Plasticization of Polymers with Supercritical Carbon Dioxide: Experimental Determination of Glass-Transition Temperatures

Paolo Alessi, Angelo Cortesi, Ireneo Kikic, Febe Vecchione

Chemical, Environmental and Raw Materials Engineering Department (DICAMP),University of Trieste, Piazzale Europa 1, 34127 Trieste, Italy

Received 6 February 2002; accepted 8 July 2002

ABSTRACT: High-pressure partition chromatography, a modification of the inverse gas chromatography technique, is presented as suitable technique for the study of the plasticization effect of carbon dioxide on the following polymers: poly(methyl methacrylate), polystyrene, and bisphenol A–polycarbonate. Polymers in the presence of a compressed gas or a supercritical fluid become plasticized; this means that their glass-transition temperatures (T_g's) can be lowered by 10s of degrees, which causes changes in their mechanical and physical properties. CO_2-induced plasticization has an important impact on many polymer processing operations in which the T_g depressions of the polymers can be evaluated. The experimental results are discussed and compared with data available from literature for each polymer we considered. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2189–2193, 2003

Key words: chromatography; glass transition; swelling

INTRODUCTION

Supercritical fluid technology has already demonstrated applicability in the area of polymer processing. Carbon dioxide is the most commonly used supercritical fluid because of its well-known properties.[1] Moreover, its small size allows gas penetration into a polymer more easily than do larger liquid solvents. Therefore, sorption processes are more rapid, and the operating conditions can be adjusted continuously with pressure and temperature.[2]

The sorption of CO_2 into polymers results in swelling and changes in the mechanical and physical properties of those polymers. The most important effect is the reduction of the glass-transition temperature (T_g), often simply called plasticization.[3]

From a thermodynamic point of view, two factors determine the good interaction of a plasticizer with a given polymer: the intermolecular forces between the polymer and the plasticizer, which must be of the same order of magnitude of the polymer–polymer interactions,[4] and the molecular size of the diluent. The efficiency of a plasticizer, which can be defined as the T_g depression for a given diluent concentration, increases as molecular size decreases; therefore, a small molecule will diffuse between the polymer segments more easily than a large molecule.

CO_2-induced plasticization has an important impact on many polymer processing operations, such as the separation and fractionation processes of polymers for impurities extraction; impregnation and extraction of additives; membranes conditioning; production of microparticles, foams, gels, and fibers; and polymerizations in supercritical media. In all of these applications, the polymer is plasticized, and so the T_g depression of the polymer should be evaluated.[5–8]

The T_g depression is a function of the gas concentration in the polymer. When the diluent concentration increases, the polymer T_g is progressively reduced. This happens because the interchain distance, the mobility of the polymer segments, and so the free volume of the system increase as well the plasticizer concentration.

Therefore, a knowledge of the influence of the diluent on the T_g, which results from the sorption at elevated pressure, is essential for determining the optimal conditions for the previously mentioned processes: for example, in the gas separation membrane processes, plasticization is not a desirable feature because plasticized membranes lose their permselectivity.[9,10]

DETERMINATION OF THE T_G DEPRESSION

In the literature, mechanical and thermal techniques have been used to investigate the plasticization of polymers by supercritical fluids.

The mechanical investigation is based on the change of the polymer creep compliance at the glass-transition state.

Correspondence to: P. Alessi (paoloa@dicamp.univ.trieste.it).

Journal of Applied Polymer Science, Vol. 88, 2189–2193 (2003)

Wissinger and Paulaitis[4,11] measured the creep compliance of poly(methyl methacrylate) (PMMA) and polystyrene (PS), in the presence of compressed CO_2, to identify the polymer glass transition. The CO_2 pressure, corresponding to a concentration in the polymer that is sufficient to decrease the T_g of the system, can be obtained from sorption data, finding a direct relationship between T_g and the amount of CO_2 dissolved in the polymer.

The creep compliance of a polymer $J(t)$ in the presence of CO_2, at constant temperature and pressure, is time dependent as reported in the following equation:

$$J(t) = \frac{\varepsilon(t)}{\sigma_0} \tag{1}$$

where σ_0 is the applied tensile stress and $\epsilon(t)$ is the strain at the time t.

At a fixed temperature, the creep compliance, function of the CO_2 pressure, can change over two orders of magnitude at the glass transition.

Previously, the same technique was used by Wang et al.[12] to study the plasticization of PS in the presence of compressed CO_2. They observed a minimum in the T_g versus pressure curve, a consequence of two opposite effects: a dilution effect and a hydrostatic pressure effect. At low pressures, the dilution effect dominated, whereas at high pressures, the second effect took over.

Condo et al.[2] described a model to predict the polymer T_g depression as a function of the dilution pressure. The model was developed with lattice fluid theory and the Gibbs–Di Marzio criterion, which asserts the zero entropy at the T_g.

Successively, Condo and Johnston[4] measured the creep compliance of CO_2/PMMA and CO_2/poly(ethyl methacrylate) systems to determine T_g as function of CO_2 pressure. The experimental data were corrected for the swelling effect of the polymer and the buoyancy. The retrograde vitrification was confirmed in the two CO_2–polymer systems.

The thermal technique utilizes high-pressure calorimeters to determine T_g. The advantage of this technique is related to the gas pressure, which is kept constant during the experimental measurement to prevent any possible desorption of the gas.

Handa et al.[6] measured the change in the T_g of a CO_2/poly(2,6-dimethyl phenylene oxide) system by means of a high-pressure differential scanning calorimetry (DSC) cell. Sequentially, Handa et al.[7] compared the plasticization of PMMA produced by different plasticizers, such as carbon dioxide, methane, and ethylene.

Zhang and Handa[8] examined, again with a high-pressure DSC cell, the T_g depression behavior for three polymers, PS, polycarbonate (PC), and poly(vinyl chloride), in carbon dioxide. Referring to PC, Zhang and Handa observed significant deviations in the experimental T_g values with the data obtained by conventional DSC under ambient pressure.

The high-pressure partition chromatography technique was then suggested for this study to investigate the T_g depression of a polymer in supercritical CO_2.

PARTITION CHROMATOGRAPHY AT HIGH PRESSURE

Gas chromatography is a technique based on the partition of a volatile solute between a mobile gas phase and a stationary phase, liquid or solid. This technique is called *inverse gas chromatography* (IGC) when the stationary phase (i.e., a polymer) is the object of interest.

As reported by Braun and Guillet,[13] the first application of IGC was the study made by Smidsrod and Guillet in 1969 for the characterization of poly(*N*-isopropylacrylamide).

In IGC, the obtained experimental data are the specific retention volumes of solutes injected in the stationary phase at different temperatures (V_g^0's), defined as follows:

$$V_g^0 = \frac{F_m}{w} j \frac{P_O - P^0_{H_2O}}{760} \frac{273}{T_a} (t_R - t_a) \tag{2}$$

where F_m is the mobile gas phase flow, w is the stationary phase weight, P_O is the outside column pressure, T_a is the flow meter temperature, $P^0_{H_2O}$ is the water vapor pressure at T_a, $(t_R - t_a)$ is the net retention time, t_a is the inert retention time, and j is the James–Martin factor, which considers the pressure drop in the chromatographic column.

In the ICG technique, the retention mechanism of a solute in a polymer depends on the state of the latter; the plot of the retention volume logarithm versus the reciprocal of the temperature is called a retention diagram, from which it is possible to observe the phase transitions of the polymer.

For a semicrystalline polymer, three characteristic temperatures are evidenced: T_g, softening temperature, and melting temperature (T_m).

In the temperature range below T_g, the diffusion of the solute in the polymer bulk phase is precluded, and so the retention mechanism is only due to surface adsorption. At T_g, the solute penetration begins, and the retention volume increases with temperature. For temperatures above T_m, the behavior is linear, corresponding to the bulk adsorption in the totally amorphous polymer.

High-pressure partition chromatography is a modification of the IGC technique; it is used for T_g depression determination of a polymer, used as a stationary

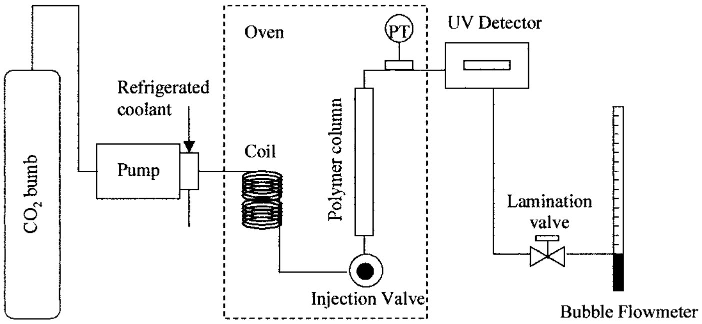

Figure 1 Experimental apparatus.

phase, in compressed CO_2, which acts as the mobile phase and in which an appropriate solute is injected.

When the partition of a solute as the ratio of its fugacity in the mobile and the polymer phases is considered, at a fixed pressure the fugacity of the solute in the CO_2 phase changes linearly with the temperature; therefore, this modification does not determine the characteristic Z shape of the retention diagram.[14]

EXPERIMENTAL

The polymers, PMMA, PS, and PC, were supplied by Sigma-Aldrich (Milan, Italy), with molecular weights (MWs) of 93,000, 240,000, and 64,000, respectively. The organic solvents, 1-butanol and chlorobenzene, were also provided by Sigma-Aldrich. CO_2 was supplied by SIAD (Bergamo, Italy) (purity of 99.98%).

The apparatus we used for the experimental measurements is shown in Figure 1. It consisted of a supercritical fluid chromatograph (SFC 300, Fisons Instruments, Beverly, MA), constituted by a syringe pump and an oven containing the polymer column, and an ultraviolet (UV) detector (Spectromonitor 3200, Thermo Separation Products, Riviera Beach, FL).

Liquid carbon dioxide was pumped into a coil, where it reached the system temperature, and then into the column (length = 250 mm, inside diameter = 3.7 mm, outside diameter = 4 mm), filled with the polymer supported on Chromosorb 100/120. The solutes were injected in the fluid phase just before the column by means of an automatic actuation-injecting valve. After the column, a pressure transducer (DS Europe, Milan, Italy) was placed to monitor the pressure value. For each experiment, the pressure drop in the column was below 0.1 bar. After the column, the outlet stream flowed through the high-pressure UV detector, the lamination valve (Swagelok SS-31RS4 micrometering valve, Solon, OH), and finally, the bubble soap flow meter that measured the CO_2 flow at atmospheric pressure.

The experimental measurements were made at two pressures (80 and 100 bar), whereas the temperature ranges were chosen according to the glass-transition temperature at atmospheric pressure (T_g^o) of each considered polymer.

RESULTS AND DISCUSSION

Before beginning the investigation of the CO_2 plasticizing effects, we determined T_g^o for PMMA by IGC in the presence of an inert gas (nitrogen at 5 bar); we made this measurement to test the validity of the IGC method, comparing the experimental values with the T_g^o's supplied by Sigma-Aldrich and those determined by the DSC technique.

For both the partition chromatographies at low pressure with N_2 and high pressure with CO_2, the injected solutes were chosen among polar compounds such as alcohols, esters, and aromatics. The choice was made on the basis of the evidenced retention time, response sensitivity, and reproducibility of the peak maximum. After the screening, the solute injected in nitrogen, for the T_g^o determination of PMMA was 1-butanol. For the experimental measurements in carbon dioxide, the selected solutes were 1-butanol for PMMA and PS and chlorobenzene for PC.

In Table I, the T_g^o values provided by Sigma-Aldrich are compared with those obtained experimentally with nitrogen at 5 bar and by the DSC technique. The table shows substantial agreement for the T_g^o values of the three sets of data.

The experimental results obtained by high-pressure chromatography technique are discussed next for each polymer.

PMMA

The plasticizing effect of CO_2 was investigated with 1-butanol as a solute at 80 and 100 bar in the temperature range 5–60°C.

TABLE I
Comparison Between T_g Values

Polymer	T_g (°C)	T_g exp (°C; DSC)	T_g exp (°C; N_2)
PMMA	105	107	103
PS	100	104	—
PC	150	147	—

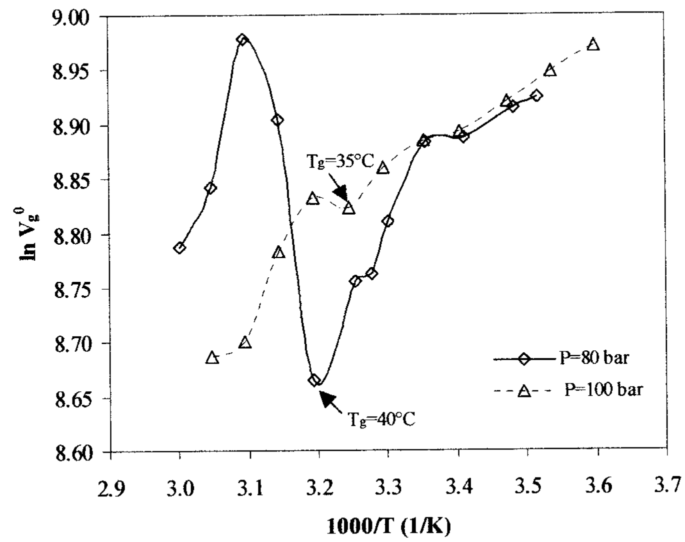

Figure 2 Retention diagrams for the PMMA/1-butanol system.

In Figure 2, relative retention diagrams are shown; the strong CO_2 plasticizing effect on PMMA was evident at 80 bar with a T_g of 40°C and at 100 bar with a T_g of 35°C.

Figure 3 shows a comparison between the experimental depression of PMMA (reported as the T_g/T_g^o ratio) and the values from Wissinger and Paulaitis[4,11] by creep compliance measurements and from Handa et al.[7] by high-pressure calorimetry; when the data of the latter was extrapolated, good agreement was obtained.

The different T_g depressions could be explained either by the difference between experimental methods or by the different characteristics of the polymer samples, that is, the different MWs.

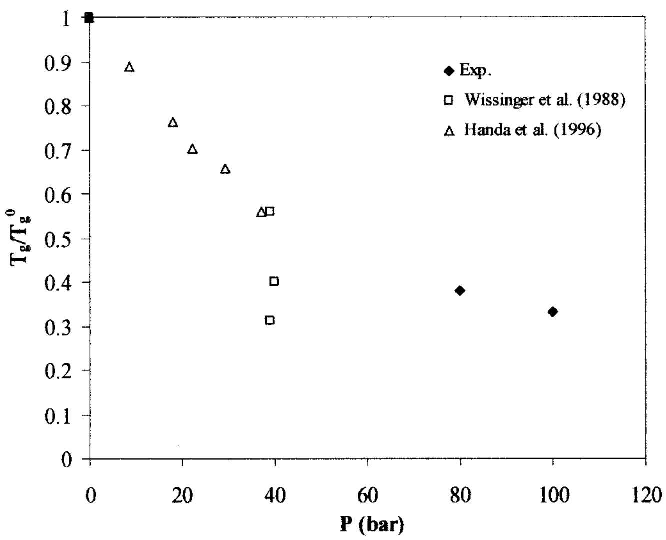

Figure 3 Comparison between PMMA T_g depressions.

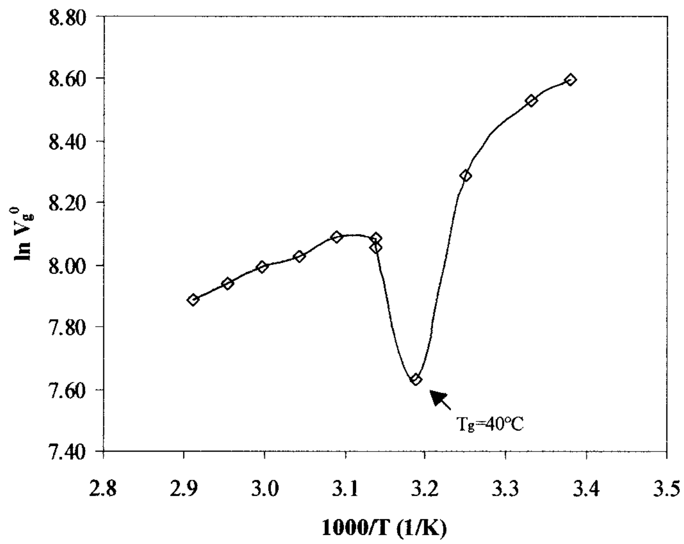

Figure 4 Retention diagram for the PS/1-butanol system at 80 bar.

PS

The plasticizing effect was investigated with 1-butanol as a solute at 80 bar in the temperature range 23–70°C.

In Figure 4, the retention diagram is shown; a T_g of 40°C was evident, representing a great plasticization effect of the CO_2 for this polymer also.

In Figure 5, the T_g depression (reported as the T_g/T_g^o ratio) of PS is compared with the one obtained by Wissinger and Paulaitis[4,11] with the creep compliance method and by Zhang and Handa[8] with the high-pressure DSC technique; as before, the T_g value measured in this work could be obtained by extrapolation of the latter experimental data set.

CO_2 had a great plasticizing effect on the PS studied by Wissinger and Paulaitis when compared to the PS adopted in this study and the one used by Zhang et al.

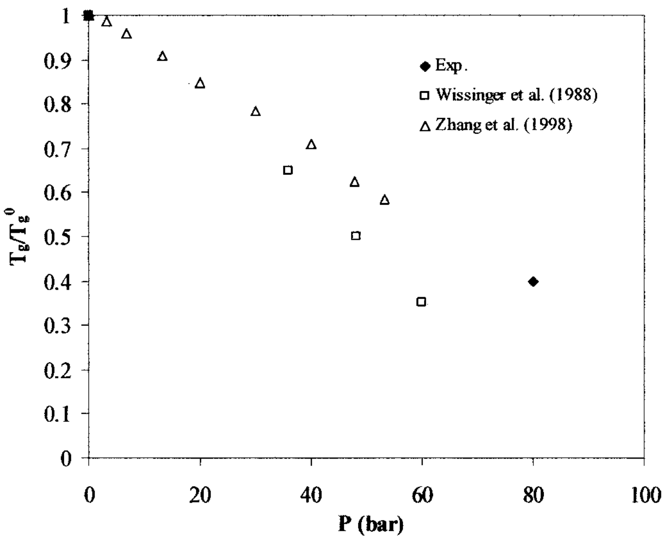

Figure 5 Comparison between PS T_g depressions.

Also for PS, the different trend in the T_g depression could be justified by the diversity of the techniques and of the samples of polymers investigated.

Bisphenol A–PC

The measurement was made at 80 bar with chlorobenzene as a solute in the temperature range 40–90°C.

In Figure 6, the retention diagram is reported; it was possible to observe a local minimum corresponding to a temperature of 75°C.

A similar T_g was found when the experimental data obtained by Zhang and Handa[8] were interpolated for a PC with a T_g^o of 145°C, very close to the 150°C of the polymer considered in this study (see Fig. 7).

CONCLUSIONS

In this study, a high-pressure chromatography technique was used to investigate the plasticization of polymers in compressed carbon dioxide.

The technique, based on retention diagram determinations, can be used for determining the T_g's of a polymer at different pressure values.

The method was applied to PMMA, PS, and PC and showed the plasticizing effect of the supercritical diluent on each polymer. All the systems evidenced a clear T_g depression function of the imposed pressure.

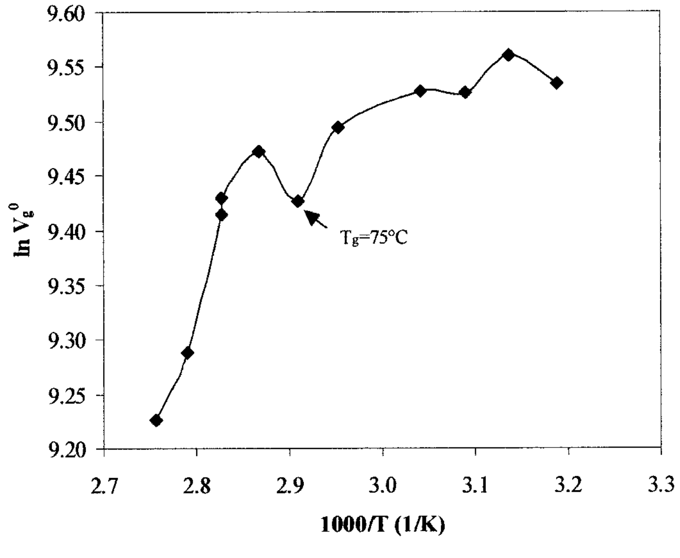

Figure 6 Retention diagram for the PC/chlorobenzene system at 80 bar.

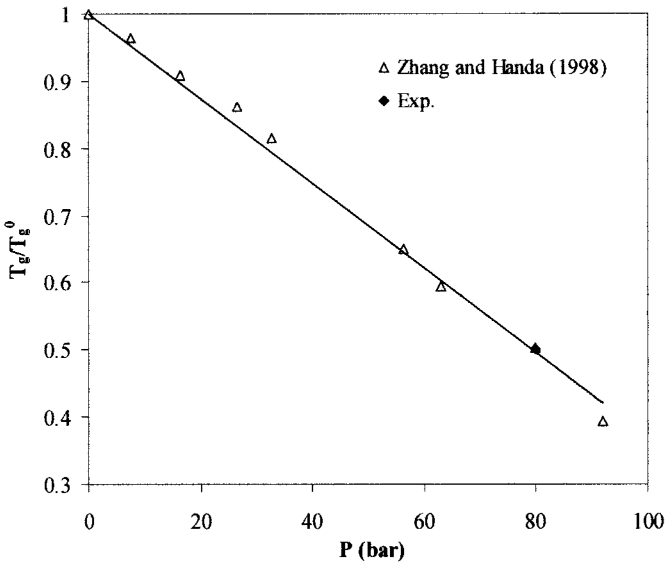

Figure 7 Comparison between PC T_g depressions.

Resulting in its rapid applicability, the high-pressure chromatography is suggested as a useful alternative technique for the study of the plasticization of polymers.

References

1. Kazarian, S. G.; Brantley, N. H.; West, B. L.; Vincent, M. F.; Eckert, C. A. Appl Spectrosc 1997, 51, 491.
2. Condo, P. D.; Sanchez, I. C.; Panayiotou, C.; Johnston, K. P. Macromolecules 1992, 25, 6119.
3. Kazarian, S. G. Polym Sci C 2000, 42, 78.
4. Wissinger, R. G. Ph.D. Thesis, University of Delaware, 1988.
5. Condo, P. D.; Johnston, K. P. J Polym Sci Part B: Polym Phys 1994, 32, 523.
6. Handa, Y. P.; Lampron, S.; O'Neill, M. J Polym Sci Part B: Polym Phys 1994, 32, 2549.
7. Handa, Y. P.; Kruus, P.; O'Neill, M. J Polym Sci Part B: Polym Phys 1996, 34, 2635.
8. Zhang, Z.; Handa, Y. P. J Polym Sci Part B: Polym Phys 1998, 36, 977.
9. Pope, D. S.; Koros, W. J.; Hopfenberg, H. B. Macromolecules 1994, 27, 5839.
10. Bos, A.; Punt, I. G. M.; Wessling, M.; Strathmann, H. J Membr Sci 1999, 155, 67.
11. Wissinger, R. G.; Paulaitis, D. R. J Polym Sci Part B: Polym Phys 1991, 29, 631.
12. Wang, W. C. V.; Kramer, E. J.; Sachse, W. H. J Polym Sci Polym Phys Ed 1982, 20, 1371.
13. Braun, J. M.; Guillet, J. E. In Advances in Polymer Science; Springer: Berlin, 1976; p 108.
14. Vilcu, R.; Leca, M. In Polymer Thermodynamics by Gas Chromatography; Elsevier: Amsterdam, 1990; p 127.