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Interferometric observation of the process of CO₂ dissolving into PMMA under high pressure

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Abstract

In situ interferometric observation of the process of CO₂ dissolving into PMMA (polymethyl methacrylate) was carried out at high pressure and room temperature, in view of the interest to polymer foam technology. By analysing interferograms, the phase shift of a laser beam transmitted through the sample (the phase is related to the dissolved gas content and polymer thickness) was obtained as a function of time and pressure. At constant pressure, the phase shift initially increased over time and reached a maximum value, and then decreased asymptotically to a constant value as equilibrium was approached. In addition, the equilibrium value of the phase shift increased with increase in pressure for pressures lower than the glass transition pressure P_g , and decreased at pressures higher than P_g . Thus, the optical properties exhibited during the process of the gas dissolving were drastically different for the glassy state and the rubbery state of the polymer.

1. Introduction

Microcellular and ultramicrocellular foams [1, 2] have been attracting much attention due to their superior mechanical and thermal stability as compared to conventional foams with much larger cell size. Recently, it became known that certain polymer–gas systems show retrograde vitrification behaviour—that is, they undergo a rubber-to-glass transition on heating [3, 4]. At low temperature, the gas solubility is quite high at relatively low pressure and the high dissolved gas content may give a high cell density. What is more, the low temperature may facilitate better control of the cell growth and may lead to production of finer cells. So, a new technique for producing polymers with very fine cell structure by taking advantage of this retrograde vitrification behaviour was proposed [3, 4].

In order to determine the inner structure of foamed plastics, such as bubble size and/or bubble number density, both the rate of diffusion and the solubility of CO₂ in the polymer are

important. But there is no established technique for measuring the dissolved gas concentration *in situ*.

As a trial, in the present study, interferometric observation of the process of dissolving CO₂ into PMMA at high pressure and room temperature was carried out, to establish an efficient *in situ* measurement technique.

2. Experimental details

The shape of the PMMA sample was a circular disc, 5 mm in diameter and 0.52 mm in thickness. The high-pressure vessel used can apply pressure up to 6 MPa. After installing the sample, the vessel was evacuated for 6 h at 80 °C to degas the polymer. The temperature was kept at 20 °C and the CO₂ pressure P was kept at fixed values up to the CO₂ saturated vapour pressure (=58 atm).

An optical Mach–Zehnder interferometer system was used for the observation of the gas dissolving into the polymer (figure 1). A reference path and a test path interfere with each other in the optical system. The interferograms were obtained for the circular polymer and were analysed by a signal processing procedure based on moire phase shift interferometry [5].

The intensity of the inlet interferogram I is related to the phase distribution profile ϕ by

$$I(x, y) = a(x, y) + b(x, y) \cos[2\pi x/P + \phi(x, y)] \quad (1)$$

where $a(x, y)$, $b(x, y)$, and P are the bias, amplitude, and pitch, respectively. In order to obtain $\phi(x, y)$, three reference interferograms with a phase difference of $\pi/2$ with respect to each other were digitally composed in the signal processor as the carrier fringes. Three moire interferograms with intensities I_j ($j = 1, 2, 3$) were created using the inlet interferogram and the three reference interferograms, and the intensities are given as follows:

$$I_j(x, y) = a'(x, y) + b'(x, y) \cos[\phi(x, y) + (j - 1)\pi/2] \quad (2)$$

where $a'(x, y)$ and $b'(x, y)$ are the bias and amplitude, respectively. The two-dimensional phase distribution profile $\phi(x, y)$ is obtained using equation (2) as

$$\phi(x, y) = \tan^{-1}[(I_3 - I_2)/(I_1 - I_2)] + \pi/4. \quad (3)$$

3. Results and discussion

Figure 2 shows sequential pictures of phase distribution profiles obtained from the interferograms. The change of greyscale level from black to white indicates a phase change of the laser beam, $\Delta\phi$, by 2π . A phase shift by 2π corresponds to an optical path difference of λ (= 632.82 nm: the wavelength of the He–Ne laser used). In figure 2(a), a black spot appeared in the centre of the sample and increased in area (figures 2(b)–(d)). In figure 2(e), the greyscale became white again. This indicates that the phase changed by 2π from figures 2(a) to (e). The greyscale level repeatedly changed from black to white.

Figure 3 shows the time variation of the phase shift $\Delta\phi$ at the centre of the sample for various values of the CO₂ pressure P . A phase shift of 2π was taken as the unit in the figure. Unusual optical behaviour was observed during the dissolving of the gas into the polymer. In all cases, the value of $\Delta\phi$ increased at first; however, it reached a maximum value. Then, $\Delta\phi$ decreased over time and asymptotically approached a constant value as equilibrium was approached.

The time necessary for saturation of gas in the polymer became shorter as P increased. This must be caused by the higher diffusion coefficient of CO₂ for the rubbery state of the polymer at higher pressure. (The glass transition pressure P_g is 46 atm at $T = 20$ °C.)

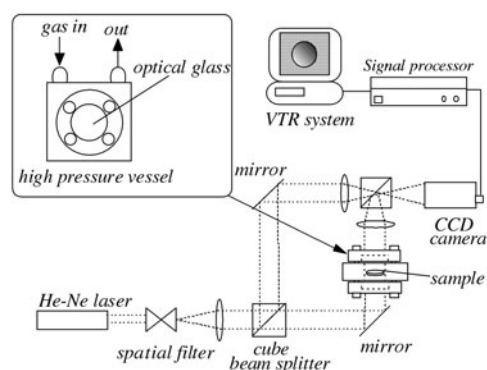


Figure 1. The optical Mach-Zehnder interferometer system used for the observation of the gas dissolving, and its combination with the high-pressure vessel.

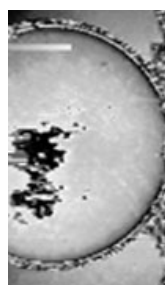


Figure 2. Sequential pictures of phase distribution profiles in the disc sample. A change of the greyscale level from black to white indicates a phase change of the laser beam by 2π .

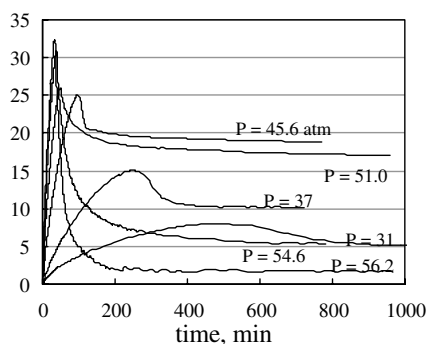


Figure 3. The time variation of the phase shift of the polymer sample as a function of the CO₂ pressure at $T = 20^\circ\text{C}$.

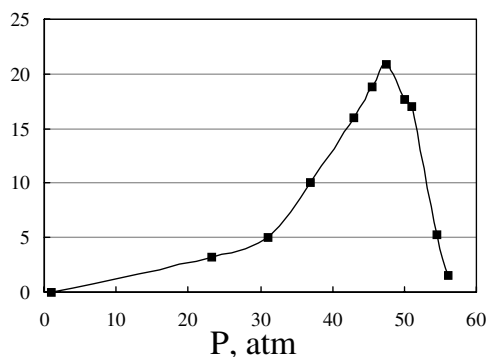


Figure 4. The equilibrium phase shift $\Delta\phi_{eq}$ as a function of the pressure at $T = 20^\circ\text{C}$.

While the gas is dissolving, the gas concentration in the polymer is not uniform, because the gas dissolves from the surface. Therefore, the results mentioned above were averaged values of $\Delta\phi$ through the thickness of the polymer. In view of this, it is advantageous to obtain the equilibrium value of $\Delta\phi$ in the final stage of each run. Hereafter, we denote $\Delta\phi$ in the equilibrium condition as $\Delta\phi_{eq}$. In this condition, the state of the polymer and the dissolved gas concentration are uniform. The relationship between $\Delta\phi_{eq}$ and P was obtained, as shown in figure 4. In the range of pressure below P_g , i.e. for the glassy state of polymer, the values of $\Delta\phi_{eq}$ increased with increase of P . However, in the range of pressure above P_g , i.e. for the rubbery state of the polymer, the values of $\Delta\phi_{eq}$ decreased with increase of P . Therefore, the gas solubility and the swelling of the sample (i.e., the increase in sample thickness) are highly dependent on the state of the polymer.

The relationship between the phase shift $\Delta\phi$ and the related parameters is as follows:

$$\Delta\phi = (h_0\Delta n + n_0\Delta h + \Delta n\Delta h)(2\pi/\lambda) \quad (4)$$

where n_0 is the initial refractive index of the polymer sample at $P = 1$ atm, h_0 is the initial sample thickness, λ is the wavelength of the He-Ne laser, Δn and Δh are the changes in n and h , respectively, when high-pressure CO₂ is installed in the vessel. The value of $\Delta\phi$ increases

when the sample thickness increases and when the refractive index of the sample increases. The refractive index is related to the dissolved gas concentration, the state of the polymer, and so on. However, in the present study, it is rather difficult to obtain the sample thickness and the gas concentration separately. Below, the present results are compared with the results obtained by other techniques.

In situ Raman spectroscopic observation showed qualitatively that the amount of CO₂ in the polymer increased monotonically and finally reached a constant value [6]. It was also shown by gravimetry that the weight of the sample absorbing CO₂ increased monotonically [4]. At this stage of research, it is quite difficult to decide why the phase shift, which is related to the gas concentration in the polymer, has a maximum value and then decreases. And the question of why the dependence of the equilibrium phase shift on pressure for the rubbery state is drastically different from that for the glassy state was unresolved. In order to investigate the properties of the polymer during the phase transition from the glassy state to the rubbery state, a detailed investigation of the process of gas dissolving into PMMA over extended ranges of temperature and pressure will be necessary.

In addition, if the thickness change of the sample, Δh , was obtained by using a different technique, it would be possible to obtain the refractive index of the polymer using equation (4). Since the solubility can be obtained by gravimetry, the calibration line between the refractive index and the dissolved gas concentration will be obtained. This means that a quite effective *in situ* technique for measuring the dissolved gas concentration could be established using interferometry.

4. Conclusions

In the present study, interferometric observation of the process of CO₂ dissolving into PMMA under high pressure was carried out. The phase shift of a laser beam transmitted through the sample was detected as a function of time and pressure. At constant pressure, over time, the phase shift initially increased and reached a maximum value, and then decreased asymptotically to a constant value as equilibrium was approached. In addition, the equilibrium value of the phase shift increased with increase in pressure for pressures lower than the glass transition pressure, and decreased at pressures higher than P_g . If some related parameters are obtained, interferometry can be an efficient *in situ* technique for monitoring the process of gas dissolving into polymer. In addition, it was found that optical properties of polymer exhibited during the process of gas dissolving undergo drastic changes at the phase transition from the glassy state to the rubbery state.

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