Effect of CO$_2$ Sorption and Desorption on the Creep Response of Polycarbonate

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In this article, experimental results on the effect of CO$_2$ sorption and desorption on the creep response of polycarbonate (PC) are presented. Tensile specimens machined from PC sheets were exposed to CO$_2$ and the absorbed gas mass fraction ranged from 0.045 to 0.12. The creep/creep recovery response of as-received PC, saturated PC, and saturation-cycled PC was characterized. It was found that the saturated PC showed a creep behavior similar to heating the PC to its glass transition temperature. The creep compliance of saturation-cycled PC was found to change with the desorption or aging time. The tests on PC saturated and then desorbed for up to 60 days showed that the effects of exposure to CO$_2$ on PC creep properties persist long after the gas has left the polymer, and could be permanent. POLYM. ENG. SCI., 45:1639–1644, 2005. © 2005 Society of Plastics Engineers

INTRODUCTION

In an earlier work, Wing et al. [1] reported on the creep response of polycarbonate (PC) and microcellular polycarbonate (MCPC). MCPC is a novel cellular material with cells on the order of 10 μm and a cell density on the order of 10^{10} cells per cm^3. Kumar and Weller [2] describe a two-stage process to produce MCPC. The first stage consists of saturating the polymer with CO$_2$ gas in a pressure vessel at room temperature. In the second stage, the gas-saturated polymer is removed from the pressure vessel and heated above its glass transition temperature. Bubble nucleation and growth ensue in the polymer upon heating, and the cells are limited in size by the high viscosity of the polymer near the glass transition temperature. At the appropriate time, the foamed polymer is quenched in room temperature water to prevent further bubble growth. The gas in the cells and in the polymer matrix eventually diffuses out to the atmosphere. This class of cellular polymers has come to be known as solid-state foams, as the process temperatures are in the vicinity of the glass transition temperature of the polymer. A brief review of solid-state microcellular foams can be found in Kumar [3].

The motivation for studying the effect of CO$_2$ sorption and desorption on the creep of PC is in the context of understanding the creep behavior of MCPC. In the process of producing MCPC, the polymer is subjected to a cycle of CO$_2$ sorption and desorption. It has been recognized by Seeler and Kumar [4] and Kumar et al. [5] that the gas sorption phase of the microcellular process may affect the mechanical properties of the polymer foam matrix. Therefore, it is expected that the creep response of MCPC will depend on both the foam microstructure as well as on the effect of the cycle of gas sorption and desorption on the PC matrix.

It has been well documented by Crissman [6], Crook and Letton [7], Nishitani et al. [8], Peretz and Weitsman [9, 10], and Zapas and Crissman [11] that amorphous polymers exhibit time-dependent response to an applied load; Yee et al. [12] showed that this response becomes more vigorous with an increase in temperature. Also, when polymers are cooled to below their glass transition temperature, the glass formation process begins. Immediately after cooling below the glass transition temperature, the material is in a non-equilibrium state and its free volume continues to evolve toward equilibrium. Changes in the mechanical (viscoelastic) behavior associated with changes in the glassy structure have come to be known as "physical aging" [13].

Several researchers have studied the effect of nonreacting gases on the mechanical behavior of polymers. Seeler and Kumar [4] investigated the effect of CO$_2$ saturation and desorption on the fatigue life of PC. They reported that the fatigue life of the saturation-cycled PC exceeded that of unprocessed PC by up to a factor of 30. The increase in fatigue life was found to be a function of the CO$_2$ saturation

pressure. Wissinger and Paulaitis [14] have reported that the glass transition temperature, T_g, of polymethyl methacrylate (PMMA) and polystyrene (PS) are reduced by CO_2 sorption. Change in modulus of silicone elastomer as a function of nitrogen gas pressure has been studied by Briscoe and Zakaria [15]. Chan and Paul [16] found that a cycle of gas sorption and desorption has lasting effects on the gas sorption, and thermal and static mechanical properties of glassy polymers. They attributed the effects to the increase in free volume of the polymer that results from a saturation cycle. Hojo and Findley [17] reported increased creep in PC tubes pressurized with CO_2. In an article on the effects of physical aging and CO_2 absorption in bisphenol-A-PC, Risch and Wilkes [18] found that absorbed CO_2 dramatically reduced the glass transition temperature of PC with linear dependence on absorbed mass fraction.

EXPERIMENTAL

Specimen Preparation

ASTM type IV tensile specimens were chosen for use in this study. The specimens were machined to the specifications of ASTM D638. Type IV tensile specimens have a specified gage length of 25 mm and a throat width of 6 mm. The specimens were machined from 1.57-mm-thick sheets of LEXAN 9034 PC with a density of 1.20 g/cm^3. Holes were drilled in the center of both grip portions of the specimens at the time of manufacture. The holes were drilled to locate the self-aligning pins in the grips used to hold the specimens.

Polymer sheets are commonly produced by extrusion, resulting in some alignment of molecular chains in the polymer matrix and anisotropy in the physical properties of the polymer. All of the specimens used in this study were machined from the PC sheets with the same relative orientation to eliminate variations due to extrusion-induced anisotropy. Residual stresses in tensile specimens disturb the otherwise uniform uniaxial stress field produced by uniaxial loading. The specimens were inspected under a polariscope to determine the amount of machining-induced residual stress. Based on this inspection, it was found that the machining did not develop significant residual stresses.

The tensile specimens used to study the effects of exposure to CO_2 gas on the creep behavior of PC were placed in a pressure vessel and exposed to a CO_2 environment for 60 hours at various pressures at room temperatures. Table 1 lists the parameters of the gas sorption process used to produce these tensile specimens. Observation of specimens under a polariscope revealed no significant residual stresses in any of the specimens due to CO_2 saturation. These saturated specimens were tested immediately after removal from the pressure vessel.

TABLE 1.   Processing conditions for PC specimens.

CO_2 saturation pressure	Saturation time	Mass fraction of gas absorbed
5.5 MPa	60 hours	0.119
4.8 MPa	60 hours	0.104
4.1 MPa	60 hours	0.0886
3.5 MPa	60 hours	0.0756
2.7 MPa	60 hours	0.0583
2.1 MPa	60 hours	0.0454

Creep Test Equipment and Procedure

The creep/creep-recovery tests were performed using dead-weight tensile loading. An electric weight trolley car was employed to smoothly lower and raise the weights. Self-aligning grips were employed to load the specimens. Strains in the tensile specimens were measured using an MTS 632.11b strain gage based contacting extensometer. The strains were recorded using a computer-controlled data acquisition system. The data acquisition system was capable of recording strains as high as 0.374 with a resolution of 0.0015. Strain data was collected at various time intervals over the entire creep/creep-recovery test period. The creep/creep-recovery tests consisted of an 8-hour creep period, followed by a 2-hour creep-recovery period. All tests were performed at ambient room temperature and conditions.

Creep/Creep-Recovery Tests

The first series of creep/creep-recovery tests were performed on "as-received" polycarbonate specimens that were not exposed to CO_2 gas. These tests were conducted to characterize the viscoelastic and viscoplastic response of the LEXAN 9034 PC prior to testing the "saturated" PC. The as-received PC tensile specimens were tested at eight stress levels ranging from 13.8 to 51.7 MPa. At least three tests were performed at every stress level tested.

PC tensile specimens saturated at 5.5 MPa were subjected to creep/creep-recovery tests at stress levels ranging from 13.8 to 34.5 MPa to evaluate the effect of CO_2 saturation on the creep response. In addition, creep/creep-recovery tests were performed on specimens saturated at pressures ranging from 2.1 to 5.5 MPa, as listed in Table 1, to determine the effect of saturation pressure on the creep behavior. These creep/creep-recovery tests were performed at a stress level of 20.7 MPa.

The effect of CO_2 desorption on the creep response was investigated by testing specimens that had been saturated and then desorbed for times ranging from 6 to 60 days. The creep/creep-recovery experiments at various desorption periods were conducted at a stress of 20.7 MPa.

A separate series of creep/creep-recovery tests were conducted on specimens that had been initially saturated at 5.5 MPa and then allowed to desorb for 60 days. These specimens were tested at stress levels of 13.8, 20.7, and 34.5 MPa.
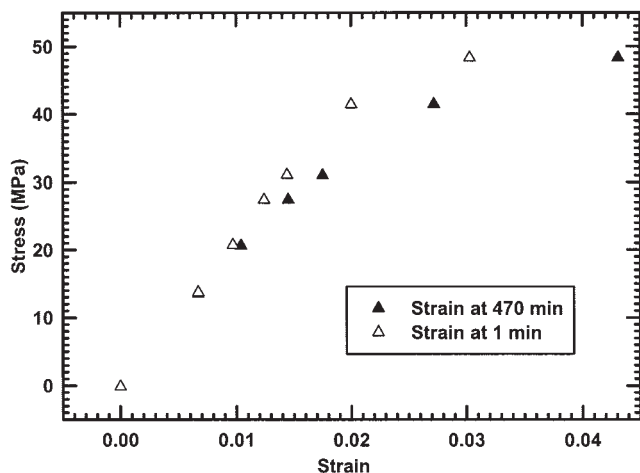
FIG. 1. An isochronous curve for as-received polycarbonate.

Desorption Experiments

To determine the desorption rate of CO_2 gas from the PC matrix, several specimens were first saturated in CO_2 gas at 5.5 MPa for a period of 60 hours. These specimens were then removed from the pressure vessel and the desorption rate of the CO_2 gas from the PC matrix was determined by weight loss. Weights were measured using a Mettler AE240 balance with a resolution of 10 μg. Desorption data was collected until the amount of CO_2 remaining in the PC specimens was approximately 1% of the amount at saturation.

RESULTS

Creep Behavior of PC

No appreciable creep was observed in the as-received PC within the resolution of the data acquisition system, at stress levels of 13.8 MPa or below. An isochronous stress-strain curve using strain data obtained at 1 minute and 470 minutes from the initial loading time is shown in Fig. 1. From this data, the creep response of PC was found to be nonlinear at stress levels above 24 MPa. Creep and recovery data at several stress levels are shown in Fig. 2. At the stress level of 51.7 MPa the creep strains induced in the PC at the end of 8 hours approached 6%.

Creep Behavior of Saturated PC

Figure 3 shows the creep response of saturated and as-received PC at stress levels of 20.7 and 34.5 MPa. At the 20.7 MPa stress level there is a small increase in the creep strains of the saturated specimens. However, at the 34.5 MPa stress level the effect of the dissolved gas on the creep is significant. The exposure to CO_2 has a pronounced effect on both the time-dependent response of the material as well as its instantaneous response. From the instantaneous response at the 34.5 MPa stress level in Fig. 3, the tensile modulus of as-received PC is estimated to be 2.6 GPa, while the tensile modulus of saturated PC is approximately 1.7 GPa, a drop of some 35%. This magnitude of drop in the modulus is analogous to the behavior we might expect upon heating the polymer to a temperature near the glass transition temperature of PC.

PC tensile specimens were saturated with CO_2 gas at six saturation pressures ranging from 2.1 to 5.5 MPa for a period of 60 hours. These specimens were then subjected to creep/creep-recovery tests at a stress of 20.7 MPa. The results of these tests are shown in Fig. 4. We see that the creep response of PC is insensitive to saturation pressure in the range from 2.1 to 5.5 MPa. Thus, increasing the concentration of the dissolved CO_2 beyond the 4.54% at 2.1 MPa (see Table 1) does not appear to further influence the creep response at this stress level.

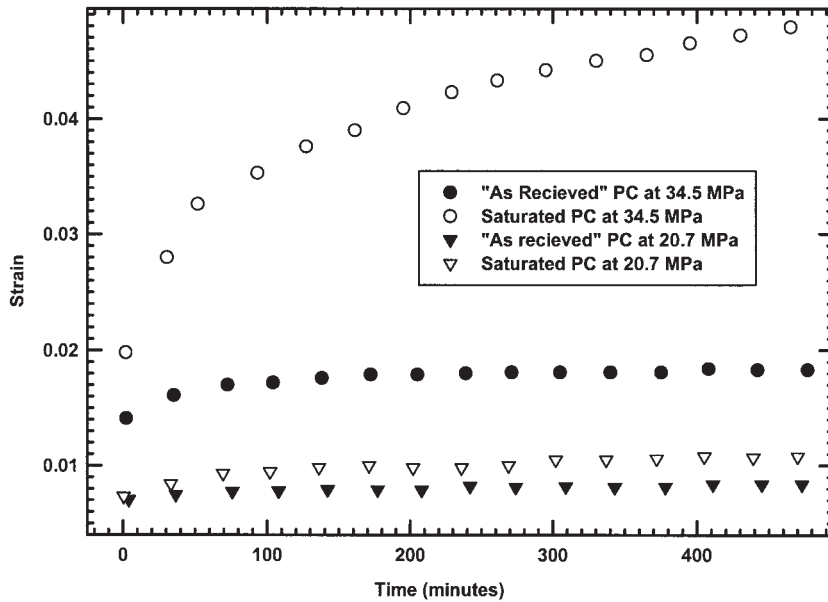FIG. 2. Creep/creep-recovery response of as-received polycarbonate at several stress levels.
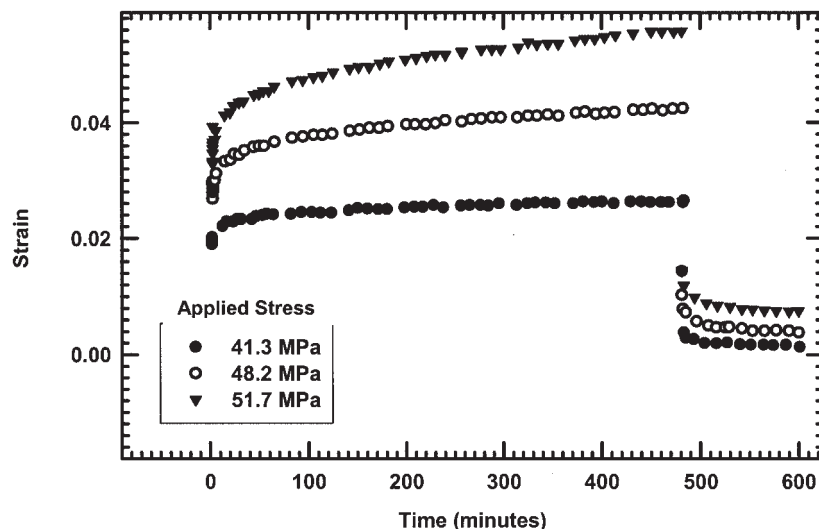
FIG. 3. A comparison of the creep response of "as received" PC and CO_2 saturated PC. The saturated PC specimens were exposed to carbon dioxide at 5.5 MPa for 60 hours.

Desorption of CO_2 from Saturated PC

Figure 5 shows the result from the desorption experiment. Here, we have plotted the percent of gas remaining in a 1.5-mm-thick PC specimen saturated at 5.5 MPa and then left at atmospheric pressure to desorb at room temperature, as a function of time. It can be seen that almost 70% of CO_2 leaves the specimen within one day and the specimens have less than 1% of gas remaining after approximately 11 days. This data is in agreement with that of Seeler and Kumar [19] who report that it takes another 8 days for the last 1% of gas to leave the specimen.

Creep Behavior of Saturation-Cycled PC

Figure 6 shows data from the creep/creep-recovery tests performed on saturation-cycled PC specimens with desorption times ranging from 6 to 60 days at a stress of 20.7 MPa.

Several observations can be made from this data. First, we see that as the desorption time increases the creep response of the saturation-cycled PC appears to approach that of the as-received PC. Second, we observe that the creep compliance of PC specimens continues to vary over the 60 days of desorption although, as seen from Fig. 5, only approximately 1% of CO_2 remains in the PC after 11 days of desorption, and no measurable amount of gas remains after 19 days of desorption [19].

Figure 7 shows creep/creep recovery data for specimens saturated at 5.5 MPa and then allowed to desorb for 60 days at stress levels ranging from 13.8 to 34.5 MPa. The behavior is compared to as-received PC at the same stress levels. For saturation-cycled PC the creep behavior is seen be linear at stress levels of 20.7 MPa and lower. At low stress levels the creep response of the saturation-cycled PC is similar to that of as-received PC. However, at a higher stress level of 34.5
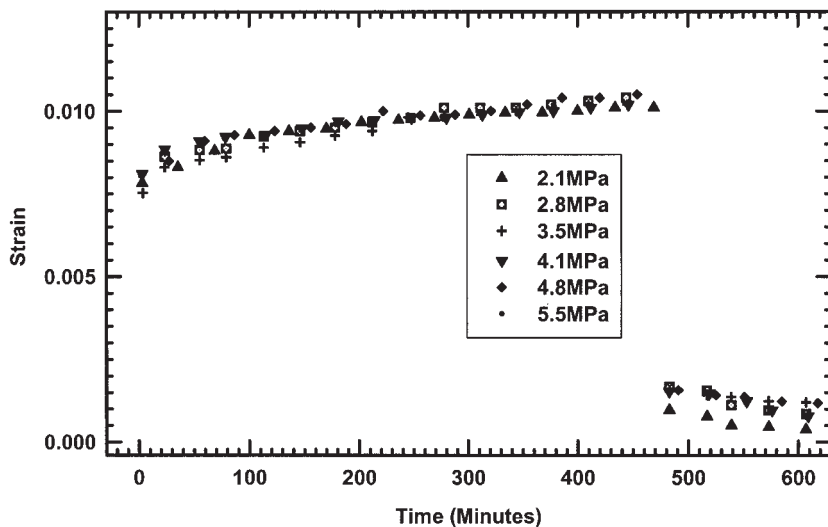

FIG. 4. Creep/creep-recovery behavior of polycarbonate saturated with CO_2 at 6 different pressures ranging from 2.1 to 5.5 MPa and tested at a stress level of 20.7 MPa. At this stress level, the creep behavior of PC with different levels of carbon dioxide concentration is quite similar.
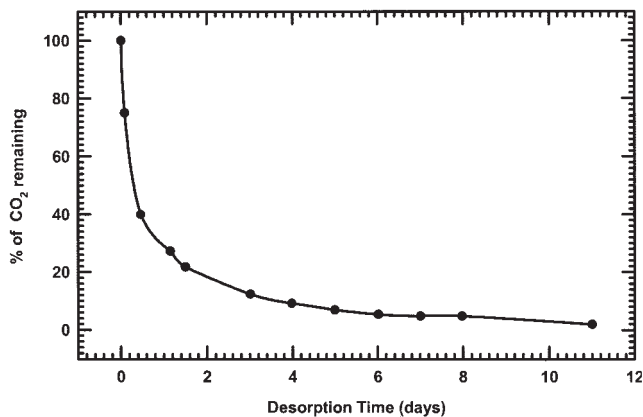
FIG. 5. Plot of CO_2 remaining in a 1.5-mm-thick PC specimen as a function of desorption time at atmospheric pressure. The 100% CO_2 corresponds to a specimen saturated at 5.5 MPa. Note that approximately 1% of the gas remains in the specimen after 11 days of desorption.

MPa, the saturation-cycled PC shows considerably more creep than the as-received PC. Thus, the effect of CO_2 saturation on PC creep behavior persists even after 60 days from the time of saturation.

DISCUSSION

It is clear from the data presented that when the PC is saturated with CO_2 at 2.1 MPa (corresponding to a gas concentration of 4.54%) or a higher pressure, the creep initiates at a lower stress and the PC becomes more compliant. These observations are consistent with the finding that the dissolved gas lowers the glass transition temperature of the polymer by increasing the molecular mobility [2, 14, 18]. This effect on the glass transition can be quite significant. For example, for PC saturated with CO_2 at 4.8 MPa, Kumar and Weller [2] estimate that the glass transition temperature lowers from 150°C for virgin or as-re-

ceived PC to 87°C, a change of 63°C. Interestingly, increasing the concentration of dissolved CO_2 beyond 4.54% by using a higher saturation pressure does not lead to a further increase in PC creep response (Fig. 4).

The tests on saturation-cycled specimens showed that after PC is saturated with CO_2, and is then allowed to desorb at atmospheric pressure, the creep compliance continues to change with time. After 11 days of desorption, the PC compliance is still significantly higher than the as-received PC (Fig. 6). This trend continues for specimens desorbed (or "aged") for 60 days after saturation (Fig. 7), indicating that the effect of CO_2 saturation-cycling is long-lasting and could be permanent. This observation is consistent with Seeler and Kumar [19] who report that the yield strength of saturation-cycled PC tested after 62 days of desorption was 26% lower than the as-received PC. Since the amount of gas dissolved in the specimen drops to about 1% of the concentration after 11 days (Fig. 5) and only trace amounts of gas remain in the matrix after this time, the persistent change in creep compliance of PC can not be explained on the basis of enhanced molecular mobility caused by the dissolved gas. It is suggested that saturating PC with CO_2 increases free volume and the material structure continues to evolve during desorption of CO_2. After all the gas has left, which in this study takes about 20 days, the properties still change with time, showing continued physical aging. These findings parallel those of Risch and Wilkes [18] who found that PC samples that had been aged after absorbing a mass fraction of 0.07–0.10 of CO_2 showed thermal and mechanical behavior similar to that of polymer quenched from above T_g with identical absorbed mass fraction of gas.

SUMMARY

The effect of CO_2 sorption and desorption on the creep response of PC was studied. Tensile specimens machined from PC sheets were exposed to CO_2 and the absorbed gas

FIG. 6. Creep/creep-recovery data from test performed on specimens saturated at 5.5 MPa with desorption times ranging from 6 to 60 days. All tests were conducted at a stress 20.7 MPa. Note after 60 days of desorption the response approaches that of "as received" polycarbonate.
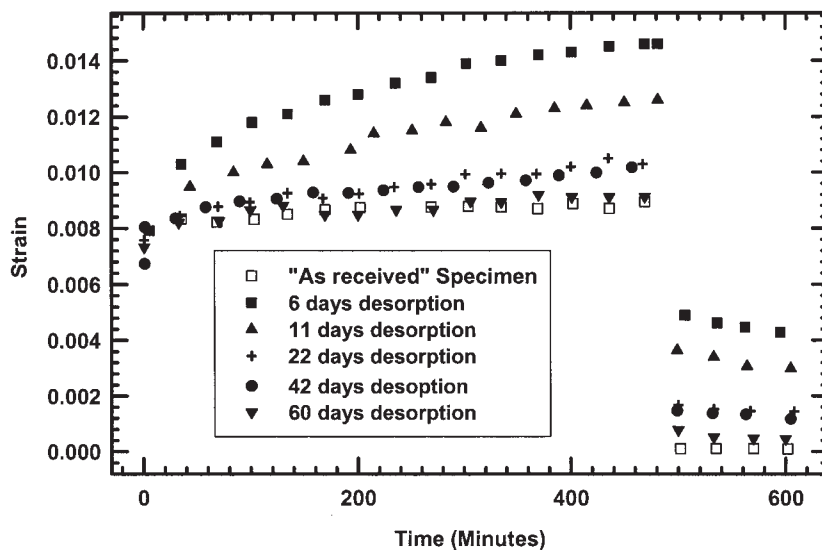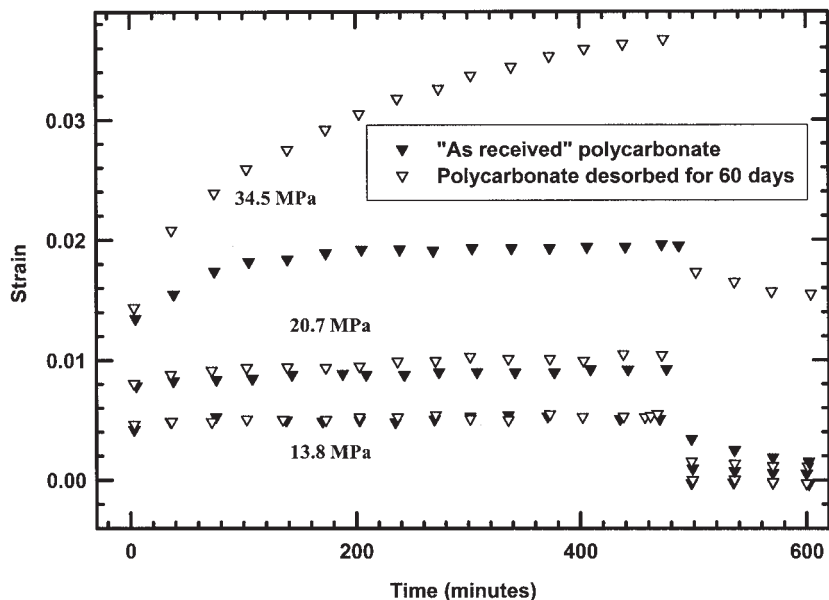
FIG. 7. A comparison of the creep/creep-recovery behavior of "as received" polycarbonate with saturation-cycled PC at various stress levels. The saturation was at 5.5 MPa and the desorption time was 60 days. Note that at 34.5 MPa stress, the saturation-cycled PC still shows a significantly higher creep compared to the as-received PC.

mass fraction ranged from 0.045 to 0.12. The creep/creep recovery response of as-received PC, saturated PC, and saturation-cycled PC was characterized. It was found that the saturated PC showed a creep behavior similar to heating the PC to its glass transition temperature. The creep compliance of saturation-cycled PC was found to change with the desorption or aging time. The tests on PC saturated and then desorbed for up to 60 days showed that the effects of exposure to CO_2 on PC creep properties persist long after the gas has left the polymer, and could be permanent.

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