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Characterization of High-Density Polyethylene Prepared at Low Pressure

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Synopsis

A high-density polyethylene prepared at low pressures is characterized with respect to density, microscopic examination, mechanical properties, and diffusion. The data for the slowly cooled, nonisothermally crystallized polymer clearly indicate that the method of preparation grossly affects the final properties of the polymer.

INTRODUCTION

In recent years, numerous observations have been accumulated showing that surface layers of a polymer arising from contact with another phase (particularly a solid) differ in structure and properties from the polymer at fairly large distances from the phase boundary.[1]

In the present paper, we have prepared samples of polyethylene in contact with both a low- and a high-surface-energy substrate to evaluate their influence on a variety of physicochemical properties of the polymer. The polymer samples were crystallized from the melt at low pressures (~1 atm) but for quite long periods of time.

EXPERIMENTAL

Sample Preparation

Polyethylene used in this study was an unfractionated Marlex 6050 with a weight-average molecular weight ($\bar{M}_w$) of 79,000. Three different specimens of polyethylene film (10 mil) were prepared for dynamic mechanical measurements using a Vibron Dynamic Viscoelastometer, Model DDV-II, manufactured by the Toyo Measuring Instruments Co., Ltd., Japan.

Sample A was molded for 30 min at 170°C between polytetrafluoroethylene (PTFE) sheets (10 mils) and quenched rapidly by passing cold water through the press platens. The polyethylene was separated easily from the PTFE and the dynamic mechanical properties were examined.

Two additional 10-mil polyethylene samples were prepared in the following manner. Samples B and C of polyethylene were prepared between 10-mil sheets of aluminum (B) and FEP Teflon films (C) at 170°C for 30 min. The composites were cooled rapidly in the press. Samples of the com-

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posites were sealed in glass tubes in which the air had been replaced by pure nitrogen. The tubes were then immersed and kept for a period of 24 hr in a silicone oil bath maintained at 142°C. The rate of cooling of the oil bath was adjusted to 2°C/day from 142° to 105°C, 4°C/day from 105° to 50°C, and 8°C/day from 50°C to room temperature. Samples A, B, and C are nonisothermally crystallized polyethylenes. Sample C was removed quite easily from the FEP Teflon composite by peeling, while the composite containing sample B was exposed to dilute hydrochloric acid (0.1*N*) to free the polymer. No oxidation was observed when samples were examined using ATR spectroscopy.

RESULTS AND DISCUSSION

Density

The density of samples A, B, and C was measured in a density gradient column containing a 1:1 mixture of diethylene glycol and isopropyl alcohol maintained at 23°C. Density values are given in Table I. The differences between the densities of samples A and samples B and C obviously depend upon the rate of cooling.

TABLE I
Density Values for Samples A, B, and C at 23°C

Sample	ρ, g/cm^3
A	0.957
B	0.989
C	0.988

Microscopy

Samples A, B, and C were examined by microscopy to detect any unusual morphologic change. Sections of the samples were taken transverse to the film direction. A typical result for samples B and C is shown in Figure 1. There apparently is no evidence for the usual spherulitic structure. In addition, it appears that the thickness of the lamella is well below that of the extended chain crystals of Wunderlich.[2]

Dynamic Mechanical Properties

One of the unusual characteristics of slow-cooled materials is their lack of ductility. This was readily noted in the course of cutting specimens of suitable size for viscoelasticity measurements. Sample C was extremely fragile. Upon cooling, the specimens broke repeatedly in the clamps of the Vibron instrument. As a result, we were able to collect viscoelastic data for sample C only at temperatures above 0°C.

The loss tangent and dynamic moduli values of the three samples are shown in Figure 2. The loss modulus (E'') curve of sample A exhibits a

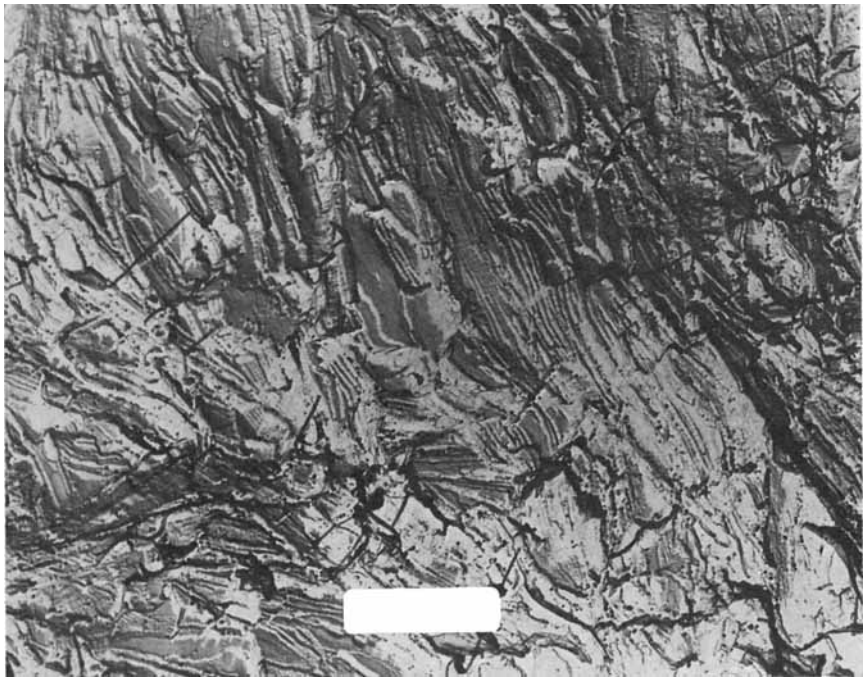

Fig. 1. Microscopic examination transverse to the film direction.

broad γ dispersion. It was previously reported by Matsuoka, Ishida, and Aloisio[3] that polyethylene γ-transitions can be separated into a γ_c relaxation in crystals and a γ_a relaxation in the amorphous glassy region. The γ_a dispersion, the higher temperature peak of the two, occurs at $-110°C$ for sample A. The γ_c relaxation which manifests itself as a shoulder in the E'' curve of sample A probably has its peak between $-140°$ and $-160°C$. In comparison, the γ_c relaxation is virtually absent in sample B. The γ_c relaxation has been ascribed to the motion of segments in the defects or near the surface of crystals. Our dynamic mechanical results therefore suggest that the crystals in sample C have fewer imperfections than sample A. It is also noted that although the γ_a peak temperature for sample B also occurs at $-110°C$, the magnitude of the loss tangent is reduced when compared with that of sample A. The loss tangent of a highly crystalline material is a direct measure of the intensity of the molecular relaxation. We therefore conclude that there are fewer amorphous segments undergoing γ_a relaxation in sample B. This conclusion is consistent with the high density of the sample.

The α relaxation process in linear polyethylenes usually extend from room temperature to about 100°C.[4] The peak temperature of α dispersion is located near 70°C but can be shifted by quenching or annealing. While many different mechanisms of α relaxation have been proposed,[5] it appears that both amorphous and crystalline segments participate in the relaxation

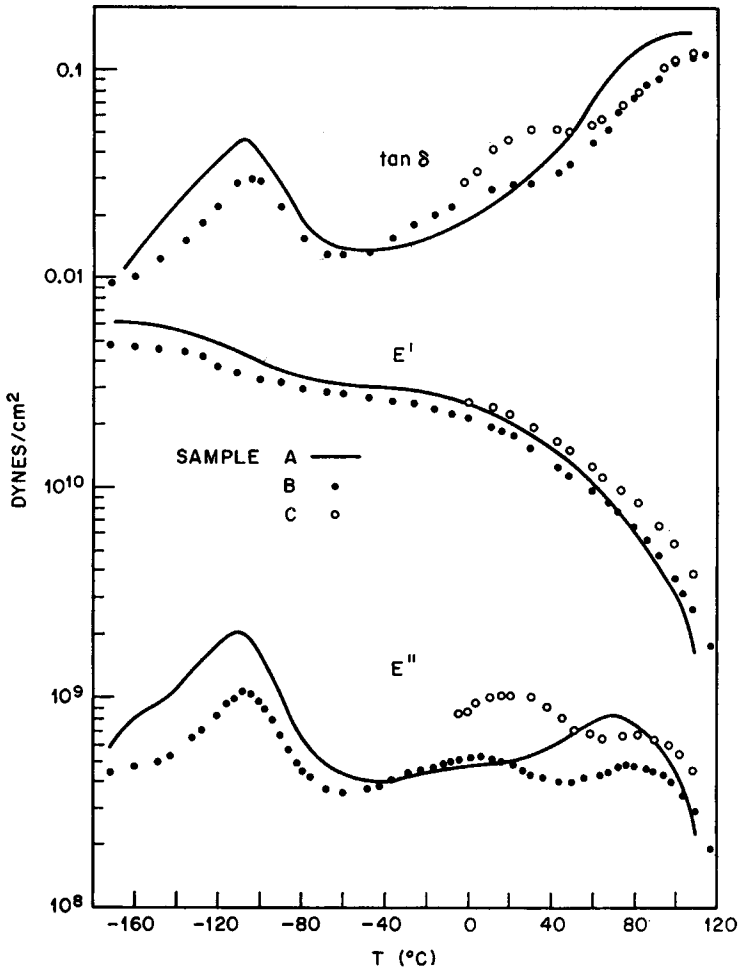

Fig. 2. Dynamic mechanical properties of high-density polyethylene prepared at low pressure.

process. In fact, Takayanagi[4] used the terms α_c and α_a dispersions. The α_a dispersion, however, has never been clearly separated from the α_c dispersion.[4] In examining the loss modulus curves of the two slow-cooled specimens, it is readily seen that two transitions are present at temperatures above $-60°C$. The high-temperature transitions with peak temperature of 80°C for both samples undoubtedly represent α_c processes. The lower-temperature transitions, with peak temperatures at 0° and 20°C for samples B and C, respectively, are most likely α_a relaxations, in Takayanagi's nomenclature. To our knowledge this is the first instance that a well-defined α_a dispersion, uncoupled with α_c process, is clearly identified. We tentatively suggest that during slow crystallization there are present some amorphous segment links near the crystal surface which are not severely

constrained by the crystallites and are able to undergo micro-Brownian motion independent of the segments in the crystalline region.

We have also noted that the storage moduli (E') of the slow-cooled materials, although higher in crystallinity, are nearly the same as the modulus values of sample A. The modulus of a crystalline polymer represents a complex combination of the contributions of the amorphous and crystalline regions. Since the morphology of the slow-cooled materials is not the same as that of sample A, a simple explanation cannot be offered at this time.

The unusual dynamic mechanical properties of samples B and C cannot be ascribed to possible degradation during the slow-cooling process because the two samples regain the properties of sample A upon molding under ordinary conditions.

Finally, it appears that sample B, crystallized in contact with aluminum, had slightly different viscoelastic characteristics from sample C which was crystallized in contact with Teflon. The role of the substrate with which the polymer melt is in contact during crystallization will be the subject of another communication.

Diffusion

The diffusion of toluene vapor in polyethylene was studied by the differential absorption method[6] with the use of a Cahn electrobalance. Toluene was chosen because the rate of absorption obeyed Fickian diffusion equations. All our experiments were conducted at 30°C. The equilibrium

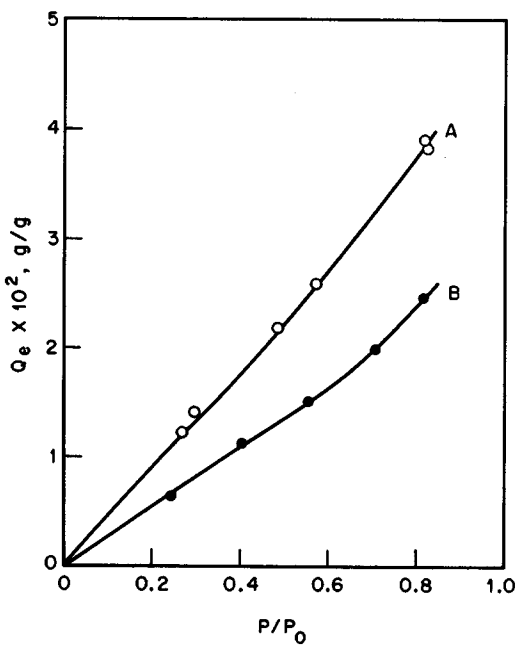

Fig. 3. Solubility of toluene in polyethylene.

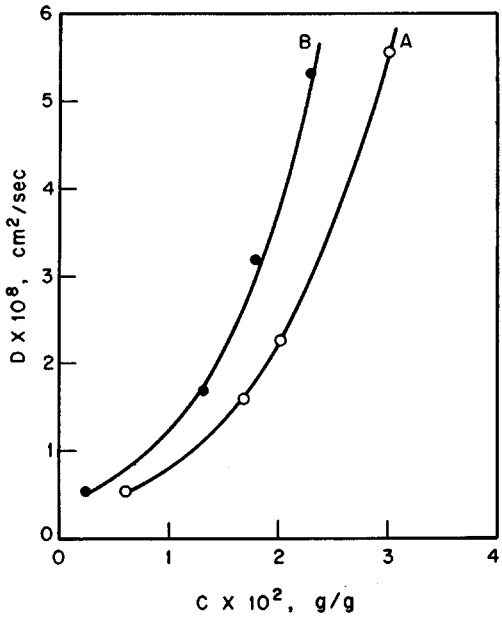

Fig. 4. Diffusion constants of toluene in polyethylene

amount of toluene vapor (Q_e) absorbed by each sample is plotted against relative vapor pressure in Figure 3. The sorption isotherms for samples A and B are nearly linear up to vapor activity of about 0.7. However, the amount of vapor absorbed by sample B is only 64% of that for sample A. This is expected from the lower amorphous content of sample B.

In Figure 4, the diffusion constant is plotted against the arithmetic average concentration of the vapor in the polymer during each differential absorption step. The concentration dependence of the diffusion constant can be represented, for both samples, by the expression

$$D = D(0)\exp \alpha c$$

where $D(0)$ is the diffusion constant extrapolated to zero concentration of the penetrant and α describes the concentration dependence. The values of $D(0)$ are 2.9×10^{-9} and 3.8×10^{-9} cm^2 sec^{-1} for samples A and B, respectively; the corresponding values of α are 1.05×10^2 and 1.18×10^2.

It is of interest to note that the diffusion constants are higher in sample B, which has a lower amorphous content, then in sample A. This unusual observation is presumably a reflection of the morphologic features of sample B. In a highly crystalline material, diffusion along lamella boundaries may play an important role. Furthermore, if our interpretation of the mechanical relaxation in the room temperature region is correct, the amorphous segments in sample B, although fewer in number, may actually possessed high degree of mobility. It is likely that both factors contribute to the large magnitude of the diffusion constant.

CONCLUSIONS

We have characterized by density measurements, microscopy, dynamic mechanical spectra, and diffusion experiments three samples of high-density polyethylene: one quenched from the melt, a second cooled slowly in contact with a chemically etched aluminum surface, and a third cooled slowly in contact with a Teflon surface. In summary, we cite the following observations:

1. The absence of spherulitic structure in the micrographs of both slowly cooled samples.
2. The presence of both amorphous- and crystalline-phase gamma transitions in the sample which was slowly cooled in contact with aluminum.
3. The presence of both amorphous- and crystalline-phase alpha relaxations for both slowly cooled samples; the quenched sample shows only a single alpha relaxation.
4. Slight difference in the viscoelastic behavior of both slowly cooled samples.
5. Higher diffusion constants for the slowly cooled sample (in contact with aluminum) than for the more amorphous quenched sample.

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