Long-Term Volume Relaxation of Bisphenol A Polycarbonate and Atactic Polystyrene

Christopher G. Robertson and Garth L. Wilkes*

Polymer Materials and Interfaces Laboratory, Chemical Engineering Department, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0211

Received October 12, 1999
Revised Manuscript Received March 22, 2000

Introduction. A few years ago, a study by Wimberger-Friedl and de Bruin[1] appeared in the literature and provided convincing evidence against the general picture of physical aging as a self-limiting process. Upon quenching an amorphous polymer from above the glass transition temperature into the glassy state, densification occurs in the nonequilibrium glassy state as the material attempts to achieve the preferred thermodynamic state. The decrease in free volume and configurational entropy during this physical aging process is thought to enact a corresponding decrease in mobility which, in turn, further limits the ability of the material to relax and densify. This circular process, which is known as self-limitation or self-retardation, is generally considered to be responsible for the dependence of isothermal volume relaxation on log(aging time), as opposed to linear time, during the aging process induced by a quench into the glassy state. The data obtained by Wimberger-Friedl and de Bruin for bisphenol A polycarbonate (PC) aged at 23 °C indicated that the rate of decrease of volume with respect to log(aging time) was constant up to an aging time of $\approx 10^7$ s where a transition to a much greater volume relaxation rate was noted. These results were clearly in opposition to the self-limitation concept.[2−4]

In view of the significance of these prior findings, the goal of our study was to independently evaluate the long-term volume relaxation behavior of PC near room temperature. Also, investigation of the densification behavior of another common glassy polymer, atactic polystyrene (PS), was performed in order to inspect whether the unusual volume relaxation behavior of PC, if observed, was specific to that material or general to polymeric glasses.

Experimental Details. The polymers utilized in this investigation were Makrolon 2608, a bisphenol A polycarbonate produced by Bayer, and an atactic polystyrene material manufactured by Dow which has the resin designation 685D. The approximate number-average molecular weight for the PC material was 16 500 g/mol, and the number- and weight-average molecular weights for the atactic polystyrene were 174 000 and 297 000 g/mol, respectively.[5] The T_g values were 147 and 103 °C respectively for PC and PS. These glass transition temperatures were obtained using a calibrated Perkin-Elmer DSC7 during heating at 10 °C/min following a quench into the glassy state at 200 °C/min.

Glass dilatometers were constructed using precision glass tubing with an inner diameter of 1.829 ± 0.0004 mm for the capillary portion. The tubing was obtained from Ace Glass. A very large amount of film for each material (≈ 60 g) was placed inside a dilatometer and sealed. Triple-distilled mercury was then used to fill the dilatometers under vacuum conditions. The filled dilatometers were then degassed under vacuum for approximately 2 days, and the dilatometers were allowed to stand for 1 day upon removal of the vacuum. The encased polymer samples were annealed for 15 min at $T_g + 20$ °C in a Haake model N4-B oil bath and then rapidly quenched into the glassy state by immersion of the dilatometers in an ice water bath. The dilatometers were then placed into an insulated oil bath kept at room temperature. The reference time which was used as the zero aging time was 15 min after the dilatometers were placed into the room temperature oil bath after removal from the ice water bath. The aging temperature was predominantly between 20 and 22 °C, but extremes of 19 and 24 °C were noted throughout the aging interim which was 2 years. However, during measurement of the mercury height in the capillaries using a cathetometer manufactured by Gaertner Scientific Corp., the oil bath temperature was controlled to temperatures between 21.35 and 21.42 °C. A Haake D1 circulating heater was used to heat the oil bath when necessary for measurements, and liquid nitrogen was employed when some measure of cooling was required. The temperature of the bath and the dilatometers contained therein was assessed using a precision thermocouple made by Ertco-Hart (model 850). Because of the small temperature discrepancies, the height measurements were corrected on the basis of the thermal expansion behavior for the polymer samples and the mercury.

Results and Discussion. The densification results for PC which were assessed in this study confirm the volume relaxation behavior noted by Wimberger-Friedl and de Bruin.[1] The long-term volume relaxation data for PC which were obtained during aging at ca. 21 °C are presented in Figure 1. A change in volume relaxation rate was clearly observed from the measured densification, and this occurred in the aging time vicinity of 10^7 s, comparable to the previous study. Our data prior to the apparent transition indicated a volume relaxation rate of 1.9×10^{-4}, which is essentially identical to the rate of approximately 2×10^{-4} determined by Wimberger-Friedl and de Bruin. However, the aging rate after the transition of our data indicated a much slower relaxation rate than their data (ca. 20×10^{-4} compared to ca. 60×10^{-4}). This latter issue may simply reflect the fact that Wimberger-Friedl and de Bruin performed their measurements up to a final aging time of ≈ 7 years compared to the 2 year experimental time frame used in this present study; our aging investigation may not have been performed for enough time to completely traverse the transition to the new fully developed volume relaxation rate.

Wimberger-Friedl and de Bruin speculated that the apparent transition may represent the realization of the glass transition. This hypothesis opposes the principle of a Vogel temperature which is the temperature limit where the equilibrium segmental relaxation times corresponding to the α-relaxation (glass transition) appear to diverge to infinity. The Vogel temperature for PC is ≈ 100 °C.[6] This suggests that the observation of the glass transition near room temperature should not occur, assuming that equilibrium relaxation times in the glassy state follow an extrapolation of the segmental

---

* To whom correspondence should be addressed.

10.1021/ma991696n CCC: $19.00

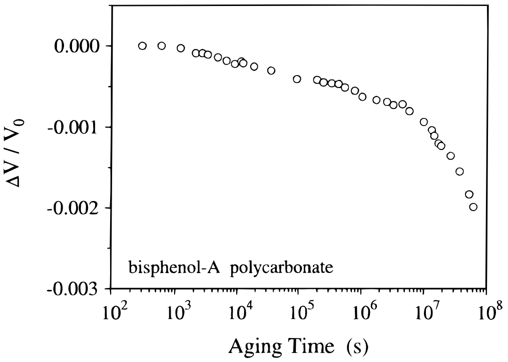

Figure 1. Volume relaxation data for bisphenol A polycarbonate during aging at 21 °C. The negative slope of the data defines the volume relaxation rate.

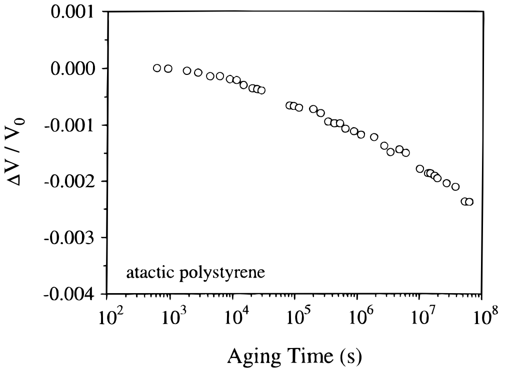

Figure 2. Volume relaxation data for atactic polystyrene during aging at 21 °C. The negative slope of the data defines the volume relaxation rate.

response observed above the glass transition temperature region. Both experimental work by O'Connell and McKenna[7] and a theoretical foundation established by Di Marzio and Yang,[8] however, suggest that the equilibrium glassy state is characterized by Arrhenius behavior which departs from the non-Arrhenius Vogel–Fulcher or Williams–Landell–Ferry scaling[9] observed above the glass transition region. Even so, the mechanical stress relaxation results reported by O'Connell and McKenna[7] for the *equilibrium glassy state* provided an activation energy of 9.58×10^5 J/(mol K), which suggests that is should take on the order of 1×10^{50} s, a time scale in great excess of 10^7 s, to observe the glass transition at temperatures near ambient conditions.

We also monitored the volume relaxation behavior of atactic polystyrene at 21 °C in parallel with the aging study of bisphenol A polycarbonate. The observed decrease of volume with log(aging time) for PS is given in Figure 2, and the data are characteristic of a self-limiting aging process. The volume relaxation rate assessed from these data was 5.4×10^{-4}, which is consistent with existing literature data for PS.[10]

A critical question that needs to be answered is why PC displays the peculiar densification while PS exhibits the typical self-retarded aging behavior. One obvious distinction between PS and PC is the ability of the latter to crystallize, albeit slowly, from the melt state. The driving force for densification of PC may, therefore, be altered compared to that experienced by noncrystallizable polymers in the glassy state. The aging response associated with the nonequilibrium nature of the PC glass may be accompanied by a sluggish analogue to the development of density fluctuations as precursors to ordered crystalline regions which are observed above the glass transition region in semicrystalline polymers.[11,12] *It is important to point out that no evidence of crystallinity was noted using differential scanning calorimetry for the PC material following our 2 year aging experiment.* The above discussion represents pure speculation; the possibility that the ability of a polymer to crystallize can affect the densification process in the nonequilibrium glass is offered merely as a thought argument. What is quite clear from this research is that a more systematic investigation of the long-term aging behavior of other glass-forming polymers at various temperatures must be accomplished before any understanding can be acquired concerning the unusual densification behavior of PC.

Acknowledgment. The authors acknowledge funding provided by the Eastman Chemical and Phillips Petroleum Companies. Appreciation is expressed to Gregory McKenna for reviewing the manuscript and providing useful comments.

References and Notes

(1) Wimberger-Friedl, R.; de Bruin, J. G. *Macromolecules* **1996**, *29*, 4992.
(2) Kovacs, A. J. *Fortschr. Hochpolym.-Forsch.* **1964**, *3*, 394.
(3) Scherer, G. W. *Relaxation in Glass and Composites*; Wiley: New York, 1986.
(4) Struik, L. C. E. *Physical Aging In Amorphous Polymers and Other Materials*; Elsevier: New York, 1978.
(5) Shelby, M. D. Ph.D. Dissertation, Virginia Polytechnic Institute and State.
(6) University, 1996.
(7) Mercier, J. P.; Groenincks, G. *Rheol. Acta* **1969**, *8*, 516.
(8) O'Connell, P. A.; McKenna, G. B. *J. Chem. Phys.* **1999**, *110*, 11054.
(9) Di Marzio, E. A.; Yang, A. J. M. *J. Res. Natl. Inst. Stand. Technol.* **1997**, *102*, 135.
(10) Ferry, J. D. *Viscoelastic Properties of Polymers;* Wiley: New York, 1980.
(11) Greiner, R.; Schwarzl, F. R. *Rheol. Acta* **1984**, *23*, 378.
(12) Marand, H., private communication.
(13) Wang, Z.-G.; Hsiao, B. S.; Sirota, E. B.; Agarwal, P.; Srinivas, S. *Macromolecules* **2000**, *33*, 978 and references contained therein.

MA991696N