Anisotropy and Dimensions of Blow-Molded Polyethylene Bottles

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A commercial blow-molding grade, high-density polyethylene resin was employed to produce cylindrical bottles in a commercial reciprocating screw-extrusion blow-molding machine. The distributions of thickness, crystallinity, birefringence, and impact strength were obtained at various positions. The thickness is greatest near the parting lines, while minimum thickness occurs at the top and bottom of the bottle. The thickness tends to be uniform in the middle section, in agreement with earlier studies of the parison during processing. Density and crystallinity distributions are closely associated with the distribution of thickness and its effect on the cooling rates prevailing during molding. Frozen stresses and birefringence are largest at the outer surface, where cooling rates are highest. The impact strength is lowest near the parting line. Photomicrographs suggest that this is associated with internal flow and crystallization phenomena.

INTRODUCTION

Commercial bottles must satisfy performance criteria that are compatible with the intended application of the bottles. However, it is well known that blow-molded polyethylene bottles exhibit a significant variation in thickness from point to point. Associated with this thickness distribution, there are observable distributions of mechanical and permanence characteristics. These distributions are the direct result of the thermo-mechanical history of the resin during the various stages of the blow molding process.

The limited amount of reported work in the area of ultimate properties of blow-molded articles (1-6) represents attempts to correlate empirically some property (in some cases, not very well defined) of the blow-molded article (e.g., haze, drop-impact resistance, shrinkage, "appearance," etc.) to operating conditions (e.g., extrusion rate, temperature, blow pressure, etc.) and to some resin parameters (e.g., melt index or resin density). The thermo-mechanical history and the microstructure, which have not heretofore been investigated, represent the necessary links between resin properties, operating conditions, and ultimate bottle properties.

In the following discussion, we summarize some of the results of an experimental program designed to study the distribution of thickness, crystallinity, density, impact properties, and birefringence in blow-molded polyethylene bottles. The data will be analyzed in relation to the thermo-mechanical history experienced by the material during the molding process.

EXPERIMENTAL

A commercial blow-molding grade, high-density polyethylene resin, designated as Resin D, was employed in the study. The density of Resin D was 0.960 g/cm^3 with melt index of 0.40.

The variation of shear viscosity with shear rate and temperature for Resin D was determined employing both the Instron Capillary Rheometer and the Rheometrics Mechanical Spectrometer. The results for 200 and 225 C are shown in *Fig. 1*. In addition to shear viscosity, the capillary extrudate swell of the material, $B(t)$, was measured as a function of time and temperature, in conjunction with the Instron Capillary Rheometer and a specially designed attachment to minimize

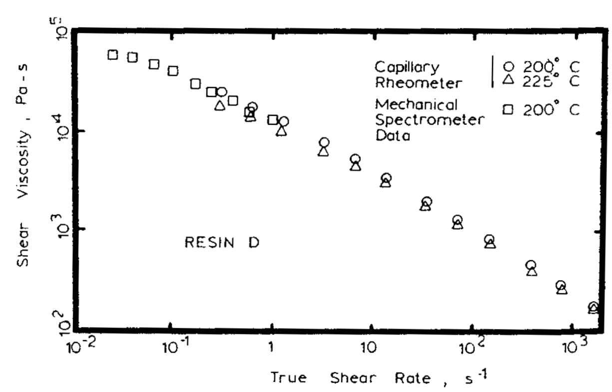

Fig. 1. Shear viscosity behavior of Resin D.

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the effects of drawdown (gravity) and cooling. The results are shown in *Fig. 2*. The significance of the above and other rheological properties in relation to the blow-molding behavior of the material will be the subject of another report. Information regarding the details of the apparatus and experimental procedure may be found elsewhere (7).

An Impco, model A13-R12, reciprocating screw-extrusion blow-molding machine was employed in conjunction with a commercial bottle mold possessing a uniform cylindrical cavity. The cylindrical section of the cavity had a diameter of 8 cm and a length of 20 cm.

Extrusion temperature was set at 200°C and blow pressure at 0.62 MPa. The mold temperature was 13°C, and the extrusion speed was monitored to be 45 g/s.

The blow-molded samples were cut so that the cylindrical sections of the bottles were separated. The separated cylindrical sections were further cut along one of the parting lines yielding a flat sheet. The cylindrical sections were further divided into 24 vertical strips, each 1 cm in length. The thickness distributions were determined over 1 cm intervals from top to bottom, employing a micrometer. The average density at various positions was determined employing a density gradient column. In order to determine density distribution in the thickness direction, samples cut at various positions in the bottle were microtomed using a microtome manufactured by Reichert. For reference, three coordinate axes were defined as indicated in *Fig. 3*. The x-axis represents the axis of the cylindrical bottle, the y-axis is in the direction of the cut and flattened circumferences, and the z-axis is in the direction of the thickness of the bottle.

The crystallinity and the birefringence distributions of the microtomed samples between the outer and inner surfaces of the moldings were determined in the y-z

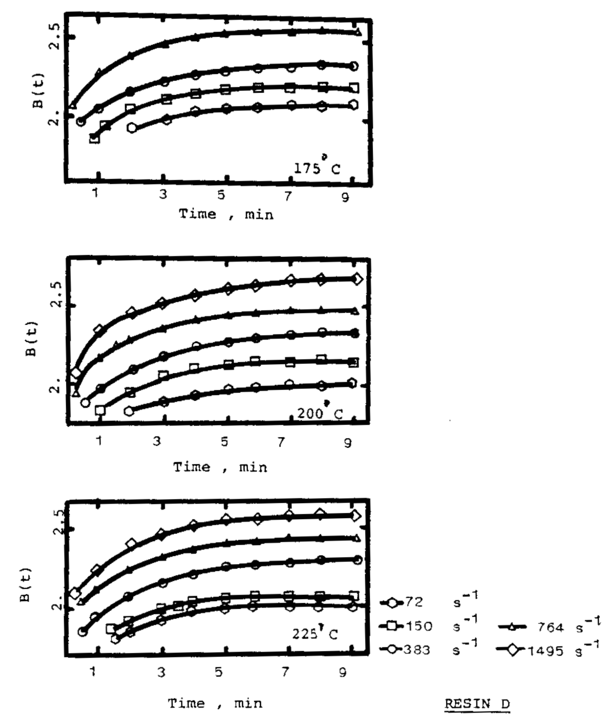

Fig. 2. Die swell behavior of Resin D.

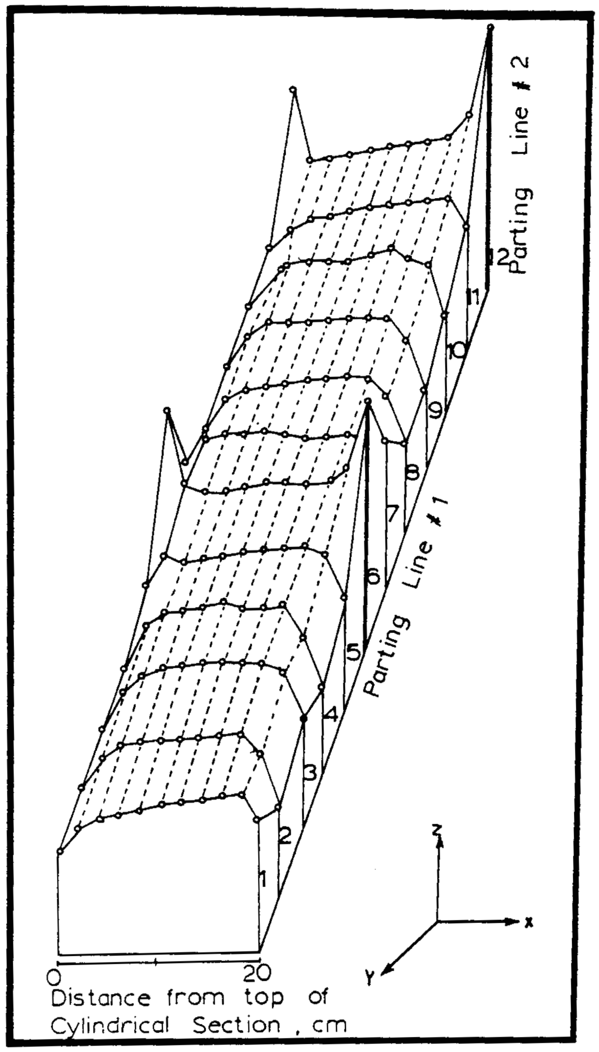

Fig. 3. Typical three-dimensional thickness distribution in blow-molded samples.

plane. The birefringence experiments were carried out employing a Reichert "Zetopan Pol" polarization microscope, in conjunction with a rotary compensator with quartz combination plates, manufactured by Ehringhaus. The morphology of the samples, microtomed in the x-y and x-z planes, was investigated and photographed under polarized light employing the Reichert polarized microscope.

For impact tests, the cylindrical sections of the blow-molded samples were divided uniformly into six rectangular sections with dimensions of 8 · 10 cm^2. Two of the test locations coincided with the parting line. The impact properties of the samples were determined employing the High Speed Impact Tester recently developed by Rheometrics, Inc., employing various cross-head speeds.

RESULTS AND DISCUSSION

A typical three-dimensional thickness distribution of the cylindrical sections of the blow-molded samples is shown in *Fig. 3*. The thickness is greatest at and around the parting lines (e.g., Positions 6 and 12), and it varies substantially along these lines. The minimum thickness is observed to occur at the top and bottom portions of various positions, excluding the parting lines and their vicinity. With respect to circumferential distributions, thickness varies significantly along the top and bottom portions of the cylindrical sections from a maximum at the parting lines to a minimum at Positions 4 and 9, which are situated at 90° from the plane of the parting lines. At other positions, located 4-16 cm from the top of the cylindrical section, the thickness is more uniform and does not vary significantly along the circumference. The variation of bottle thickness may be related to observed variations in the parison during extrusion (7-9) and inflation (10, 11).

Typical distributions of average density at various locations around the circumference are shown in *Fig. 4*. The density varies considerably around the circumference. The maximum values of density are observed at the parting lines where the thickness is maximum. The relationship between the thickness and density distributions in blow-molded samples is illustrated in *Fig. 5*. The density appears to increase linearly with thickness. The increase of the density with increasing thickness may be attributed to the lower rates of cooling associated with thicker specimens, since lower cooling rates permit higher levels of crystallinity (7). This behavior emphasizes the very important role of thickness control in extrusion blow-molded parts.

The distribution of crystallinity between the outside and inside surfaces of the blow-molded specimens at a position with a thickness of 1.6 mm is shown in *Fig. 6*. Crystallinity increases from a minimum at the outside

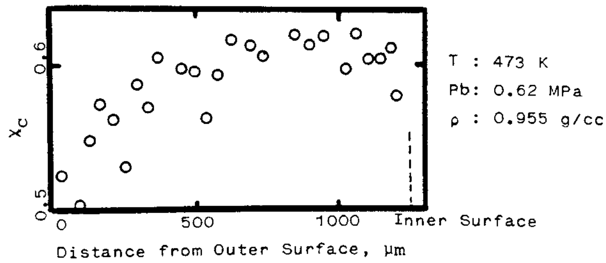

Fig. 6. Variation of crystallinity with distance from the surface.

surface, where the polymer contacts the mold cavity surface during the cooling stage, to a maximum close to the inside surface. The variation of crystallinity between the two surfaces should again be mainly influenced by the prevailing cooling rates during the cooling stage (7).

It should be noted that the material at or close to the outside surface, which solidifies immediately, should retain the orientation arising from the previous deformation history, while the material at or close to the inner surface has available a substantially longer duration of time for the relaxation of orientation under more favorable thermal conditions. As shown in *Fig 7*, optical anisotropy or birefringence indeed generally increases from a maximum at or close to the outer surface to a minimum at or close to the inner surface of the blow-molded articles. Moreover, it has been observed that birefringence is greater for higher blow pressures and lower extrusion temperatures. These observations are related to the effects of pressure and temperature on the frozen-in hoop stress in the molded bottles. Higher

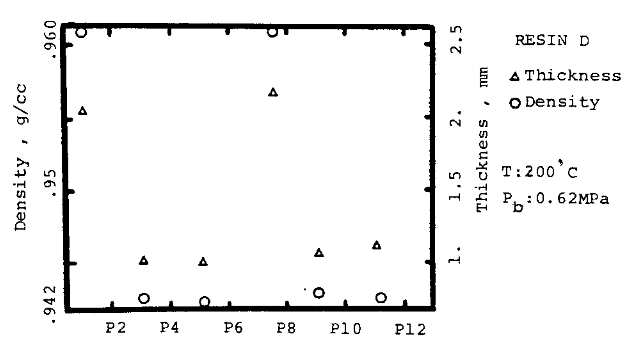

Fig. 4. Variation of density at various positions.

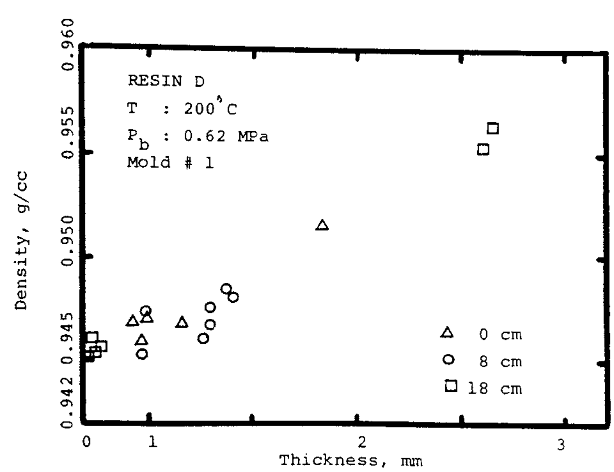

Fig. 5. Relationship between density and thickness.

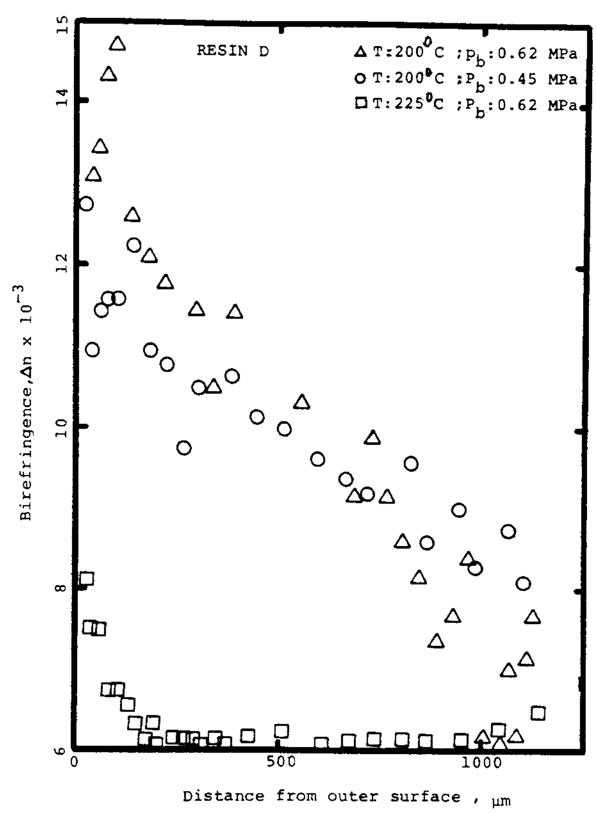

Fig. 7. Variation of birefringence with distance from the surface.

blow pressures result in higher strain rates during inflation, as demonstrated in *Fig. 8*. The strain rate, $\dot{\epsilon}(t)$, has been based on experimental cinematographic data obtained during the inflation stage, and it is defined as follows:

$$\dot{\epsilon}(t) = \frac{dD_2(t)}{dt}\frac{1}{D_2(t)} \quad (1)$$

where $D_2(t)$ represents the measured outside diameter at time t during inflation. Also, higher blow pressures must be associated with larger hoop stresses, $\tau(z, t)$, defined at height, z, and time, t, as follows:

$$\tau(z, t) = \frac{PR(z, t)}{b(z, t)} \quad (2)$$

where P is the blow pressure, R is the radius, and b is the thickness of the parison. The role of the lowering of temperature is to raise the effective extensional viscosity of the material, which again should contribute to raising the hoop stresses.

Typical variations of the values of the impact energy at yield, Ey, and impact energy at break, Eu, normalized with respect to the thickness of various positions tested, is shown in *Fig. 9*. The only statistically significant variation in properties is observed when the test locations coincide with the parting lines (positions designated with PL). At the parting lines, the energy at break and yield is significantly lower than at other positions.

Photomicrographs of samples, which were microtomed perpendicular to the bottle axis at various positions around the circumference of blow-molded samples, are shown in *Fig. 10*. Dark bands were observed at both parting lines due to the squeezing flow of the parison during clamping of the mold. Furthermore, there are arc-shaped flow lines, which appear to be composed of brighter and larger irregular-shaped spherulites, in the vicinity of the parting lines. The combined effects of the "weld-line"-type structures

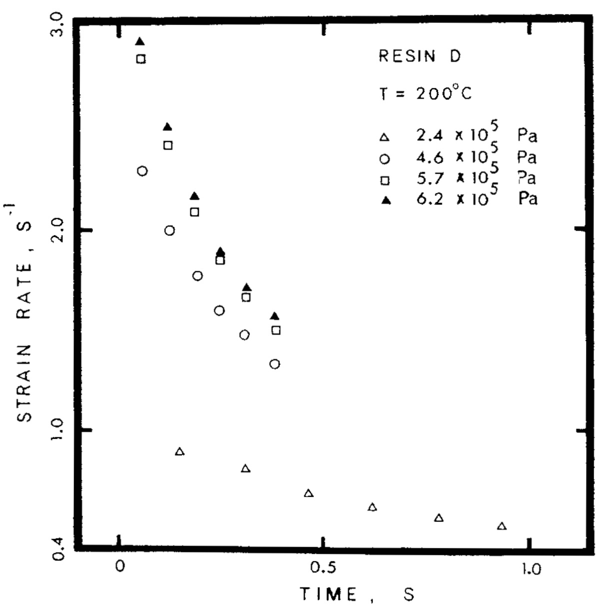

Fig. 8. Effect of blow pressure on strain rate during inflation.

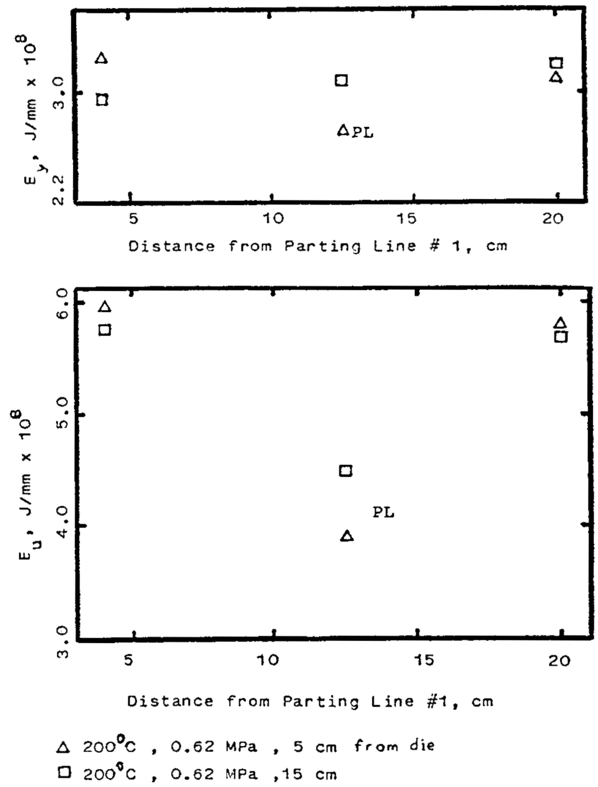

Fig. 9. Variation of energy at yield, E_y, and energy at break, E_u, with distance from the parting line.

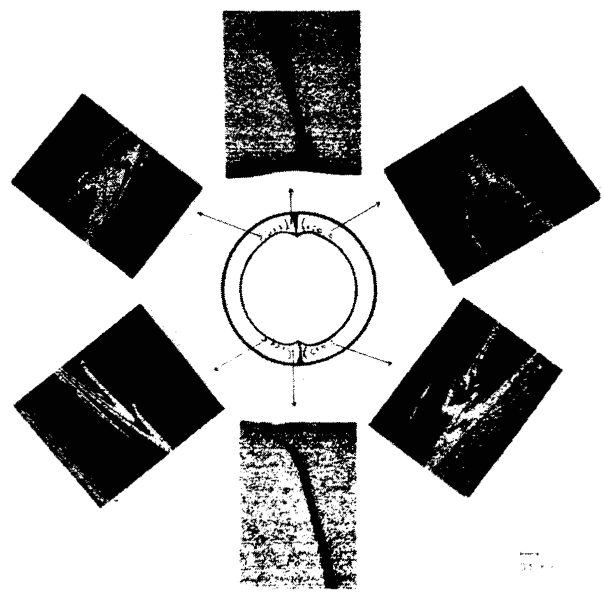

Fig. 10. Photomicrographs illustrating internal flow and crystallinity near the parting line.

and the irregularly-shaped spherulites may result in the lower values of impact strength of the samples at these positions, as shown in *Fig. 9*.

CONCLUSIONS

The results of this study suggest that, in the absence of careful control schemes, the thickness of extrusion blow-molded articles varies considerably both in the axial and circumferential directions. Such variation may be attributed to phenomena occurring during the parison-formation, clamping, and inflation stages. The prevailing thickness distribution during the blow-molding process leads to variations in cooling rates and, consequently, to variations in the distribution of density (crystallinity), birefringence (orientation), and ultimate properties. Moreover, it is found that the material at the parting line exhibits low-impact strength associated with morphological and orientation characteristics that are significantly different from those observed at other positions in the blow-molded article.

REFERENCES

1. H. Frank and W. Wengler, *Verpack Runds*, **22**, **10**, 1382 (1971).
2. M. Dixon, *Plast. Inst. Trans. J.*, **13** (1963).
3. J. Terenzi, R. Griffith, and C. Deeley, *SPE ANTEC Tech. Papers*, **13**, 745 (1967).
4. W. Daubenbechel, *Kunststoffe*, **66**, **7** (1976).
5. W. Kendall, *Plast. Inst. Trans. J.*, **49** (1963).
6. S. Hirata and A. Kishimoto, *Polym. Eng. Sci.*, **10**, 235 (1970).
7. D. M. Kalyon, Ph.D. Thesis, McGill University, Montreal (1980).
8. D. Kalyon, V. Tan, and M. R. Kamal, *SPE ANTEC Tech. Papers*, **25**, 992 (1979).
9. D. Kalyon, V. Tan, and M. R. Kamal, *Polym. Eng. Sci.*, **20**, 6 (1980).
10. M. R. Kamal, V. Tan, and D. Kalyon, *Polym. Eng. Sci.*, in print.
11. M. R. Kamal, D. Kalyon, and V. Tan, in "Rheology, Applications," Vol. 3, pp. 149-155, edited by G. Astarita, G. Marrucci, and L. Nicolais, Plenum Press, New York (1980).
12. G. Capaccio and J. Ward, *Polymer*, **16**, 239 (1975).