Rapid Measurements of Elastic Modulus and Density in Polypropylene Sheet During Aging

J. S. BAUM and J. M. SCHULTZ, *Department of Chemical Engineering, University of Delaware, Newark, Delaware 19711*

Synopsis

New methods for rapidly obtaining elastic modulus and density measurements during isothermal polymer aging are given. The elastic measurements are performed using a Rockwell hardness tester. In this case, the elastic recovery is measured. Rapid density measurements are performed using a "double drop" density gradient column method. Here, a fully aged and a freshly quenched specimen are dropped simultaneously into the column. Simultaneous column height differences directly measure the density difference of the two specimens. The results of these two experiments extend previously reported aging measurements to relatively low times of aging. A log (time) law for both properties is found to the smallest times measured.

INTRODUCTION

Commercial processing of isotactic polypropylene usually involves quenching from the melt. The semicrystalline microstructure of this material develops during and after the quench. The crystalline units form rapidly and exhibit their asymptotic density change within the time necessary to quench a specimen to room temperature and take one x-ray diffraction scan (~15 min).[1-3] On the other hand, the macroscopic density increases with the logarithm of aging time at room temperature.[1,3] This chain rearrangement is reflected in a hardening of the material.

In the aging of polypropylene, the density and tensile modulus are of special interest, since these properties should be interrelated by micromechanical models (see, for example, ref. 4). A previous study by Kapur and Rogers[5] has shown that the tensile modulus, as well as the density, increases logarithmically with aging time. Therefore, relatively large, and predictable, changes should occur in the first few minutes of aging. However, previous work has probed only the time spectrum from 1 hour after quenching, and most of the data have been gathered from one day to a week after quenching. The purpose of the present work is to report new techniques and results for measuring the changes in elastic modulus and density in small time increments immediately after quenching.

EXPERIMENTAL

Sample Preparation

Samples of Hercules ProFax high crystallinity molding grade isotactic polypropylene, $\frac{3}{8}$ in. thick, were prepared for this study. A heated hydraulic press was first preheated to 210°C. Polypropylene pellets were placed in a rectangular mold and sandwiched between two ferrotype plates, which were in turn supported

by two $\frac{1}{4}$-in. (0.64 cm) steel plates. The mold and the polypropylene pellets were heated at 210°C for 15 min under minimal pressure. The sample was then compressed at 6000 psi (4.2×10^6 kg/m^2) and held there for 30 min at the same temperature. The mold was placed into the quenching bath (water at room temperature) immediately after the pressure was released.

A suitable test specimen must have a clean surface and lay flat on the test support. Ferrotype plates were used for molding the polypropylene to ensure a smooth, clean surface. Owing to the thickness of the polypropylene sample, it should not be removed from the mold while it is being quenched and is still hot, to avoid buckling of the sample. The samples were allowed to remain in the quenching bath for a full minute before removal from the mold.

Elastic Modulus Measurement

Small time changes in the elastic modulus of aging polypropylene were measured using a Rockwell hardness tester. For a given applied load, the distances of indentation and recovery measured by the Rockwell tester can be related to an elastic modulus.

The Rockwell test measures the depth of penetration of a metal ball indenter into the plastic under an applied load, as shown in Figure 1. Each increment on the Rockwell C scale corresponds to 2 μm of penetration. The depths of penetration during loading and subsequent recovery are related to an elastic modulus using an empirical test procedure developed by Baer et al.[6] Drawing on the elastic theory of Hertz[7] and empirical observation, Baer et al. derived an expression for the tensile modulus E in terms of indentation measurements:

$$E = \frac{0.346 W}{(d_1 - d_2)(d_1 D)^{1/2}} \tag{1}$$

where W is the applied load in pounds, D is the diameter of the indenting metal ball in inches, and d_1 and d_2 are the depths of penetration and recovery, respectively, as shown in Figure 1. In these experiments, a load of 60 kg was used. For polypropylene, these depths d_1 and d_2 are on the order of ten thousandths
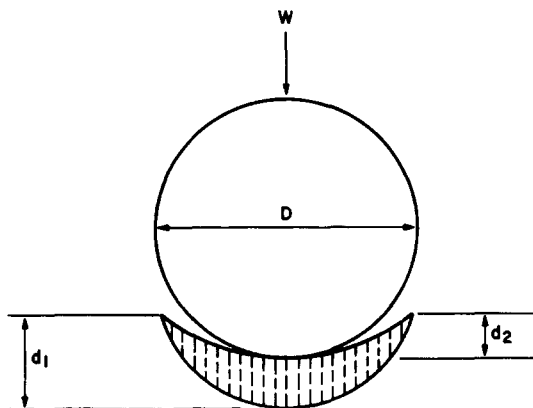

Fig. 1. Indentation of polymer specimen by ball indenter under an applied load. The depths d_1 and d_2 represent the indenter depth under plastic plus elastic strain and plastic strain only, respectively.

of an inch. For these experiments, a special $\frac{3}{4}$-in. ball indenter was constructed. Although Baer did all of his work using an Instron testing machine, any device capable of accurate measurement of the depth of penetration can be used.

The time factors involved in the application and release of the load are important, owing to the creep and recovery behavior of polypropylene. Following the guidelines for Rockwell testing of plastic given in ASTM D785-65, the major load (60 kg) was applied within 10 sec of fixing the specimen in place with the minor load (10 kg). After 15 sec of application, a reading (d_1) is taken and the major load released. The recovered depth (d_2) is then read after another 15 sec. These time intervals for the testing are quite critical to the resulting modulus and should be kept to 15 (+1, −0) sec.

Density Measurement

Small time changes in the density of the quenched polypropylene were measured using a density gradient column, using a miscible mixture of carbon tetrachloride and toluene. To obtain rapid estimates of the sample's changing density, a "double drop" technique was used. A freshly quenched sample and an infinitely aged sample (at least a week old) were placed into the column simultaneously. The samples' positions in time were measured at small time intervals using a cathetometer.

The most accurate readings were obtained using small (1.5×10^{-2} cm^3) symmetrical samples. The effects of tumbling and drag on the samples as they settle were then minimized. Figure 2 shows typical settling curves for two pieces of
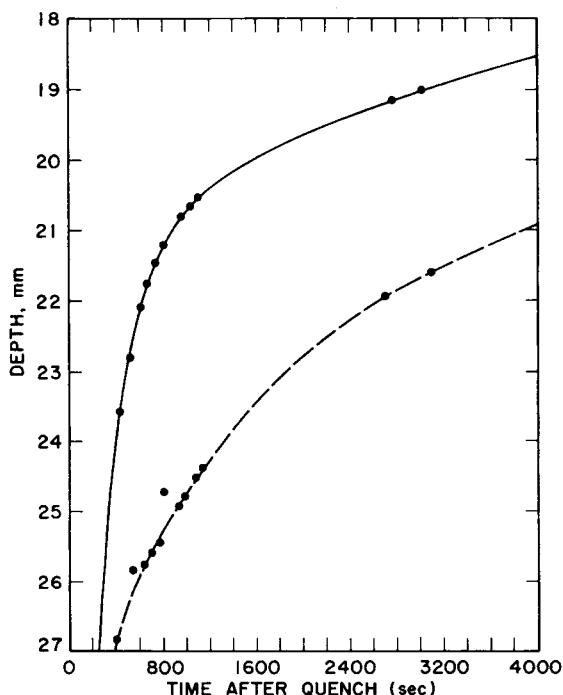

Fig. 2. Typical settling curves for aged (dashed line) and aging (solid line) polypropylene in a density gradient.
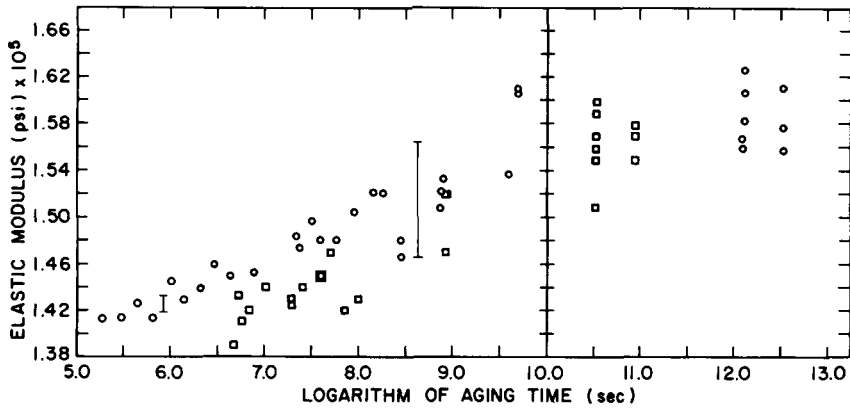
Fig. 3. Elastic modulus vs. natural logarithm of aging time. Circles and squares represent two different specimens. Error bars shown for two different modulus levels.

polypropylene. All of the settling curves are of the same general shape. They vary in detail because of the differences in the ultimate densities of the two pieces and the differences in the density gradients. Using such graphs, the instantaneous difference in apparent density between the freshly quenched piece and the fully aged piece will be proportional to the difference in column height at any time. A plot of the apparent density difference $\Delta\rho$ versus time can then be extracted from the settling curves.

RESULTS

Modulus

Figure 3 shows the elastic modulus as a function of the logarithm of the time for two samples aging at 25°C. A linear relationship exists down to an earliest reading of 3 min and 15 sec after quench. This confirms a similarly linear relationship presented by Kapur and Rogers[5] but extends the results to much lower aging times. The specimens of Kapur and Rogers show a larger change in the elastic modulus than was found here using indentation measurements. However, the data of Kapur and Rogers were obtained from tensile tests and cannot be compared absolutely to the moduli obtained here. The present values are actually surface-related moduli. In addition, the molecular weight of the polypropylene used by Kapur and Rogers was different from ours. The similarity of the aging functions is what is significant.

TABLE I
Average Rates of Density Change for Three Room-Temperature Aging Runs

Average density change; g/cm³/sec	Data taken
1.52×10^{-7}	April 27, 1979
1.59×10^{-7}	April 12, 1979
1.56×10^{-7}	April 27, 1979

Density

Figure 4 is a plot of the apparent density difference between an aging specimen and a control specimen. This curve is typical of the case in which both specimens are small and have identical rodlike geometry. (When such a match does not exist, the $\Delta\rho$–t curve exhibits either a hump or an exaggerated slope at times below 20 min). These data parallel those of Schael,[1] as shown in Figure 5. Differences in the absolute initial density depend, however, on differences in the material used and in small differences in the method of preparation. The "double drop" method effectively extends the existing data toward time zero and reaffirms the logarithmic time dependence of the polypropylene density.

Average rates of change of density over the time period 1800–6400 sec after quenching are given in Table I. The results of three identical runs are shown there. The reproducibility of this result is evident.

DISCUSSION

Methods for the measurement of elastic modulus and density in small time increments have been established. Using these methods, the previously reported logarithmic dependences have been shown to extend to the early stages of aging. As in the earlier work of Schael,[1] both elastic modulus and density are reported here. Schael showed a linear relationship between the tensile modulus and the
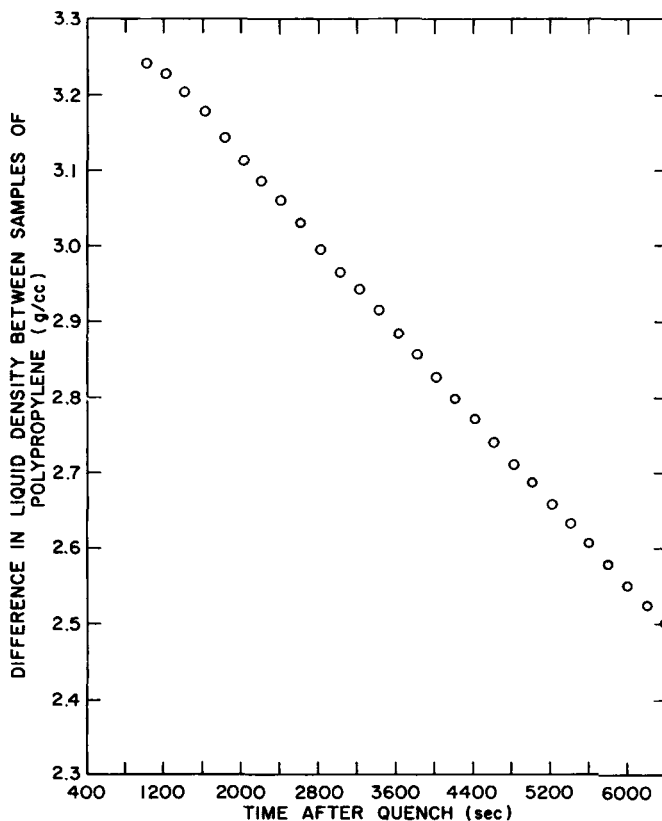

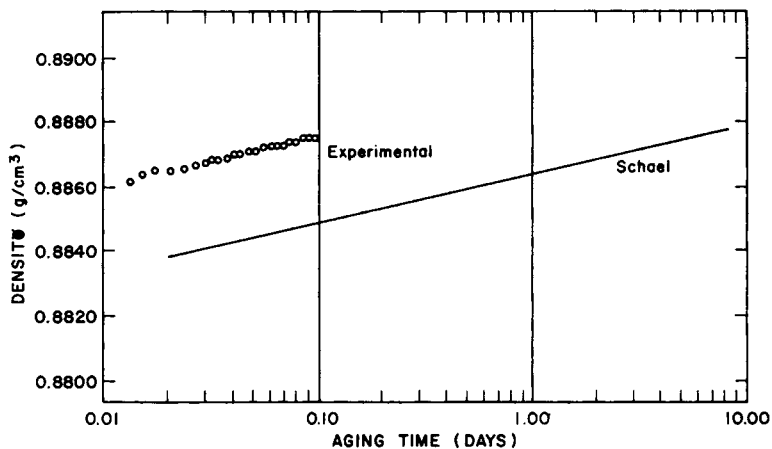Fig. 4. Apparent density difference between an aging and a fully aged specimen.

Fig. 5. Comparison of "double drop" density data with those of Schael.[1]

density of 7.7×10^9 (kg/m^2)/(g/cm^3). The ratio derived in the present is 3.1×10^9 (kg/m^2)/(g/cm^3). The differences in the two figures is most probably due primarily to differences in the material used and in the nature of the elastic modulus measurement.

References

1. G. W. Schael, *J. Appl. Polym. Sci.*, **10**, 901 (1966).
2. D. M. Gezovich and P. H. Geil, *Polym. Eng. Sci.*, **8**, 210 (1968).
3. M. K. Agarwal, M.Ch.E. Thesis, Univ. of Delaware, 1980; *Polym. Eng. Sci.* (to appear).
4. R. L. McCullough, in *Treatise on Materials Science.* Vol. 10B, *Properties of Solid Polymeric Materials*, J. M. Schultz, Ed., Academic, New York, 1977.
5. S. Kapur and C. E. Rogers, *J. Polym. Sci. Part A-2*, 2107 (1972).
6. E. Baer, R. E. Maier, and R. N. Peterson, *SPE J.*, (Nov. 1961).
7. A. E. H. Love, *The Mathematical Theory of Elasticity*, 4th ed., Dover, New York, 1927, p. 183.