

Heterogeneous Nucleation and Crystallization of Polyethylene with Gold: Dilatometry

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Synopsis

Heterogeneous nucleation and crystallization data for polyethylene at a gold interface are reported. Isothermal crystallization is investigated by dilatometry. Avrami plots of the crystallization data suggest that the gold surface acts as a suitable nucleating agent resulting in heterogeneous nucleation and two-dimensional crystal growth at the polyethylene melt-gold interface. The deviation of measurements from Avrami's equation suggests the presence of intercrystalline links during the final growth stages of isothermal crystallization. A closely packed lamellar model is given for heterogeneous nucleation and two-dimensional crystallization which results in high density and rod-like crystals.

INTRODUCTION

While considerable attention has been focused on a detailed examination of the surface structure of polymer single crystals, comparatively little effort has been directed toward examining the interfacial structure of polymers at the substrate-polymer interface. However, in recent years, the possibility of regulating the dimensions (and number) of spherulites in polymer materials by introducing into the polymers a small amount of a finely dispersed additive¹ has been attracting the attention of numerous investigators.^{2,3} Kargin and co-workers⁴⁻⁶ have shown that the mechanism by which these additives act involves the formation (by adsorption) on the surface of the solid particles of the nucleating agent of ordered regions of the polymer, which act as crystallization centers. Such ordered regions are retained on the surface of the nucleating agent at high temperatures of the polymer melt when homogeneous crystallization centers (in the bulk of the melt) are completely decomposed.

Recently,⁷ we have shown that thin films of polyethylene nucleated and crystallized at low pressures in contact with gold foil have densities in excess of 0.99 g/cm³ and heats of fusion in excess of 70 cal/g.

In this study, we report the kinetics of heterogeneous nucleation of polyethylene on finely divided gold powders using dilatometric techniques.

EXPERIMENTAL

A linear polyethylene, Marlex 6050, was used throughout this study. Two types of gold powder were used as nucleating agents. One was a

precipitated gold powder prepared by Fisher Scientific Co., and the other, a flake powder prepared by Engelhard Industries, Inc. The precipitated powder was 99.95% pure and had an average particle size of 1 μ . The flake powder was 99.9% pure and had a particle size of 15 μ and a surface area (by the BET adsorption method) of 2.13 m²/g.

Powdered polyethylene was prepared by precipitation from a 3.2% xylene solution (110°C). The xylene solution was slowly cooled down to room temperature without stirring. The particle size was less than 3 μ .

Prior to use, the gold powders were extracted with xylene in a Soxhlet extractor for ten days. The gold powders were dried under vacuum at 110°C for seven days, then mixed with the polyethylene powder using a mortar and pestle. The mixture was dried in a glass tube at 0.02 mm Hg pressure at 110°C for 40 days. The drying temperature was controlled by immersion of the glass tube in a silicone bath at 110°C. After 40 days, the temperature of the silicone bath was raised to 170°C and maintained at this temperature for 1/2 hr to allow the gold powder to be wetted by the polyethylene melt to produce a void-free specimen. Samples for the dilatometer study were prepared in a high-pressure mold⁸ kept at 0.87 kbar and 190°C for 15 min. Upon cooling, the sample was removed from the mold and placed in a standard dilatometer tube. The dilatometer tube was evacuated to 0.025 mm Hg pressure and heated up to 170°C and maintained at this temperature for 24 hr in a well-regulated silicone oil bath ($\pm 0.5^\circ$). A temperature of 170°C was necessary to remove any residual nuclei that might persist in the melt.⁹ The samples were then transferred quickly to an adjacent silicone bath which was adjusted to 131 $\pm 0.05^\circ$ C. The specific volume data reported in this study are those obtained at 131 $\pm 0.05^\circ$ C.

RESULTS AND DISCUSSION

The Avrami equation has proven to be of considerable importance in the study of the kinetics of nucleation and growth of crystalline polymers. The Avrami equation may be expressed as¹⁰

$$\log \left(\frac{V_\infty - V_t}{V_\infty - V_0} \right) = kt^n \quad (1)$$

where t is the crystallization time, V_0 is the specific volume of the polyethylene melt at $t = 0$, V_t and V_∞ are the specific volumes of the polymer at crystallization time $t = t$ and $t = \infty$, respectively, and k and n are constants.

Avrami plots of our measurements are shown in Figure 1. The presence of gold in the samples exhibits an accelerating effect on the isothermal crystallization of polyethylene. The extent of nucleation and crystallization appears to depend not only on the amount of gold but also on the surface area of gold. The reasonably good fit of the Avrami equation with exponent $n = 3$ for unfilled polyethylene, the solid line in Figure 1, suggests that crystallization of polyethylene from melt is typically a three-dimensional crystal growth. Deviation of the experimental data from Avrami's equation with the exponent $n = 3$ during the final crystallization stage might result from interlamellar crystal type (intercrystalline links) growth.¹¹

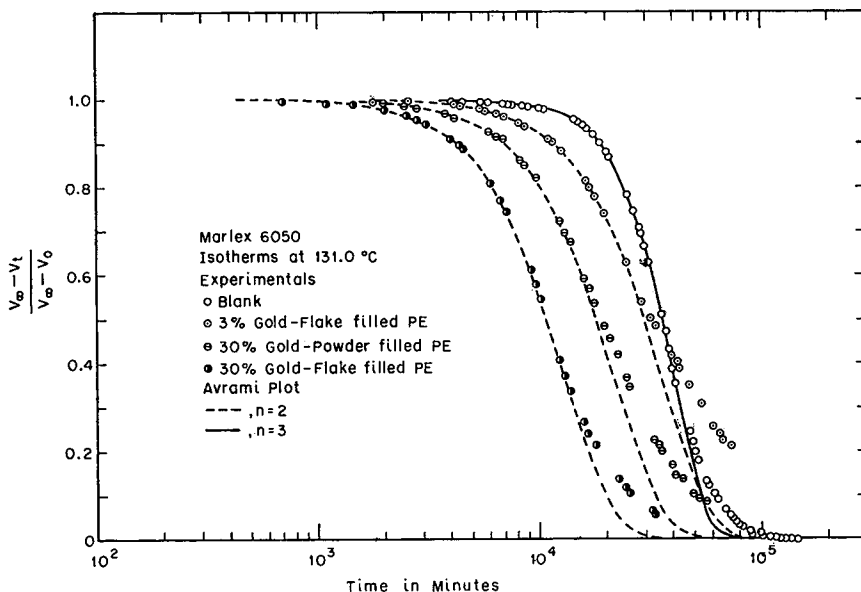


Fig. 1. Crystallization isotherms for gold-filled polyethylene Marlex 6050 samples at $131.0 \pm 0.05^\circ\text{C}$.

From the fit between the three gold-filled polyethylene samples and Avrami's equation with exponent $n = 2$, it appears that heterogeneous nucleation and two-dimensional growth are reasonable mechanisms for the crystallization of the gold-filled polyethylene. During the final crystallization stages for the three gold-filled specimens, deviations from the Avrami equation suggest the growth of interlamellar crystals (intercrystalline links).¹¹

In a previous report, we showed that when polyethylene was rather slowly heterogeneously nucleated and crystallized in contact with a gold foil (10^{-3} deg/min), the morphology of the polyethylene consisted of rod-like crystals which grew from gold surface into the bulk of the polymer (cf. Fig. 2). The gold-nucleated and crystallized polyethylene film ($\sim 2.5 \mu$) also had an extremely high density and high heat of fusion.¹²

In the case of slow cooling of the polyethylene melt (nonisothermal crystallization from high temperatures), the adsorbed polyethylene chains at the gold surface appear to act as the primary nuclei for crystallization. The relationship between lamellar thickness L and crystallization temperature T was given by Hoffman and Lauritzen¹³ as follows:

$$L = \frac{4\sigma_e}{\Delta H_f - T\Delta S_f} = \frac{4\sigma_e}{\Delta H_f \left(1 - \frac{T}{T_m}\right)} \quad (2)$$

where, σ_e is the surface free energy of the chain-folded surface, T_m is the equilibrium melting temperature of the polyethylene crystal, and ΔH_f and ΔS_f are the enthalpy and entropy of fusion, respectively.

Equation (2) suggests that an increase in the crystallization temperature T should result in lamellar thickening of the polyethylene. The high density of the surface region of polyethylene, which was nucleated and crystallized on the gold surface, may be due to a lamellar thickening process. Tightly packed lamellar crystals that are nucleated in contact with the

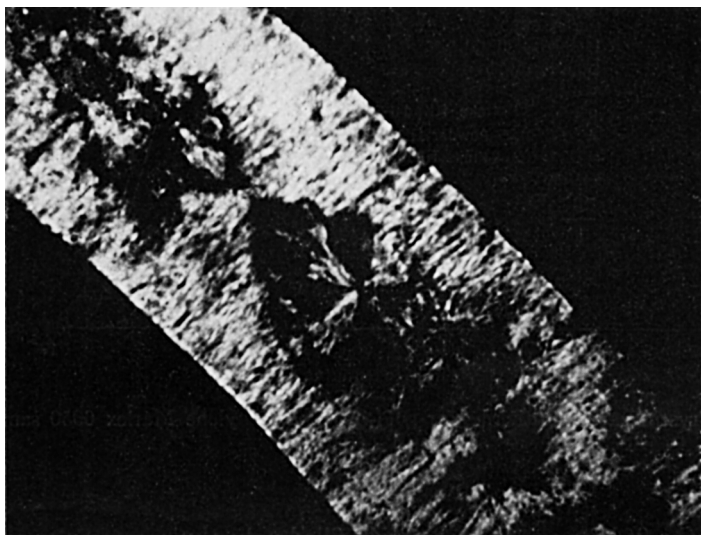


Fig. 2. Example of a rod-like crystal of Marlex 6050 polyethylene grown at the gold-polyethylene interface. Rate of cooling is $0.020^{\circ}\text{C}/\text{min}$.

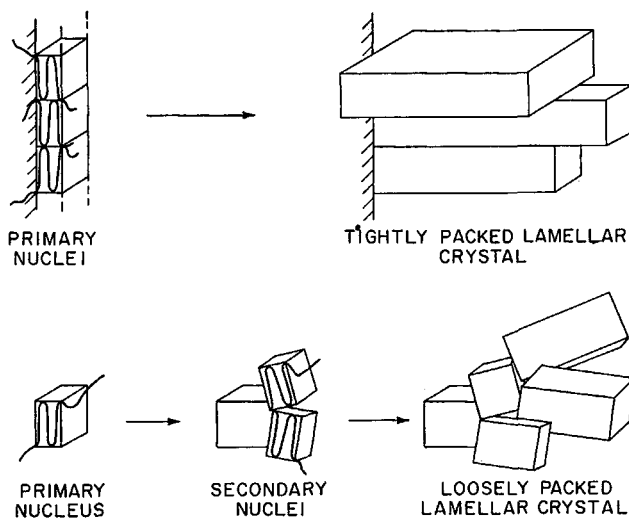


Fig. 3. Models of crystal growth: (a) heterogeneous nucleation by gold surface and two-dimensional crystal growth; (b) heterogeneous nucleation and three-dimensional crystal growth.

gold surface and grow in a two-dimensional manner may facilitate formation of a high-density interfacial region.

Figure 3 shows a suggested model of the crystal growth under two different conditions: (a) heterogeneous nucleation by a gold surface and associated two-dimensional crystal growth and (b) heterogeneous nucleation and three-dimensional crystal growth.

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