

PBA Solubility Measurement

Using Teledyne Isco Syringe Pumps

Overview

The solubility of physical blowing agents plays a key role in the manufacturing of plastic foams^[1]. This solubility study aims to investigate the amount of gas that can dissolve in polymer melt at a given temperature and pressure. Volumetric and gravimetric methods have been widely used to measure the solubility of different blowing agents and their blends in polymers^[2-3]. However, the gravimetric method requires an equation of state (EOS) to compensate for the buoyancy effect of swelling^[4]. Magnetic suspension balance (MSB), a gravimetric method, is one of the most commonly used apparatus to measure solubility. It requires a pump with a controller to dose the gas. Since solubility is a function of pressure at a given temperature, a high pressure pump with a controller plays a vital role for measuring solubility. The stability and accuracy of the measurement strongly depend on the pump and controller, such as the Teledyne Isco syringe pump.

Theory and Approach

The solubility of a physical blowing agent (CO₂, N₂, butane, etc.) in a polymer melt has a significant effect on polymer processing. The knowledge of gas solubility and the effects of dissolved gases on the physical properties of a polymer melt, such as swollen volume, isothermal compressibility, and thermal expansion coefficient, are important in various polymer processing operations.

Since the 1950s, numerous efforts have been made to investigate the solubility of gases in polymer melts through a variety of approaches, including experimental measurements and theoretically thermodynamic calculations. All previous studies found in literature that considered solubility of gas in molten polymer can be categorized into three classes:

- Experimental measurements (pressure decay, piezoelectric sorption, gas-liquid chromatography, and gravimetric methods etc.)
- Theoretically thermodynamic calculations (Flory-Huggins, Sanchez-Lacombe (SL)^[5], Simha-Somcynsky (SS)^[6], statistical associating fluid theory (SAFT)^[7] equation of state (EOS) etc.)
- Experimental measurements with theoretical compensation

Of these approaches, the last is the most widely preferred and used by researchers. Therefore, we propose a general approach that combines an experimental solubility measurement and thermodynamic models. First, a gravimetric method is carried out to experimentally

measure the gas sorption in a polymer melt. From this, we obtain information regarding the gas sorption in the polymer or apparent solubility ($X_{apparent}$) which does not consider the volume swelling effect. Secondly, the thermodynamic model is applied to calculate the phase equilibrium (theoretical solubility, X_{theory}) and swollen volume of polymer, V_s . Thirdly, the theoretically predicted swollen volume, V_s , can be used to complete the correction of the apparent solubility, $X_{apparent}$, and then obtain the actual solubility or corrected solubility, $X_{corrected}$.

Experimental Procedure

A schematic of the MSB and working procedures is shown in Figure 1.

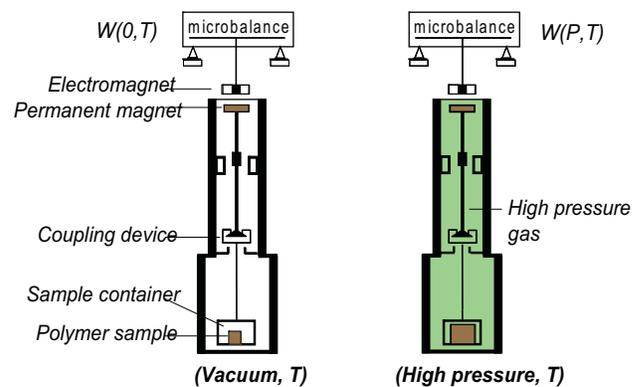


Figure 1: Schematic of MSB System

Before commencing the sorption experiment, a sample is placed in the absorption chamber, degassed in vacuum, and preheated to a designated temperature. The balance readout at vacuum ($P=0$) and temperature (T) is recorded as $W(0, T)$. The high pressure gas is then injected into the sorption chamber and sorption occurs. At the final saturation stage, the weight readout from the balance is recorded as $W(P, T)$ at pressure (P) and temperature (T). Hence, the weight gain from the dissolved gas in the polymer, W_g , is calculated by employing the following equation:

$$W_g = W(P, T) - W(0, T) + \rho_{CO_2}(V_B + V_P + V_S) \quad (1)$$

where ρ_{CO_2} is the gas density, V_B is the volume of the sample holder (including the sample container and measuring load coupling device), V_P is the volume of the pure polymer sample without swelling at pressure P and temperature T , and V_S is the swollen volume of the polymer/gas sample mixture, caused by the dissolution

of gas into the polymer sample. By ignoring the swollen volume term (V_s) of Equation 1, the measured weight gain is treated as the apparent weight gain $W_{g, apparent}$

$$W_{g, apparent} = W(P, T) - W(O, T) + \rho_{CO_2}(V_B + V_P) \quad (2)$$

Then the apparent solubility $X_{apparent}$ and corrected solubility $X_{corrected}$ can be calculated as follows:

$$X_{apparent} = W_{g, apparent} / m_{sample} \quad (3)$$

$$X_{corrected} = X_{apparent} + (\rho_{CO_2} \times V_s) / m_{sample} \quad (4)$$

where m_{sample} is the mass of the sample.

Data Analysis

Solubilities of different physical blowing agents and their blends have been substantially measured in our lab through use of the MSB and Isco syringe pump setup (Figure 2)^[1-6]. Extensive work has been done on the solubility measurements of CO₂, N₂, HFC134a, HFC152a, and HFC134a/HFC152a blends in polypropylene (PP), polypropylene nanocomposite (PP-PNC), polylactide (PLA), Ethene/Octene copolymer, and polystyrene (PS)^[4, 8-12] by using MSB, SS-EOS, and SL-EOS. It has been observed that the swelling effect is more significant at higher pressures and temperatures. It has also been noted that the swelling ratios determined by using various EOS are not same at the same temperature and pressure. Consequently, the solubility also differs for various EOS.

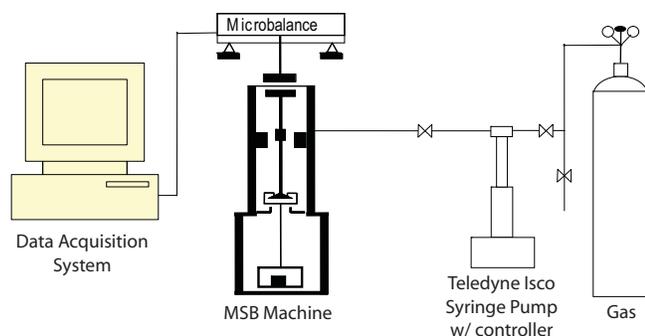


Figure 2: MSB-Isco syringe pump setup

The solubility measurements are done at a constant pressure and temperature. The pressure is developed using a Teledyne Isco Model 260D syringe pump module and Series D pump controller. The controller can be programmed for different pressures and time durations while keeping the temperature constant, resulting in efficient control and significant time savings.

The graphs shown in Figures 3 and 4 are the successful investigations of the solubilities of CO₂ in polypropylene (PP) melt at temperatures 180, 200, and

220 °C, and pressures up to 4500 psi^[4] using the MSB set-up. The two theoretical models, based on SL and SS EOS, were developed to predict the volume swelling. Based on the proposed approach, it was found that the long chain branched PP exhibits less expandability due to the entangled molecular chain structure. Therefore, the total amount of gas that can dissolve into the polymer is decreased.

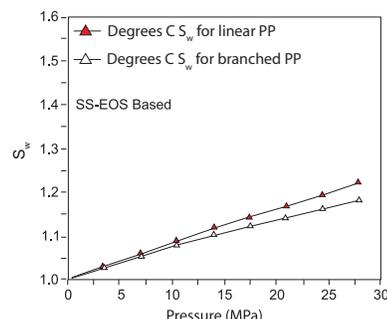


Figure 3: Swelling behavior of linear and branched PP/CO₂ mixtures at 180, 200, and 200 °C

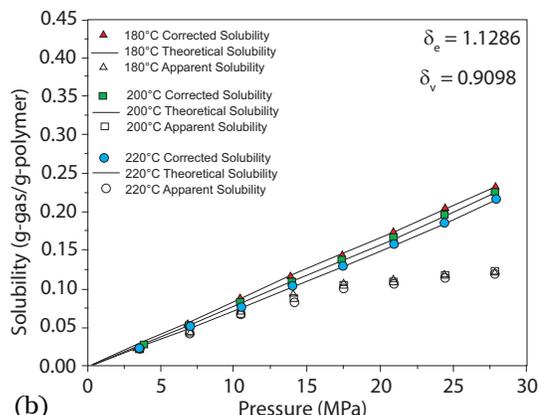
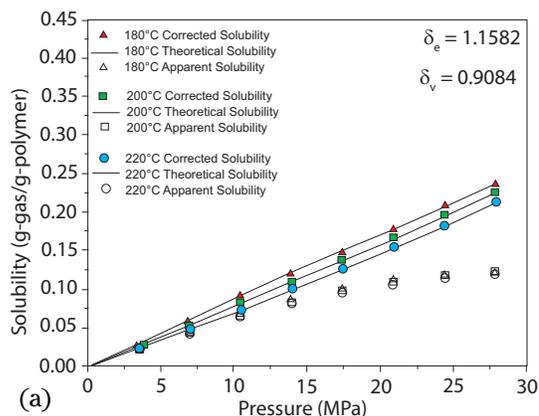


Figure 4: Solubility of CO₂ in (a) linear PP and (b) branched PP

REFERENCES

- 1) Xu, X.; Park, C.B.; Xu, D.; Pop-Iliev, R. "Effects of Die Geometry on Cell Nucleation of PS Foams Blown with CO₂." Polymer Engineering and Science: 43(7), 1378-1390. 2003.
2. Sato, Y.; Takikawa, T.; Takishima, S.; Masuoka, H. "Solubilities and diffusion coefficients of carbon dioxide in polyvinyl acetate and polystyrene." J. Sup. Fluids: 19, 187-198. 2001.
3. Sato, Y.; Takikawa, T.; Yamane, M.; Takishima, S.; Masuoka, H. "Solubility of carbon dioxide in PPO and PPO/PS blends." Fluid Phase Equilibria: 194-197, 847-858. 2002.
4. Li, G.; Wang, J.; Park, C.B.; Simha, R. "Measurement of Gas Solubility in Linear/Branched PP Melts." Journal of Polymer Science: Part B: Polymer Physics. Accepted 18 April, 2007.
5. Sanchez, I.C.; and Lacombe, R.H. "An elementary molecular theory of classical fluids. Pure fluids." J. Phys. Chem., 80: 2352-2362. 1976.
6. Simha, R.; Xie, H. "Applying lattice-hole theory to gas solubility in polymers." Polymer Bulletin, Berlin, 40: 329-335. 1998.
7. Huang, S.H.; and Radosz, M. "Equation of state for small, large, polydisperse and associating molecules." Ind. Eng. Chem. Res., 29: 2284-2294. 1990.
8. Hasan, M.M.; Li, G.; Park, C.B. "The PVT and Solubility Behaviors of the Nanocomposite/gas Mixtures." UKC, Korean-American Scientists and Engineers' Conference, San Diego, August 14-17, 2008.
9. Li, G.; Li, H.; Wang, J.; Park, C.B. "Investigating the Solubility of CO₂ in Polypropylene Using Various EOS Models." Cellular Polymers, 25(4): 237-248. 2006.
10. Li, G.; Gunkel, F.; Wang, J.; Park, C.B.; Altstädt, V. "Solubility Measurements of N₂ and CO₂ in Polypropylene and Ethene/Octene Copolymer." Journal of Applied Polymer Science, 103 (5): 2945-2953. 2007.
11. Li, G.; Lia, H.; Turng, L.S.; Gong, S.; Zhang, C. "Measurement of gas solubility and diffusivity in polylactide." Fluid Phase Equilibria, 246: 158-166. 2006.
12. Li, G.; Leung, S.N.; Hasan, M.; Wang, J.; Park, C.B.; Simha, R. "A thermo-dynamic model for ternary mixture systems – gas blends in a polymer melt." Fluid Phase Equilibria, 266: 129-142. 2008.

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Teledyne Isco

P.O. Box 82531, Lincoln, Nebraska, 68501 USA
Toll-free: (800) 228-4373 • Phone: (402) 464-0231 • Fax: (402) 465-3091
E-mail: IscoInfo@teledyne.com

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