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Raman Spectroscopic Investigation of the Phase Behavior and Phase Transitions in a Poly(methyl methacrylate)–Carbon Dioxide System

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ABSTRACT: Laser Raman spectroscopy, in conjunction with an optical high-pressure cell, was used to investigate the poly(methyl methacrylate)–carbon dioxide system. The Raman shifts associated with carbon dioxide molecules in the gas phase and those dissolved in the polymer were used to derive sorption kinetics of carbon dioxide and the carbon dioxide-induced phase changes in the polymer. Measurements were made in the temperature and pressure ranges in which this system is known to exhibit retrograde vitrification behavior. The Raman results on the sorption kinetics and on the onset of plasticization were in agreement with those obtained by gravimetric and calorimetric techniques, respectively. This technique provides a versatile and rapid way of characterizing polymer–gas systems and information that so far has been obtainable only through painstaking and time-consuming techniques. © 2003 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 41: 2214–2217, 2003

Keywords: polymers; gas; sorption kinetics; phase transitions; phase behavior; Raman spectroscopy; thermoplastics

INTRODUCTION

The process for making microcellular foams with physical blowing agents is now well established,[1] by which a polymer is saturated with a gas, such as carbon dioxide (CO_2) or N_2, and then either the pressure is suddenly released at a temperature slightly above the glass-transition temperature (T_g) of the polymer–gas system or the pressure is released slowly to the ambient pressure and the system is rapidly heated to a temperature between T_g and the softening point of the neat polymer. The thermodynamic instability thereby introduced brings about phase separation in the polymer–gas solution, causing the dissolved gas to nucleate, expand, and escape the polymer matrix and leave behind a morphology with small, closed cells. Typically, the cells are 1–100 μm in diameter, and the cell density is 10^8 to 10^{10} cells cm^{-3}.

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The cell size and density depend on the amount of gas occluded in the polymer matrix and the processing conditions. It has been reported[2,3] that foams with a cell size lower than 1 μm and a cell density higher than 10^{12} cells cm^{-3} can be made by the saturation of poly(methyl methacrylate) (PMMA) with CO_2 at ambient or slightly elevated temperatures and at pressures of 13–30 MPa. These foams with submicrometer cellular morphologies are called *ultramicrocellular foams*. Recently, a new route to making ultramicrocellular foams has been found:[4] first, PMMA is saturated with CO_2 at 0 °C and 3.3 MPa, and then the solution is heated to the foaming temperature. With this process, ultramicrocellular foams with 0.35-μm cells, a cell density of 10^{14} cells cm^{-3}, and foam densities as low as 0.116 g cm^{-3} have been produced.[4]

As noted previously, knowledge of the amount of gas dissolved in the polymer and the sorption kinetics and knowledge of the changes in T_g of the polymer due to the dissolved gas, which, in turn, help to determine the appropriate foaming temperature, are central to producing foams with the desired morphology. Customarily, we have employed gravimetric techniques to measure gas solubility and sorption kinetics and thermal techniques to detect phase transitions in the polymer–gas systems.[4,5] These techniques are painstaking and time-consuming but, nevertheless, have proven to be invaluable in delineating the retrograde behavior that leads to the process for making ultramicrocellular foams under milder conditions of temperature and pressure. An experimental technique that can provide comparable information, but is more versatile and rapid, is clearly desirable. In this article, we report the development of a laser Raman spectroscopic technique for characterizing polymer–gas systems over extended ranges of temperature and pressure, and we apply it to the PMMA–CO_2 system to demonstrate its utility.

EXPERIMENTAL

The PMMA used had a T_g of 95 °C, a weight-average molecular weight of 108,500, and a number-average molecular weight of 56,700. PMMA sheets around 0.5 mm thick were obtained by compression molding. High-purity, bone-dry CO_2 was used.

A schematic of the apparatus used to measure Raman shifts in polymer–gas systems is shown in Figure 1. The cross-sectional view of an optical high-pressure cell, approximately 2 cm^3 in volume, is shown. A 15-mm-thick glass window was installed in the center of the top side of the cell. The depth and the inner diameter of the cell were 10 and 16 mm, respectively. The temperature of the cell was controlled by a cooling unit, and the whole cell, except the glass window, was covered by insulation. The temperature was measured to ±0.1 °C with a thermocouple inserted into a thermowell in the side wall. The polymer sample, typically 5 mm in diameter and 0.5 mm thick, was set at the center of the cell. Compressed CO_2 was introduced into the cell to the desired pressure and allowed to equilibrate with the polymer sample. The pressure was measured to ±0.01 MPa.

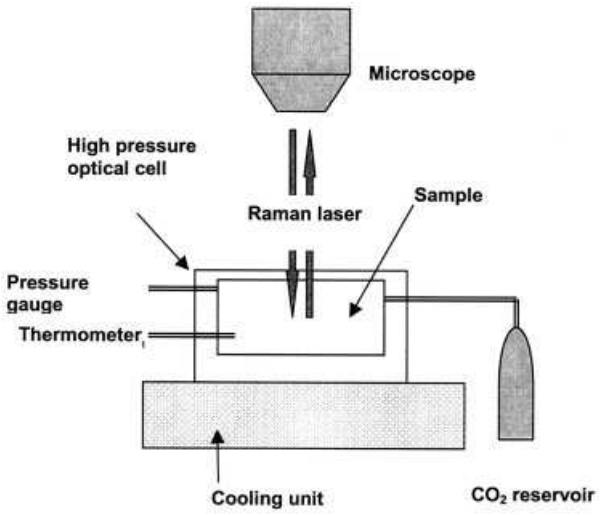

Figure 1. Cross-sectional view of the high-pressure optical cell used for Raman laser scattering.

The dissolution of CO_2 in the polymer sample was followed by *in situ* Raman spectroscopy with a laser Raman microprobe spectrometer (Jobin Yvon Ramanor T64000). The incident laser beam was irradiated onto the sample through the object lens and the glass window. The light source was an argon-ion laser, the wavelength and power of which were 514.5 nm and 100 mW, respectively. The laser beam was condensed to a 1 μm in spot diameter using its microscopic system. During the measurements of the Raman shifts, the Raman beam was focused at about 0.15 mm from the upper surface of the sample. The integration time for each measurement was 10 s, and the average of six measurements was stored as the spectrum. The Raman shift in the PMMA–CO_2 system at 0 °C was measured at pressures of 2.4, 3.0, and 3.3

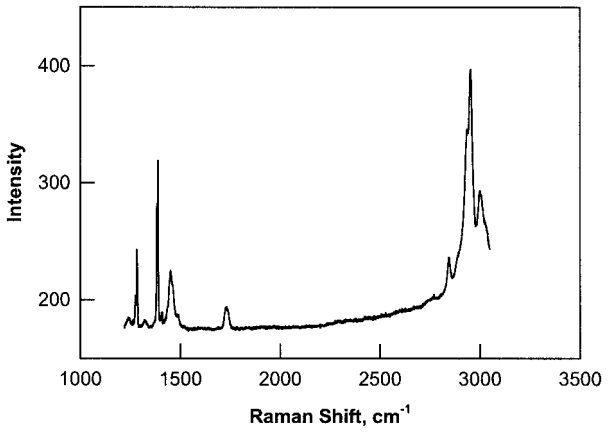

Figure 2. Raman spectrum for the PMMA–CO_2 system at 3.0 MPa and 0 °C.

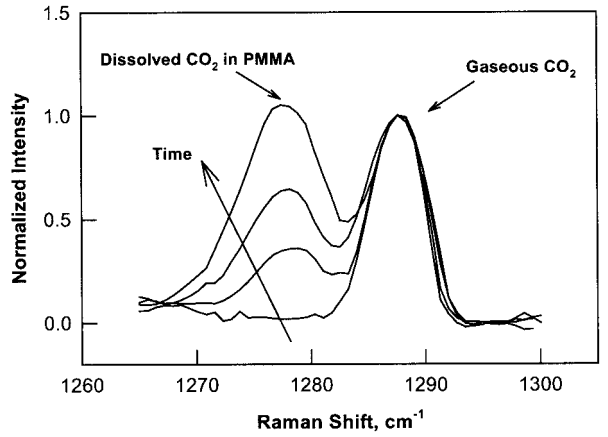

Figure 4. Time dependence of the growth in the peak intensity of the Raman peak due to dissolved CO_2.

MPa. A fresh sample was used for each pressure study.

RESULTS AND DISCUSSION

A typical Fourier transform Raman spectrum of the PMMA–CO_2 system at 3.0 MPa of CO_2 pressure and 0 °C is shown in Figure 2. The spectrum contains peaks due to CO_2 in the gas phase and CO_2 dissolved in PMMA and due to PMMA itself. Several characteristic peaks of PMMA can be observed at 1454 and 1734 and between 2840 and 3010 cm^{-1}.

Peaks due to CO_2 molecules occurring between 1250 and 1450 cm^{-1} are shown in detail in Figure 3. The relatively larger peaks at 1287 and 1390 cm^{-1} are attributed to the gaseous CO_2 in the cell.

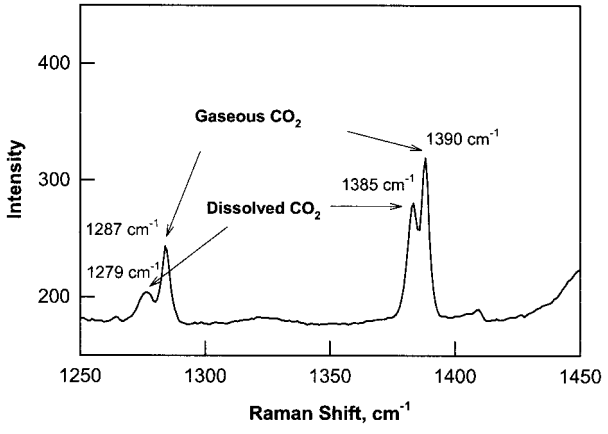

Figure 3. Raman shift due to gaseous CO_2 and CO_2 dissolved in PMMA at 3.0 MPa and 0 °C.

Two smaller peaks at 1279 and 1385 cm^{-1} are attributed to the CO_2 molecules dissolved in PMMA. This shift to lower frequencies with respect to the free gas phase has been observed in other systems when the molecules are transferred from the gaseous state, where all modes are activated to a confined state in which translational and rotational modes are restricted and the barrier to vibrational and stretching modes is affected as well. For example, the occlusion of CO_2 molecules in clathrate hydrates shifts[6] the Raman signature at 1287 to 1277 cm^{-1} and the one at 1390 to 1380 cm^{-1}. The broadening of the Raman bands for dissolved CO_2, as noted in Figure 3, was also observed for occluded CO_2.[6]

The evolution of the Raman peaks due to dissolved and gaseous CO_2 at 1279 and 1287 cm^{-1}, respectively, with time is shown in Figure 4, in which peaks due to dissolved CO_2 with increasing intensity correspond to increasing equilibration time. The intensities (taken as the peak height at its maximum) of the dissolved peak are plotted after normalization with respect to the corresponding intensities for gaseous peaks. The results clearly show that the Raman analysis can be used to follow the approach to phase equilibrium in polymer–gas systems.

Figure 5 shows the ratio of the intensities of the peaks at 1279 and 1287 cm^{-1} due to dissolved and gaseous CO_2, respectively, plotted against time. The results are shown for various gas pressures, and these plots essentially reflect the kinetics of sorption of CO_2 in PMMA. As expected, the kinetics become faster as the pressure is increased at a given temperature. Also shown in Figure 5 are the sorption kinetic results at 3.3

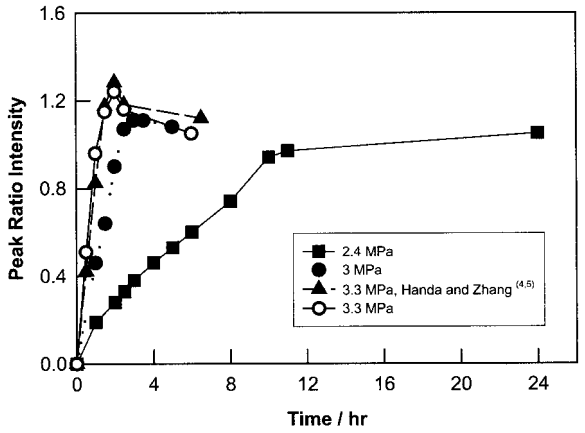

Figure 5. Ratio of the intensities of the peaks at 1385 and 1390 cm^{-1} due to dissolved and gaseous CO_2, respectively, at various times and pressures.

MPa reported previously from gravimetric measurements.[4]

The kinetic data from this investigation were converted into the dimensionless scale for the y axis by dividing the amount absorbed at different times by the equilibrium solubility. The timescale for the data in ref. 4, which refers to a sample 1.25 mm thick, was converted into the timescale of this investigation by multiplication with a factor that is the ratio of the square of the thickness of this sample to the square of the thickness of the sample used in ref. 4. The agreement between the two sets of results is remarkably good. On the basis of this comparison, the kinetic profiles observed in the Raman results can be attributed to the existence of the glassy state at 0 °C and 2.4 MPa and to the existence of the rubbery state at 0 °C and 3.3 MPa, the latter assignment being based on the retrograde vitrification measurements reported previously.[4,5]

The retrograde vitrification phenomenon in PMMA–CO_2 and other systems[4,5,7] has been studied extensively. According to this phenomenon, a polymer–gas system can have multiple T_g's for a given gas pressure.[8] For example, PMMA exists in the rubbery state when equilibrated with CO_2 at 0 °C and 3.3 MPa. When this system is heated under a constant gas pressure, it undergoes a rubber–glass transition (hence the term *retrograde*) at 5 °C, and on continued heating, it undergoes a glass–rubber transition at 72 °C. Therefore, the rubbery state exists at temperatures below 5 °C and above 72 °C, and the glassy state exists at temperatures between them. Accordingly, in this study, the sample existed in the rubbery state at 3.3 MPa and in the glassy state at 2.4 MPa under the saturation conditions with CO_2 at each gas pressure and 0 °C. This is reflected in the results shown in Figure 5. At 2.4 MPa, the peak intensity ratio increases with time and then eventually attains an equilibrium value. However, at 3.0 and 3.3 MPa, the peak intensity ratio reaches a maximum value followed by a small but measurable drop. This occurs because at the constant gas pressure, the glassy state has higher free volume than the corresponding rubbery state. The polymer continues to dissolve more and more CO_2 with time until it undergoes transformation into the rubbery state when some of the dissolved CO_2 is expelled from the solution because of a loss of free volume.

The embryonic nucleation determines the eventual morphology attained in a foaming process. The emergence of an incipient bubble occurs when, under a certain driving force, the concentration fluctuations of dissolved gas lead to the formation of aggregates of embryos larger than the critical radius required for homogeneous nucleation. In polymers, the rubbery state permits gas molecules to undergo such concentration fluctuations. Consequently, the sorption kinetic measurement method, along with the detection of the accompanying phase change reported here, provides a valuable tool for understanding the foaming process in polymers. Its applications to the determination of gas solubilities, phase changes, bubble nucleation, and growth and the imaging of the resulting morphology will be reported in forthcoming articles.

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