

# Crystallinity and Dicumyl Peroxide Diffusivity in Low Density Polyethylene with Different Thermal Histories

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## Synopsis

The absorption diffusivity of dicumyl peroxide (DICUP) in low density polyethylene pellets that have been annealed and either cooled slowly or quenched has been measured and correlated with the corresponding changes in crystallinity as measured by DSC. Annealing at 125°C resulted in an increased crystallinity and decreased DICUP diffusivity ( $3.2 \times 10^{-7}$  cm<sup>2</sup>/s for as supplied pellet to  $5.2 \times 10^{-8}$  cm<sup>2</sup>/s for annealed and slowly cooled pellets). Quenching the annealed pellet reduced the increase in crystallinity and corresponding decrease in diffusivity. The time course of annealing and secondary crystallization processes was defined through further DSC measurements. The relationship between crystallinity and pressure for both hot press films and 4 mm diameter extrudate was found to be identical, indicating the importance of pressure on bulk crystallization phenomena regardless of the source of the pressure.

## INTRODUCTION

Plastic processing operations<sup>1,2</sup> typically involve the crystallization of the polymer melt while under stress from shear or pressure. The processing conditions<sup>3</sup> such as temperature, pressure, and shear affect the number and size of spherulites and rate of crystallization to determine the degree of crystallinity and the spatial distribution of the crystallites. Ultimately, the transport properties of the amorphous component are modified. The relationship between thermal history or processing conditions and crystallinity of low density polyethylene (LDPE) has been characterized as part of an investigation<sup>4</sup> into the effects of extrusion processing conditions on the sorption of dicumyl peroxide (DICUP) by LDPE. Such transport properties and their relationship to thermal history are of relevance for the characterization of the migration of dicumyl peroxide or other additives into or out of the polyethylene.

## MATERIALS AND METHODS

### Materials

Low density polyethylene (CIL 300 GXN 7218) was supplied by Canadian Industries Ltd. (Edmonton, Alberta) in the form of nearly cylindrical pellets (4.0 mm in diameter  $\times$  3.5 mm in length, surface to volume ratio  $\sim$  1.57

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$\text{mm}^{-1}$ ). The melt index was 2.07 (ASTMD 1238-73), density was  $928.7 \text{ kg m}^{-3}$  (ASTM D1506-68), and percent crystallinity (DSC) was  $32 \pm 2$ . Dicumyl peroxide (DICUP R, Hercules Inc., Wilmington, DL) was 98-100% active and was used without further purification.

## Sample Preparation

### *Films*

Films (50-250  $\mu\text{m}$  thick) were prepared in a laboratory hot platens press (Model P-215C, Pasadena Hydraulics Inc., Brea CA), at  $130^\circ\text{C}$  by molding as supplied LDPE pellets between sheets of aluminum foil with pressure in the range of 1000-40,000 psig. These hot press films were allowed to cool to room temperature either by maintaining them in the press under pressure and turning the heat off or by simply removing them from the press and allowing them to cool in air. After cooling, these films were kept at room temperature for 24 h prior to analysis by DSC.

### *Extruded Rods*

As-supplied LDPE pellets were extruded at various screw speeds (10-180 rpm) through a 4 mm diameter cylindrical die by a Brabender plasticorder (Model 252, C. W. Brabender, Hackensack, NJ) with a 0.75 in. screw. The pressure in the die was measured with a pressure transducer and gauge (Dynisco, Westwood, MA). The temperature in the die and along the barrel was adjusted as necessary ( $110$ - $135^\circ\text{C}$ ) to vary the die pressure at constant screw speed or to maintain a nearly constant pressure as the screw speed was varied; the latter was difficult to achieve.

### *Annealing*

As-supplied LDPE pellets were maintained for various lengths of time in an oven at annealing temperatures of 70, 90, 100, and  $120^\circ\text{C}$ . At fixed intervals, samples were removed from the oven and kept at room temperature or in ice cold water ( $\sim 0^\circ\text{C}$ ) for a minimum period of 24 h. Before further analysis, samples maintained in ice water were thoroughly dried by tissue paper.

For sorption measurements, pellets were annealed at  $125^\circ\text{C}$  for 4 h, and cooled at various rates. Some pellets were slowly cooled in the oven after switching it off while others were quenched in liquid nitrogen or in ice water ( $\sim 0^\circ\text{C}$ ) for a minimum period of 24 h. The quenched samples were examined both before and after a period of maintenance at room temperature for 24 h. The dimensions of the original pellets were preserved throughout these annealing/quenching steps.

### *Quenching*

As-supplied LDPE pellets were melted in an oven at  $140^\circ\text{C}$  for 4 h. This melt was then quenched in liquid nitrogen or ice cold water at  $\sim 0^\circ\text{C}$ . At fixed intervals, samples were removed from the quenching baths and im-

mediately investigated for crystallinity while others were maintained at room temperatures for a minimum period of 24 h before being measured by DSC.

### Differential Scanning Calorimetry

Percent crystallinity was determined with 5–10 mg of polymers by differential scanning calorimetry (DuPont 990 Thermal Analysis System, Wilmington, DE) at a heating rate of 10°C/min. The percent crystallinity was estimated using 68.4 cal. g<sup>-1</sup> as the heat of fusion of 100% crystalline polyethylene.

### Sorption Measurement

The rate of mass uptake of dicumyl peroxide was determined by suspending a LDPE sample from the balance, 1 cm above the level of molten DICUP liquid in the sample tube. The sample and DICUP temperature were chosen to complete the experiments in a reasonable time and yet minimize the thermal degradation of DICUP during sorption. In most cases the absorption process was interrupted prior to reaching equilibrium and the sample was removed from the balance and suspended from one of the stainless steel hooks arranged around the periphery of the sample tube 1 cm above the DICUP. After equilibrium had been obtained (at least 3 days later) under nearly identical conditions, the equilibrium weight of the LDPE sample was measured using the Cahn balance. Details of this modified sorption technique are provided elsewhere.<sup>4</sup>

The diffusivity was estimated from the slope of a plot of  $M_t/M_\infty$  vs.  $t^{1/2}$  using the surface-to-volume ratio of the LDPE pellet<sup>6</sup>:

$$M_t/M_\infty = 2a(Dt/\pi)^{1/2} \quad (1)$$

where  $M_t$  = mass gained at time  $t$ ,  $M_\infty$  = mass gained at equilibrium (here a separate measurement),  $a$  = surface-to-volume ratio,  $D$  = diffusivity, and  $t$  = time. The error associated with the application of this equation based on 1-dimensional diffusion to cylindrical pellets with a small aspect ratio was checked and found to be negligible.<sup>4</sup>

## RESULTS

### Pressure/Shear Rate Effects

The effect of pressure on the crystallinity of hot pressed films of LDPE prepared at 130°C is shown in Figure 1. The increase in crystallinity with an increase in pressure was found to be independent of the film thickness over the range of 50–250 μm. A similar increase in crystallinity with an increase in pressure was found for LDPE extruded at low screw speed. Here pressure at the die was increased by lowering the temperature along the barrel and in the die (temperature range, 110–135°C). The changes in crystallinity are remarkably comparable to those observed with hot pressed films at equivalent pressure.

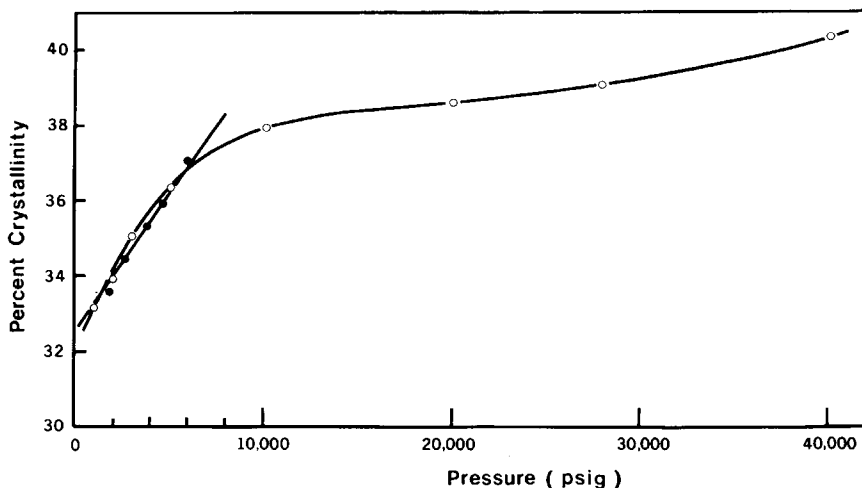


Fig. 1. Effect of processing pressure on crystallinity of low density polyethylene: (○) hot pressed films; (●) LDPE extruded at 120 rpm and temperature ranging between 110 and 135°C.

The effect of shear (i.e., screw speed) on the crystallinity of LDPE is shown in Figure 2. At low screw speed, there was no significant change in crystallinity. However, as screw speed increased from 60 to 160 rpm, the crystallinity increased sharply. This increase in crystallinity at high screw speed was attributed to the unavoidable corresponding increase in pressure, thereby causing a pressure-induced crystallization similar to that seen in Figure 1.

### Annealing/Quenching Effects

The effect of annealing LDPE pellets at various temperatures on their crystallinity is shown in Figures 3 and 4. As expected, annealing at higher temperatures resulted in significant increases in crystallinity with the crys-

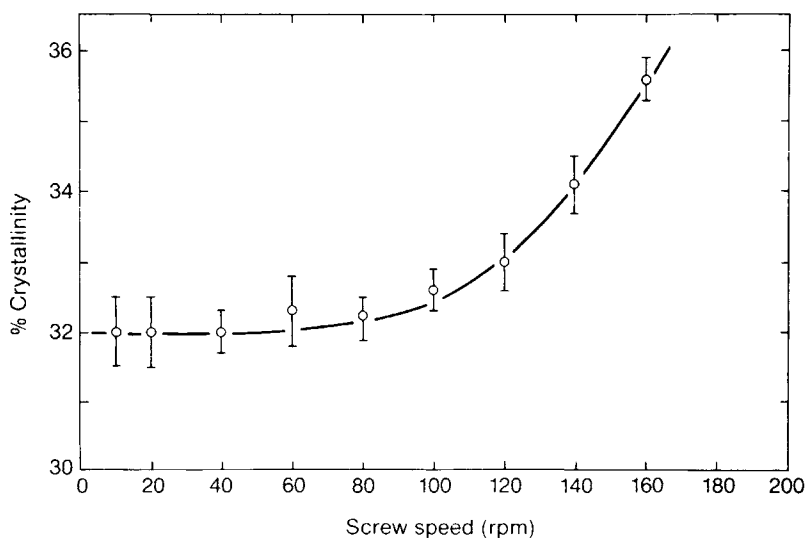


Fig. 2. Effect of extruder screw speed on crystallinity of low density polyethylene extruded at 135°C. Pressure variations (10–60 rpm, 600–1950 psig; 60–160 rpm: 1950–3800 psig).

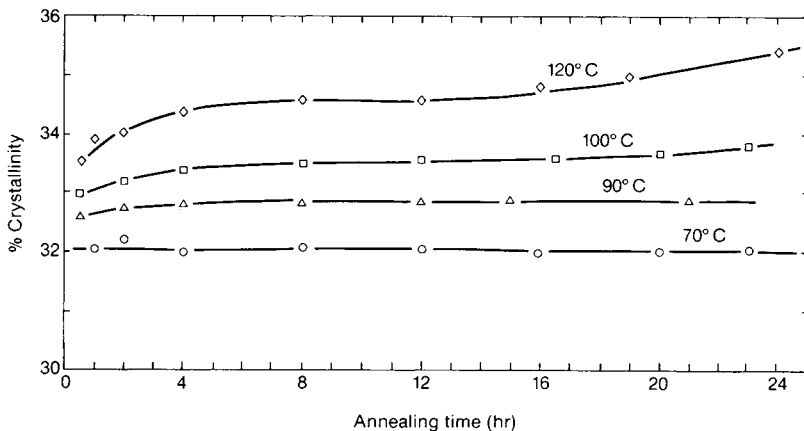


Fig. 3. Effect on annealing on crystallinity of as-supplied low density polyethylene pellets. Sample at each annealing temperature after predetermined annealing time was kept at ambient temperature for 24 h prior to crystallinity measurement.

tallinity increasing with increased annealing time. Annealing effects were absent at 70°C. Secondary crystallization appeared to progress even during the 24 h after annealing since there was a slightly higher crystallinity in those samples maintained at room temperature compared to those maintained at ~ 0°C (Fig. 4).

The effect of quenching in liquid nitrogen or in water at ~ 0°C with or without a subsequent 24-h period at room temperature is shown in Figure 5. As expected, the faster crystal growth rate associated with quenching in water at 0°C resulted in more crystalline material than when quenched in liquid nitrogen. Maintaining these quenched samples at room temperature decreased the observed difference in crystallinity. These observations reflect the balance between the enhanced nucleation rate with greater supercooling and greater crystal growth at higher temperatures.

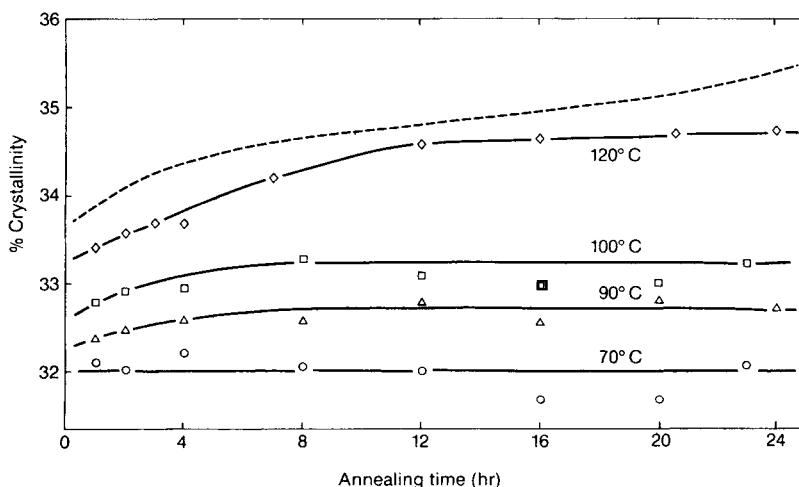


Fig. 4. Effect of annealing on crystallinity of low density polyethylene. Sample at each annealing temperature after predetermined annealing time was kept at ~ 0°C for 24 h prior to crystallinity measurement. Compare the results of Figure 3 at 120°C (---).

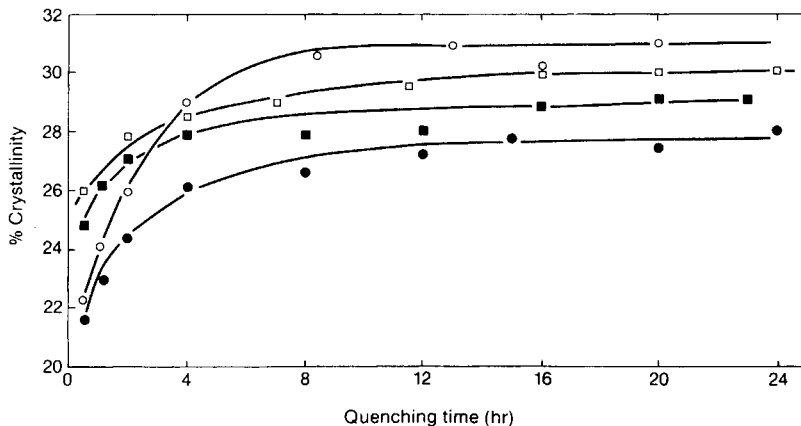


Fig. 5. Effect of quenching on crystallinity of low density polyethylene: (●) quenched in liquid nitrogen; (○) quenched in liquid nitrogen at predetermined time and maintained at ambient temperature for 24 h prior to crystallinity measurement; (■) quenched in ice cold water ( $\sim 0^{\circ}\text{C}$ ); (□) quenched in ice cold water at predetermined time and maintained at ambient temperature for 24 h prior to crystallinity measurement.

### DICUP Diffusivity

The absorption kinetics of DICUP in all thermally treated LDPE pellets exhibited the usual Fickian behavior. The equilibrium uptake values and diffusivities of DICUP obtained from these plots using eq. (1) are summarized in Table I.

Annealing as-supplied LDPE pellets near the melting point and slowly cooling them (by turning the oven off) caused a reduction in DICUP diffusivity relative to that in the original pellet. Quenching the annealed pellet in liquid nitrogen or ice water gave higher values of diffusivity relative to that which was slowly cooled. Quenching the annealed pellet in ice cold water at  $\sim 0^{\circ}\text{C}$  resulted in a lower diffusivity as compared to that of pellet quenched in liquid nitrogen. Maintaining the quenched samples at ambient

TABLE I  
Effect of Thermal History on Absorption Diffusivity and Equilibrium Uptake of DICUP in LDPE at  $70^{\circ}\text{C}$

Thermal treatment	Diffusivity <sup>a</sup> ( $\times 10^{-8}$ $\text{cm}^2/\text{s}$ )	Equilibrium uptake <sup>a</sup> ( $\times 10^{-2}$ g DICUP/g polymer)
As-supplied pellet	$32 \pm 1.2$	$7.01 \pm 0.11$
Annealed and slowly cooled	$5.2 \pm 0.16$	$7.21 \pm 0.11$
Annealed and quenched in liquid nitrogen	$9.4 \pm 0.21$	$7.65 \pm 0.09$
Annealed and quenched in ice cold water ( $\sim 0^{\circ}\text{C}$ )	$7.2 \pm 0.32$	$7.51 \pm 0.15$
Annealed and quenched in liquid nitrogen, and maintained at ambient temperature	$9.1 \pm 0.45$	$7.66 \pm 0.11$
Annealed, quenched in ice cold water, and maintained at ambient temperature	$7.2 \pm 0.38$	$7.55 \pm 0.14$

<sup>a</sup> Mean of 3-4 samples  $\pm$  standard deviation.

temperature for a period of 24 h had no significant effect on the equilibrium uptake values or DICUP diffusivities.

## DISCUSSION

The observed increase in crystallinity with increase in pressure in an extruder or hot press (Fig. 1) was presumed to be directly related to the effect of pressure on crystallization. Increasing pressure increases the degree of supercooling by increasing the melting point<sup>7,8</sup> resulting in larger lamellar thickness<sup>9</sup> and a higher degree of crystallinity. Pressure-induced crystallization of high density polyethylene as a consequence of melting point elevation has been observed directly in other studies.<sup>2</sup>

The absence of a significant effect of shear rate on crystallinity (at screw speeds  $\leq 100$  rpm, Fig. 2) was consistent with earlier reports<sup>10</sup> that only under very high shear in a ram extruder does low density polyethylene undergo chain scission or disentanglement that would affect crystallinity.

The observed increases in percent crystallinity from 32.0 to 35.5% with annealing (Fig. 3) were expected since it is well known that annealing greatly improves crystallinity.<sup>3</sup> These results are consistent with the observed decrease in DICUP diffusivity from  $3.2 \times 10^{-7}$  to  $5.2 \times 10^{-8}$  cm<sup>2</sup>/s (Table I) with annealing at 125°C followed by slow cooling.

It was presumed that annealing resulted in an increased degree of crystal perfection since, during normal melt crystallization, complex imperfect structures are obtained due to interchain entanglements and competition.<sup>7</sup> In addition, chain folding increases with increasing annealing temperature becoming quite pronounced at annealing temperatures near the melting point. This was evident in terms of the higher values of crystallinity obtained at 120°C (35.5%) after 24 h of annealing. Increases in crystallinity with an increase in melting time (Fig. 1) were consistent with previous reports,<sup>3,7,9</sup> regarding the time course of lamellar thickening that occurs with annealing.

The decrease in percent crystallinity with quenching (Fig. 4) was also consistent with earlier studies,<sup>3,6,9</sup> indicating that quenching considerably slows down the rate of crystallization. The increase in mass uptake of DICUP in quenched samples (Table I) was consistent with the increase in the amorphous contents in quenched samples.

The increase in DICUP diffusivity in the samples that were annealed and subsequently quenched as compared with that in the samples which were annealed but slowly cooled was presumably the result of a slowdown in the process of secondary crystallization due to quenching. The smaller increase in the diffusivity for the samples that were annealed and quenched in ice water ( $7.2 \times 10^{-8}$  cm<sup>2</sup>/s), relative to that for the samples quenched in liquid nitrogen ( $9.4 \times 10^{-8}$  cm<sup>2</sup>/s), suggested that the process of secondary crystallization remained more active in the pellet quenched in ice water than in liquid nitrogen. This process of secondary crystallization resulted in an increase in crystalline contents in the ice water quenched sample which was also evident from the lower equilibrium uptake of DICUP (Table I). The absence of an effect on the diffusivity and equilibrium uptake when the quenched samples were tested after 24 h at room temperature was

believed to be due to the near completion of secondary crystallization in the samples immediately after quenching.

### CONCLUSIONS

LDPE displayed variations in its crystallinity and DICUP transport properties with changes in thermal history or processing conditions. Increases in pressure either in a hot press or in an extruder resulted in an increase in LDPE crystallinity. The crystallinity of LDPE pellets increased with increase in annealing temperature while quenching resulted in an increase in the amorphous content. The effect of annealing and quenching in the diffusivity and mass uptake of DICUP in LDPE pellets paralleled the effects of these treatments on crystallinity.

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