Experimental research on swelling and glass transition behavior of poly(methyl methacrylate) in supercritical carbon dioxide

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ABSTRACT

The glass transition temperature (T_g) reduction of polymer by plasticization is a paramount thermodynamic property in polymer/diluent systems, thus effecting microcellular foaming process. Experiment was conducted in a high-pressure cell furnished with an optical channel. In this research, the swelling ratios ($\Delta V/V_0$) of polymethyl methacrylate (PMMA) in carbon dioxide (CO_2) with pressures ranging from 2 to 22 MPa were measured, thus the T_g data of PMMA was determined in the same pressure range. It was found that the swelling ratio increases with temperature but reaches the maximum at 12 MPa, instead of 22 MPa. And the glass transition temperature decreases from 380.5 to 311.4 K within the pressure range of 0.1–12 MPa but increases gradually to 323.1 K from 12 to 22 MPa. Additionally, the change of maximum saturation temperature as a function of CO_2 pressures agrees well with T_g of the polymer-CO_2 system.

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1. Introduction

A variety of industrial applications involving polymers and supercritical fluids captured attentions in recent years, especially supercritical CO_2 ($SCCO_2$). It is readily available, cheap and environmentally-friendly. Furthermore, CO_2 has a tunable solvent strength, plasticization of glassy polymers and enhanced diffusion rates over a continuum with pressure and temperature in polymers. It has high solubility in polymer even at moderate pressures, especially in PMMA as a result of the interaction between the ester groups and the carbon atom which is electron-deficient in PMMA [1]. PMMA is widely used for its large T_g depression induced by the high CO_2 solubility. The diagram of T_g-CO_2 pressure can be applied to optimize the microcellular foaming process by determining the glassy and rubbery state of the polymer-CO_2 system in saturation stage [2].

Microcellular polymeric foams are characterized as systems with uniformly distributed cells that range in size from 0.1 to 10 microns, and in density from 10^9 to 10^{15} cells/cm, and thus have favorable insulating properties against the heat, noise and electricity [3]. They are produced by saturating polymers in compressed gas. The expansion of the supersaturated system causes thermodynamic instabilities, and resulting in a foaming process [4]. Because of plasticization by $SCCO_2$, it is feasible to produce foams using a glassy polymer at temperatures substantially lower than its intrinsic T_g. Goel and Beckman [5] produced microcellular PMMA foams at temperatures as low as 313 K that is far lower than its T_g.

On account of the dissolution of CO_2 in polymers, compressed CO_2 near or slightly above the critical points (T_c = 304.3 K, p_c = 7.38 MPa) can produce substantial polymer swelling, causing significant depression of T_g [6]. For instance, a 70 K drop in T_g of PMMA at 6 MPa has been observed by Handa et al., and the depression in T_g increases with the solubility [7]. Besides *in situ* creep compliance was applied in T_g measurement [8], other methods were reported. Banerjee and Lipscomb [9] utilized a Setaram C80D microcalorimeter equipped with high-pressure cell to measure T_g of PMMA and polycarbonate (PC) as a function of CO_2 pressure. Wissinger and Paulaitis [10] explored the relationship between T_g and gas concentration. Meanwhile, differential scanning calorimeter (DSC) was applied for T_g measurement. DSC is convenient, fast, and accurate technique to determine T_g of a polymer [11]. The equilibrium CO_2 concentration in cells varies with the DSC program temperature, thus the available high-pressure cell for DSC has a typical pressure limitation and the baseline stability becomes erratic under elevated pressure [12,13], to result in less accuracy for T_g measurement.

According to the free volume theory proposed by Fox and Flory [14], along with the temperature increase, the free volume of a polymer will be changed by the swelling of CO_2; thus T_g can be determined by analyzing the relationship between the isobaric volume change and temperature. Therefore, T_g measurement by optical observation began to be conducted in larger pressure or

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temperature range according to the existence of an inflection point at T_g. Rajendran et al. [15] measured swelling and sorption behavior of the PMMA-CO_2 system in the ranges of $p = 0$–25 MPa and $T = 323$–353 K with optical observation and magnetic suspension Balance (MSB), which quickly estimates reliable swelling and sorption data. The reliability of optical observation method was also been verified in the work of Nikitin [16], a high-pressure visual cell was applied to measure the dynamics of diffusion front propagation in polymer samples during the swelling process. Chen et al. [17] experimentally measured the solubility of CO_2 in polymer by MSB and the swelling volume of the isotactic polypropylene (iPP)-CO_2 system at pressures up to 30 MPa with direct visual observation. The swelling ratio was used to correct the gas buoyancy acting on the iPP melts in the MSB measurement.

In swelling of polymer, two competitive mechanisms simultaneously affect the free volume in polymer-gas system. On one hand, the mechanical compression induced by hydrostatic pressure reduces the free volume of compressible polymer-gas system. On the other hand, the dissolved gas causes polymer to swell and increase the free volume, which is usually reported typically more significant than the former [18]. It implies that the presence of gas evidently enhances the mobility of the polymer chains, and thus creating more free volume for CO_2 molecule. The progressive increased free volume triggers an augment in solubility and diffusivity to decrease T_g. However, the relationship between hydrostatic pressure and swelling effect changes with pressure, thus altering the T_g change.

Due to the experimental method limits, T_g data of polymers at high pressure is insufficient in literature. Therefore, the change of T_g was merely regarded as depression. As for T_g at high pressure, the lack of experimental data inhibited the further study. As a consequence, the determination of the saturation temperature in foaming process was a deficiency of theoretical evidence. In this work, attempts have been made to measure the swelling ratios of PMMA at CO_2 pressure ranging from 2 to 22 MPa and achieve its T_g, in which the change in the dimension of a polymer sample was recorded with direct observation. The knowledge of the T_g–p profile provides information on the conditions under which cell nucleates, cellular morphology performs for microcellular foaming with $SCCO_2$ [19]. Accordingly, the relationship between T_g and saturation temperature in foaming can be established by illustrating the cell density as a function of CO_2 saturation pressure at a series of saturation temperatures.

2. Material and methods

2.1. Material

PMMA rods with a diameter of 2 mm and length of 60 mm (average molecular weight = 500,000 g/mol) was purchased from Mitsubishi Rayon Polymer Nantong Co. Ltd., and CO_2 (purity > 99.9%) from Xi'an Tianze Cryogenic Equipment Co. Ltd.

2.2. Experimental equipment and procedures

2.2.1. Experimental equipment

Fig. 1 manifests a schematic diagram of the self-designed visual observation apparatus for T_g measurement. It consists of a high-pressure visual cell, a zoom-stereo microscope supplied with a digital video camera, a gas-supply line, and a pump with a refrigerated circulator bath. The pressure generator and the visual cell are provided with mechanical manometers to control the pressure. The cell was also equipped with thermometer and an attemperator. Silica glass windows with thickness of 70 mm mounted were used to implement the optical channel in the high-pressure cell.
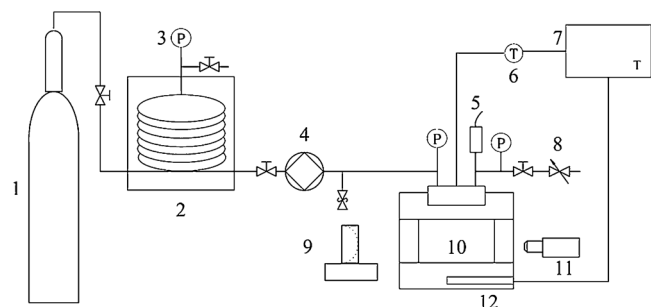
1-CO_2 cylinder; 2- refrigerated circulator bath; 3- pressure gage; 4-metering pump; 5- safety valve;

6- thermometer; 7- attemperator; 8- reducing valve; 9- illuminant; 10-high-pressure visual cell;

11-zoom-stereo microscope

Fig. 1. Experimental equipment for measuring volume change ratio of PMMA in CO_2 pressure.

2.2.2. Experimental procedure

The experimental investigation of CO_2 sorption by the PMMA samples was performed in the following manner. A cylindrical polymer sample was fixed on a self-regulating shelf inside the cell. Then the cell was sealed and CO_2 was pumped into the cell to increase pressure up to a certain value at a relatively low temperature (293 K in this work). Cylindrical sample is much easier to measure optically than films. The angle to the camera lens does not affect the accuracy, while the film or strip must be carefully placed vertically with respect to the camera lens. Despite all this, the disturbance of CO_2 with increased temperature in cell shifts the sample. After the sample was exposed to CO_2 atmosphere for 12 h, the cell began to be heated up at the rate of 5 K/30 min. During heating up, a pressure regulator was applied to remain the pressure inside the cell constant. When the image obtained by microscope was distinct and steady, the optical observations were conducted using video camera filming through the optical channel of the cell every 30 min and then analyzed by the Image-Pro Plus software 6.0 (The Media Cybernetics Co. Ltd.). To avoid PMMA samples being in viscous state, the upper limit of temperature in this work was set to be 363 K.

The swelling ratio ($\Delta V/V_0$) is defined as the ratio of the volume change (ΔV) under isobaric condition during swelling with the initial volume (V_0) of the polymer sample at ambient temperatures.

$$V_0 = \pi r_0^2 h^2$$
$$V = \pi r^2 h^2 \tag{1}$$

Variables r, r_0 and h, h_0 are the measured and initial diameters and length of samples, respectively. It is assumed that the swelling of the PMMA film was assumed isotropic, and therefore only the change in diameter was measured [20,21]. Isotropic swelling was verified by measuring the volume change in length directions from the same cylindrical sample.

$$\frac{r}{r_0} = \frac{h}{h_0} \tag{2}$$

$$\frac{V}{V_0} = \frac{\Delta V + V_0}{V_0} = \left(\frac{r}{r_0}\right)^3 \tag{3}$$

$$\frac{\Delta V}{V_0} = \left(\frac{r}{r_0}\right)^3 - 1 \tag{4}$$

The T_g data can be obtained by finding the inflection point in the plot of the $\Delta V/V_0$ *versus* increasing temperature under atmospheric pressure and CO_2 isobaric condition, respectively.