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Retrograde Vitrification of Polymers with Compressed Fluid Diluents: Experimental Confirmation

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In a recent study[1] we predicted the depression of the glass transition temperature of polymers caused by dissolution of compressed fluids using lattice fluid theory[2–5] and the Gibbs–Di Marzio criterion,[6,7] which states that the mixture entropy is zero at the glass transition. Four fundamental types of T_g behavior were identified as a function of pressure. The predictions did not contradict any available T_g data in the literature[8–11] and extended the understanding of these systems to broader ranges in temperature and pressure. A new phenomenon was discovered, retrograde vitrification, whereby a polymer undergoes a liquid to glass transition with increasing temperature. The objective of this paper is to confirm this prediction of retrograde vitrification with experimental measurements of T_g (and likewise the glass transition pressure, P_g).

Figure 1 shows the T_g depression as a function of the solubility of the compressed fluid in the polymer for the PMMA–CO_2 system.[8,9] The predictions are in excellent agreement with the experimental data. The T_g is depressed from the pure polymer value of 105 °C due to the increased flexibility and free volume introduced by the diluent, CO_2. The corresponding behavior of T_g as a function of pressure is considerably more complex according to the model[1] (see Figure 2); for example, the slope changes sign. Consider an isobaric path at 30 atm beginning at 125 °C where the polymer is a liquid. As temperature and thermal energy decrease, the segmental motion of the polymer is reduced, leading to the expected glass transition, in this case at 75 °C. Upon further cooling, the glassy polymer becomes a liquid again, a phenomenon we call retrograde vitrification by analogy with retrograde condensation for nonpolymeric systems near the vapor–liquid critical points. This unusual result is caused by an increase in the solubility of the diluent in the polymer with a decrease in temperature.

We chose to study PMMA because of the large T_g depression caused by the high solubility of CO_2. In-situ measurements of a mechanical property, specifically, the creep compliance of PMMA films in equilibrium with a compressed CO_2 phase, have been used to determine the glass transition pressure (P_g) at various temperatures.[9,10] The creep compliance is well-suited for this objective, since it changes by orders of magnitude in the region of the glass transition,[12,13] and can be measured at constant pressure and temperature, without perturbing the CO_2 phase equilibrium. This latter constraint would not be satisfied by differential scanning calorimetry, since the CO_2 solubility in the polymer changes with temperature.

For each experiment, a 3 × 150 mil polymer strip 5.5 cm in length was suspended in a Jerguson sight gauge. Attached to the bottom of the polymer strip was a weight varying from 4 to 10 g. After the system was evacuated for 1 h, the polymer strip was equilibrated with CO_2 for an additional 1 h at a given temperature and pressure. During the equilibration step the polymer strip and weights were supported by a pan. Next the pan was lowered, subjecting the polymer to a constant stress for a period of 1 h. The creep compliance (strain divided by the stress) was determined at a constant time of 15 min for the data shown in Figures 3 and 4. A reference time of 1 min was chosen to begin the strain measurements in order to remove dilation and conditioning effects that would lead to erroneously high strain values. In addition, all stress values were corrected for the buoyancy effect based on the bulk density of CO_2. In Figure 3, experimental results are shown as a function of pressure for three isotherms. The creep compliance changes over 2 orders of magnitude and exhibits a characteristic sigmoidal shape between the glassy and rubbery plateaus for each temperature.[12,13] The glass transition was defined at the midpoint between the glassy and rubbery plateau regions.[13] As the temperature decreases from 75 to 45 °C the glass transition shifts to higher pressures. This is the normally expected behavior; i.e. the T_g decreases due to the increase in the solubility of CO_2, which results from the increase in pressure. Contrary to Figure 3, the pressure of the glass transition

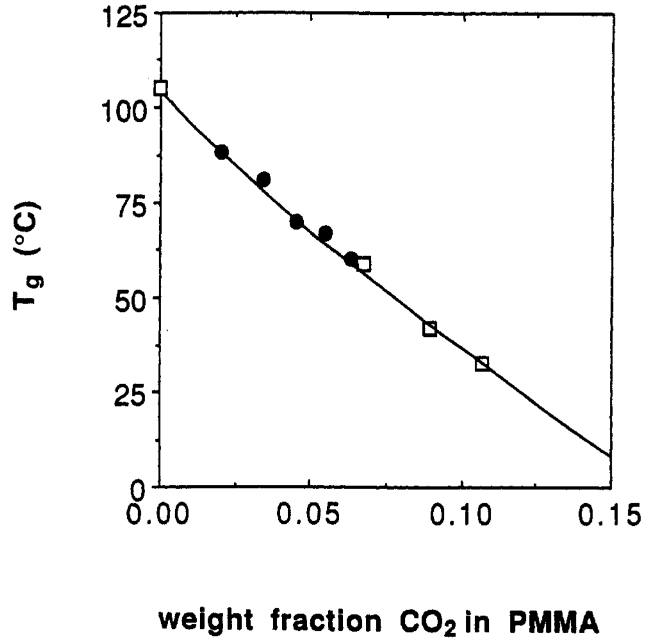

Figure 1. T_g of PMMA as a function of the solubility of CO_2 in the polymer: (●) Chiou et al.;[8] (□) Wissinger and Paulaitis;[9] (—) prediction.[1]

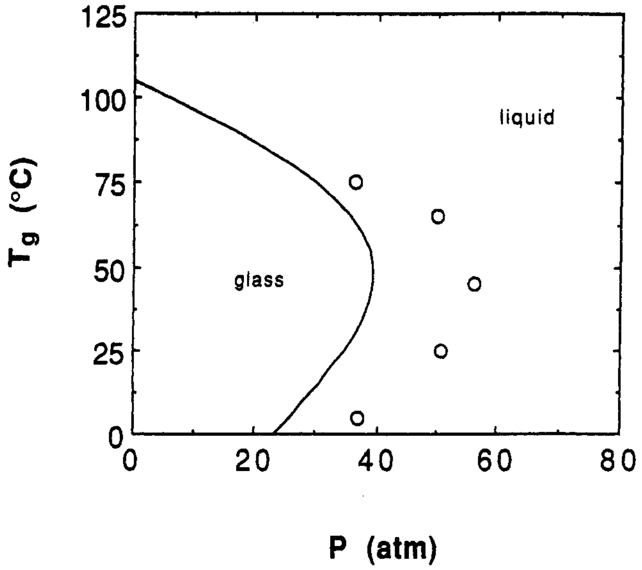

Figure 2. T_g of PMMA as a function of CO_2 pressure in the PMMA–CO_2 system: (—) prediction;[1] (○) this study.

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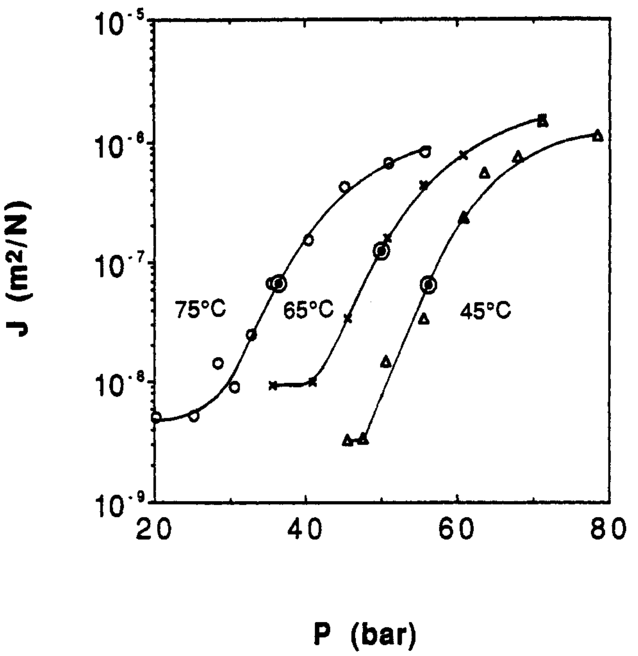

Figure 3. Creep compliance of PMMA equilibrated with CO_2 as a function of pressure: (⊚) glass transition.

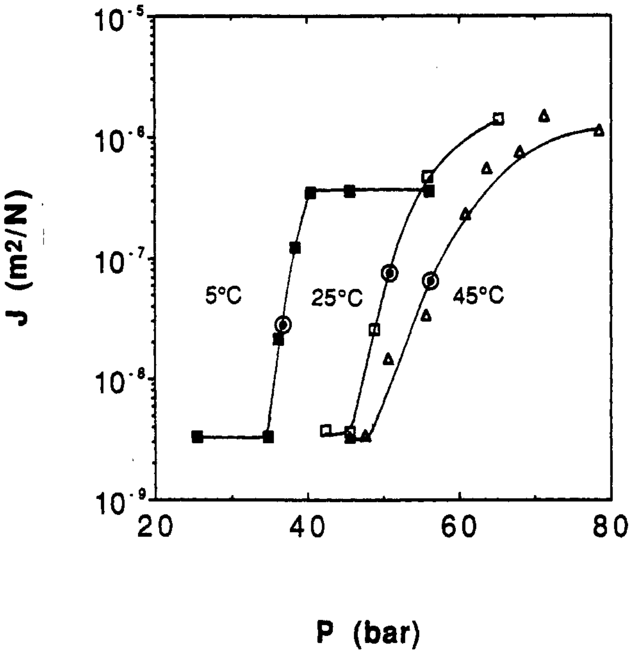

Figure 4. Creep compliance of PMMA equilibrated with CO_2 as a function of pressure in the retrograde vitrification region: (⊚) glass transition.

shifts to lower pressures with decreasing temperature from 45 to 5 °C as shown in Figure 4. Each isotherm has the same characteristic shape observed in Figure 3, and the plateau regions are well-defined. It is absolutely clear from the data that the trends are opposite in these two temperature regions. The experimental glass transition points (i.e., T_g and P_g) from Figures 3 and 4 are plotted in Figure 2. The characteristic shapes are the same for theory and experiment, although the glass transition pressures are underpredicted. The data clearly establish the existence of the previously predicted retrograde vitrification phenomenon. Two characteristic features are present in both theory and experiment. First, the slope of T_g versus P_g is positive at lower temperatures. Here a decrease in temperature causes a glass to liquid transition. Second, the P_g goes through a maximum at the boundary of the retrograde region.

As explained in more detail elsewhere[1] the retrograde behavior results from the combined effects of temperature and pressure on the solubility of a compressed fluid in a polymer. In the retrograde region, the solubility of the diluent becomes a strong function of temperature. Concisely stated, the increase in the diluent concentration with an isobaric temperature reduction overcomes the normal decrease in segmental motion. A corollary is that the pressure required to achieve the needed solubility for a glass to liquid transition decreases as the temperature decreases.

The prediction of the shape of the T_g versus pressure behavior is quite accurate, despite the difference in the P_g values. The PMMA–CO_2 interaction strength was correlated from independent sorption data of CO_2 in the polymer[14] at an arbitrarily chosen temperature of 32.7 °C. Most likely, the T_g data may be predicted with greater accuracy than in Figure 2, by adjusting the interaction strength which is somewhat temperature dependent. This will be addressed in a forthcoming paper.

It should be emphasized that it was a thermodynamic model of the glass transition that predicted the existence of the retrograde vitrification phenomenon. This model does not preclude the kinetic aspects of the glass transition. Indeed, a kinetic aspect is addressed by the Gibbs–Di Marzio criterion, albeit indirectly, by using the experimental T_g of the pure polymer to correlate a flex energy. The unique feature of this thermodynamic model is that it addresses equation of state properties, phase equilibrium, and the glass transition simultaneously using only fundamental thermodynamic relationships and the Gibbs–Di Marzio criterion of the glass transition.[1] No correlations or empirical relationships involving the T_g of the polymer–diluent mixture were employed. By successfully predicting the retrograde vitrification phenomenon, the thermodynamic model has passed one of the most rigorous tests of a glass transition model to date.

The existence of the retrograde vitrification phenomenon creates exciting opportunities in applications such as polymer processing and polymeric materials production. Polymers may be plasticized under much milder conditions of temperature than presently believed, leading to viscosity reduction and higher mass-transfer rates. These mild conditions are especially important for thermally labile substances, and the nontoxic nature of CO_2 desirable. After processing, devolatilization of CO_2 is much faster and more complete than for conventional liquid solvents.

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