A New Gas/Supercritical Fluid (SCF) Diffusivity Measurement Method for CO_2 Saturated Polymer Systems Using Optical Transmission Property

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ABSTRACT

Over the last century, polymer processes involving gas or supercritical fluid (SCF) have attracted significant attention. The attributes of a gas/SCF in polymers benefited many polymer processing applications. In many applications, the solubility and diffusivity of a gas/SCF in polymers are important parameters. A method of using an optical property to predict the solubility and diffusivity of a gas/SCF in polymers was investigated in this study. Poly(dimethylsiloxane) (PDMS) and supercritical CO_2 were used to study the relationship between its optical property and solubility & diffusivity. The optical transmission intensity decreased as pressure increased..

Keywords: Gas, Supercritical Fluid (SCF), Diffusivity, Solubility, Optical Transmission Intensity

1 INTRODUCTION

Supercritical fluids (SCFs) and gases is widely used in polymer processing. For example, plastic foam products used for light-weight structural components, heat insulation, and food packaging can be fabricated by nano-/micro-cellular foaming processes with SCFs [1, 2]; SCF is also used as a carrier in polymer impregnation, a process of depositing a solute into polymer [3, 4]. Many properties such as solubility, diffusivity, rheological properties, plasticization behavior, surface tension, and crystallization of polymers can be affected by the dissolved SCFs and gases at high temperatures and pressures. Among these effects solubility and diffusivity are most fundamental ones. Thus, it is necessary to get a correct understanding about the solubility and diffusivity of gas/SCF in a polymer under different temperature and pressure.

As diffusivity is concentration dependent, in the solvent-polymer system which relationship between refractive index and concentration is known, diffusivity could also be calculated from the refractive index theoretically. In 1936, R. Taylor et al. studied permeation of water through rubber [5]. The concentration of water was found and this enabled the diffusivity values to be calculated as a function of concentrations. In 1950, C. Robinson developed an apparatus to obtain diffusivity values of what? by measuring a refractive index [6]. All of these indicated the connection between solvent-polymer system's optical property and its diffusivity andsolubility [7]. Fiber optic sensors use optical fibers as a basis of the sensing element, where it is configured in a way so the light propagates through the optical fiber sensors to a detector. In literature, the fiber optic sensors are already used as a gas sensor and even as a sensor to obtain solubility of gas in water [8, 9]. Since fiber optic sensors have already been used as a sensor to obtain solubility of gas in water, it may be feasible to study the solubility of a gas in polymers as well.

If a fiber optic technology can be used to measure gas/SCF solubility/diffusivity in polymers, then a cost effective, simple, and miniaturized sensor may be fabricated.. This paper investigated the relationship between the optical transmission intensity and CO_2 diffusion behavior under different temperatures and pressures.

2 EXPERIMENTS

Poly(dimethylsiloxane) (PDMS, PMX-200, Xiameter) and CO_2 (99.9%, Praxair) were used in this experiments. As shown in Figure 1, a high pressure chamber placed in an oven was used to measure in-situ optical transmission intensity at different pressures and temperatures. The optical sensor was placed in the pressure chamber and connected with two optical fibers on each side. The light was transferred by the fiber, went through the optical sensor and received by optical spectrum analyzer (OSA).

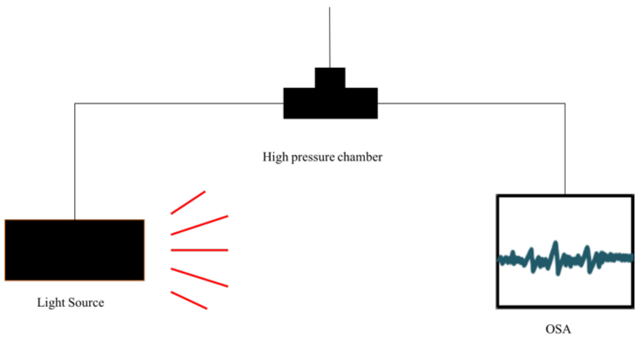

Figure 1. A schematic of optical transmission intensity measurement devices

As Figure 2 shows, the test apparatus consists of one stainless steel pipe fitting as a chamber (304 stainless steel pipe fitting), three adapters (Yor-Lok tube fitting, 1/16" tube OD and 1/8" pipe size). Each adapter was assembled with an Extreme-Pressure Polyetheretherketone (PEEK) sleeve (1/16" OD and 260 μm), a fitting ferrule (1/16" ID) and a fitting nut. The optical fiber passed through the both side of adapters in order to place the fiber optic sensor at the center of the chamber. Gap between the optical fiber and PEEK sleeve was completely sealed by fitting nut and ferrule, which made optical fiber immobilized. The chamber was filled with the PDMS through the top port of the chamber, after that, the top adapter was assembled and connected to the CO_2 tank for gas injection and pressurization.

Optical fiber based sensors have been developed for measuring environmental parameters such as temperature, pressure, humidity and chemical composition [10]. In this experiment, LPG optical fiber sensors were fabricated by a femtosecond laser (Spectra-Physic ultrafast Ti: Sapphire laser) with a 120 femtosecond pulse width and 1 kHz repetition rate at a central wavelength of 800 nm.

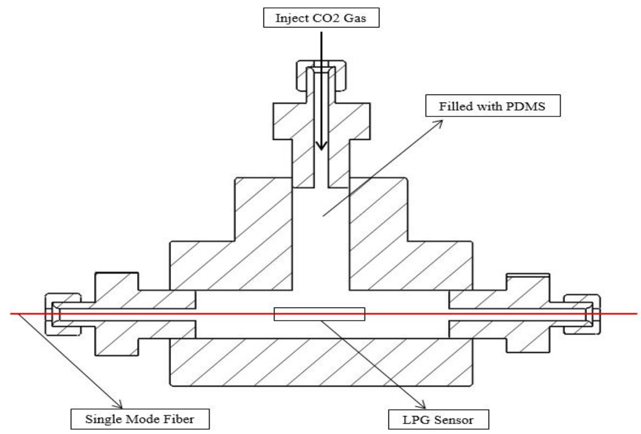

Figure 2. A schematic of the high pressure chamber with optical transmission fibers

The optical transmission intensity of a PDMS/CO_2 system under different pressures was measured at 35 °C. First, optical transmission intensity values of a PDMS/CO_2 system were measured from 0 ~120 psi.

The effect of temperatures was also investigated by recording the optical transmission intensity of a CO_2/PDMS system at the temperature range from 35 °C to 90 °C at 120 psi.

3 RESULTS AND DISCUSSION

PDMS is a viscous liquid at ambient temperatures with rheological behavior similar to that of many other high molecular weight molten polymers at their processing temperatures; therefore, it is a convenient ambient temperature analog to thermoplastic melts [11]. PDMS was chosen to absorb CO_2 because of its liquid form ata room temperature and its refractive index for total internal reflection guiding mode [12]. In this mode, light transmission intensity of a fiber sensor is highly related to the refraction index.

Optical fiber based sensors are sensitive to the refractive index of medium surrounding the fiber. If the cladding is surrounded by a material which has high refractive index, the total internal reflection is lost, and it reduces the center wavelength of the attenuation bands significantly [13-15]. J.H Chong et al. researched the sensitivity of refractive index sensor including LPGs with materials which have different refractive indices such as ethylene glycol, salt and sugar solutions, up to 1.44 refractive index [16]. It indicated that LPG sensors can operate in refractive index up to 1.44 approximately. Therefore, PDMS was chosen for the material surrounding medium of the fiber because of its low refractive index about 1.4.

To obtain the time for transmission intensity get stabilized, optical transmission intensity values of the CO_2/PDMS system during absorption were measured over time. Figure 3 shows that the transmission intensity decreased quickly in the first 30 minutes when CO_2 was injected and then stabilized. The greatest fluctuation during the last 35 minutes was smaller than 0.002 dBm.

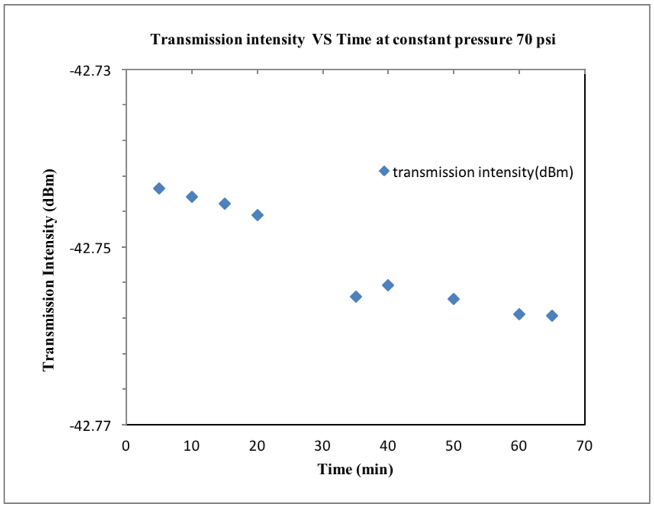

Figure 3. Transmission intensity of CO_2/PDMS system at 70 psi

The transmission intensity values of the CO_2/PDMS system with respect to pressures were measured and shown in Figure 4. Each data point was collected after the intensity value reached at steady state (~ 30 mins). These measurements were repeated three times and the standard deviations were shown by the error bars to show the repeatability. The transmission intensity decreased dramatically at low pressures and then slowed down at higher pressures.

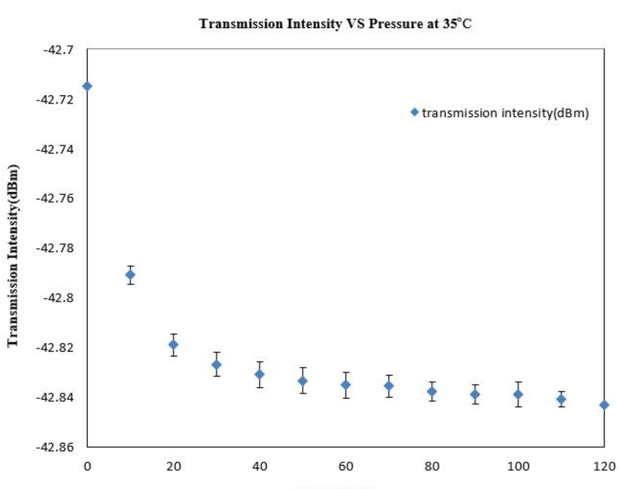

Figure 4. Transmission intensity of CO_2/PDMS system with respect to pressures

The temperature effect was also investigated in this study. The CO_2/PDMS system at 120 psi was heated up from 35 °C to 90 °C and the results were shown in Figure 5. No significant transmission intensity change was observed in this temperature range. The biggest difference was around 0.01 dBm, which is ignorable compared to the intensity change caused by pressure fluctuation.

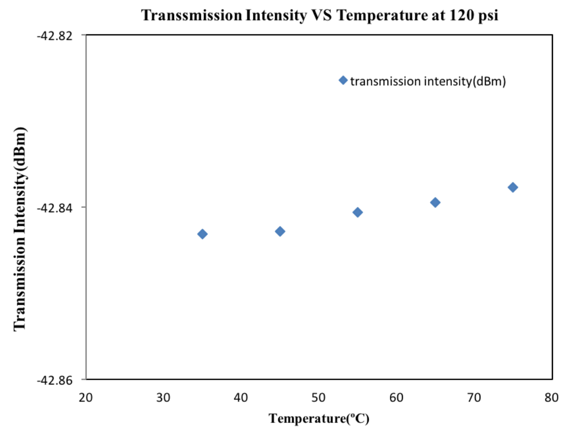

Figure 5. Transmission intensity change with respect to temperatures

4 CONCLUSION AND FUTURE WORK

This study investigated the relationship between optical transmission intensity and gas diffusivity of the CO_2/PDMS system during CO_2 absorption. Optical transmission intensity change during the CO_2 diffusion was recorded using OSA.

In the future, the optical transmission intensity values at higher pressures and temperatures will be investigated, and more experiments on various kinds of polymers will be conducted.

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