Glass transition behavior of poly(methyl methacrylate) in compressed carbon dioxide revisited – New perspectives

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1. Introduction

Poly(methyl methacrylate) is historically one of the model polymers that has been investigated for its behavior in supercritical fluids and is known to display a retrograde T_g behavior in the presence of carbon dioxide[1]. The retrograde glass transition behavior exhibited by PMMA in compressed CO_2 has been studied using high-pressure volumetric[2], thermal[3-5], sorption[3], creep compliance[6,7], chromatographic[8], quartz crystal resonator[9], and spectroscopic[10] measurement techniques. In a recent publication[11], we remarked on the wide variability of the data reported in the literature, and as illustrated further in Figure 1, we specifically noted the absence of retrograde behavior in some publications[2,8]. This talk will present recent results of a study that was undertaken to bring some clarity to potential causes of this variability in the literature. The polymer molecular weight, whether the thermal transition is approached by increasing temperature or pressure, and the heating or the pressurization rate during assessment all play a role in shifting the observed depressed glass transition, yet such information is not provided in the literature in any systematic manner.

2. Materials and Methods

The thermophysical behavior of two samples of PMMA with different molecular weights were assessed using High-Pressure Torsional Braid Analysis (HP-TBA). The properties are provided below:

Sample 1: M_w = 89,700; PDI = 2.02; T_g(°C) = 109
Sample 2: M_w = 457,000; PDI = 1.51; T_g (°C) = 124

HP-TBA is a recent technique developed in our laboratory. Briefly, it consists of a polymer impregnated fiber-glass braid attached to an inertial mass which is housed in a high-pressure chamber. An externally positioned electromagnet is used to induce oscillations of the inertial mass. The decay of the oscillations, which follows a damped sine wave, is monitored and characterized. The frequency of oscillations and the change in amplitude are related to the rigidity and mechanical loss of the polymer. The technique allows the assessment of the relative rigidity and mechanical damping as a function of temperature at a given pressure, or as a function of pressure at a given temperature.

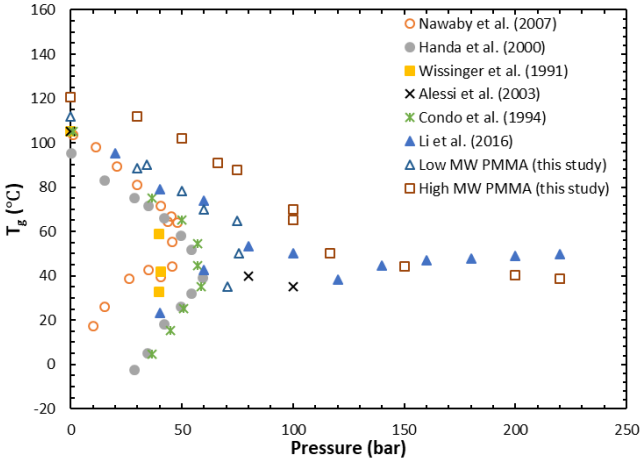

Figure 1. Glass transition behavior of PMMA-CO_2 systems. Data was read from graphs when not provided. Graph includes recent results from the present study.

The measurements were conducted in two different modes, one involving increasing temperature at constant pressure and the other involving increasing pressure at constant temperature. Constant-pressure HP-TBA temperature scans were conducted with both the Low and High MW PMMA samples in carbon dioxide at 30, 50, 75, 100, and 200 bar. Two additonal scans at higher pressures of 150 and 220 bar were conducted with the High MW PMMA sample. Constant-temperature pressure scans were conducted with both the Low and High MW PMMA sample starting from 20 bar until a transition was observed in the damping peak in real-time.

3. Results and discussion

The Low MW PMMA system displays classic retrograde behavior which was assessed by HP-TBA scans by holding temperature constant and increasing pressure and by holding pressure constant and increasing temperature. High MW PMMA does not display classic retrograde behavior; instead, the system displays a plateau-like region at higher pressures. The results from this study are shown in Fig. 2.

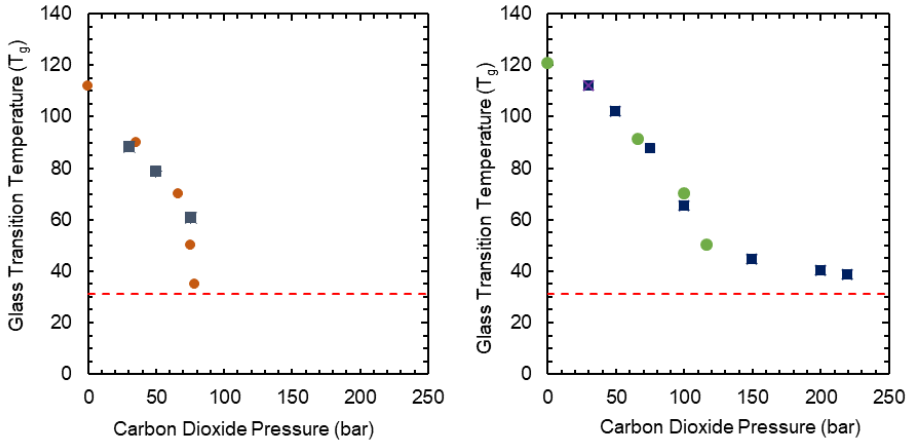

Figure 2. Glass transition temperatures of **(Left)** Low MW and **(Right)** High MW PMMA as a function if carbon dioxide pressure as determined by the HP-TBA scans. Constant-pressure temperature scan data is presented by squares (■) and constant-temperature pressure scan data is represented by circles (•). Red dashed line (-------) represents the region below the critical temperature excluded from exploration.

4. Conclusions

This investigation into the glass transition behavior of PMMA has shown that the measurement of the depression in the thermal behavior of a polymer material in the presence of dense and/or compressed fluids is nontrivial. Among the factors that may shift the observed T_g are (1) the molecular weight of their sample, (2) the diffusional time scales needed to achieve equilibrium saturation, or (3) the effect of heating and/or pressurization rates.

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