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Environmental Effects on the Structural Recovery Responses of an Epoxy Resin after Carbon Dioxide Pressure Jumps: Intrinsic Isopiestics, Asymmetry of Approach, and Memory Effect

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CO$_2$ pressure vessel for Aging/recovery experiments

ABSTRACT: Novel volume measurements on an epoxy resin subjected to carbon dioxide pressure jumps (PCO$_2$) are used to investigate the structural recovery of glassy polymers after plasticizer jumps. Previously, we had investigated an epoxy resin after plasticizer concentration jumps using relative humidity (RH) and CO$_2$ and evidenced structural recovery and physical aging responses.[1−6] In that work, two things were demonstrated: (a) qualitatively, the physical aging (after CO$_2$ and RH jumps) and structural recovery (after RH jumps) responses are similar to those observed after temperature jumps, and (b) quantitatively, the responses are not the same and, moreover, they exhibit anomalous behaviors. The purpose of the present work is to further investigate the nature of the anomalous behaviors by investigating the structural recovery response of the same epoxy when subjected to PCO$_2$-jump conditions. We provide new data using CO$_2$-jumps and show intrinsic isopiestics, asymmetry of approach, and memory effect and then compare these with similar data for temperature-jump histories. We show that the extended Kovacs−Aklonis−Hutchinson−Ramos does not adequately describe the structural recovery of the epoxy resin after PCO$_2$-jumps. This is consistent with what was previously observed in our laboratory on modeling the structural recovery data of the epoxy resin subsequent to relative humidity changes. Finally, we show a further anomaly in that the volume in CO$_2$-jump experiments seems to evolve toward a different final state[23] than it does in temperature-jump experiments, suggestive of a metastable glassy state that differs from that of the temperature-jump created glass.

1. INTRODUCTION

There have been extensive studies of the impact of structural recovery and physical aging on the mechanical and thermodynamic properties of glassy polymers.[7−13] Polymeric glass-forming materials are in a nonequilibrium thermodynamic state after cooling from above the glass transition temperature T_g to below it. Therefore, as depicted in Figure 1, when one performs a temperature jump from above T_g to an aging temperature, T_1 (below T_g), the material evolves toward the equilibrium state. Structural recovery and physical aging affect many properties of glass-forming materials, such as the mechanical, dielectric, and optical properties. Therefore, the long-term performance of the glass forming materials is dependent on the previous thermal histories of the glass.[8,14,15]

The long-term stability of polymeric glasses is also affected by the plasticizer content in the material because an increase in the plasticizer content depresses the glass transition temperature of the material.[16−29] While the impact of temperature changes on the viscoelastic and structural recovery properties of glass-forming materials is well documented in the literature,[7−13] there are few works that deal with the plasticization effect on the volume change of glassy polymers subjected to small molecule plasticizers.[1−6,22,30,31] Fleming and Koros[22] performed volume, sorption, and desorption measurements of polymers subjected to CO$_2$ molecules under isothermal conditions. The results showed large hysteresis effects for the sorption/desorption and volume dilatation/consolidation of bisphenol A−polycarbonate exposed to CO$_2$ pressures as high as 6 MPa.[22]

There has also been some work on plasticization effects of CO$_2$ on the viscoelastic behavior of polymers.[19,24,26] In these works, the mechanical properties of polymers were investigated under carbon dioxide pressure. For example, creep measurements of polymers subjected to supercritical CO$_2$ showed a retrograde vitrification phenomenon.[19,26] The retrograde vitrification behavior was also observed in calorimetric measurements of PMMA subsequent to carbon dioxide pressure changes.[29] Recently, we reported on results from creep measurements of an epoxy resin plasticized by CO$_2$,[3] and we examined the physical aging response. Also, the time−concentration superposition and the time−aging time superposition were successfully applied to the data where the PCO$_2$-jump experiments were found to be qualitatively similar to the T-jump experiments, though the responses were quantitatively different.[3] Similar results reported from our laboratory showed physical aging[4] and structural recovery[5] responses of the epoxy resin subsequent to relative humidity changes. That work demonstrated that structural recovery in the material following relative humidity jumps manifests itself in terms of intrinsic isopiestic (constant relative humidity), memory effect, and asymmetry of approach in a fashion that was qualitatively similar to the temperature-jump experiments performed by Kovacs.[7] However, the kinetics of the volume measurements under RH-jump conditions was quantitatively different from that under T-jump conditions.

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Furthermore, we had found that volume change measurements in a CO_2-prepared glass showed an anomalous high stability in spite of high volume, i.e., upon heating the material retained its high volume until ∼8 °C above the nominal glass transition temperature.[30,31]

The objective here is to further explore the impact of plasticization effects on the structural recovery response for an epoxy resin after carbon dioxide pressure jumps. We observed the signatures of structural recovery, namely the intrinsic isopiestic, asymmetry of approach, and memory effect similar to humidity and temperature jump experiments. Moreover, PCO_2-jump experiments also showed the anomalous differences between temperature and concentration glasses that were first evidenced in humidity-jump experiments. Further, we also provide evidence for the existence of a new glassy state in the PCO_2-jump formed glasses that was only suggested in the prior work[30,31] and which need to be further investigated. In addition, we use an extended form of the TNM-KAHR model[32−38] to describe the structural recovery responses of the epoxy/CO_2 system for the intrinsic isopiestic, asymmetry of approach, and memory effect; the results are discussed, and it is suggested that present results support the contention that the TNM-KAHR models are inadequate for the full description of glassy behavior and new models are required.

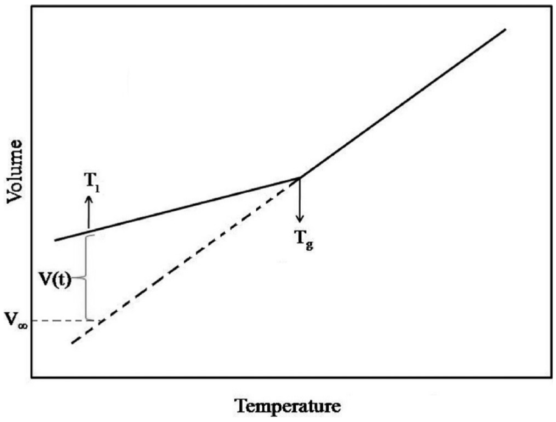

Figure 1. Schematic representation of specific volume versus temperature during cooling of a glass-forming liquid. The glass transition temperature is defined as the intersection between the liquid and the glassy lines.

2. EXPERIMENTAL METHODS

2.1. CO_2 Pressure Chamber. As described in our previous work,[3] a CO_2 pressure system was built to perform creep measurements under different CO_2 pressures. Both the temperature and the carbon dioxide pressure are controlled independently. Figure 2 shows a schematic of the experimental apparatus used in this work. The core of this apparatus is the pressure vessel into which the sample is placed. The vessel was designed and built at the National Institute of Standards and Technology for measuring the swelling of rubbers and has undergone extensive modification in our laboratory for physical aging and structural recovery measurements under carbon dioxide pressure. The vessel is made from 304 stainless steel and designed for a maximum working pressure of 8 MPa. The vessel incorporates two view ports 180° apart for viewing and backlighting purposes (see Figure 3). The cylindrical vessel has 2.25 L of inner volume. To maintain a constant temperature, the vessel was placed in a rectangular bath and completely immersed in silicone oil. The bath is heated with a 750 W Fisher immersion heater and stirred to maintain a uniform temperature using a 49 W Cole-Parmer Stir-Pak mixer. The temperature of the oil bath was controlled by an Omega controller-type (CNi 1622) to a stability of ±0.1 °C. For the delivery of the gas, 6.35 mm stainless steel tubing with a 110 MPa pressure rating is used. The pressure of the CO_2 was monitored using a pressure transducer with an absolute pressure range of 0−10.5 MPa and the pressure controlled by two Omega electrovalves type (SV128) and held stable to within 0.05 MPa. The pressure, temperature, and the electrovalves were controlled and monitored by a PC using a data acquisition board from National Instruments (Austin, TX). This apparatus was used to perform creep measurements under CO_2 pressure in our previous work[3] where a motor, controlled by the DAQ board, was used to load and unload the sample (Figure 2). However, in the present work there is no weight applied to the sample during structural recovery except the

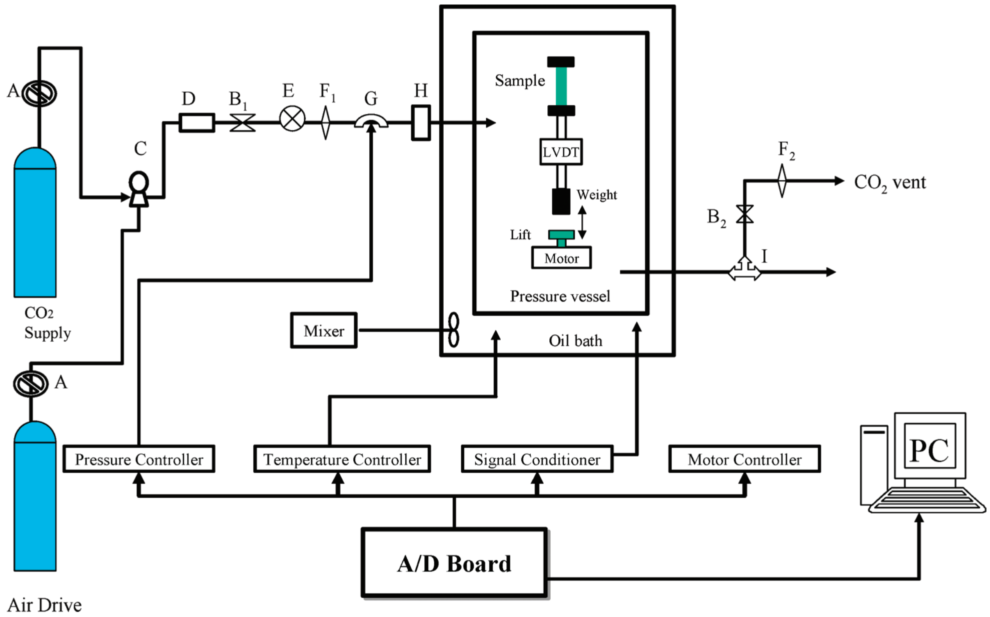

Figure 2. Creep apparatus that was built in our laboratory to perform experiments under different CO_2 pressure and temperature conditions.

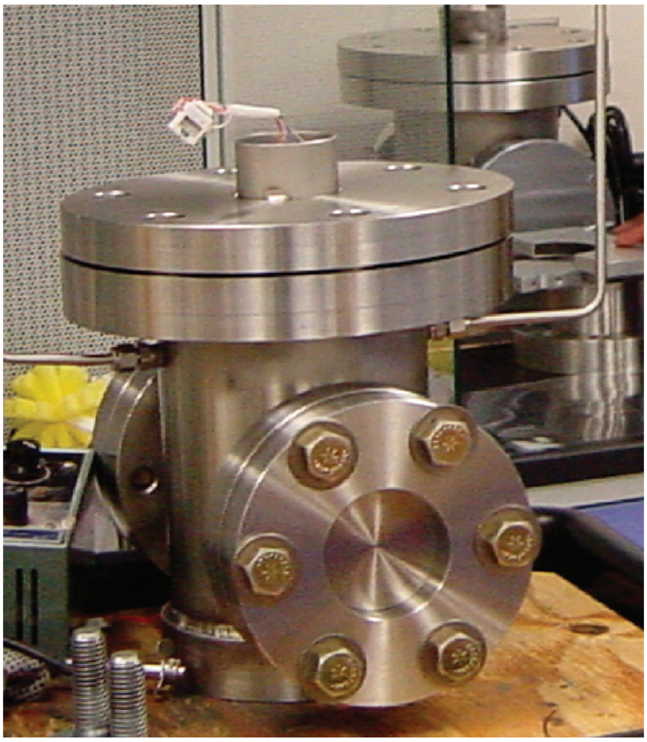

Figure 3. Pressure vessel used to perform the experiments under CO_2 pressure.

weight of the LVDT core, which is negligible. This is discussed further subsequently in section 2.5.

2.2. Operation. Prior to any sorption run, the system was evacuated using a vacuum pump for about 30 min, until the pressure reading records a pressure below atmospheric pressure. In a typical run, the valves "I", "B", and "F" on the outlet side of the vessel are closed. The pressure regulator "A" on the gas cylinder is then opened and set to the maximum desired pressure. A LabVIEW program was written to control pressure and LVDT signal during the pressurization, recovery, and depressurization steps.

For the pressurization step, the CO_2 pressure is controlled on the inlet side electronically by the automatic valve "B_1" simultaneously with a needle valve "F" for fine control of the CO_2 flow rate. The pressurization rate for all the experiments was set to 0.0016 MPa/s. In the same manner, for the depressurization step the CO_2 pressure is controlled on the outlet side by using the valves "B_2" and the needle valve "F". During the experiments under a constant pressure, the PCO_2 is monitored and controlled using automatic valves "B_1" and "B_2" in the inlet and outlet sides. The CO_2 pressure system can operate under a maximum pressure of 8 MPa. The CO_2 cylinder can deliver a maximum CO_2 pressure of 6 MPa. For pressures greater than this, a booster pump with a maximum pressure capability of 15.5 MPa can be used.

It is important to note that in the case of polymers a high depressurization rate would foam the sample. In the present experiments, foaming of the sample was avoided by ensuring that the pressurization/depressurization rate was maintained constant at 0.0016 MPa/s. The lid of the vessel is fitted with an electrical feed-through to allow connections to the electronics inside the vessel in order that the temperature and length change of the sample can be measured during the experiments. The temperature, measured inside the vessel close to the sample, was stable to within ±0.1 °C as measured by a type K thermocouple.

2.3. Signal Conditioning and Data Acquisition. The volume change of the sample is measured by monitoring the changes in the length of the sample upon carbon dioxide sorption and desorption at constant temperature. The grip displacement is measured with a linear variable differential transformer (LVDT) (HR 100, Lucas Schaevitz, Inc.) connected to a microprocessor-based signal conditioner (ATA/1000, Schaevitz). A National Instruments Data Acquisition board installed in the PC receives the displacement voltages from the LVDT conditioners. The resolution of the LVDT and associated electronics in the experimental setup is 2 μm, corresponding to a strain of <0.0001 on a typical sample length of 30 mm.

2.4. Model Epoxy Network. The samples used in these experiments were thin films of an epoxy-terminated diglycidyl ether of bisphenol A (DGEBA, DER332, Dow Chemical) cured with an amine-terminated poly(propylene oxide) (T403, Huntsman). To prepare the thin films, the resin was preheated to 55 °C for 2 h to melt any crystals. A stoichiometric mixture of the epoxy and amine was then continuously stirred and degassed for 1 h at room temperature. The degassed mixture was cast onto smooth brass molds and fully cured at 100 °C between two brass plates under a pressure of 2 atm for 24 h. Pressure is applied to prevent air bubbles from forming due to residual air and moisture in the sample. After 24 h, the heat supply was turned off and the sample was slowly cooled to 23 °C overnight. The T_g of the cured sample determined by differential scanning calorimetry (DSC) measured at a heating rate of 10 °C/min after cooling to ambient temperature from 100 °C at a cooling rate of 10 °C/min was ∼72 °C. The T_g remained stable even after the sample had been subjected to many cycles of sorption and desorption of the carbon dioxide. However, in the case of RH jumps,[4] the T_g stabilized after many sorption−desorption cycles. This could probably be due to hygrothermally induced changes in the network that saturate over relatively short times.

The thickness of the samples used for the current experiments are in the range of 50−70 μm with a length of ∼4 cm. Assuming that the CO_2 has a diffusion coefficient in the epoxy similar to that of water (it should be higher) in the epoxy, the desorption times for the CO_2 at the temperature and pressure conditions of interest are expected to be less than 2 min.[2,5] Also, we note that the glass transition behavior of the epoxy in CO_2 has been previously examined in some detail,[3] and the conditions of the experiments are such that they are carried out in the vicinity of the glass transition temperature in all cases, allowing one to make the analogy between CO_2 pressure jumps and temperature jumps. One issue that we see below is that the slopes of the sample volume vs CO_2 pressure do not show large changes upon increasing pressure. This leads to some uncertainty as to the actual glass transition pressure but does not change the actual framework of the experiments.

2.5. Volume Measurements. The volume change of the epoxy resin was determined by measuring the length change of the sample using a linear variable differential transformer (LVDT). Hence, the volume change is calculated by assuming that the length changes in all dimensions are isotropic for thin films.[22] During the experiments, the sample was subjected to a small tensile stress (∼0.07 MPa) due to the LVDT's core. Furthermore, the sample was annealed above the glass transition (i.e., at high temperature or at high PCO_2 for a time between 1 and 2 h) such that the material reaches the equilibrium or the limiting rubbery plateau. The PCO_2 or the temperature was then lowered to the desired value to perform the structural recovery measurements. Hence, we can neglect the creep of the sample due to the small weight of the LVDT's core. Measurements of the volume changes performed under different weights of the LVDT's assembly indicated that there was a negligible effect of the tensile stresses during structural recovery experiments [this work and ref 4]. It is important to note that the material reaches the limiting plateau. If the material does not reach the limiting plateau, creep during the first pressurization step leads to errors in the apparent volume change. After this cycle, the results are reproducible.

2.6. Structural Recovery Experiments. The structural recovery experiments with the epoxy films were performed in a similar manner to those reported by Kovacs after temperature jumps.[7] Here, we performed isothermal experiments after jumps in carbon dioxide pressure from above to below the glass transition CO_2 pressure (PCO_2). In addition, isobaric experiments after T-jumps from above to below T_g were performed. These T-jump experiments were performed in an oven rather than the pressure vessel in order to have a cooling rate equivalent to the depressurization rate; i.e., the conditions were chosen to keep the cooling rate and depressurization rate approximately the same, and the thermal mass of the pressure vessel was simply too great for to perform even the relatively slow T-jump experiments that would correspond to the depressurization rates. Consequently, the T-jump experiments were performed at essentially zero PCO_2.

2.6.1. Determination of the Glass Transition Carbon Dioxide Pressure PCO_{2g}. The glass transition PCO_{2g} of the epoxy resin was determined by performing an isothermal ramp in PCO_2 at different temperatures from higher to lower CO_2 concentration. The sample was first annealed isothermally at 3.9 MPa (above the nominal T_g for that CO_2 pressure and the temperatures examined here) for 1 h to erase the thermomechanical history. The temperatures at which the experiments were performed were below the glass transition temperature of the unplascized epoxy ($T_g = 72$ °C). The PCO_2 was then lowered to 0 MPa at a rate of 0.0016 MPa/s isothermally.

2.6.2. Intrinsic Isopiestics. The intrinsic isopiestic experiment is the volume measurement after a plasticizer concentration (PCO_2 or humidity) jump from above to below the glass transition concentration. This is similar to Kovac's intrinsic isotherm experiment under isobaric conditions performed after a jump in temperature from above T_g to below it.[7] The experiments were performed under isothermal conditions by increasing the PCO_2 from 0 to 3.9 MPa. The sample was then equilibrated for 1 h to erase previous history. Finally, the PCO_2 was ramped to different PCO_2 below the P_gCO_2. For all experiments, we report the time abscissa as $t - t_i$, similar to the data presentation of Kovacs,[7] and which is the time from the end of the PCO_2 ramp.

2.6.3. Asymmetry of Approach. In the isothermal asymmetry of approach experiment, the epoxy film was first equilibrated at an initial carbon dioxide pressure PCO_2 and then PCO_2 down- and PCO_2 up-jumps, of the same magnitude, were performed to the same final PCO_2. For the PCO_2 up-jump experiment at 62 °C, the sample was first annealed for 1 h at 3.9 MPa, and then the CO_2 pressure was lowered to 0.8 MPa where the sample was equilibrated for 264 h. The PCO_2 was then increased to 1.6 MPa to measure the volume change of the sample during structural recovery at this pressure. In the PCO_2 down-jump experiments, the sample was equilibrated for 1 h at 3.9 MPa to erase the previous history. The PCO_2 was then ramped to 2.4 MPa where the sample was equilibrated for 6 h, and then the CO_2 pressure was reduced to 1.6 MPa to perform the structural recovery measurements.

In the same manner, the asymmetry of approach experiments at 65 °C was performed at 1.4 MPa. In the PCO_2 down-jump experiments, the sample was first equilibrated at 2.1 MPa for 3 h and then the CO_2 pressure was lowered to 1.4 MPa. The PCO_2 up-jump experiment was performed after a jump from 0.7 to 1.4 MPa; the time to reach equilibrium at 0.7 MPa and 65 °C was 165 h. For all experiments, we report the time abscissa as $t - t_i$, similar to the data presentation of Kovacs,[7] and which is the time from the end of the PCO_2 ramp.

2.6.4. Memory Effects. The memory experiments at 62 °C were performed in two-step experiments (isothermal PCO_2 down- and up-jump experiments). The sample was equilibrated at 3.9 MPa for 1 h followed by PCO_2 jumps to 0.35, 0.75, or 1.2 MPa. In the first step, the sample was aged for 1.5 h where the sample partially recovered and did not reach equilibrium. Increasing the PCO_2 to 1.7 MPa performed the second step in these structural recovery measurements. For the experiments at 65 °C, the PCO_2 down-jump experiments were performed at $PCO_2\,(1) =$ 0.75 and 1 MPa where partial recovery occurred for 1 h after down-jumps from 3.6 MPa. The second step experiments were performed at 1.6 MPa after PCO_2 up-jumps from $PCO_2\,(1)$. For all experiments, we report the time abscissa as $t - t_i$, similar to the data presentation of Kovacs,[7] and which is the time from the end of the PCO_2 ramp. In this case it is the time from the end of the second "step" or ramp in pressure.

2.6.5. Comparison between the Structural Recovery Responses after PCO_2-Jump and T-Jump. The kinetics of the structural recovery response of the epoxy resin after T-jump was compared to that after a PCO_2-jump to the same final conditions. The final conditions of the glass are the temperature and CO_2 pressure. The isothermal structural recovery experiment after a PCO_2 down-jump was performed at 62 °C and 0 MPa after PCO_2-jump from 3.9 to 0 MPa, whereas the isobaric structural recovery experiment was performed at 62 °C and 0 MPa after a T-jump from 85 °C. For all experiments, we report the time abscissa as $t - t_i$, similar to the data presentation of Kovacs,[7] and which is the time from the end of the PCO_2 ramp in the case of the pressure-jump experiments and from the end of the temperature ramp in the T-jump experiments.

3. MODELING OF THE STRUCTURAL RECOVERY RESPONSES: THE TNM-KAHR MODEL

The TNM-KAHR[32−38] model was developed to describe the structural recovery response of glass-forming liquids subjected to temperature changes. The departure from equilibrium is defined as

$$\delta(t) = \frac{V(t) - V(\infty)}{V(\infty)} \tag{1}$$

$V(t)$ and $V(\infty)$ are the instantaneous volume and the volume at equilibrium, respectively. According to the KAHR model, the total departure from equilibrium δ_i is recovered according to the following equation:

$$-\frac{d\delta_i}{dt} = \Delta\alpha_i q + \frac{\delta_i}{\tau_i} \tag{2}$$

$q = dT/dt$ is the cooling or heating rate, $\Delta\alpha = \alpha_l - \alpha_g$ is the difference between the liquid, α_l, and glassy, α_g, thermal expansion coefficients, and τ_i is the instantaneous retardation time. The nonlinearity of the KAHR model is incorporated by assuming that the retardation times are dependent on temperature, T, and structure, δ:

$$\begin{aligned}\tau_i(T,\delta) &= \tau_{i,\mathrm{r}}\left(\exp(-\theta(T - T_\mathrm{r}))\exp\left(-(1-x)\frac{\theta\delta}{\Delta\alpha}\right)\right)\\ &\equiv \tau_{i,\mathrm{r}} a_T a_\delta\end{aligned} \tag{3}$$

where τ_{ir} is the retardation time in equilibrium at a reference temperature T_r. The shift factors a_T and a_δ characterize the dependence of the retardation times on temperature at equilibrium (or fixed δ) and on the structure δ at fixed T:

$$a_T = \frac{\tau_i(T,0)}{\tau_i(T_\mathrm{r},0)} = \exp(-\theta(T - T_\mathrm{r})) \tag{4a}$$

$$a_\delta = \frac{\tau_i(T,\delta)}{\tau_i(T,0)}\exp\left(-(1-x)\frac{\theta\delta}{\Delta\alpha}\right) \tag{4b}$$

where θ is a parameter related to the activation energy and x is a parameter that defines the degree of nonlinearity (i.e., the dependence of the retardation times on the temperature and structure); $x = 0$ implies structure dependence whereas $x = 1$ indicates a pure temperature dependence. In the KAHR model formulas, the departure from equilibrium is presented in reduced

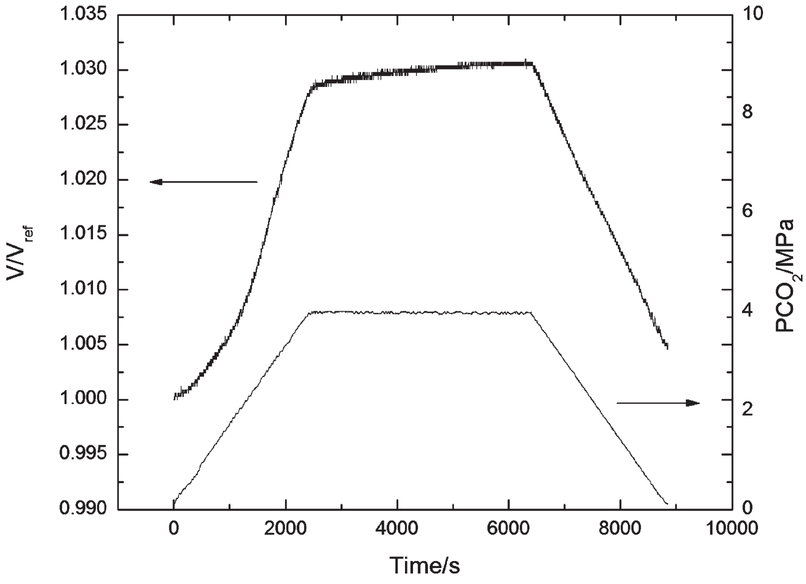

Figure 4. Volume of the epoxy resin at 62 °C as a function of time during the pressurization, annealing, and depressurizations steps. The pressure history during the experiment is also shown in the figure.

time (u) by applying the Boltzmann superposition (in linear viscoelasticity):

$$\delta(u) = \Delta\alpha_T \int_0^u \exp\left(-\left(\frac{u-u'}{\tau_0}\right)^\beta\right) \frac{dT}{du'}\, du' \qquad (5a)$$

The nonexponential nature of the relaxation behavior observed in glass-forming liquids is accounted for by introducing the Kohlrausch–Williams–Watts (KWW)[39,40] function in eq 5a, which was originally proposed by Moynihan.[36] The reduced time u is related to the shift factors:

$$u = \int_0^t \frac{d\xi}{a_T a_\delta} \qquad (5b)$$

The KAHR model was previously extended in our laboratory[4] to describe the structural recovery responses of the epoxy resin subsequent to relative humidity changes. We follow here the same methodology presented in that work[4] to represent the structural recovery responses of the epoxy resin after carbon dioxide pressure jumps.

4. RESULTS

4.1. Volume Change during Isothermal Carbon Dioxide Pressure Ramps. We present results for the volume measurements of the epoxy resin after isothermal carbon dioxide pressure changes during pressurization, annealing, and depressurization steps. Figure 4 shows the volume change at 62 °C of the epoxy sample as a function of time during the pressurization, annealing, and depressurization steps. The pressurization and depressurization rates were well controlled at 0.1 MPa/min. Figure 4 also shows the carbon dioxide pressure profile during these steps. It is seen in the figure that the volume change of the sample follows the PCO$_2$ histories. We note here that the results shown in the figure are based on relative measurements of the volume (i.e., the length change of the sample), which are slightly different from dilatometric volume measurements performed under isobaric[7,12,13] and isothermal[41−43] conditions.

Figure 5a,b shows the isothermal volume change at 62 and 65 °C of the epoxy sample as a function of carbon dioxide pressure during the depressurization ramp. In these figures, the volume change is normalized to its initial value at equilibrium where the CO$_2$ pressure reaches a maximum during the annealing step (i.e., 3.9 and 3.6 MPa for the experiment at 62 and 65 °C, respectively). Figure 5a,b shows that the epoxy/CO$_2$ system exhibits a glass transition in carbon dioxide pressure under isothermal conditions. This is similar to that observed in temperature and relative humidity experiments.[4] However, the observed PCO$_2$ glass transition appears weaker than a normal temperature glass transition, and this is perhaps due to the antagonistic effects of CO$_2$ concentration and the hydrostatic pressure. This weak transition is similar to that observed by Colucci et al. in isochoric experiments.[41] At 62 °C, the sample has a PCO$_2$ glass transition of 2.85 MPa, whereas the PCO$_{2g}$ at 65 °C is 2.25 MPa. Figure 5a,b also shows the difference between the coefficient of concentration expansion, $\Delta\chi$PCO$_2$, in the rubbery $\chi_{(l)}$ and the glassy state $\chi_{(g)}$ of the epoxy sample at 62 and 65 °C. The values of PCO$_{2g}$ and χPCO$_2$ are listed in Table 1.

It is worth noting that one assumption we use in our experiments is that CO$_2$ pressure is directly related to the volume or mass uptake of the CO$_2$ in the sample. As discussed previously,[3] this is an approximation, but it would be extremely difficult to measure the sample concentration and control the CO$_2$ pressure to keep constant concentration in the sample. Hence, we apply effectively a constant chemical potential surrounding the sample.[3] We think that this approximation is reasonable and not the cause of the observed differences in behavior relative to temperature-jump behavior reported below.

4.2. Intrinsic Isopiestics. Figure 6a shows the results from the intrinsic isopiestic experiments for the epoxy resin at 62 °C. The results for the intrinsic isopiestic experiments at 65 °C are shown in Figure 6b. The isothermal volume measurements at 62 and 65 °C indicate that the time to reach the equilibrium state increases with increasing carbon dioxide pressure, and the magnitude of departure from equilibrium increases with increasing the magnitude of the PCO$_2$-jump. These results are similar to

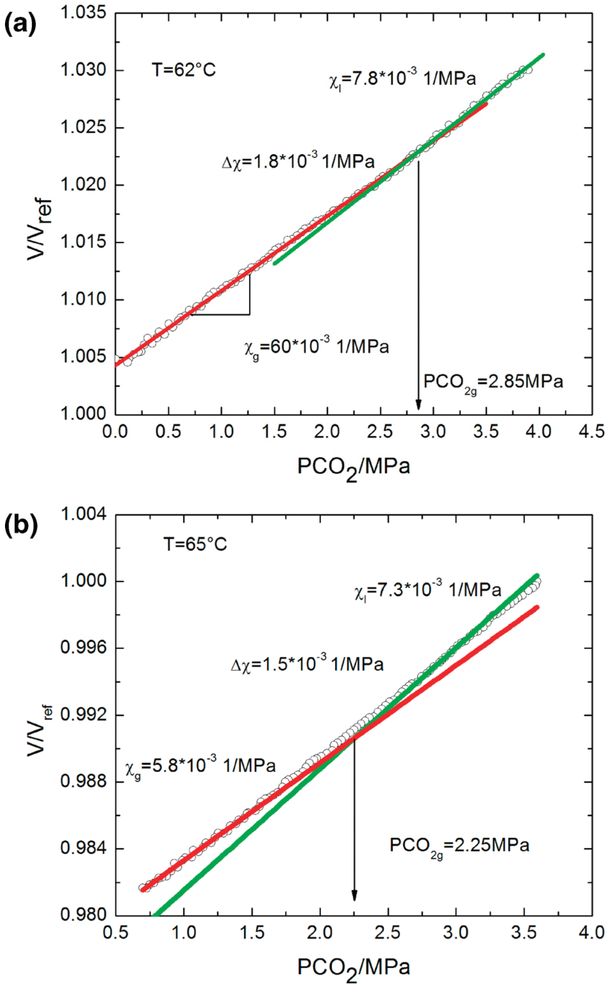

Figure 5. Volume versus PCO_2 at (a) 62 °C and (b) 65 °C for the epoxy resin during the depressurization step. Parts a and b confirm that the epoxy/CO_2 system shows a glass transition in CO_2 concentration.

Table 1

	62 °C	65 °C
PCO_{2g}/MPa	2.85	2.25
$\chi_{PCO_2(l)}$ (1/MPa)	7.8×10^{-3}	7.3×10^{-3}
$\chi_{PCO_2(g)}$ (1/MPa)	6×10^{-3}	5.8×10^{-3}
$\Delta\chi_{PCO_2}$ (1/MPa)	1.8×10^{-3}	1.5×10^{-3}

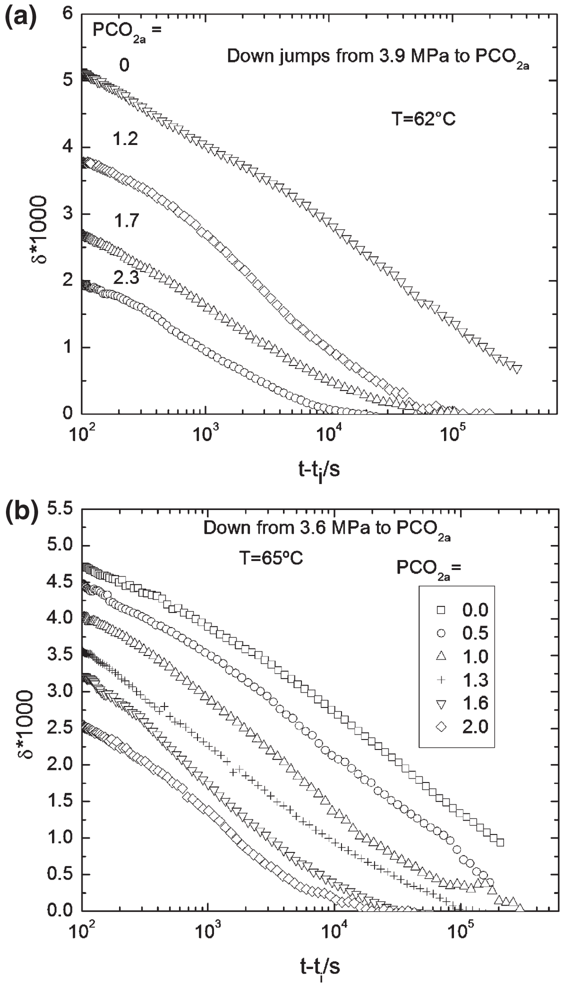

Figure 6. Intrinsic isopiestics at (a) 62 °C and (b) at 65 °C for the epoxy resin.

the intrinsic isotherms after temperature changes performed by Kovacs[7] and also to those performed by Zheng and McKenna on the same material after RH-jump experiments.[4] For the experiments performed at low PCO_2, the volume at equilibrium was calculated by linear extrapolation of the volume at equilibrium at high carbon dioxide pressures. The results reported in the present work on the intrinsic isopiestics at different temperatures are qualitatively similar to the intrinsic isotherms though the values of the departure from equilibrium (δ) at different CO_2 pressures are higher than those observed in T-jump experiments.

4.3. Asymmetry of Approach. Figures 7a and 7b present the results of isothermal asymmetry of approach experiments at 62 and 65 °C, respectively. It is seen in the figures that the isothermal volume responses of the epoxy resin after PCO_2 up- and down-jumps, to the same final conditions with the same magnitude, are asymmetrical. The approach to equilibrium is slightly different; the volume response after PCO_2 down-jump is faster than that for the PCO_2 up-jump experiment. Also, the magnitude of the departure from equilibrium δ after an up-jump is higher than that after a down-jump. Thus, the structural recovery response is nonlinear and this is analogous to what is observed in T-jump[7] and RH-jump experiments.[4]

4.4. Memory Effect. Figures 8a and 8b show the results of the memory experiments performed at 62 and 65 °C. These figures show that the epoxy/CO_2 system exhibits the classic memory effect or crossover. Maxima are seen in the departure from equilibrium vs aging time for both experimental temperatures. Such results reflect both the history dependence of the response and the existence of a distribution of relaxation times in the structural recovery kinetics after carbon dioxide pressure jumps. The memory experiments after PCO_2 changes are similar to those observed in T-jump[7] and relative humidity[4] experiments. We remark, as well, that Horn and Paul have seen the impact of memory effect and recognized it as such, in their investigations of permeability in CO_2 environments.[44]

4.5. Modeling of Structural Recovery Responses of the Epoxy/CO_2 System. In this section, we model the structural recovery responses of the epoxy/CO_2 system using the TNM-KAHR

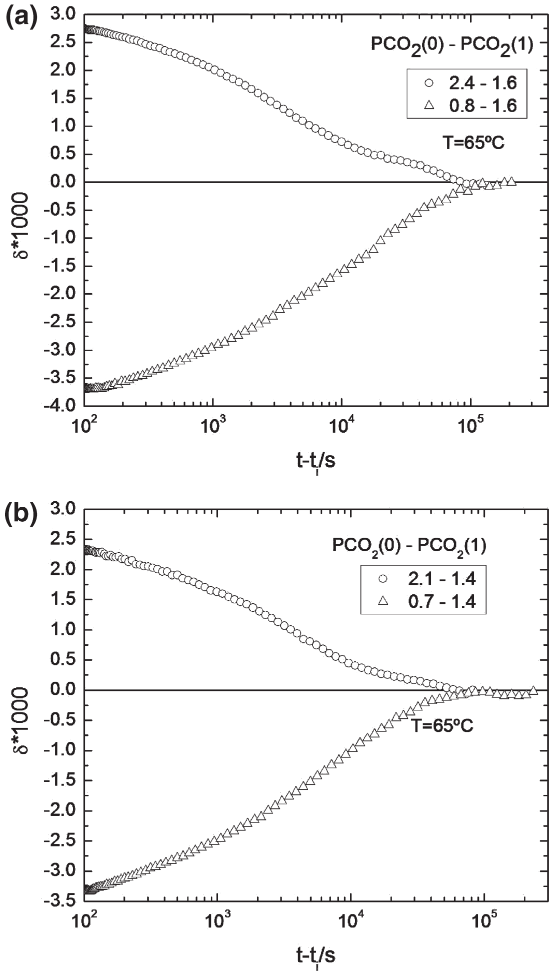

Figure 7. (a) Asymmetry of approach experiments at 62 °C. The sample was equilibrated at 2.4 MPa for 10 h and for 100 h at 0.8 MPa. (b) Asymmetry of approach experiments at 65 °C for the epoxy. The sample was equilibrated at 2.1 MPa for 10 h and for 100 h at 0.7 MPa.

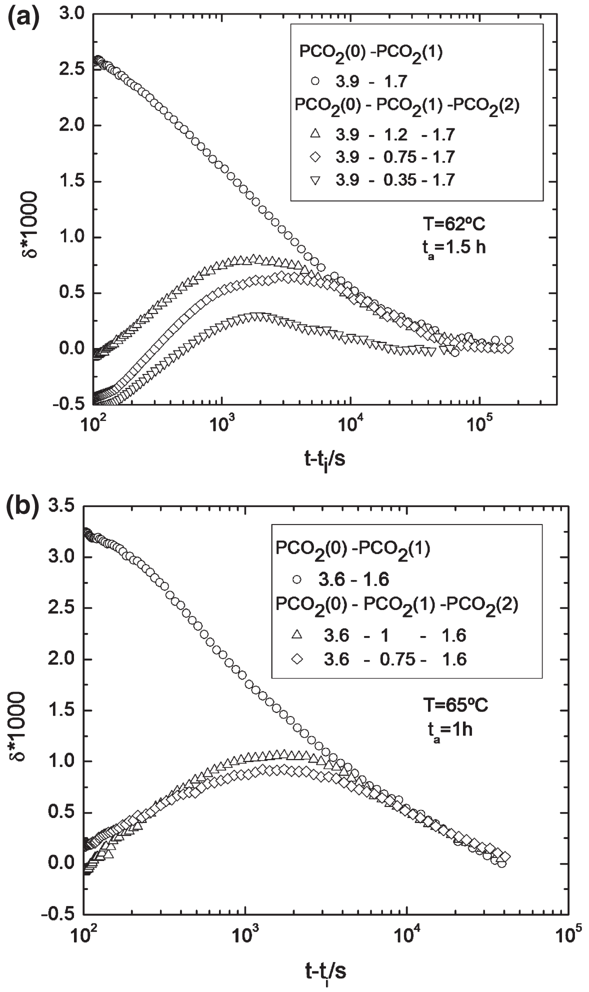

Figure 8. (a) Memory experiments at 62 °C. The sample was partially aged at 1.2, 0.75, and 0.35 MPa for 1.5 h. (b) Memory experiments at 65 °C. The sample was partially aged at 1 and 0.7 MPa for 1 h.

model. It is known that the TNM-KAHR model does not quantitatively describe the structural recovery responses of glass-forming liquids after temperature changes.[11,45,46] We show here, as it was reported in prior work,[4] that the modified TNM-KAHR model does not capture the full range of the structural recovery experiments (isotherms or isopiestics, asymmetry of approach, and memory effect) for the plasticizer jump histories.

Figure 9a shows the TNM-KAHR model curve fit to the intrinsic isopiestic experiment of the epoxy at 62 °C after a PCO_2 ramp from equilibrium to 2.3 MPa. The parameters used to model the data are determined experimentally and listed in Table 2. The differences between the coefficient of concentration expansion, in the liquid and the glassy states, $\Delta\chi$, and the glass transition pressure (concentration), PCO_{2g} (the reference concentration), are determined from Figure 5a. The parameter θ, which is a form of activation energy, is obtained from the CO_2 concentration dependence of the shift factor, $a_{PCO_2} = \exp(-\theta(PCO_2 - PCO_{2r}))$ (i.e., θ is determined from the slope of shift factor of the intrinsic isopiestic curves (Figure 6a) vs $1/PCO_2$). The values of x and β were obtained using the multidimensional Marquardt optimization algorithm.[47] It is important to note that in the TNM-KAHR model the four independent parameters—τ_0, x, θ, and β—can, in principle, be determined from independent measurements. For example, θ or the activation energy can be obtained from the dependence of T_g on cooling rate,[11,38,48,49] whereas the pre-exponential factor, τ_0, is determined from θ and T_g at a given cooling rate.[11] The parameter β can be estimated from structural recovery experiments after linear jumps in temperature.[50] However, the nonlinearity parameter, x, can only be obtained from independent measurements when special assumptions are made and is generally obtained using curve-fitting procedures.[11,51,52]

The methods mentioned above were successfully used to determine the TNM-KAHR parameters to describe the isobaric structural recovery responses of polymers after T-jump experiments.[12,38,48,49,51,52] However, it was difficult to apply these methods to the isothermal structural recovery experiments of the epoxy resin after PCO_2 jumps. For example, it was implausible to estimate the activation energy from the dependence of the PCO_2 glass transition on the depressurization rate. This is because the experiments under carbon dioxide pressure for the thin films of the epoxy resin are difficult to perform and the range of depressurization rates that could be used is small.

Referring to Figure 9a, it is shown that the TNM-KAHR model does not describe well the intrinsic isopiestic data of the

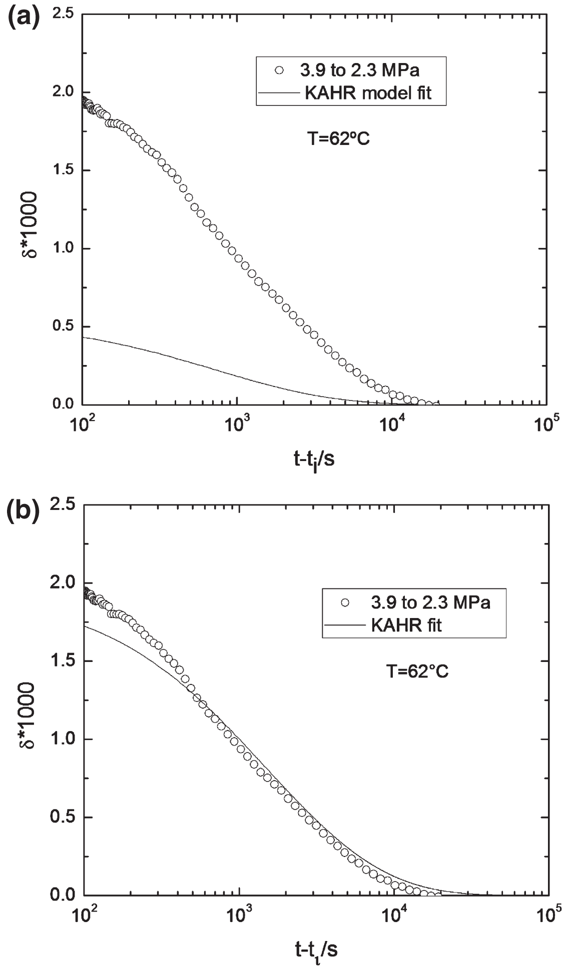

Figure 9. (a) TNM-KAHR model curve fit to the intrinsic isopiestic of the epoxy resin at 2.3 MPa and 62 °C. (b) TNM-KAHR model fit to the intrinsic isopiestic at 2.3 MPa for the epoxy resin at 62 °C. The fitting procedure was modified by changing the TNM-KAHR model parameters (see Tables 1 and 2).

Table 2

parameters	values	parameters	values
x	0.3	τ_{ref} (s)	100
β	0.14	$\Delta\chi PCO_2$ (1/MPa)	0.0018
θ	0.1	PCO_{2ref} (MPa)	2.85

epoxy resin at 2.3 MPa and 62 °C. This might be due to the fact that the difference between the coefficient of concentration expansion ($\Delta\chi$) is higher than that determined from Figure 5. This is seen in Figures 6a and 6b where the intrinsic isopiestic data of the epoxy at different temperatures show high volume change compared to those observed in T-jump experiments.[7] For this reason, we increased the values of ($\Delta\chi$) and τ_0 parameters to provide better model fits to the PCO_2 data. We show in Figure 9b the TNM-KAHR model curve fit to the intrinsic isopiestic of the epoxy resin at 2.3 MPa and 62 °C using different model parameters. The model parameters are listed in Table 3. A good agreement between the TNM-KAHR model and the data is observed in Figure 9b.

Table 3

parameters	values	parameters	values
x	0.6	τ_{ref} (s)	550
β	0.52	$\Delta\chi PCO_2$ (1/MPa)	0.0033
θ	0.1	PCO_{2ref}	2.6 MPa

The TNM-KAHR model curve fits to the intrinsic isopiestic data of the epoxy resin at 62 °C are shown in Figure 10a. The model parameters are listed in Table 3. This figure shows that the KAHR model can describe, at least qualitatively, the isopiestic data at 62 °C. Figures 10b and 10c show the KAHR model calculations compared to the asymmetry of approach and memory effect experiments of the epoxy resin at 62 °C. The model parameters used in the calculations are those for the intrinsic isopiestics at 62 °C. It is shown in Figures 10b and 10c that the calculated δ values are lower than those for the asymmetry of approach and memory effect experiments of the epoxy sample at 62 °C. This is similar to what is observed in modeling the asymmetry of approach and memory effect experiments of the epoxy resin after RH jumps.[4] We note that Zheng and McKenna[4] modeled the isopiestic experiments under RH conditions using the model parameters determined from the RH asymmetry of approach experiments. It was reported that the calculated δ values were higher than those for the RH isopiestics experiments.[4] This implies that the model parameters are history dependent for its application in RH experiments.[4] This is a known problem of the TNM-KAHR type of model. The PCO_2-jump results presented here are yet another case, where these models do not completely capture the structural recovery behavior of the glassy materials. The conundrum of the continuing findings of lack of agreement between the behavior of glasses and the current models available to describe them was discussed two decades ago in one of the Relaxations in Complex Systems meetings organized by K. L. Ngai, and a discussion session was held that showed even then that there were recognized deficiencies in the models. Refer to McKenna et al.[53] for the summary of the discussion of the various models including the TNM-KAHR type models and why it is difficult to find a universal model for explaining the phenomenon of structural recovery. There is also recent work by Caruthers and co-workers[54−61] that shows some promise but also seems to have the same difficulties as the present models, though the Caruthers model also includes mechanics of the behavior. The suggestion here is that there needs to be a radical rethinking of the current models to explain not only the present plasticization-jump experiments but also temperature-jump experiments. Other work using novel temperature perturbation methods by Simon and Bernazzani[62] also come to this conclusion.

CO_2-Formed Glass vs Temperature-Formed Glass. In this section, we compare the structural recovery responses of the epoxy resin after jumps in temperature and CO_2 to the same final conditions of the glass that are defined by temperature and PCO_2. The final conditions of the glassy state are 62 °C and 0 MPa. Figure 11 exhibits a comparison between the intrinsic isopiestic at 62 °C and the intrinsic isotherm at 0 MPa. This figure shows that the volume change of the CO_2-formed glass is much higher than that for the temperature-formed glass despite the fact that the final state of the glass is the same (62 °C and 0 MPa). However, the time to reach the equilibrium state for the concentration glass is much longer than that for the temperature glass. This indicates that the kinetics of the structural recovery under carbon dioxide pressure conditions is very different from that under temperature conditions. This anomalous behavior is similar to that reported in

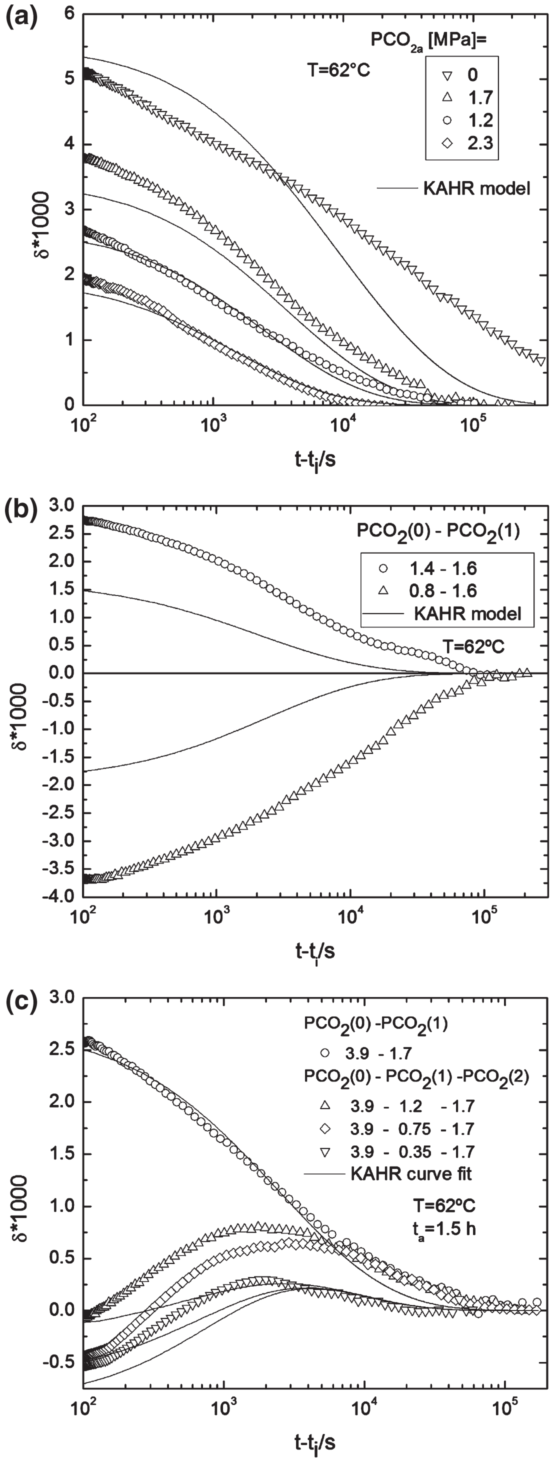

Figure 10. (a) TNM-KAHR model curve fits to the intrinsic isopiestics at 62 °C. (b) TNM-KAHR model curve fit to the asymmetry of approach experiments at 62 °C. The model parameters were defined from the curve fits to the intrinsic isopiestics at 62 °C shown in (a) (see text). (c) TNM-KAHR model curve fit to the memory effect experiments at 62 °C. The model parameters were defined from the curve fits of the intrinsic isopiestics at 62 °C shown in (a).

previous works[3−5] where the physical aging (after CO$_2$ and RH jumps) and structural recovery (after RH jumps) responses of the epoxy resin were different from those after temperature jumps.

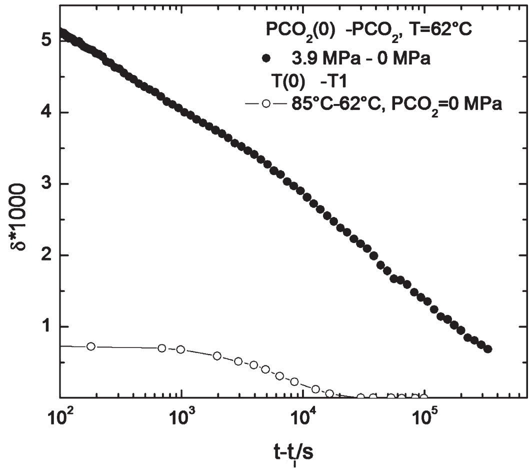

Figure 11. Comparison between the intrinsic isopiestic (concentration glass) and intrinsic isotherm (temperature glass) for the epoxy resin after jumps from the equilibrium state to the same final conditions of the glass.

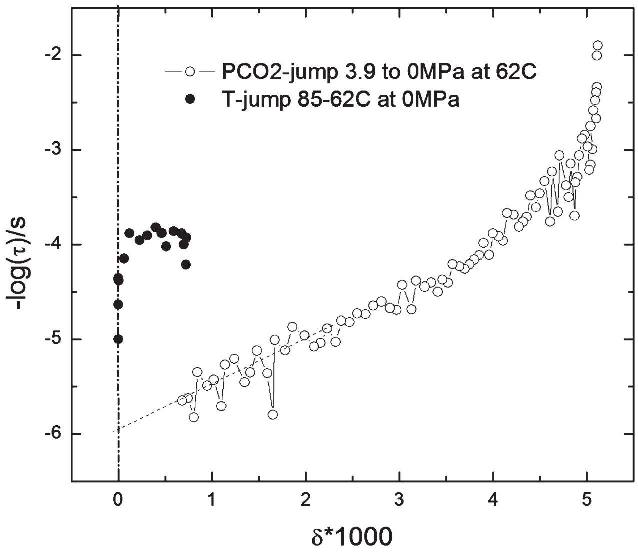

Figure 12. τ-effective retardation times for the concentration and temperature glasses.

We show in Figure 12 another comparison, in terms of the effective retardation times (τ-effective), between the PCO$_2$-formed glass and the temperature glass. The τ-effective parameter (τ_{eff}), as defined by Kovacs,[7] can be calculated from the departure from equilibrium, δ, as $\tau_{\text{eff}}^{-1} = (-1/\delta)(d\delta/dt)$. The τ-effective parameter was frequently used to analyze the asymmetry of approach responses of glassy polymers[7,63−65] by plotting τ_{eff}^{-1} versus the departure from equilibrium, δ. In the Kovacs' structural recovery experiments of PVAc, τ_{eff}^{-1} evolves as the material approaches the equilibrium state due to the nonexponentiality and the nonlinearity of the structural recovery responses.[7] In the up- and down-jump experiments to the final condition of the glass (i.e., the same final temperature), Kovacs reported that the for the up-jump experiments τ_{eff}^{-1} were longer than those for the down-jump experiments. In addition, Kovacs observed a gap between the values of τ_{eff} in the up- and down-jump experiments at equilibrium, $\delta = 0$. This is known as the τ_{eff} paradox.[7]

Referring to Figure 12, it is clear that the kinetics of the structural recovery response of the concentration glass is different from that of the temperature glass. The aspect that the glass created from the CO_2-jump is more stable in spite of the higher free volume than is the glass created by a T-jump is similar to what was found for RH-jump experiments[4,5] and consistent with our prior results on CO_2-jump glasses.[3,30,31] However, unlike the case for the RH-jump experiments, the responses do not seem to converge to the same value as $\delta \rightarrow 0$, i.e., as the equilibrium is approached. This results leads to the interesting question of whether the CO_2-plasticizer alters the material properties even after their complete removal from the system and the "equilibrium" attained in the concentration formed glass is an actual equilibrium state. A similar question has been addressed in enthalpy recovery studies after temperature jumps where Li and Simon[66] show results that support the idea that the recovery is complete and the (extrapolated) equilibrium liquid line is reached at long structural recovery times, while Cowie and coworkers suggest that the equilibrium line is not reached.[67,68] In the case of the RH-jump experiment,[4,5] the final "equilibrium" achieved was independent of the path as just discussed. It appears that the CO_2-created glass may "equilibrate" in a metastable state—a conclusion that requires further investigation. The results are consistent with work done previously in our group by Alcoutlabi, Banda, and McKenna[30] on temperature and PCO_2 concentration formed glasses (not exactly in equilibrium conditions) to the same final conditions have established the point that the temperature formed glasses are denser than the concentration formed glasses and more stable. In the case of the RH-glasses, while they were found to relax more slowly than the T-glasses, they came to have the same final behaviors in the apparent equilibrium state, which is not the case here for the PCO_2-glasses. Clearly the results here merit further investigation.

5. SUMMARY AND CONCLUSIONS

We have performed volume measurements for an epoxy resin subsequent to carbon dioxide pressure changes and observed that the epoxy sample showed structural recovery responses after changes in CO_2 concentration. The structural recovery was manifested as isopiestics, asymmetry of approach, and memory effect and is qualitatively similar to results to Kovacs' structural recovery experiments after temperature jumps[7] and to those after relative humidity jumps reported on the same material.[4,31] We used an extended form of the TNK-KAHR model[4] to describe the structural recovery responses of the epoxy resin after changes in CO_2 concentration. While the model qualitatively represented the structural recovery responses of the epoxy/CO_2 system, it did not quantitatively describe the three signatures of the structural recovery responses of the epoxy/CO_2 system. This is consistent with the modeling work of Zheng and McKenna[4] reported on the epoxy resin in relative humidity-jump conditions. Such lack of agreement between model and experiment is a known weakness of the TNM-KAHR model in describing the structural recovery responses of glass-forming liquids.

In addition, the volume measurements of the epoxy resin showed anomalous behavior in the structural recovery responses between temperature-jump formed glasses and the CO_2-jump formed glasses. At high excess volumes the CO_2 glass shows slower dynamics than the temperature glass. This anomalous behavior is similar to that observed in the physical aging (under CO_2 and RH-jump conditions) and the structural recovery (under RH) experiments.[3−5] However, unlike the case of the RH-jump glass, the CO_2-jump glass does not seem to age to the same state as the temperature glass, suggesting that the CO_2-jump glass is creating a new metastable equilibrium glassy state. Further research is warranted to confirm and to understand the reported observations.

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