Effects of Physical Aging and Carbon Dioxide Absorption in Bisphenol-A Polycarbonate

BRIAN G. RISCH and GARTH L. WILKES*

Department of Chemical Engineering, Polymer Materials and Interfaces Laboratory, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

SYNOPSIS

Thermal and mechanical behavior of bisphenol-A polycarbonate was studied as a function of thermal history and absorbed mass fraction of CO_2. Physical aging at 120°C for one week produced dramatic changes in both the thermal and mechanical behavior. Gas absorption studies indicated that although initial diffusion was somewhat retarded in the aged samples, both aged and unaged polycarbonate samples showed identical equilibrium absorbed gas values at 6500 K Pa and identical gas desorption behavior. Absorbed CO_2 was shown to dramatically reduce the glass transition of polycarbonate indicating that CO_2 plasticizes polycarbonate. Additionally, samples which had been aged and absorbed a mass fraction of 0.07–0.10 of CO_2 showed thermal and mechanical behavior identical to that of a glass quenched from above T_g with identical absorbed mass fraction. Once the absorbed gas was desorbed, the thermal and mechanical properties were similar to those of a glass freshly quenched from above T_g. This study demonstrates that sufficient CO_2 gas absorption followed by desorption reverses physical aging in polycarbonate. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The well-known process of physical aging is a phenomenon associated with the nonequilibrium nature of the glassy state.[1] As an amorphous polymer is cooled from above its glass transition temperature, both the segmental mobility and the molar volume of the polymer decrease. When the glass transition temperature is reached, there is a dramatic decrease in segmental relaxation. At this point the segmental relaxation rate may no longer accommodate volume relaxation to the equilibrium value within a reasonable time frame. As a result excess free volume is frozen into the system. Even at temperatures below the glass transition temperature, however, some localized segmental relaxation may occur over a much longer time frame. As a result the equilibrium glassy state is approached and a decrease in excess free volume occurs through the process of physical aging. Bartos et al. have observed the rate of volume relaxation in polycarbonate and illustrated that the

rate of volume relaxation increases rapidly with storage temperature at temperatures below T_g.[2]

Physical aging has been shown to dramatically influence the mechanical properties of glassy polymers due to the increase in relaxation times associated with decreased free volume.[3,4] Lee has shown that the logarithm of the permeability coefficient decreases linearly with the inverse of the specific free volume of glassy polymers,[5] and Kapur and Rogers have shown that physical aging decreases the diffusion coefficient of glassy polymers.[6] Therefore, it is well documented that physical aging affects the gas absorption properties of glassy polymers.

Recently, interest has increased in processing polymers with compressed gases especially in the production of thermoplastic microcellular foams.[7–9] Bisphenol polycarbonate (PC) has been used in these studies due to its good impact strength and high glass transition temperature. The effects of physical aging on the glass transition and mechanical properties of PC have been studied earlier by several others.[3,5,10] A great deal of research has been undertaken to determine the effects of processing or utilizing polymers in the presence of a pressurized gas especially for polymer applications as gas-per-

meable membranes. Depending on the solubility and pressure of the gas, the effects of the pressurized gas on the physical properties of the polymer may be varied. If a polymer is placed in the presence of a nonsoluble pressurized gas or in a soluble pressurized gas at pressures well above the saturation pressure, the effect is to impose an isostatic pressure on the polymer reducing segmental mobility and increasing the glass transition.[11] However, if a polymer is placed in the presence of a soluble pressurized gas near or below saturation pressure, the gas diffuses into the polymer and acts as a low-molecular-weight diluent. Condo et al. have shown that polymers with compressed fluid diluents may exhibit significantly depressed glass transition temperatures.[12,13] Berens noted that depending on the previous thermal and/or vapor treatment of a polymer, sorption kinetics may be widely varied.[14] The work of Berens and others led to the development of kinetic sorption models which included contributions due to conventional Fickian diffusion, a relaxation-controlled contribution, plus the role of the absorbed gas as a plasticizer.[14-17] Studies on the sorption and dilation in polycarbonate indicated that previous conditioning with various pressures of carbon dioxide led to dramatic effects in sorption and dilation behavior.[18,19] Sanders studied the effects of penetrant induced plasticization in the CO_2–polyethersulfone (PES) system.[20] Sanders illustrated that CO_2 plasticizes PES by observing a dramatic depression of the glass transition temperature which accompanied a decreased tensile modulus and increased elongation to break with increasing amounts of absorbed CO_2.[20] Sanders also noted that exposing PES to high-pressure CO_2 altered the nonequilibrium state of the polymer, altering effects of physical aging. This study addresses the effects of processing physically aged and unaged polycarbonate with pressurized CO_2 on thermal and mechanical properties.

EXPERIMENTAL

Samples utilized in this study were General Electric LEXAN® bisphenol-A polycarbonate slabstock (2.5 mm) and thin films (15 mils). To ensure samples were not plasticized by atmospheric gases (CO_2 or H_2O), all samples were stored in a vacuum desiccator for one week at room temperature before experiments unless otherwise specified. Samples were then heated to 160°C (ca. 10°C above T_g) for 5 min and then rapidly cooled to room temperature before physical aging or testing of unaged samples. Physical aging was carried out in a vacuum oven for one week

at either 100 or 120°C. All differential scanning calorimetry (DSC) runs were performed on a Seiko DSC 220C or DSC 210 at a heating rate of 10°C/min unless otherwise specified. The instruments were calibrated with indium and sapphire standards. Samples were thick enough so that negligible gas desorption occurred during experimentation.

The stress–strain behavior of the PC films were made using a Model 1122 Instron tensile tester interfaced to a computer for data collection and stress calculation. Dogbone specimens were cut from films of thickness ranging from 15 to 18 mils. The stressed, cross-sectional area of the samples was 10 by 2.5 mm. Again the sample thickness was large enough to ensure that negligible gas desorption occurred during the experiments. Three to five samples were tested in each case to note reproducibility.

Gas absorption behavior was measured by placing from 5 to 10 aged and freshly quenched samples in a cylindrical high-pressure cell of interior diameter of 50 mm and height of 150 mm. Samples were pressurized with coleman grade 4 CO_2 (99.99% purity) at a pressure of 6500 k Pa (900 psi). Before pressurization the pressure cell was evacuated with a vacuum pump.

RESULTS AND DISCUSSION

The extent of physical aging was indicated by the area of the well-known exothermic peak occurring at the glass transition. Figure 1 illustrates the effects of physical aging for 1 week at 100 and 120°C. As
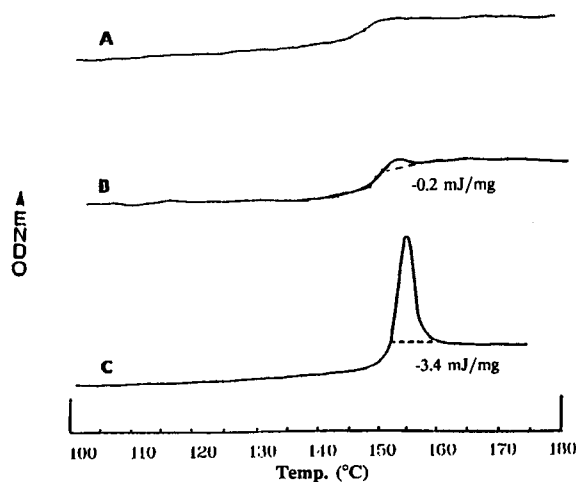
Figure 1 DSC scans of polycarbonate as a function of thermal history: (A) Quenched from 160°C, (B) quenched from 160°C and annealed for 7 days at 100°C, and (C) quenched from 160°C and annealed for 7 days at 120°C.

expected, the effect of physical aging on the glass transition was much more notable in the samples aged at 120°C than those aged at 100°C. In order to determine the effects of physical aging on gas absorption and permeability, absorbed gas mass fraction was measured as a function of time and previous thermal history (see Fig. 2). For a given thermal history, the values of absorbed mass fraction obtained from each of the 5 to 10 samples measured varied by no more than 0.1%. Within the sensitivity of our measurements, differences in absorbed mass fraction as a function of thermal history were only noticeable at short times; after gas absorption occurred for 72 h, no differences were evident in absorbed gas mass fraction. At this point no further significant additional gas absorption occurred; thereby indicating that all three samples had nearly identical equilibrium values. As seen in Figure 3, when similar measurements were made to follow the desorption of CO_2, no difference was noted in the desorption behavior of the three samples, indicating that the effect of previous thermal history on the permeability of the samples was eliminated. Carbon dioxide desorption occurred very rapidly in the initial stages, where significant gas desorption occurred in a matter of minutes. No significant amount of CO_2 was measurable after a week of desorption. The rapid initial rate of CO_2 desorption and the fact that samples with different thermal histories showed

identical behavior suggested that absorbed CO_2 plasticized the samples as well as erased the previous effects of physical aging. This hypothesis was verified by observing the glass transition in a freshly quenched sample and comparing it to a sample that had been annealed at 120°C for 7 days and then saturated with CO_2 gas which was then allowed to desorb for 190 h. As seen in Figure 4, no differences were evident in the glass transition temperature of the two samples and the characteristic exothermic thermic peak was eliminated. Figures 5 and 6 illustrate the systematic effects of absorbed mass fraction of CO_2 on the glass transition temperature of polycarbonate as observed by DSC. These DSC experiments were performed at a heating rate of 20°C/min to minimize gas desorption during heating. (The increased heating rate shifted the observed T_g from 150°C at a rate of 10°C/min to 152.5°C at a rate of 20°C/min) As shown in Figure 6, the depression of the glass transition temperature of polycarbonate suggests a strong linear dependence on absorbed mass fraction of CO_2 ($R^2 = 0.97$). The onset of foaming at temperatures slightly above T_g prevented the runs from being continued beyond this point, note runs E, F, and G were therefore stopped at temperatures below those of runs A–D. Significant T_g depressions due to high levels of dissolved gas in other glassy polymers have recently been observed experimentally in other studies.[21-23] The results ob-
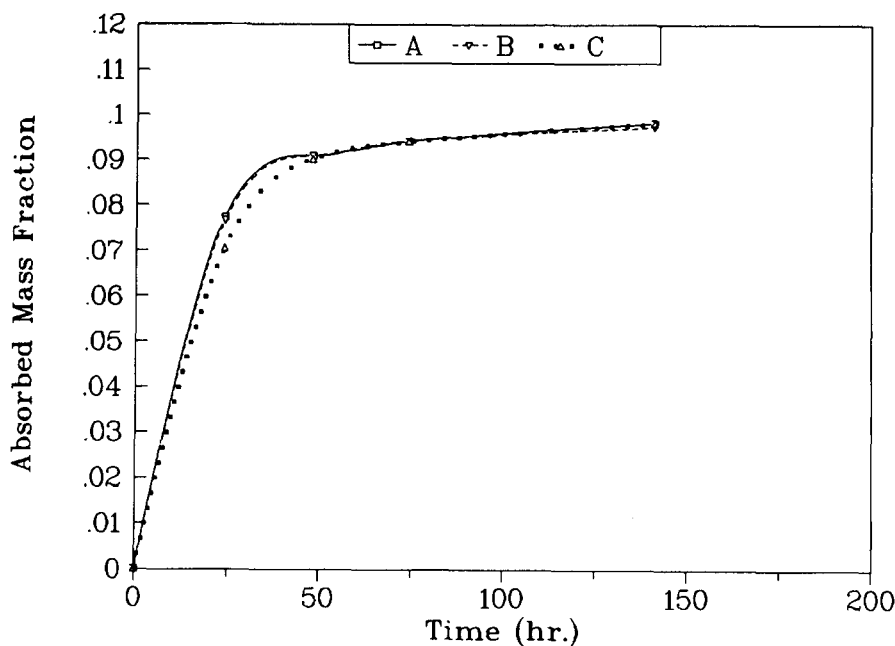

Figure 2   Absorption of CO_2 in polycarbonate: effects of physical aging: (A) Quenched from 160°C, (B) quenched from 160°C and annealed for 7 days at 100°C, and (C) quenched from 160°C and annealed for 7 days at 120°C.
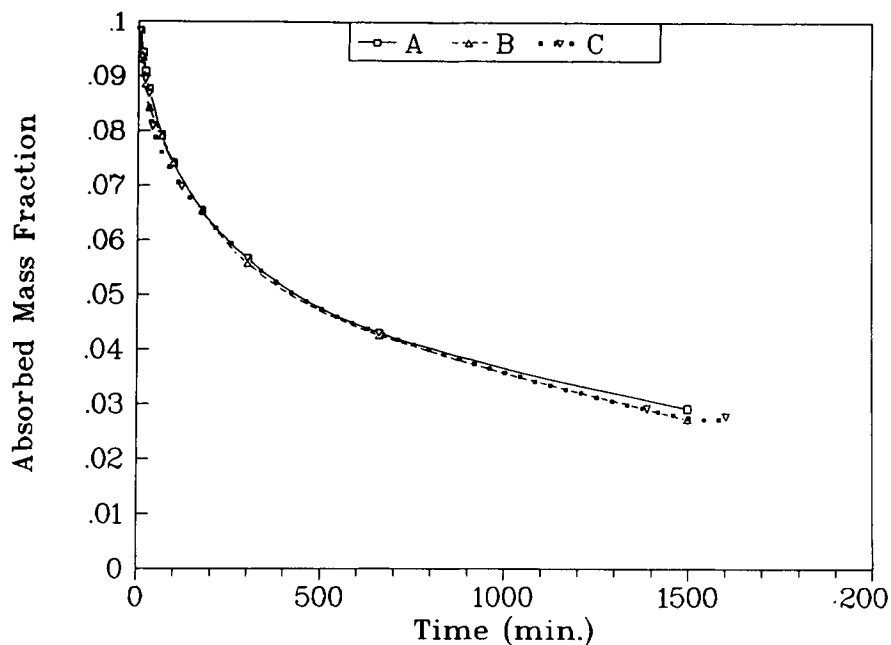
Figure 3 Desorption of CO_2 from polycarbonate: effects of physical aging: (A) Quenched from 160°C, (B) quenched from 160°C and annealed for 7 days at 100°C, and (C) quenched from 160°C and annealed for 7 days at 120°C.

tained for CO_2 in polycarbonate agree very well with theoretical predictions of the glass transition temperature of polymer–fluid diluent systems based on the phenomenological models used to describe T_g behavior.[11,24] Thus, the T_g of a polymer–gas system is governed by the absorbed mass fraction which, in turn, is governed by the temperature, pressure, and solubility of the gas in question. Extrapolation of our data leads to a ca. 100°C depression of the glass
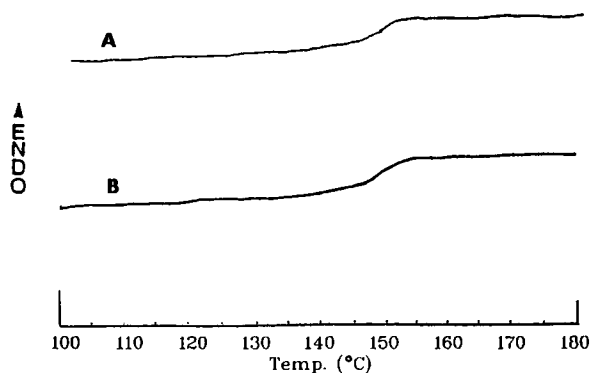

Figure 4 Effects of gas absorption and desorption on the glass transition of polycarbonate: (A) Freshly quenched from 160°C and (B) quenched from 160°C, annealed at 120°C for 7 days, saturated with CO_2 gas at 900 psi (absorbed mass fraction = 0.10), and then desorbed for 190 h.

transition of polycarbonate with an absorbed mass fraction of only 10% CO_2.

The results of the gas absorption, gas desorption, and thermal analysis experiments suggested that CO_2 gas would plasticize polycarbonate samples and gas supersaturation followed by desorption could eliminate the effects of physical aging. Figure 7 illustrates the dramatic change in stress–strain behavior caused by physical aging for 1 week at 120°C. For our testing conditions, samples quenched from above the glass transition temperature show an average yield stress of 58 MPa while those aged for 1 week at 120°C show an average yield stress of 73 MPa, an increase of 26%! The aged samples also showed decreased elongation to break at this crosshead speed. Figure 8 illustrates the effect of absorbed CO_2 on the stress–strain behavior of aged and unaged polycarbonate. The stress–strain behavior showed no dependence on previous thermal history for samples containing a mass fraction of CO_2 greater than or equal to 7%. Although there was a 10% difference in absorbed mass fraction between samples placed in the pressure cell for 24 h at 900 PSI and those which were saturated at 900 PSI (1 week), there were no significant difference in yield stress (see Fig. 8). In both cases an average yield stress of about 40 kPa was observed, a decrease of 31% when compared to the value for a freshly quenched sample and a decrease of 45% when com-
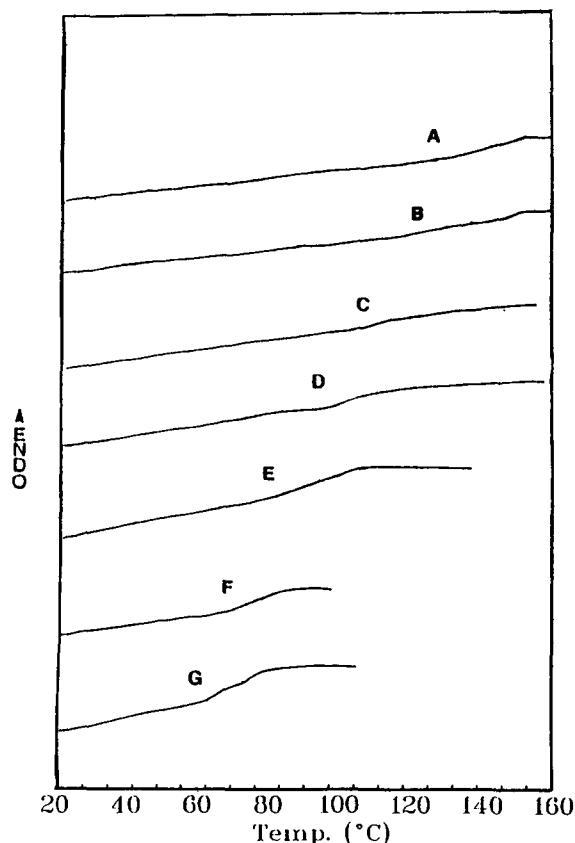
Figure 5 Systematic decrease in glass transition of polycarbonate as a result of absorbed CO_2: (A) Absorbed mass fraction = 0.015, T_g = 143°C; (B) absorbed mass fraction = 0.024, T_g = 134°C; (C) absorbed mass fraction = 0.033, T_g = 123°C; (D) absorbed mass fraction = 0.040, T_g = 106°C; (E) absorbed mass fraction = 0.055, T_g = 94°C; (F) absorbed mass fraction = 0.073, T_g = 78°C; and (G) absorbed mass fraction = 0.090, T_g = 73°C.

pared to the value for a sample physically aged at 120°C for 1 week. Samples which were saturated with CO_2 showed an increased elongation to break compared to samples which were allowed to absorb CO_2 for 24 h, although scatter of roughly 10% was observed in these values. This behavior may be attributed to the significant plasticization effect of CO_2 on polycarbonate. Similarly, as illustrated in Figure 9, after desorption for 1 week there were no appreciable differences between samples saturated with CO_2 gas at 900 psi and those pressurized for 24 h, although slight differences in elongation to break were observed. Once desorption was essentially complete (after 1 week), the yield stress of the samples increased to 45 MPa, a value 22% less than a freshly quenched sample! In all cases, once significant gas absorption occurred, no distinction could be made between aged and unaged samples based
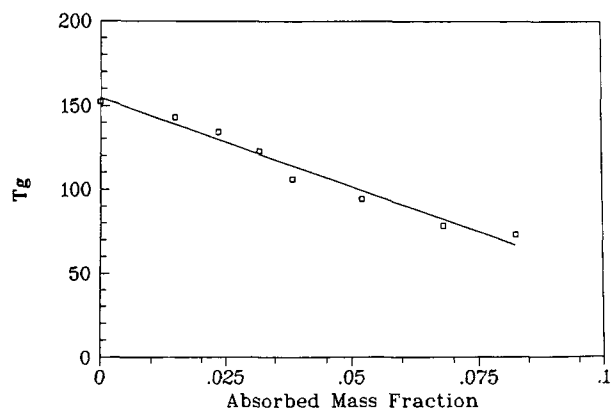

Figure 6 Effect of absorbed CO_2 on the glass transition of polycarbonate: T_g vs. absorbed mass fraction.

on mechanical behavior. Figures 7, 8, and 9 dramatically illustrate the effects of gas supersaturation on aged and unaged polycarbonate samples. As illustrated in Figures 7 and 8, once an appreciable amount of CO_2 enters the system, the system becomes plasticized. As saturation is reached, the effects of previous thermal history are eliminated. This is due to the increase in segmental relaxation rates caused by the CO_2 plasticizer. Since the system is still well below its glass transition temperature, gas diffusion rates are still much more rapid than segmental relaxation rates. Thus, as the CO_2 gas desorbs from the supersaturated polymer diluent system, excess free volume, and a small fraction of the original gas molecules, are left in the sites once occupied by gas molecules. As a result some "excess" free volume may be "pumped" into a glassy polymer by gas absorption and desorption. The presence of increased excess free volume and residual CO_2 mol-
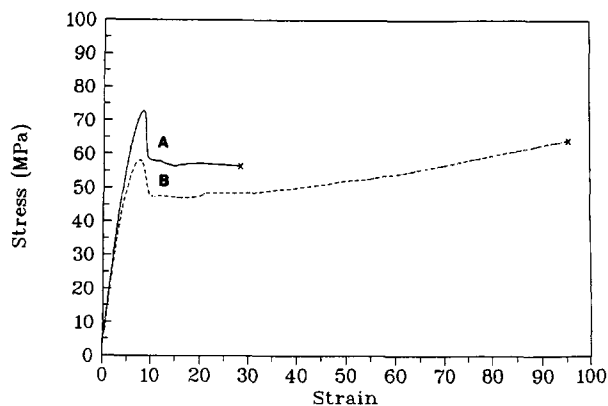

Figure 7 Stress–strain behavior for polycarbonate: effects of physical aging: (A) Quenched from 160°C and annealed for 1 week at 120°C: yield stress = 73 MPa and (B) freshly quenched from 160°C: yield stress = 58 MPa.

ecules is indicated by the dramatic decrease in yield stress observed in samples which were gassed and degassed.

CONCLUSIONS

The effects of physical aging and gas supersaturation were studied for the bisphenol-A polycarbonate CO_2 system. Samples which were aged at 120°C for 1 week and quenched showed dramatic evidence of physical aging in thermal as well as in mechanical behavior. Gas absorption studies indicated that although initial diffusion was somewhat retarded in physically aged samples, both aged and unaged polycarbonate samples showed identical equilibrium absorbed gas values at a pressure of 6500 kPa as well as essentially identical gas desorption behavior. Absorbed CO_2 was shown to dramatically reduce the glass transition temperature of polycarbonate with a linear dependence on absorbed mass fraction. Additionally, samples which had been aged and absorbed a mass fraction of 0.07–0.10 of CO_2 showed thermal and mechanical behavior identical to that of a quenched glass with identical absorbed mass fraction. Once absorbed gas was nearly totally desorbed, samples behaved as if they were freshly quenched from above T_g. The effects of physical aging and gas absorption are important when processing polymers with pressurized gases such as in
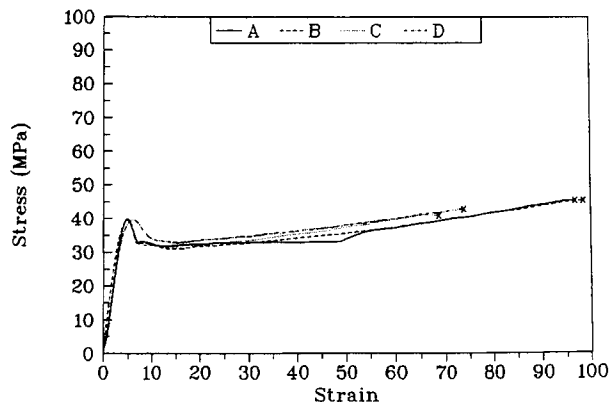

Figure 8 Stress–strain behavior for polycarbonate: effects of gas absorption: (A) Quenched from 160°C and held at a CO_2 pressure of 900 psi for 7 days: absorbed mass fraction = 0.10. (B) Annealed for 7 days at 120°C and held at a CO_2 pressure of 900 psi for 7 days: absorbed mass fraction = 0.10. (C) Quenched from 160°C and held at a CO_2 pressure of 900 psi for 24 h: absorbed mass fraction = 0.078. (D) Annealed for 7 days at 120°C and held at a CO_2 pressure of 900 psi for 24 h: absorbed mass fraction = 0.070.
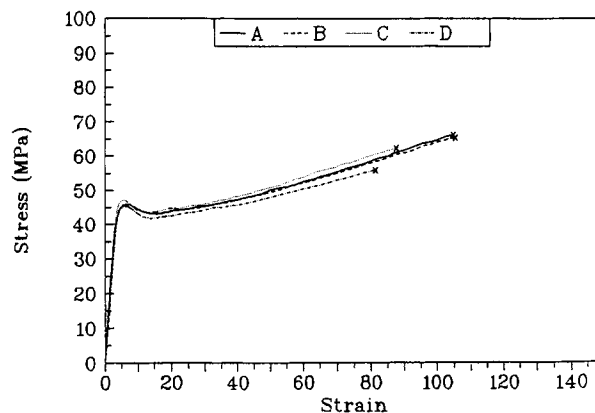

Figure 9 Stress–strain behavior for polycarbonate: effects of gas absorption and desorption. (A) Quenched from 160°C, held at a CO_2 pressure of 900 psi for 7 days (absorbed mass fraction = 0.10), and desorbed for 1 week. (B) Annealed for 7 days at 120°C, held at a CO_2 pressure of 900 psi for 7 days (absorbed mass fraction = 0.10), and desorbed for 1 week. (C) Quenched from 160°C, held at a CO_2 pressure of 900 psi for 24 h (absorbed mass fraction = 0.078), and desorbed for 1 week. (D) Annealed for 7 days at 120°C, held at a CO_2 pressure of 900 psi for 24 h (absorbed mass fraction = 0.070), and desorbed for 1 week.

the production of microcellular foams. This study suggests that although mechanical and thermal properties of aged and unaged polycarbonate may be markedly different, after processing with high-pressure CO_2, properties are independent of previous physical aging and only a function of absorbed mass fraction of CO_2. In the case where pressurized CO_2 is used to produce microcellular polycarbonate, it is important to recognize the effects of physical aging, the effects of the absorbed gas as a plasticizer, as well as the effects that the processing history may have on the excess free volume of the system. Finally, this study suggests that gas absorption followed by desorption can be a feasible method of reversing physical aging in glassy polymers.

REFERENCES

1. A. J. Kovacs, *Polym. Sci.*, **30**, 131 (1958).
2. J. Bartos, J. Muller, and J. A. Wendorff, *Polymer*, **31**, 1678 (1990).

3. K. Neki and P. H. Geil, *Macromol. Sci.-Phys.*, **B8**, 295 (1973).
4. L. C. E. Struik, *Physical Aging in Amorphous Polymers and Other Materials*, Elsevier, New York, 1978.
5. W. M. Lee, *Org. Coat. Plast. Chem.*, **39**, 341 (1978).
6. S. Kapur and C. E. Rogers, *J. Polym. Sci., Phys. Ed.*, **10**, 2107 (1972).
7. V. Kumar, J. Weller, and H. Hoffer, *Symposium on Processing of Polymers and Polymeric Composites*, ASME winter annual meeting, A. A. Tseng and S. K. Soh, Eds., **MD-19**, 197–212 (1990).
8. V. Kumar and J. E. Weller, *Polymer Preprints*, **31**(1), 501 (1992).
9. S. K. Goel and E. J. Beckman, *Polymer Preprints*, **31**(1), 506 (1992).
10. D. C. McHerron, Ph.D. Thesis, Virginia Polytechnic Institute and State University, Blacksburg, VA, 1991.
11. J. M. O'Reilly, R. S. Stein, G. Hadziioannou, and G. D. Wignall, *Polymer*, **24**, 1255 (1983).
12. P. D. Condo, I. C. Sanchez, C. G. Panayiotore, and K. P. Johnston, *Macromolecules*, **25**, 6119 (1992).
13. P. D. Condo and K. P. Johnston, *Macromolecules*, **25**, 6730 (1992).
14. A. R. Berens, *J. Appl. Polym. Sci.: Polym. Phys. Ed.*, **17**, 1757 (1979).
15. Y. Kamiya, T. Hirose, Y. Naito, and K. Mizoguchi, *J. Appl. Polym. Sci.: Part B: Polym. Phys.*, **26**, 159 (1988).
16. S. M. Jordan, W. J. Koros, and J. K. Beasley, *J. Membr. Sci.*, **43**, 103 (1989).
17. E. S. Sanders, S. M. Jordan, and R. Subramanian, *J. Membr. Sci.*, **74**, 29 (1992).
18. D. S. Pope, G. K. Flemming, and W. J. Koros, *Macromolecules*, **23**, 2988 (1990).
19. Y. Kamiya, K. Mizoguchi, T. Hirose, and Y. Naito, *J. Appl. Polym. Sci.: Part B: Polym. Phys.*, **27**, 879 (1989).
20. E. S. Sanders, *J. Membr. Sci.*, **37**, 63 (1988).
21. J. S. Chiou, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **30**, 2633 (1985).
22. H. Hachisuka, T. Sato, T. Imai, Y. Tsuijita, A. Takizawa, and T. Kinoshita, *Polym. J.*, **22**, 77 (1990).
23. R. G. Wissinger and M. E. Paulaitis, *J. Polym. Sci., Part B. Polym. Phys.* **29**, 989 (1991).
24. J. M. Gordon, G. B. Rouse, J. H. Gibbs, and W. M. J. Risen, *J. Chem. Phys.*, **66**, 4971 (1977).