Absorption of Dicumyl Peroxide by Extruded Polyethylene: Difference between Surface and Bulk Morphology

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Synopsis

Under some conditions, the absorption of dicumyl peroxide (DICUP) at 70°C by extruded low density polyethylene (LDPE) displayed features which are characteristic of two-stage sorption. For example, the initial slope of the DICUP absorption curve (plot of M_t/M_∞ against $\sqrt{t}$) reflecting diffusion in the surface region was 2.5 times higher than the slope of the second stage (reflecting diffusion in the bulk) for 4-mm-diameter LDPE rods extruded at 130°C and 180 rpm (die pressure = 6000 psig). Only a single stage curve was evident in the same rod with its surface removed or in smaller diameter extrudate. Increasing the screw speed from 10 to 45 rpm at nearly constant extrusion pressure (1800–2380 psig) resulted in an approximately 50% decrease in the initial (first stage) slope with a negligible effect on the second stage slope. Increasing the die pressure (4900–6000 psig), by decreasing the extrusion temperature, at constant screw speed (125 rpm) resulted in an almost threefold decrease in the second stage slope without apparent effect on the first stage slope. Photomicrographs demonstrated the presence of distinct surface and bulk morphologies with evidence of a transcrystalline surface layer oriented perpendicular to the surface at low screw speeds and larger spherulites in the bulk of the high pressure extrudate. Such morphological features and the observed dependence of the two stage sorption curves on extrusion conditions are consistent with the surface and bulk morphology of the extruded LDPE rod being dependent on the screw speed and die pressure, respectively. These uptake curves were determined by modifying the classical sorption technique to separate the measurement of the equilibrium uptake from the continuous recording of the slow changes in mass during absorption. This techique may be useful in the characterization of the migration process in other plastic/penetrant systems where diffusion is too slow to be measured by conventional means.

INTRODUCTION

The migration of various additives, such as plasticisers, initiator fragments and crosslinking agents, is becoming of increasing concern to the plastics industry[1] because of the potentially adverse impact of these additives on the environment or the media (e.g., food) that come into contact with the finished plastic. Additive migration can also result in heterogeneities in polymer properties because of localized changes in additive concentration.

However, standard techniques[2] for characterizing diffusion of organic compounds in polymers are not well suited to this problem. These additives are generally of higher molecular weight than the classical organic vapours whose diffusivities are measured by sorption or permeation methods. In order for these methods to be effective high surface-to-volume ratios of the polymer (i.e., thin films or ground polymer) must be used so that experi-

ments can be completed in a reasonable period of time with these large and therefore relatively slow molecules. Unfortunately, this prevents investigation of the effect of processing variables on the transport process since processed product (i.e., resin pellets, injected-molded specimens) are generally too thick for sorption or permeation studies. Since morphological differences may exist between the finished product and the thin film, extrapolation from the latter to the finished product is difficult.

As a model system and because of its interest in the making of crosslinkable polyethylene, we have modified the classical sorption technique to determine the diffusivity of dicumyl peroxide (mol wt = 270) in extruded samples of low density polyethylene of low surface to volume ratio. The modified technique simply entails the separate measurement of the initial rate of mass uptake (absorption) or loss (desorption) and the final equilibrium uptake. The effects of extruder temperature, screw speed, and die pressure on the morphology of the extruded polymer have been inferred from their effects on the diffusivity of dicumyl peroxide.

MATERIALS AND METHODS

Materials. Low density polyethylene (CIL 300GXN7218) was supplied as nearly cylindrical pellets (4.0 mm diameter × 3.5 mm long, surface-to-volume ratio = 1.57 mm^{-1}). The melt index was 2.07 (ASTM D1238-73), density was 928.7 kg/m^3 (ASTM D1506-68), and crystallinity (DSC) was 32 ± 2%. Dicumyl perixode (DICUP R, Hercules Inc., Wilmington, Del.) was 98–100% active and was used without further purification.

Sorption Measurement. A Cahn electrobalance (Model 2000, Cahn Instruments, Cerritos, Calif.) was used for all measurements (Fig. 1). The balance was contained within a glass bottle (14 cm diameter × 30 cm long), which could be evacuated by an ordinary laboratory vacuum pump (Welch 8392-4, Skokie, IL.) and the pressure monitored with a mercury manometer. For experiments at 70°C, for example, the pressure was maintained constant throughout the measurement period at 2.4 cm Hg.

Sample and DICUP temperature were maintained at 40–70°C (± 0.1°C) by circulation of hot water (water bath circulator RC3, Lauda, Federal Republic of Germany) through the jacketed tube.
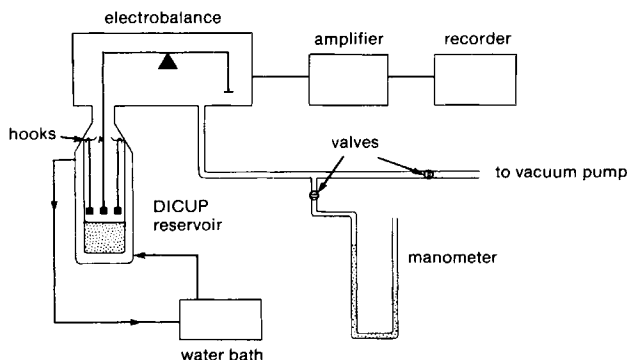

Fig. 1. Schematic diagram of the sorption apparatus showing hooks from which pellets were suspended for equilibration.

The rate of mass uptake was determined by suspending a LDPE sample from the balance, 1 cm above the level of molten DICUP liquid in the sample tube. In most cases the absorption process was interrupted prior to reaching equilibrium and the pellet 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. To check the validity of this method, the entire sorption curve was measured at a single time for some samples.

For the single stage absorption curves the diffusivity was estimated from the slope of a plot of M_t/M_∞ vs. $t^{1/2}$ using the surface-to-volume ratio of the LDPE pellet.[3]:

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

where M_t = mass gained at time t, M_∞ = 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: (1) the diffusivity at 70°C of as supplied pellets with the ends sealed with aluminum foil (radial diffusion only) could not be distinguished from that measured with the ends exposed and (2) applying the integrated concentration profile for combined radial and axial diffusion at long time[4] to the experimental data at 70°C, in as supplied pellets resulted in a diffusivity 3.6% lower than that obtained with radial diffusion only.

For two-stage absorption curves, the results are reported as the slopes of each stage of the plot of M_t/M_∞ against $t^{1/2}$ or after conversion to quantities with the same units as diffusivity using

$$\text{"diffusivity"} = (\text{slope})^2\pi/4a^2 \tag{2}$$

The quotation marks are used to distinguish this "diffusivity" from the proper diffusivity, used in Fick's law to describe the diffusion process and to underscore the limited conceptual insight offered by this parameter, particularly for the second stage of absorption.

Extrusion. LDPE pellets were examined as supplied and after extrusion at various screw speeds (10–180 rpm) through cylindrical dies (1–4 mm diameter) by a Brabender plasticorder (Model 252, C.W. Brabender, Hackensack, N.J.) with a 0.75 in. screw. Pressure in the die was measured with a pressure transducer (Dynisco, Westwood, Mass.). The temperature in the die and along the barrel was adjusted as necessary (115–136°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 extremely difficult. The surface of one sample (130°C, 180 rpm, 6000 psig) was removed by simple cutting with a sharp scalpel blade to examine the effect of this on the absorption kinetics.

Optical Microscopy. Pellets were cross-sectioned perpendicular to the extrusion direction (the cylindrical axis) by an ultramicrotome (Model MT-1, Serval) to yield sections 10–12 μm thick. These were mounted in Canada balsam (Fisher Scientific, Toronto, Ont.) and observed under polarized light with an optical microscope (Vanox, Olympus, Japan) with a polarizing attachment (AP-1) and camera (PM-10-A).

RESULTS

Absorption kinetics for DICUP in as supplied pellets at temperatures ranging from 40°C to 70°C are shown in Figure 2 as a plot of M_t/M_∞ against $t^{1/2}$. Except for the measurements at 70°C, M_∞ was determined separately from M_t as described in the Methods section. The observed linearity is characteristic of Fickian diffusion with the continued linearity beyond $M_t/M_\infty = 0.6$, suggestive of a concentration-dependent diffusivity (diffusivity increasing with increase in concentration).[5]

The dependence of diffusivity on temperature was consistent with an Arrhenius type relationship with an activation energy of 41.6 kJ/mol (Fig. 3). The values of equilibrium DICUP uptake were represented by a linear function of the logarithm of the equilibrium uptake (mass of DICUP/mass of polymer) vs. reciprocal temperature (Fig. 3). Identical values of equilibrium uptake of "DICUP" were obtained using the modified sorption technique as were obtained by allowing the polymer pellet to achieve the equilibrium saturation in one step in a routine sorption experiment.

The effects of extrusion pressure and screw speed on the absorption kinetics are shown in Figure 4 for 4 mm diameter samples extruded at 130°C. Under some processing conditions, the curves of M_t/M_∞ against $t^{1/2}$ lost their linear, Fickian features, and assumed the characteristic shape of two-
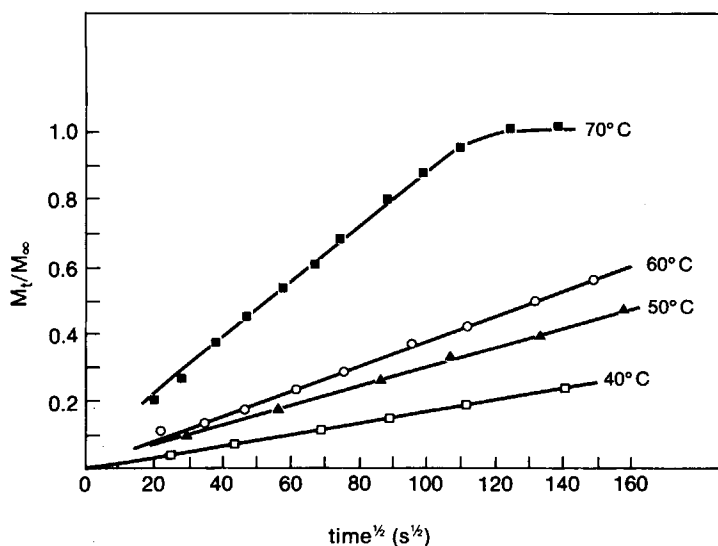

Fig. 2. Absorption curves of DICUP in as supplied pellets of LDPE at different temperatures. M_∞ measured separately for temperatures < 70°C.
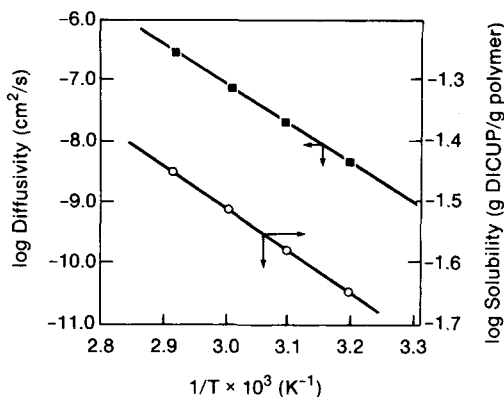
Fig. 3. Effect of temperature on diffusivity and equilibrium uptake of DICUP in LDPE as supplied pellets.

stage sorption. Rather than interpreting the observed "two-stage sorption" as reflecting changes in the surface concentration due to a slow surface relaxation process as is done classically.[6,7] We attributed this behavior to differences in surface and bulk morphology in the extruded pellets.

Two stage behavior was absent in the absorption curves obtained with smaller diameter pellets (Fig. 5), suggesting the presence of a more homogeneous pellet without a morphologically distinct surface layer. Removal of the surface of a pellet produced at the highest screw speed and extrusion pressure resulted in a single stage uptake curve with diffusivity (6.5×10^{-9} cm²/s) comparable to the "diffusivity" from the second stage in the original
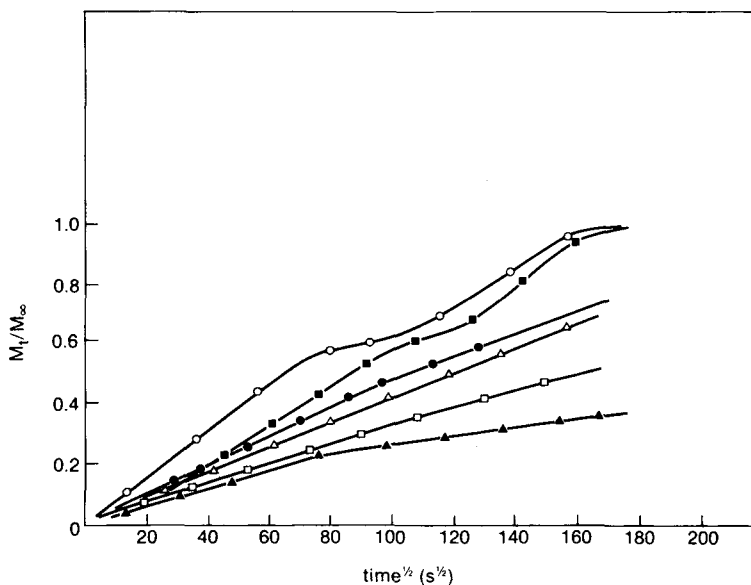

Fig. 4. Absorption curves at 70°C of DICUP in LDPE pellets extruded at 130°C. Screw speed ω (rpm) and P (psig): (○) 10, 180 0; (■) 35, 2500; (●) 60, 3800; (△) 85, 4500; (□) 145, 5500; (▲) 180, 6000.
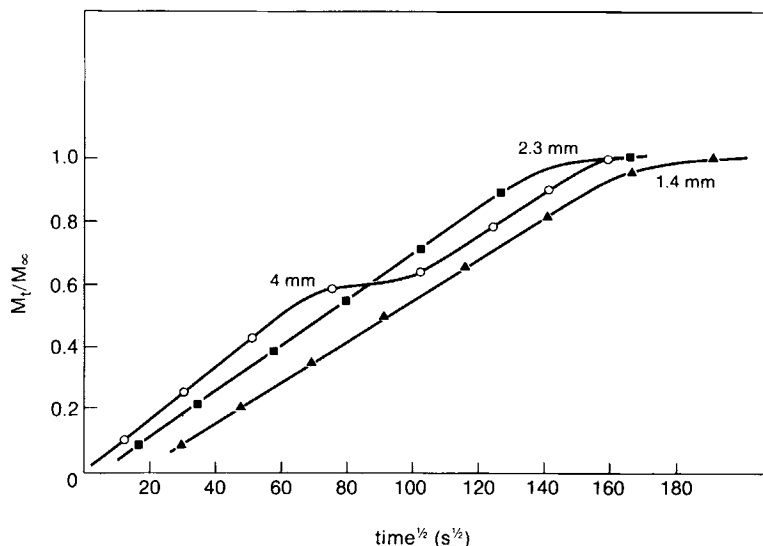
Fig. 5. Effect of pellet diameter on absorption curves at 70°C of DICUP in LDPE pellets extruded at 10 rpm: 4-mm diam, 130°C, 1800 psig; 2.3-mm diam, 134°C, 2200 psig; 1.4-mm diam, 136°C, 2800 psig.

pellet (5.3×10^{-9} cm^2/s). The "diffusivities" in the two-stage case were those determined from the slopes of each of the stages using eq. (2) and are listed in Table I. Increasing screw speed from 10 to 180 rpm at 130°C with a corresponding increase in die pressure from 1800 to 6000 psig resulted in a tenfold reduction in the first stage "diffusivity" and a fortyfold reduction in the second stage "diffusivity."

The presence of a distinct surface layer was confirmed by optical microscopy of thin sections of extruded pellets. Pellets extruded at low screw speed [Fig. 6(a)] appear to have a thin surface layer ($\sim$200 μm) with a crystal structure oriented perpendicular to the surface (i.e., radially) overlaying a fine spherulitic core structure. Pellets extruded at higher speeds and correspondingly higher pressure [Fig. 6(b)], exhibit a slightly different surface morphology: While there is evidence of a surface region, there is

TABLE I
Apparent "Diffusivities" of DICUP in 4-mm-Diameter Extruded LDPE[a]

Screw speed (ω)	Die pressure (psig)	"Diffusivity" (cm^2/s)[b]	
		First stage	Second stage
10	1800	3.5×10^{-7}	2.3×10^{-7}
35	2500	3.0×10^{-7}	2.2×10^{-7}
60	3800	8.5×10^{-8}	3.5×10^{-8}
85	4500	6.2×10^{-8}	3.3×10^{-8}
140	5500	4.5×10^{-8}	2.1×10^{-8}
180	6000	3.2×10^{-8}	5.3×10^{-9}

[a] Die Temperature = 130°C.
[b] As calculated from slope of M_t/M_∞ vs. $t^{1/2}$ plot using eq. (2).
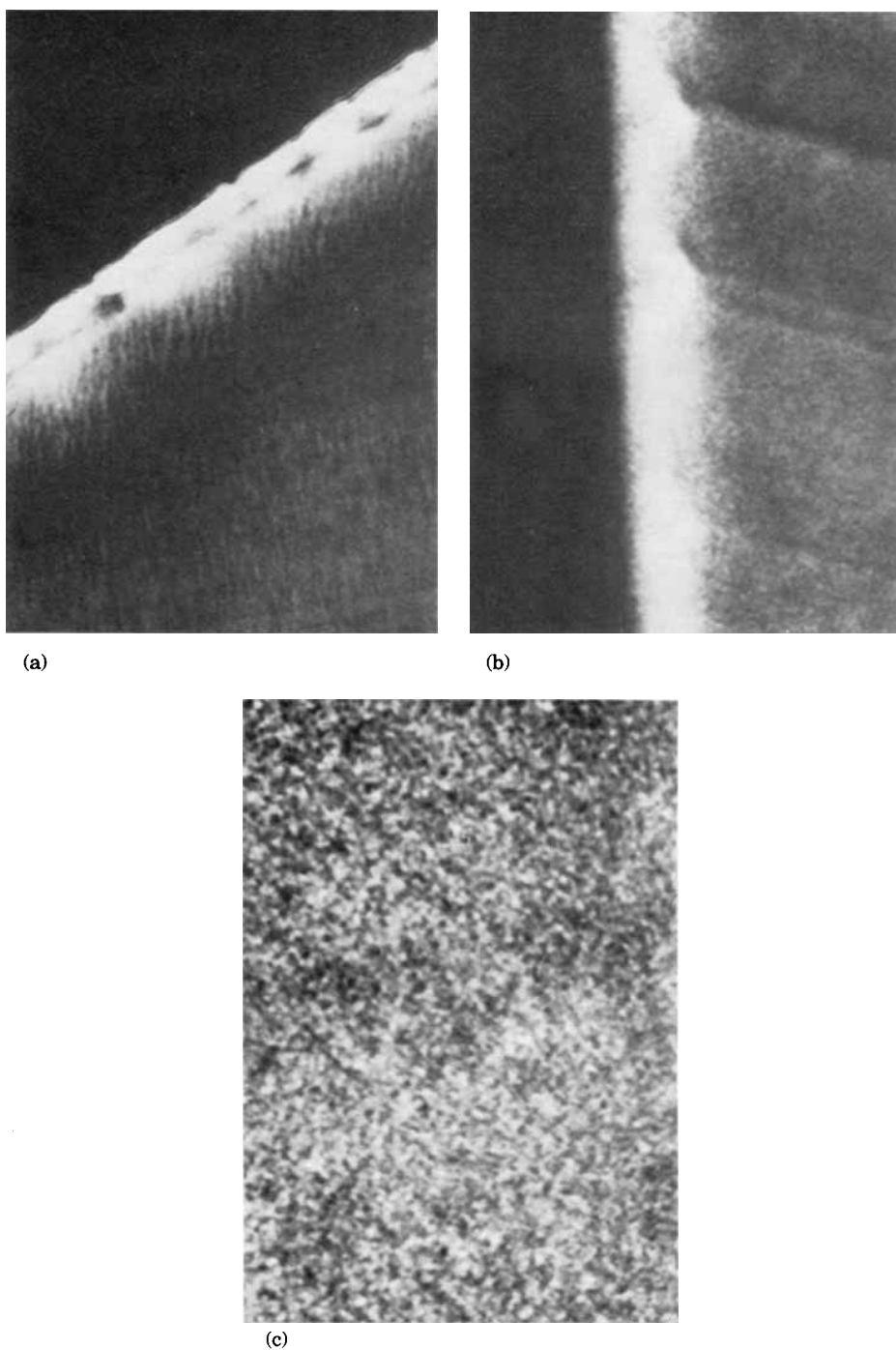
(a)

(b)

(c)

Fig. 6.   Photomicrographs of pellets extruded at various conditions: (a) surface, 130°C, 40 rpm, 3800 psig; (b) surface 130°C, 140 rpm, 5500 psig; (c) bulk, 110°C, 180 rpm, 6000 psig.

no orientation distinction between surface and bulk. In the latter pellets, the bulk spherulites appear larger than those prepared at low pressure. The spherulite size is more evident in the bulk of other samples extruded at high pressures [Fig. 6(c)].

Related effects of screw speed and extrusion pressure were also apparent in the absorption kinetics. Increasing the screw speed at nearly constant pressure (1800–2380 psig) resulted in smaller initial slopes in the two-stage sorption curves for 4 mm diameter pellets with only a small effect on the slope of the second stage (Fig. 7); the extrusion temperature was increased to minimize the impact of the increasing screw speed on extrusion pressure. On the other hand, the slope of the second stage decreased with increasing pressure ("diffusivities": 4.1×10^{-8} to 5.0×10^{-9} cm^2/s) for the same diameter pellets (Fig. 8) extruded at 125 rpm and decreasing temperatures without significant effect on the first stage slopes (apparent "diffusivity" = $4.1 \times 10^{-8} \pm 0.31 \times 10^{-8}$ cm^2/s). There was also no effect of screw speed on the slopes of the linear sorption plots obtained with 1.45 mm diameter pellets (Fig. 9) which were presumed to have no distinct surface layer.

DISCUSSION

The routine sorption method was used to investigate the transport rates of DICUP in as supplied pellets at 70°C. This sorption temperature was selected in order to complete the experiments in a reasonable time and yet minimize the thermal degradation of DICUP during sorption. Subsequently, the sorption technique was modified to determine separately the initial mass uptake and the equilibrium saturation of DICUP in as-supplied pellets under identical conditions. Identical values of diffusivities were obtained
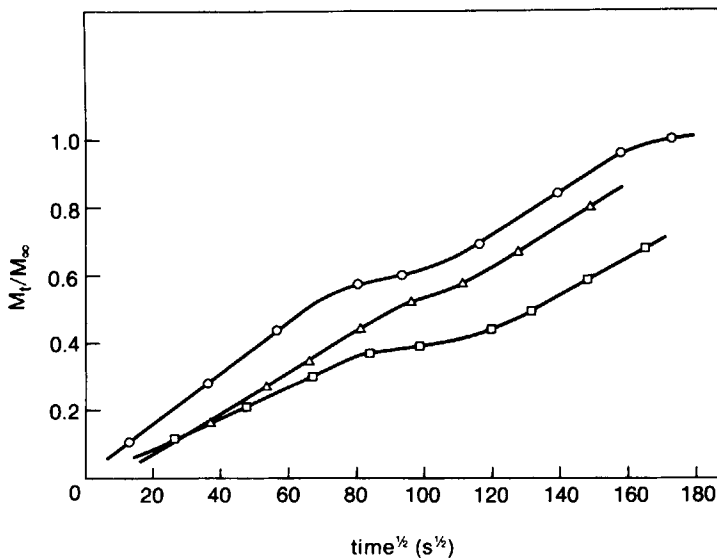
Fig. 7. Effect of increasing screw speed at nearly constant die pressure on the absorption curves at 70°C of DICUP in 4-mm extruded LDPE: (○) 10 rpm, 1000 psig; (△) 30 rpm, 2150 psig; (□) 45 rpm, 2350 psig.
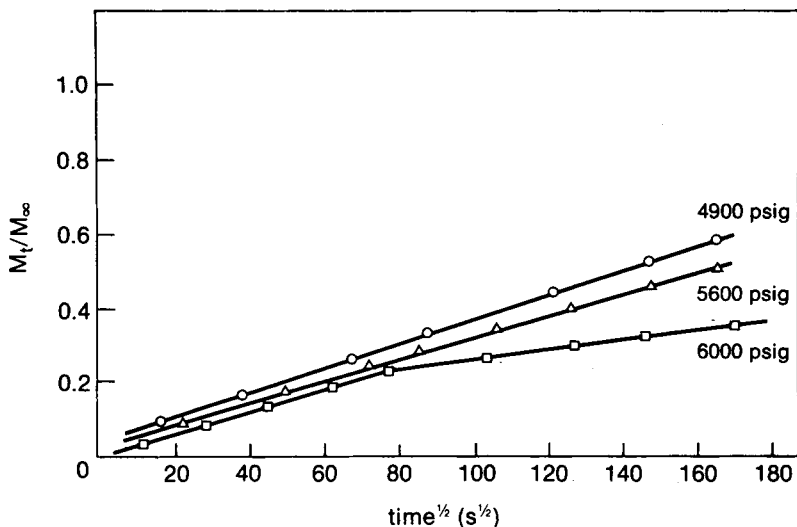
Fig. 8.   Effect of increasing extrusion pressure, at constant screw speed (125 rpm) on the absorption curves at 70°C of DICUP in 4-mm extruded LDPE.

from the two methods, justifying the use of the modified method at lower temperatures.

Concern over changes in pellet morphology during sorption were not considered important since there was no appreciable change in percent crystallinity in these pellets over a long period of time at sorption temperatures indicating the absence of annealing effects. Also, the equilibrium uptake was independent of sample size (pellet sections of different thickness), indicating the absence of an effect of sorption time on pellet crystallinity.
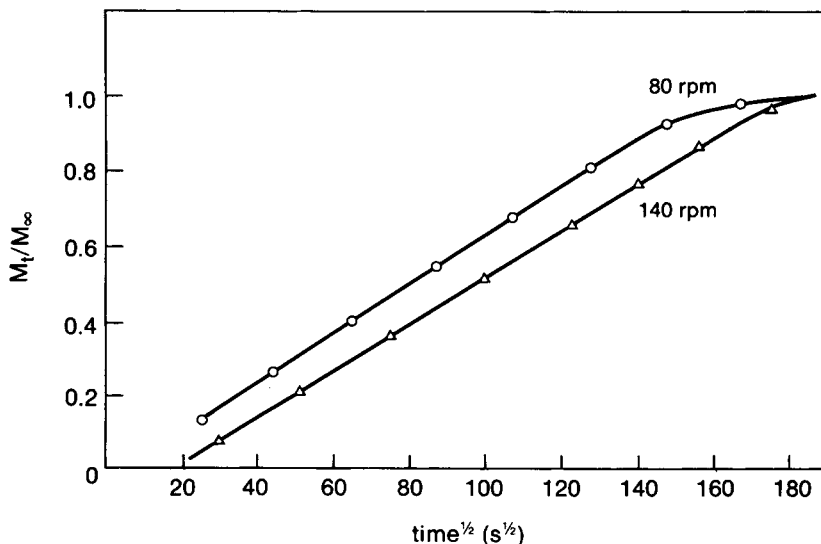

Fig. 9.   Absorption kinetics of DICUP at 70°C in 1.4-mm diameter LDPE pellets extruded at 80 and 140 rpm. $D = 5.6 \times 10^{-8}$ cm²/s.

The photomicrographs (Fig. 6) are clear evidence of the presence of distinct surface and bulk morphologies in the 4 mm diameter extruded samples, the appearance of which are dependent on processing conditions. The surface layer was presumed to arise from nucleation at the die/melt interface and propagation inwards, to form the observed "transcrystalline" structure. Crystallization in the bulk occurred during the quiescent cooling of the extruded rod, to yield the conventional spherultic structure. Schonhorn[8] observed a transcrystalline layer in polyethylene films molded against high energy substrates which acted as nucleation sites for crystals which grew undirectionally into the interior. Similar transcrystalline layers have been reported for a polyamide,[9,10] a polyurethane,[11] and for a polyethylene quenched in ice water.[11]

The DICUP absorption measurements have been interpreted to show the dependence of surface and bulk morphology on screw speed and pressure during extrusion. The initial rate of sorption which would be determined by the morphology of the surface was affected by screw speed and not by die pressure while the second stage (reflecting diffusion through the bulk of the pellet) was dependent on die pressure. The inability to keep extrusion pressure absolutely constant while varying screw speed (Fig. 7) makes it impossible to rule out an effect of screw speed on the second stage slope; nonetheless, this effect is at most small compared to the effect of die pressure. At lower screw speeds, the residence time of the melt in the die is greater, providing the opportunity for greater surface nucleation and hence a greater degree of surface orientation [compare the surfaces of Figs. 6(a) and 6(b)]. In addition, the surface of the extrudate as it exits from the die is cooled more rapidly than the interior with the resultant formation of finer spherulites than the bulk. As screw speed is increased, the temperature gradient at the surface becomes more significant[12] resulting in enhanced difference in crystallization behavior between the surface and bulk. Such differences have beem noted by Eby with ice water quenched polyethylene.[11] Contact angle measurements are underway to distinguish these two factors.

That the surface layer is more permeable than the bulk, as was observed here (higher first stage slope), is consistent with the results of Eby,[11] who measured the diffusion constant of ethane in polyethylene with and without a transcrystalline layer created by quenching. It was presumed that the transcrystalline layer provided a more direct, less tortuous, path to the interior with appropriately higher diffusivity. As the screw speed increased at nearly constant extrusion pressure (Fig. 8) the difference between first and second stage slopes ("diffusivities") decreased, suggesting that at least over this range of extrusion conditions, the transcrystalline layer had a decreasing impact.

The effect of die pressure presumably arises from the differences in crystallite size that result from the effect of pressure on crystallization in the bulk. Increased pressure, increases the degree of supercooling by increasing the melting point,[13] resulting in a larger lamellar thickness[14] and a higher degree of crystallinity.[15] Based on the photomicrographs, this higher crystallinity is manifested as larger crystals, which apparently create a greater impedance to diffusion than the smaller spherulites of pellets formed at lower pressures. This accounts for the effect of die pressure on the second

stage slope evident in Figure 4. The decrease in second stage slope in Figure 8 arises from a combined effect of increased pressure on the melting point and the lowered die temperature.

CONCLUSIONS

The classical sorption technique has been modified to investigate the slow absorption of dicumyl peroxide in extruded low density polyethylene (LDPE). The modified technique entailed the measurement of equilibrium uptake of the penetrant separately from the continuous recording of mass change. This method has been used to demonstrate the presence of a distinct surface layer in 4 mm diameter extruded LDPE rod, through the appearance of uptake curves with the characteristics of two-stage sorption. The nature of the surface layer, at least in terms of its diffusivity to dicumyl peroxide, was dependent on extruder screw speed while the bulk was more dependent on die pressure. This behavior has been related to the orientation of the transcrystalline surface layer at low screw speeds and the larger spherulites in the bulk of samples extruded at high pressures.

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