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An *In Situ* Study of Plasticization of Polymers by High-Pressure Gases

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ABSTRACT: A high-pressure differential scanning calorimetric technique is described for studying polymer plasticization by compressed gases at pressures to 100 atm. The *in situ* measurements avoid problems due to gas desorption encountered with conventional DSCs, thus providing an accurate way to determine the change in glass transition temperature, T_g, with pressure, p. The entire T_g–p curve can be established in less than 2 days. The glass transition was observed as a sharp step in the case of 100–200-μm thin samples, whereas thicker samples gave a broad transition; highly reproducible results were obtained for the thin samples. For PS–CO_2, the measured T_gs under various pressures were found to be in good agreement with literature values. Results for the systems PS–HFC134a, PVC–CO_2, and PC–CO_2 are also reported. © 1998 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 36: 977–982, 1998

Keywords: compressed gases; polymer; plasticization; high-pressure DSC

INTRODUCTION

A glassy polymer is easily plasticized as a low molecular weight species dissolves in it and, as a result, its glass transition temperature T_g is lowered. The extent of depression in the T_g depends on pressure p of the gas or its concentration in the polymer matrix.[1] A knowledge of the T_g–p behavior of a given polymer–gas system is an important parameter for developing processes for making polymer foams[2]; it provides information on the conditions under which the morphology of the growing cells can be arrested in the case of macrocellular foams and, additionally, on the conditions under which the cell nucleation and growth will take place in the case of microcellular foams. Such T_g–p information is also required for characterizing the optimum temperature–pressure window within which a gas separation membrane should be used,[3] and for extracting unreacted species from manufactured plastics.[4]

A variety of techniques such as NMR,[5] X-ray diffraction,[6] dielectric relaxation,[7] creep compliance,[8] dynamic mechanical response,[9] gas solubility and permeation,[10] ambient pressure DSC,[11,12] and high-pressure calorimetry,[13,14] have been used to infer plasticization of polymers by compressed gases. In most of these techniques, either the thermodynamic state of the polymer–gas system or the glass-to-rubber transition is not well defined. An often-used method to determine T_g of polymers is differential scanning calorimetry. It is the simplest of the techniques to use, and it provides fast and accurate information on the glass to rubber transition. Ambient pressure DSC has been used[11] to scan polymer samples presaturated with the gas to obtain the plasticized T_g. Such a procedure can produce reasonable results provided the loss of gas during sample handling and scanning is minimal. It is also possible to scan a polymer–gas system in a sealed high-pressure DSC pan. However, the pressure in the system does not remain constant during the scan, and it is also not possible to unambiguously define the thermodynamic state of the system.[12,13] High-

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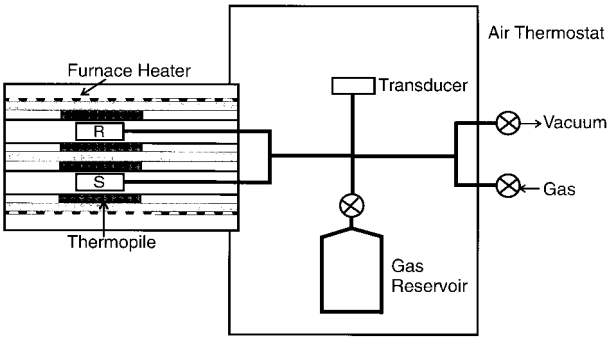

Figure 1. A schematic of the Tian–Calvet heat-flow DSC design, and of the high pressure vessels and the pressurizing manifold.

pressure cells available for conventional DSCs suffer from the same problems; in addition, the baseline stability deteriorates under elevated pressures,[13] and the pressure range available is somewhat limited. Thus, a desirable extension of the regular DSC technique will be a high-pressure DSC where only the polymer sample, and not the entire DSC, is pressurized, and the polymer in equilibrium with the gas phase can be scanned.

Recently, we developed a technique for measuring directly the changes in T_g of a polymer as a function of the gas pressure.[14] The equipment used was a Tian–Calvet heat-flow microcalorimeter (Setaram, Model BT2.15) modified for high-pressure work. Though this technique gave highly reproducible results, the speed of data generation left a lot to be desired. Because only slow scans rates, typically 5–10°C h^{-1}, are possible with the BT2.15, only one heat-cool cycle is possible in 24 h. Thus, it can take several days to generate a complete T_g–p curve. There is now available a DSC121 from Setaram that is also based on the Tian–Calvet principle. It, in fact, is a miniaturized version of the BT2.15 but can be operated just like a DSC. The systems PS–CO_2 and PS–HFC134a have been investigated in terms of producing macrocellular foams[15,16]; and PVC–CO_2 and PC–CO_2 in terms of producing microcellular foams.[17,18] The system PC–CO_2 has also been investigated for gas separation applications.[19] In this article, we report the use of DSC121 for *in situ* determination of the compressed gas-induced plasticization of polymers.

EXPERIMENTAL METHODS

The Setaram DSC121 is not like a conventional DSC. It has a rather massive furnace with two symmetrical cavities containing the reference and the sample vessels (Fig. 1). Each vessel is surrounded by a thermopile, and the differential output of the thermopiles is measured as a function of time and temperature. Again, unlike the conventional DSCs, the internal volume of the high-pressure vessel is quite large and a sample up to 0.15 cm^3 can be used. The temperature and energy scales of the DSC were calibrated by measuring the heat capacities of sapphire over the range −40 to 400°C, and by measuring the melting points and heats of melting of high purity gallium, indium, tin, and zinc. The calibrations were then tested by measuring the heat capacities over the range −40 to 150°C and the melting characteristics of benzoic acid.

For high-pressure work, the vessels were connected to a gas handling manifold, as shown in Figure 1. The pressure rating of the vessels used was 100 atm. The volume of the gas reservoir was much larger than that of the vessels, so that during a scan the pressure in the system did not change. A Setra pressure transducer (Model 204) was used to monitor pressure in the system. After installing the sample, the system was evacuated for a few hours to degas the polymer, and then both reference and sample sides were pressurized to the desired value. The reference vessel was equipped with alumina powder of about the same volume as the polymer sample so that the pressure–volume work done by the gas in both vessels was about the same during the scan. The sample was held at a constant temperature (usually 35°C), and sufficient time allowed for the polymer

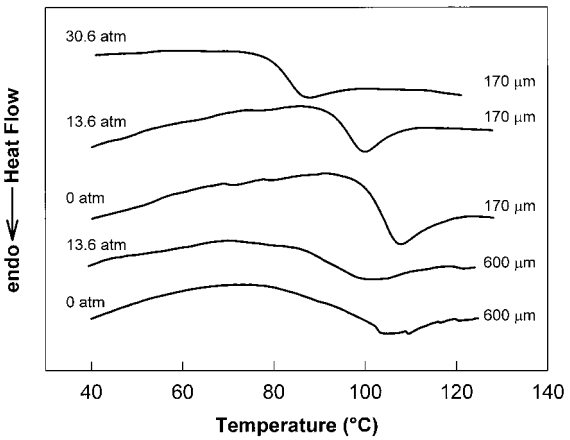

Figure 2. *In situ* and *ex situ* DSC scans on PS–CO_2. PS films of different thickness were saturated with CO_2 at 35°C and 30.6 atm, then scanned under the pressure indicated on each curve.

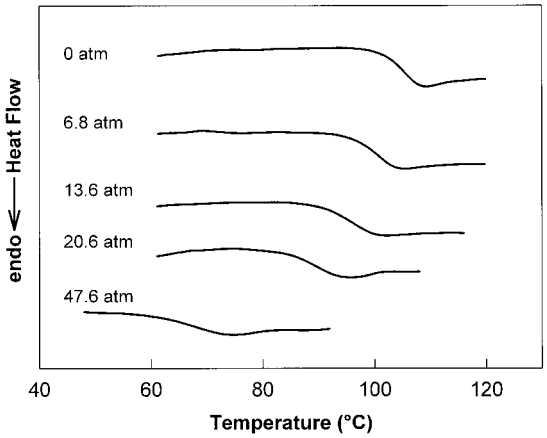

Figure 3. Some representative DSC scans at various pressures for the system PS–CO_2; thickness of the PS samples was in the range 100–200 μm.

to attain equilibrium gas solubility. The sample was then scanned, while still in contact with the gas, at 5°C min^{-1}, usually from 15°C to a temperature about 20 degrees above T_g. The starting temperature of the scan, the pressure in the system, and the temperature of the thermostat housing the pressure reservoir were selected such that no condensed phase of the gas was encountered during the scan. The scans for which the gas-saturated polymer remained in contact with the compressed gas are termed *in situ* scans, where the gas pressure was partly or completely released after the polymer had been saturated with the gas are termed *ex situ* scans.

Polystyrene (PS) used was Scott C-35 with a T_g of 104°C, M_w = 258,000, and M_n = 103,000. PS films, 100 to 200-μm thick, were solvent cast and then dried and annealed in a vacuum oven at 120°C; a detailed procedure for preparing the films is reported elsewhere.[20] Thicker PS films (600 to 700 μm) were also used and were prepared by compression molding at 190°C and then air quenched. Polycarbonate (PC), T_g = 145°C, and unplasticized poly(vinylchloride) (PVC), T_g = 77°C, films, each 100 μm thick, were obtained from Goodfellow. Another sample of PVC containing 7.5 wt % additive (Royal Plastics Geon 103EPF76) was provided to us by Prof. Chul Park of University of Toronto. It was compression molded into a film, about 100 μm thick, at 190°C and then air quenched. Its T_g was 61°C. The T_gs of the as-received and the molded samples were the same, indicating no deterioration of the sample during the high temperature treatment.

High purity CO_2 (SFE grade) was obtained from Air Products and 1,1,1,2-tetrafluoroethane (HFC134a) was obtained from Elf Atochem North America.

RESULTS AND DISCUSSION

The advantage of using high-pressure DSC to study compressed gas-induced polymer plasticization is that gas pressure can be kept constant during the measurements and the obtained results are truly correlated to the applied pressure. Some representative *in situ* and *ex situ* scans on PS–CO_2 at various pressures after PS was saturated with CO_2 at 35°C and 30.6 atm are shown in Figure 2. Glass transition occurred at 81.5°C when the sample was kept under the initial conditioning pressure of 30.6 atm, but moved to higher temperatures when the scanning pressure was reduced or totally released. For the latter case, the pressure was reduced slowly over several minutes in order to avoid foaming of the sample. The increase in T_g is due to the loss or desorption of CO_2 from the polymer during the scan, and is controlled by the gas diffusion behavior under the working pressure. For thin films, CO_2 in the saturated polymer quickly equilibrates with the gas phase during the scan such that the measured T_g is almost independent of the initial conditioning of the polymer, and depends entirely on the pressure during the scan. For thicker films, the diffusion from the central part cannot catch up with the heating process so that a CO_2 solubility gradient develops in the sample during the scan, resulting

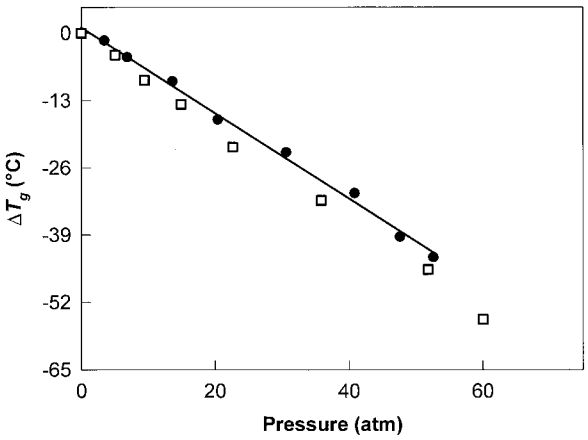

Figure 4. Depression in the glass transition temperature, ΔT_g, of PS plotted against the CO_2 gas pressure. (●), This work; (□), O'Neill and Handa.[14] The curve is drawn to show trend in the data.

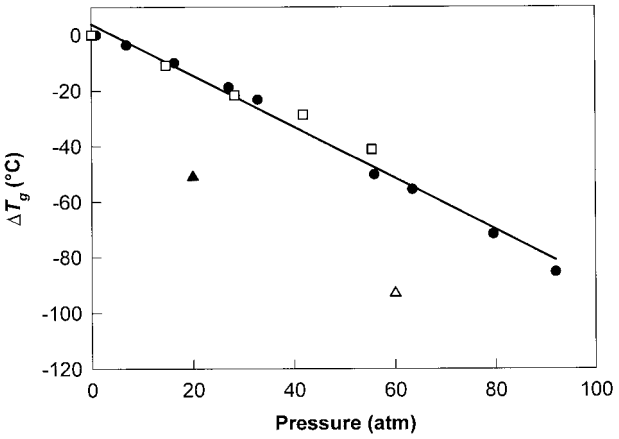

Figure 5. Depression in the glass transition temperature, ΔT_g, of PC plotted against the CO_2 gas pressure. (●), This work; (□), Banerjee[20]; (▲), Chiou et al.[11]; (△), Hachisuka et al.[12] The curve is drawn through our data points to show the trend.

in a very broad glass transition with an increased average T_g.

In conventional DSC, it is not possible to avoid gas desorption during the scan. Although thick samples and fast scan rates can be used to reduce gas desorption, the thickness effect shown in Figure 2 may still broaden the glass transition and, thus, introducing a larger uncertainty in the T_g values obtained. Furthermore, when the solubility in the central part of the thick sample is significantly unmatched with the scanning pressure, i.e., the initial gas pressure used to achieve the solubility is much higher than the pressure in the system during the scan, foaming may occur in that part of the sample with the elevated solubility. In such a case, endotherms that arise due to gas desorption or nucleation and bubble growth can be detected by DSC. The unusual post-T_g signal fluctuation in the bottom curve in Figure 2 is considered to be due to such effects; indeed, small bubbles were found in the scanned samples. Such effects, also reported by other workers,[11] cause noise in the post-T_g baseline, and may introduce further error in the determination of T_g.

The *in situ* DSC outputs at various pressures for the system PS–CO_2 are shown in Figure 3. A decrease in T_g is clearly seen with increasing pressure. The midpoint of the step transition was taken as the T_g at the given pressure. The results are plotted in Figure 4 as ΔT_g against the gas pressure where $\Delta T_g = T_{g,0} - T_g$; $T_{g,0}$ and T_g being the glass transition temperatures of the parent polymer and the polymer–gas system, respectively. Also shown in Figure 4 are the results for PS–CO_2 obtained previously using the microcalorimeter.[14] The agreement between the two sets of results is quite good. The microcalorimeter (Setaram, Model BT2.15) required a sample size of about 2 g, whereas a typical sample size used with the DSC121 was about 55 mg. Furthermore, the whole T_g–p curve could be established with the DSC in the time it took to obtain one or two data points with the microcalorimeter. Thus, the high-pressure DSC technique described here provides a quick and accurate way to study the plasticization of polymers by compressed gases.

The T_g–p behavior in the system PC–CO_2 is shown in Figure 5. Also shown in the figure are the results from previous studies.[11,12,20] There is fairly good agreement between our data and those of Banerjee.[20] The latter results were obtained using a C80 calorimeter from Setaram. This calorimeter is also based on the Tian–Calvet heat-flow principle, and is intermediate in size between the microcalorimeter we used previously[14] and the high-pressure DSC used in this work. The other literature values, obtained using conventional DSCs, deviate significantly from the curve in Figure 5. These values were obtained by scanning under ambient pressure a sample previously saturated with the gas,[11] and by scanning a non-equilibrium mixture of the components in a sealed pan.[12] In both cases, the DSC signals showed multiple step changes, any of which could be taken as the glass transition.

The T_g–p behavior for the system PVC–CO_2 is shown in Figure 6. Both neat PVC and PVC

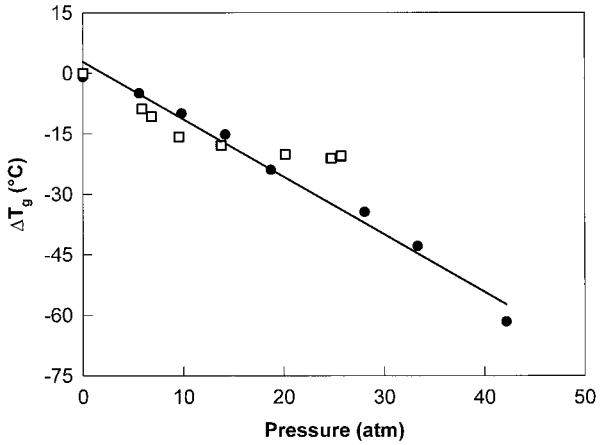

Figure 6. Depression in the glass transition temperature, ΔT_g, of PVC plotted against the CO_2 gas pressure. (●), Neat PVC; (□), PVC containing 7.5% by weight additives. The curve is drawn to show trend in the data.

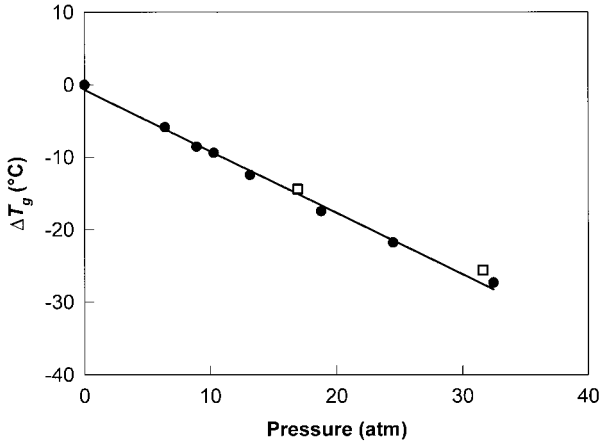

Figure 7. Depression in the glass transition temperature, ΔT_g, of PS plotted against the HFC134a gas pressure. (●), Sample scanned under the gas pressure; (□), sample saturated with HFC134a and then scanned under ambient pressure; thickness of the PS samples was in the range 100–200 μm. The curve is drawn to show trend in the data.

containing 7.5 wt % additive were used in this work. Like the PS–CO_2 and PC–CO_2 systems, a linear relationship is obtained for neat PVC, indicating that the plasticization follows Chow's model.[13,14,22] However, for the PVC containing the additive, the depression in T_g is higher at lower pressures and appears to approach a limiting value at higher pressures. Such a curvature is not predicted by the various theories of glass transition in polymer-diluent systems.[23,24] Obviously, the unusual behavior can be attributed to the presence of the additive. Also, it is worth noting that the additive-containing sample was found to show unusual CO_2 sorption and desorption behavior.[25] The approach to limiting T_g values usually happens under much higher pressures,[14,26] which is not the case here or when the T_g is lowered to the temperature where the polymer was saturated with the gas, which may be the case here.

The T_g–p profile for the system PS–HFC134a is shown in Figure 7. Critical temperature of HFC134a is 101°C.[27] Consequently, the polymer was saturated with the gas at 110°C. After saturating the polymer, the DSC was cooled down to room temperature while maintaining the air thermostat at 110°C. As the DSC cooled, pressure in the system was also reduced such that no condensed phase of the gas was encountered.[13,14] The sample was then scanned under a pressure that was same or lower than the pressure under which it was equilibrated with the gas at 110°C. The infinite dilution diffusion coefficient of HFC134a in PS is about 4×10^{-11} cm^2 s^{-1} at 30°C and about 1.2×10^{-8} at 120°C.[28] For comparison, the corresponding value for CO_2 is about 1.2×10^{-7} at 50°C.[28] Consequently, the rather low diffusion coefficient of HFC134a ensured that the solubility of the gas did not change over the time scale of the experiment. As shown in Figure 7, identical T_gs were obtained from scans conducted under ambient conditions and under the gas pressure. On the other hand, as shown in Figure 2, the rather high diffusivity of CO_2 leads to different T_gs when a saturated sample is scanned under various pressures.

As seen in Figures 4 and 7, the plasticizing effects induced by the dissolved CO_2 and HFC134a are almost the same, about -0.8°C atm^{-1}, implying similar solubility behaviors. Consequently, any differences in the cellular morphologies obtained with these two blowing agents will be dictated largely by the difference in their diffusivities.

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