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On the Plasticization of Poly(2,6-dimethyl phenylene oxide)† by CO_2

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SYNOPSIS

Change in the glass transition temperature, T_g, of poly(2,6-dimethyl phenylene oxide), PPO, due to the dissolved CO_2 has been measured as a function of the gas pressure, p, using a high-pressure DSC cell. At 61.2 atm, the highest pressure studied, T_g is depressed by 31.6°C. The depression in T_g is found to be linear with pressure, with dT_g/dp of −0.5°C atm^{-1}. The experimental results are in fair agreement with those calculated from a quasi-lattice solid-solution model for polymer-diluent systems. The present results, however, differ markedly from a recent investigation on PPO-CO_2 system which reported a depression in T_g of 226°C at 60 atm and a dT_g/dp of −3.8°C atm^{-1}. © 1994 John Wiley & Sons, Inc.
Keywords: plasticization • poly(2,6-dimethyl phenylene oxide) • PPO-CO_2 • glass transition

INTRODUCTION

The plasticization of polymers by compressed gases has been the subject of a number of recent investigations.[1-9] There are a number of applications in which we encounter polymer-gas systems. These include formation of microcellular plastics[10] and foams,[11] extraction[12] from and impregnation[13] into polymers of additives using supercritical fluids, and gas separation membranes.[14] In all these applications, it is important to know the temperature, T, and pressure, p, conditions under which the polymer gets plasticized. In the case of gas separation membranes, the plasticization renders the membrane useless as it loses most of its permselectivity.[15,16] Consequently, a knowledge of the change in the glass transition temperature, T_g, of the polymer as a function of the gas pressure helps define the T-p window within which the membrane will give an optimum performance.

Compressed gases like CO_2, N_2O, and C_2H_4 can dissolve to appreciable levels in polymers causing depression in T_g by tens of degrees.[9,17] Recently Hachisuka et al.[4] reported a remarkable plasticization effect of CO_2 on poly(2,6-dimethyl phenylene oxide), PPO, where T_g is depressed by 226°C at a gas pressure of 60 atm. In gas separation membranes, plasticization effects are usually observed as anomalous sorption and permeation during measurements at elevated pressures.[15,16] Sorption and permeation of several gases, including CO_2, through PPO membranes has been investigated at 35°C and pressures to 26 atm.[18-20] No plasticization effects have been observed in these studies; in fact, PPO performs quite well for separating CO_2—CH_4 mixtures at pressures to 26 atm. In the light of the CO_2-induced plasticization effect reported by Hachisuka et al.,[4] PPO would not be expected to function as an efficient separation-membrane at higher pressures where membranes actually are used in practice. This, combined with the rather very strong plasticization effect reported by Hachisuka et al., has led us to reinvestigate the effect of compressed CO_2 on T_g of PPO.

A variety of techniques have been used to determine compressed-gas-induced plasticization effects. Some techniques like NMR,[21] dielectric relaxation,[22,23] and gas sorption, and permeation[16] provide mostly an indirect evidence of plasticization in the sense that either the thermodynamic state of the system or the glass ⇌ rubber transition point is not well defined. Quantitative information on the change

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in T_g of a polymer when contacted with a high pressure gas was obtained by Chiou et al.[2] by equilibrating the polymer with the gas and then scanning the polymer-gas solid-solution in a DSC under ambient pressure, assuming that the solubility of the gas in the polymer did not change much during sample handling and during the scan. Hachisuka et al.[4] also used differential scanning calorimetry (DSC) with high pressure pans containing PPO-CO_2 mixture under pressure. High-pressure static creep compliance measurements were used by a few investigators[1,6,24] to establish the T_g-p profiles. Recently, Handa et al.[9] and O'Neill and Handa[17] used a high-pressure heat-flow calorimeter to make in situ measurements of the change in T_g as a function of the gas pressure. The results were found to agree with those obtained by ambient pressure DSC[2] and high-pressure creep compliance measurements.[1,6] In this work, we used a high-pressure DSC cell for establishing the T_g-p profile in PPO-CO_2 system. This technique was chosen over our high-pressure heat-flow calorimeter because only a limited quantity of PPO was available to us and also because the temperature range of our calorimeter is 190°C whereas T_g of PPO is over 210°C. However, the methodology used was the same as that developed for our high pressure calorimeter.

EXPERIMENTAL

PPO (General Electric) was in the form of a fine powder. It was used as such for some measurements and pressed as a pellet for other measurements. The sample size was about 8 mg when used as powder and about 16 mg when used as pellet. Bone dry CO_2 of minimum purity 99.8% was obtained from Matheson.

A 2910 DSC coupled to a 2100 Operating System (TA Instruments) was used. The glass transition temperature of PPO, T_{g0}, was obtained by heating the powder sample in a regular DSC cell to 240°C, quenching it to room temperature using ice-cold water, and then scanning it at 10°C min^{-1} under a dry nitrogen flow of 50 ml min^{-1}. The DSC was then equipped with a high-pressure cell[25] from TA Instruments, PDSC, for making T_g measurements on the PPO-CO_2 system. The PDSC is simply the regular DSC cell enclosed in a pressure vessel. Measurements at elevated pressures are made by filling the pressure vessel with the compressed gas. In these measurements, not only the sample but the entire cell is subjected to the gas pressure. The PDSC is rated for use at pressures to about 70 atm. However, with low-pressure CO_2, it was found that the baseline was a bit noisy and had a slight curvature to it. These baseline characteristics became worse with pressure and at ca. 55 atm, the baseline had extensive noise and the curvature also became quite amplified. Fortunately, these characteristics were dominant only at temperatures to ca. 150°C beyond which, the temperature range of interest for the present application, the cell performed reasonably well. Baseline calibrations at temperatures to 250°C were first performed at CO_2 pressures of 13.6, 27.2, 40.8, and 54.4 atm, using two empty hermetically sealed pans with holes punched in the center of the lids. After baseline calibrations, the sample-side pan was replaced with one containing a PPO pellet and a hole punched in the center of the lid. The sample was heated to a temperature about 10°C above T_{g0}, the cell pressurized with CO_2 to 13.6 atm, kept at this temperature for 10 min, and then cooled to room temperature by placing ice packs on and around the cell. The sample was then scanned at 10 or 20°C min^{-1} to a temperature about 10°C above the new T_g. The CO_2 pressure was then increased to 27.2 atm and the new T_g determined as before. This procedure was repeated at 40.8 and 54.4 atm. The pressure was then decreased in steps of 13.6 atm and T_g measurements made again at 40.8, 27.2, and 13.6 atm. The two sets of measurements gave T_g's, at the corresponding pressures, to within ±0.4°C. It should be noted that before starting a scan at each pressure, the DSC was programmed with the baseline calibration parameters pertaining to that pressure.

A few measurements were also made at 34.0, 54.4, and 61.2 atm. For these, PPO was used in the powder form, a fresh sample was used at each pressure, and the baseline calibration parameters were obtained by interpolating or extrapolating the calibration parameters determined above. Also, for these measurements, the cell was first pressurized, then heated to about 10°C above the estimated T_g, and the polymer-gas system allowed to equilibrate for 10 min. The cell was then cooled back to room temperature and then scanned at 10°C min^{-1}, and the T_g determined from the second scan.

It should be noted that in all the measurements, care was taken to avoid cooling the cell to a temperature below the condensation temperature of the gas. Also, the pressure in the cell increased during the scan. For this reason, the pressure was always adjusted at ca. 10°C above T_g so that during the scan the pressure in the system, at the transition event, was almost the same as the nominal pressure.

RESULTS AND DISCUSSION

Some representative DSC outputs at various pressures are shown in Figure 1. The output signals are normalized to unit mass of PPO; however, they have been shifted vertically for the sake of clarity. Despite the rather higher noise level than usually observed in normal DSC scans, the glass transition step is well resolved. T_g was taken as the temperature at the midpoint of the step. The results on the change in T_g of PPO as a function of CO_2 pressure are given in Table I and shown in Figure 2. The results from the present work are shown by the hollow symbols; a line is drawn through the points to aid the eye. There is good agreement between the measurements made on the pellet and the powder samples.

The results of Hachisuka et al.[4] are shown in Figure 2 by the filled circles, and again a line is drawn through the points to aid the eye. There is a large disparity between the two sets of results. The present results show that there is only a slight decrease in T_g of PPO at pressures to 60 atm whereas the literature values show a very strong plasticization effect. Our results give a value of $-0.5°C\ atm^{-1}$ for dT_g/dp and those of Hachisuka et al. a value of $-3.8°C\ atm^{-1}$. For comparison, values of $-0.2°C\ atm^{-1}$ for polystyrene-CH_4 and $-0.9°C\ atm^{-1}$ for polystyrene-CO_2 and polystyrene-ethylene systems have been reported previously.[1,6,17] At higher gas pressures, an effect opposite to plasticization comes into play due to the hydrostatic pressure exerted by the gas. Thus, at higher CO_2 pressures, T_g of PPO is not expected to drop any more than what is already shown by our results in Figure 1 because any further decrease in T_g due to the elevated pressure would be offset by an increase in T_g due to the hydrostatic effect. This cancellation of the plasticization effect by the hydrostatic effect has been observed previously.[1,17] Thus, we do not anticipate to see a strong plasticization effect as reported by Hachisuka et al.

There is a significant difference in the way PPO was conditioned in the two experimental studies. Our approach has been to maintain the polymer-gas equilibrium over the temperature range of the scan, taking care to avoid any condensed phase of the gas.[9,17] The approach used by Hachisuka et al. was to seal PPO and an appropriate amount of dry

Table I. T_g Values for the PPO-CO_2 System at Various Gas-Pressures

p/atm	T_g/°C
0.0	216.0
13.6	211.4
27.2	203.6
34.0[a]	202.1
40.8	195.8
54.4	185.2
54.4[a]	193.0
61.2[a]	184.4

[a] Sample used in powder form; used as a pellet for the other measurements.

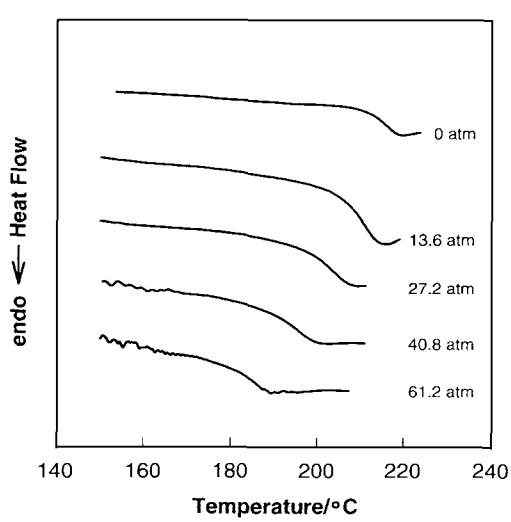

Figure 1. PDSC scans for PPO-CO_2 at various gas-pressures.

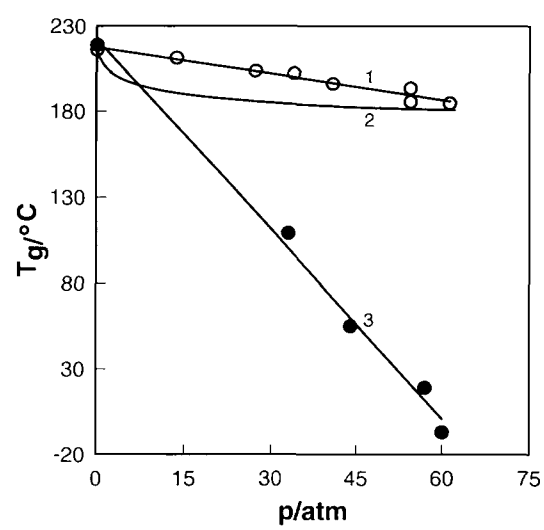

Figure 2. Change in T_g of PPO as a function of the gas pressure. ○—this work; ●—Hachisuka et al.[4] Curves 1 and 3 are drawn through the data points to aid the eye; curve 2 is calculated from eqs. (1)-(3).

ice in a DSC pan, equilibrate the system at 25°C, quench it to −60°C, and then scan it from −50°C. The pressure generated by CO_2 was calculated from an equation of state. However, at −50°C, the saturation vapor pressure of CO_2 is[26] 6.8 atm and, therefore, all their scans started with PPO in contact with liquid CO_2. The presence of a condensed phase complicates DSC measurements in that the DSC output becomes quite erratic. In Hachisuka et al.'s work, the DSC output showed a number of steps indicating that a true PPO-CO_2 equilibrium among various phases of CO_2 and between PPO and CO_2 was not established. For such outputs, the choice of a step as glass transition becomes somewhat subjective. Furthermore, the authors reported T_gs of 19 and −7°C at 57 and 60 atm, respectively, conditions under which CO_2 exists as a liquid.[26] Thus, it appears that the state of the system was not well defined in their study. From the information available in Hachisuka et al., it cannot be ascertained whether the transitions reported by them refer to PPO with much higher loadings of CO_2 than possible with CO_2 in the supercritical state.

Chow[27] proposed a relationship to account for the change in T_g of polymers due to sorbed vapors or liquids. Later on, this relationship was shown by Chiou et al.[2] to apply equally well to polymer-gas systems. Recently, a number of models[7,8] have been proposed to explain the plasticization effects of compressed gases and the rather complex phase behavior observed when T_g of the polymer is depressed to the critical temperature, T_c, of the compressed fluid. However, if $(T_{g0} - T_c)$ is large then Chow's simple model works as well as the more sophisticated recent models.[8,28] In the light of the large disparity between the two sets of measurements in Figure 2, our intent here is to show what the T_g-p profile for PPO-CO_2 would be and not to go into a detailed analysis of the results. For this purpose, we can use the simple model proposed by Chow. According to this model,

$$\ln(T_g/T_{g0}) = \beta[\theta \ln \theta + (1 - \theta)\ln(1 - \theta)] \quad (1)$$

$$\beta = \frac{zR}{M_p \Delta C_p} \quad (2)$$

$$\theta = \frac{M_p}{zM_d} \frac{\omega}{1 - \omega} \quad (3)$$

where M_p and M_d are the molar masses of the polymer repeat unit and the gas, respectively, R is the gas constant, ΔC_p is the heat capacity change associated with the glass transition of the pure polymer, ω is the gas solubility in the polymer, and z is the lattice coordination number that depends on the sizes of the gas molecule and the polymer repeat unit. The calculated T_gs using $\Delta C_p = 0.265$ J K^{-1} g^{-1} reported by Karasz et al.[29] and the gas solubilities by Chern et al.[18] are shown by curve 2 in Figure 2. Chiou et al.[2] found that for polymers with small repeat units, such as polystyrene and poly(methyl methacrylate), a good fit of experimental results was obtained using $z = 1$ whereas for polymers with larger repeat units, such as polycarbonate, $z = 2$ gave a good fit. For PPO, we used $z = 1$. The effect of using $z = 2$ is to shift downward the curve 2 in Figure 2 by about 10°C; the shape of the $T_g - p$ profile remains the same. It should be noted that the calculated values refer to the gas solubilities at 35°C whereas in the DSC experiments the gas content of the polymer decreases slightly during the scan. Accordingly, the agreement between experimental and calculated values improves as T_g decreases. Nevertheless, the calculated $T_g - p$ profile is similar to the one measured by us. We, therefore, conclude that CO_2 induces only a weak plasticization effect in PPO, in agreement with the theoretical predictions for high T_g polymers-CO_2 systems.[7,8]

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