for clear determination of the boundary between polymer and substrate. This function is clear shown by the comparison of figure 6 and figure 7. The thickness of glass sheet performs as a reference of the length measurement, which reduce error introduced by the lens adjustment. Because it can preserves its initial shape and size in the CO₂ environment, and change with the lens adjustment.

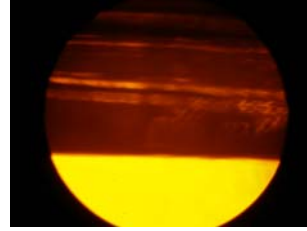
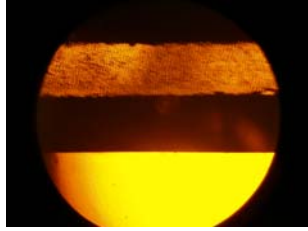


Fig. 6: Using glass sheet as substrate Fig. 7: Without using glass sheet

The swelling ratio is defined as:

$$\text{Swelling Ratio} = (V_t - V_0) / V_0$$

where V_t is volume of polymer sample at t time and V_0 is initial volume of sample. The value of swelling ratio versus time is showed in figure 4. The swelling ratio increases sharply with time goes up at the beginning stage, and then level off. In fact, the first stage of swelling curve reveals a linear relationship with time. It is directly related to the Fickian behavior^[12,13]. However the large degree of swelling with time actually distorts following region of the curve, which approaches the swelling equilibrium.

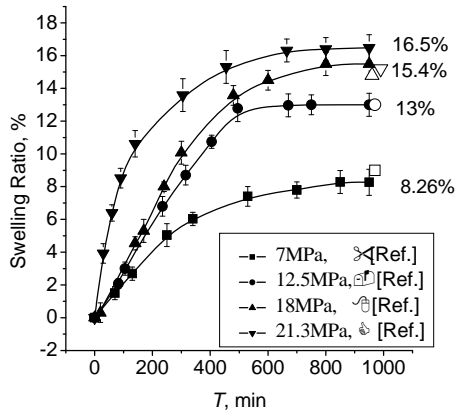


Fig. 8: Swelling kinetics of PS exposed to CO₂ at 50 °C

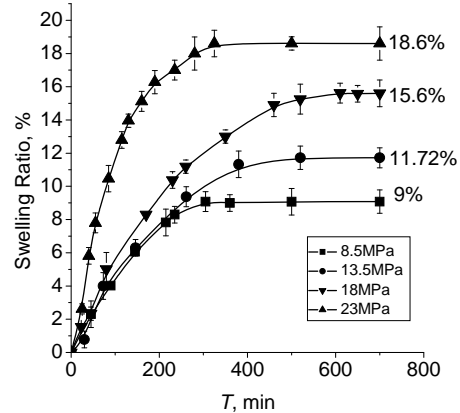


Fig. 9: Swelling kinetics of PS exposed to CO₂ at 60 °C

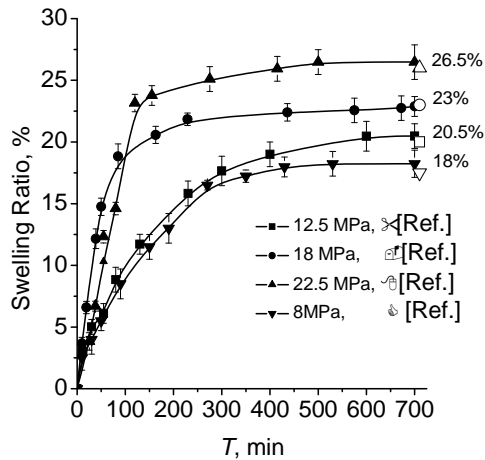


Fig. 10: Swelling kinetics of PMMA exposed to CO₂ at 50 °C

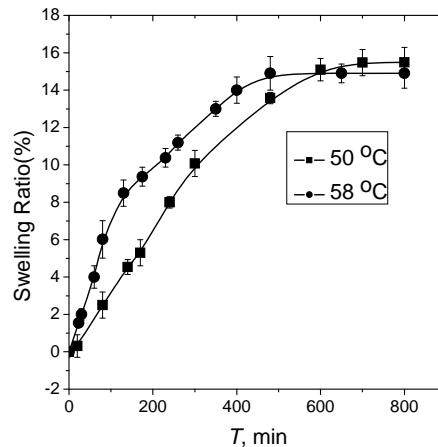


Fig. 11: Swelling kinetics of PMMA exposed to CO₂ at 17 MPa

Figure 8, figure 9 and figure 10 show the swelling kinetics of PS and PMMA in contact with CO₂ at various condition. Reasonable agreement of the equilibrium swelling values are found between this work and previous literature^[10] at similar temperature. The effects of pressure on the kinetics of swelling are examined. According to the result, it is found that the equilibrium swelling ratio increase while pressure goes up. Moreover, the initial sloped of the swelling curves increases with pressure, which indicate higher diffusion coefficient at higher pressure, due to higher gradient. However, the unusual trend at 22.5 MPa in figure 10 may be caused by the force of high pressure of CO₂.

Figure 11 shows the effect of temperature on the kinetics of swelling at a fixed pressure. As shown in the figure, the initial slopes of the swelling curves at the two temperatures are different and increase with temperature. It suggests that the diffusion coefficient of the system increases with temperature. The time required to reach equilibrium at 50 °C is more than that at 58 °C. One possible explanation for this phenomenon is that there is more energy at higher temperature provided for polymer chains to move. Then CO₂ molecule is easily to penetrate into the polymer matrix. Also, we can find equilibrium swelling ratio is smaller at higher temperature which conforms to Henry's Law.

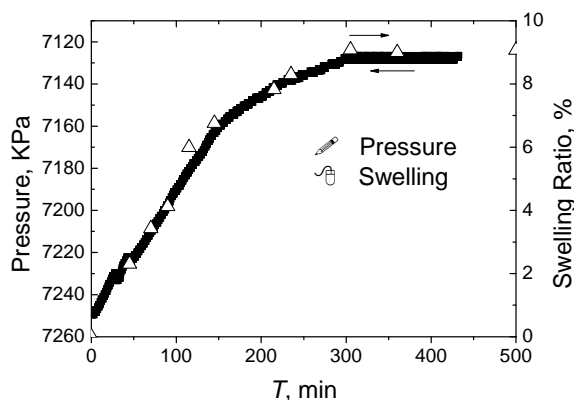


Fig. 12: Comparison of diffusion and swelling behavior of PS exposed to CO₂ at 60 °C and 8.5 MPa.

Beside the swelling measurement, we investigate the relationship between the volume change of polymer and the diffusion behavior of scCO₂. The same polymer plane sheet was put into the oven. By using pressure-decay method, the pressure drop curve with time is shown in figure 12. It is found that there is a strong correlation between the CO₂ diffusion and the polymer sample swelling. It shows that the sorption and swelling of polymer under CO₂ atmosphere occur simultaneously.

Conclusion:

Experiments of swelling measurement have been carried out to verify the intended function. The accuracy of the experiments has been investigated based on the obtained data. Increased pressure enhanced the extent of swelling, while a decrease in the equilibrium swelling ratio is observed with increasing temperature. According to the comparison of diffusion and swelling behavior, there is a strong correlation between the CO₂ diffusion and the polymer sample swelling.

Acknowledgements:

This work has been supported by Chinese National Science Foundation Grants: 20676031 and partially supported by STCSM Nano-Foundation: 05nm05039.

References:

- [1] Sameer P. Nalawade, Francesco Picchioni, *et al.* Progress in polymer science, 2005: 1–25.
- [2] David L. Tomasko, Hongbo Li, *et al.* Ind. Eng. Chem. Res. 2003, 42: 6431-6456.
- [3] S. G. Kazarian. Polymer Science, Ser. C, 2000, 42: 78–101.
- [4] Dehua Liu, Hongbo Li, *at al.* Macromolecules 2005, 38: 4416-4424.
- [5] Arvind Rajendran, Barbara Bonavoglia, *et al.* Ind. Eng. Chem. Res., 2005, 44: 2549-2560.
- [6] N. M. B. Flichy, S. G. Kazarian, *et al.* J. Phys. Chem. B, 2002, 106: 754-759.
- [7] Vito Carla, Ke Wang, *et al.* Macromolecules 2005, 38: 10299-10313.
- [8] Tomoko Fujiwara, Tetsuji Yamaoka, *et al.* Biomacromolecules 2005, 6: 2370-2373.
- [9] E. Piccinini, M. Giacinti Baschetti, *et al.* Journal of Membrane Science, 2004, 234: 95–100.
- [10] Maria Pantoula, Joachim von Schnitzler, *et al.* J. of Supercritical Fluids, 2007, 39: 426–434.
- [11] Davis P K, Lundy G D, *et al.* Ind. Eng. Chem. Res., 2004, 43(6): 1537-1542.
- [12] J. Crank. The mathematics of diffusions, Oxford, U.K., (1975).
- [13] Joseph R. Royer, Joseph M. DeSimone, *et al.* Macromolecules 1999, 32: 8965-8973.