

LETTERS TO THE EDITORS

The Properties of Marlex Crystallized at High Pressure

Objects molded of polyethylene can be considered to be in a quenched state, to a certain extent. Annealing would reduce the number of noncrystalline segments which are in a state of quasi-equilibrium, but one is by no means assured that an equilibrium density has been reached.

Under atmospheric pressure, a higher density is generally obtained when crystallization occurs at a higher temperature. Mandelkern¹ has obtained a Marlex sample with density of 0.982 g./cm.³ by crystallizing it at atmospheric pressure for 40 days and cooling it to 25°C. Under a much higher pressure, a density as high as this can be obtained in a much shorter time (ca. 2-4 hr.). Table I shows the density of Marlex polyethylene crystallized at high hydrostatic pressure. The crystallization temperature for the sample of 0.981 g./cm.³ density shown here corresponds to about 14°C. below the melting temperature under 1200 atm., while Mandelkern's sample was crystallized at about 7°C. below the melting temperature. Since the temperature coefficient of crystallization is extremely high in polyethylene,^{2,3} the difference in the amount of supercooling for the above two cases would understandably result in a very large difference between the rates of crystallization. Since the difference in thermodynamic potential between the metastable liquid state and the stable crystalline state would determine the critical crystal size⁴ (or the chain folding period)^{5,6} these two samples would expectedly possess different crystalline textures in spite of the coincidence in density.

The results of x-ray diffraction studies on a pressure-crystallized sample and an injection-molded sample are shown in Figure 1. Although the difference in the peak Bragg angles cannot be concluded as real on the basis of just these data, the difference in the peak intensities for the 110 plane ($2\theta \approx 21.6^\circ$) is unmistakably clear. The spread of intensities around the 110 peak is narrower (Fig. 2). This indicates that the difference in density between the two samples is due largely to the crystallinity. A comparison of dynamic moduli⁷ also supports this view. The real modulus of a pressure-crystallized sample was found to be greater than that of an injection-molded sample at all frequencies between 10^{-3} and 100 cycles/sec., while for their loss tangents the relation was reversed.

TABLE I

Densities of Marlex (M.I. = 8) Crystallized at Different Temperatures and Pressures^a

Pressure, atm.	2600	2600	1700	1300	1200
Temperature, °C.	150	160	160	160	160
Density, g./cm. ³	0.966	0.968	0.971	0.977	0.981

^a Samples were crystallized at the specified conditions for 2 hr. and cooled to 25°C. This material exhibits a density of 0.95-0.96 g./cm.³ when compression-molded.

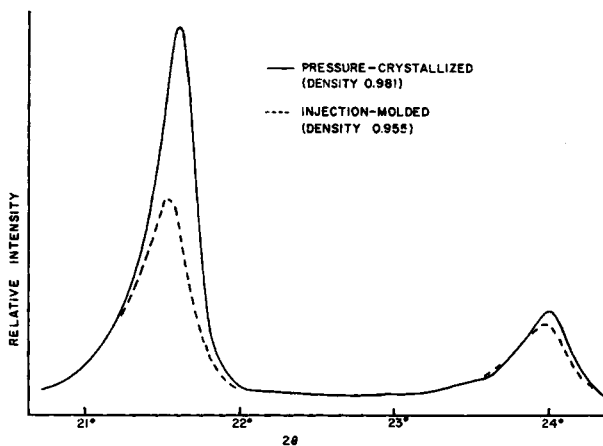


Fig. 1. X-ray diffraction for the pressure-crystallized sample (density 0.981 g./cm.³) and an injection-molded sample (density 0.955 g./cm.³).

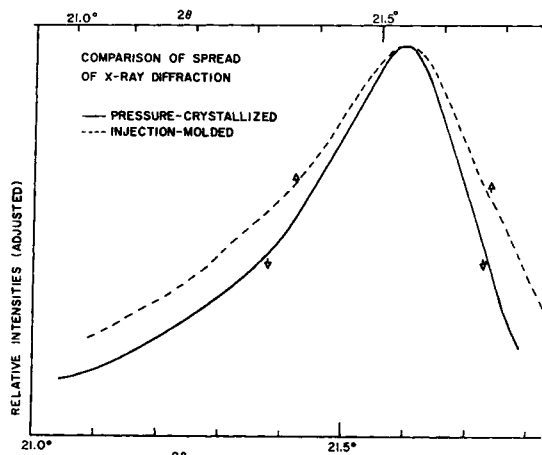


Fig. 2. Replot of data shown in Fig. 1 to compare the ratio of the peak height to the spread at 110 plane. The intensity of the injection-molded sample has been amplified by 1.8 times to match the peak heights.

A high density material thus obtained seems to attain an even higher density upon annealing under atmospheric pressure. Slichter⁸ has shown that a sample with a density of 0.971 g./cm.³ (crystallized at 160°C. under a hydrostatic pressure of 1700 atm. for 2 hr. and cooled to 25°C.) can be annealed to consistently higher densities (up to 0.979 g./cm.³) by raising the temperature of annealing (up to 130°C.). Nuclear magnetic resonance tests were made on these specimens by the same author, and the relative abundance of the narrow component was found to decrease from 0.060 to 0.036 upon annealing at increasing temperatures, suggesting that the overall crystallinity increases with the increase in density.

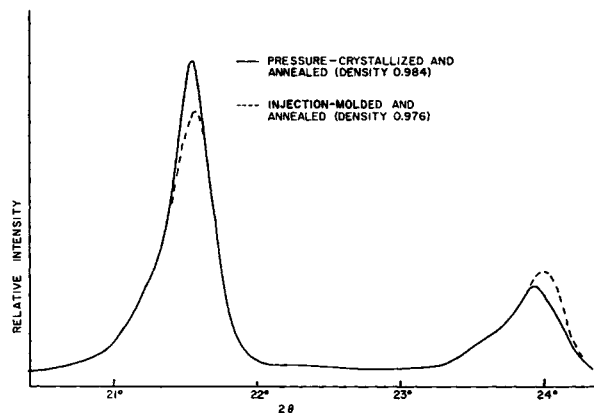


Fig. 3. X-ray diffraction for the pressure-crystallized and injection-molded samples after annealing. Densities are 0.984 and 0.976 g./cm.³, respectively.

While the high density resulting from the high pressure of crystallization thus seems largely due to the high degree of crystallinity, this general increase in crystallinity does not seem to be the only characteristic of the high pressure process. After the data shown in Figure 1 were taken, the same two samples were annealed for 17 hr. at 120°C., for 5 hr. at 129°C., and for 16 hr. at 110°C., successively. Upon cooling the specimens down to 25°C., the densities of the molded sample and the high pressure-crystallized sample were both found to have increased to 0.977 and 0.984 g./cm.³, respectively. The x-ray diffractions of these samples after annealing are shown in Figure 3. Although the 110 peak of the pressure-crystallized sample still remains higher than that of the originally molded sample, the 200 peak of the latter has increased above that of the denser material. Also by comparing the x-ray results on the pressure-crystallized specimen before and after annealing, it was found that the 110 peak had decreased after annealing, even though the density has increased. The fact that the ratio of the 110 peak to the 200 peak for the pressure-crystallized sample is greater than that for the ordinary sample (both annealed and unannealed) confirms that there are some morphological differences between the two. There should then be a difference in some physical properties, even if these two are of an identical density. This view is supported by the experiments of Brazier and Maxwell⁹ on some fracture properties of Marlex polyethylene crystallized at various pressures and temperatures. Long-time brittle fracture tests were made on these specimens, since this has long been suspected to be sensitive to the crystalline texture of polyethylene.¹⁰ The results show that samples with identical densities exhibit markedly different fracture characteristics depending on the pressure of crystallization.

Summary

By inducing crystallization in linear polyethylene by hydrostatic pressure, an unusually high density can be attained. Such a high density seems largely due to high crystallinity. The high density material thus prepared can generally be annealed to even a higher density. The crystalline texture of such a material is different from that of an ordinary molded sample.

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On Melting Characteristics of Linear Polyethylene

Dilatometric data on semicrystalline polymers, both above and below their melting temperatures are numerous, and linear polyethylene has perhaps been investigated most often.¹⁻³ These data usually differ in some details. Difficulties arise because (1) below the melting point the existence of equilibrium is uncertain, since the density of the polymer depends on the conditions of crystallization and also because (2) the volume-temperature curve is sensitive to the rate of heating.

In this study, dilatometric measurements were made on Marlex 6000 type 50 linear polyethylene. A commercial dilatometer (Scientific Glass No. 1025) was modified for the purpose, and a procedure similar to that by Bekkedahl⁴ was followed. An automatic temperature control system designed by J. L. Lundberg of these laboratories was used. It controlled the bath temperature within 0.01°C., for an indefinite period of time.

Dilatometric measurements were first taken on a compression-molded sample (density 0.963 at 23°C.) at two different rates of heating. On the first run, a heating rate of 1°C./42 hr. (in increments of 0.2°C.) was employed near the melting point. After this run was complete, the bath and the sample were allowed to cool to 20°C., and the second experiment was made on the same sample (somewhat denser as the result of slow cooling) at the rapid heating rate of 10°C./hr.

It is clear from the results shown in Figure 1 that a rapid rate of heating induces partial melting at lower temperatures. Furthermore, it was also noticed during the experiment that some volume increase would immediately follow an initial temperature increase, but when the temperature was kept constant at this new level the volume would de-