Glycerol Contact Angle Measurements on Exterior and Interior Surfaces of Polyethylene Rods: Difference between Surface and Bulk Morphology

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Synopsis

A difference between surface and bulk morphologies of extruded low density polyethylene (LDPE) has been observed through measurement of the contact angle of glycerol on both exterior and interior surfaces of the extrudate. The sessile drop contact angle on the exterior surface of LDPE rods prepared in a Brabender plasticorder increased with increasing screw speed (40–180 rpm) and correspondingly increased die pressure at each extrusion temperature (110–130°C). On the other hand, the sessile drop contact angle on the interior surface of LDPE rod, exposed by grinding, decreased with increased screw speed. Qualitative trends were identical with exterior contact angle measured by the Wilhelmy plate method or with the interior surface exposed by fracture. Contact angle variations were interpreted in term of density or crystallinity to suggest that the bulk or interior crystallinity increased with increasing die pressure (even at constant screw speed), while the crystallinity of the exterior decreased with increasing screw speed (even at nearly constant die pressure). The difference between surface and bulk morphologies was consistent with that deduced from DICUP absorption kinetics and optical microscopy [*J. Appl. Polym. Sci.*, **29**, 2383 (1984)], although differences were noted in the effect of screw speed on surface morphology.

INTRODUCTION

A difference between surface and bulk morphology of extruded low density polyethylene rods was noted in a previous investigation using optical microscopy and the sorption of dicumyl peroxide at 70°C.[1] This paper reports on contact angle measurements that confirm this difference in morphology.

A considerable effort has been expended in determining the relationship between the contact angle of a liquid on a polymer surface and the physical properties (e.g., molecular weight distribution, density, crystallization behaviour, etc.) of a polymer. Roe[2] and Lee, Muir, and Lyman[3] have indicated that the density of the surface layer can be important in determining the ultimate wettability. Schonhorn and Ryan[4] showed that a variation in the surface density of a polymer resulted in a change in the critical surface tension of wetting and devised a relationship between surface crystallinity and wettability. A theory to discribe the effect of a polymer phase transition (e.g., melting) on surface tension has been devised.[5] Schonhorn[6] investigated the

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heterogeneous nucleation and crystallization of polyethylene against high energy surfaces (e.g., metal, metal oxides, and alkali halide crystals) by contact angle measurements using glycerol as the wetting liquid. Contact angle data were used to determine the crystallization conditions required to maximize polyethylene adhesion to an aluminum substrate.

The difference in the crystallization behaviour between the surface and the interior of 4 mm diameter low density polyethylene (LDPE) rods was investigated by measurement of the glycerol contact angle on both exterior and interior surfaces.

MATERIALS AND METHODS

Materials

Low density polyethylene (CIL 300 GXN 7218) was supplied by Canadian Industries Ltd. (Edmonton, Alberta, Canada) 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 mm^{-1}). The melt index was 2.07 (ASTMD 1238-73), density was 928.7 kg m^{-3} (ASTM D1506-68), and percent crystallinity (DSC) was 32 $\pm$ 290.

LDPE was extruded at various screw speeds (40–180 rpm) through a cylindrical die (4 mm diameter) by a Brabender plasticorder (Model 252, C. W. Brabender, Hackensack, NJ) with a 3/4 in. screw. The increase in pressure in the die with the increase in screw speed or temperature was measured with a pressure transducer (Dynisco, Westwood, MA). The temperature in the die and along the barrel was adjusted as necessary (110–130°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.

Surface Preparation

Exterior surfaces were prepared by washing in distilled water only. Interior surfaces of these rods were exposed by two methods:

(i) Fracture. Notches were made in the surface of the extruded rods (Fig. 1) using a sharp knife. The rods were immersed in liquid nitrogen and fractured along the notches by hand. Small regions of the resulting interior surface were found to be sufficiently flat for sessile drop measurements. Exposed surfaces were washed with distilled water.

(ii) Grinding. Extruded rods were secured in a lucite block and then embedded in a room temperature curing epoxy resin (Ancamine 1770, Shell Canada, Toronto, Ontario, Canada) as shown in Figure 1. These blocks were then ground on a horizontal grinding wheel (Buchler Ltd., Evanston, IL), to expose the interior. The exposed surfaces were polished and washed with distilled water.

Contact Angle Measurement

Both sessile drop and Wilhelmy plate methods were used to determine the contact angle of glycerol (99.8% pure, anhydrous, Baker Chemical Co., Phillipsburg, NJ) on the exterior surfaces of the extrudate. Only the sessile drop method was used on the interior surfaces.

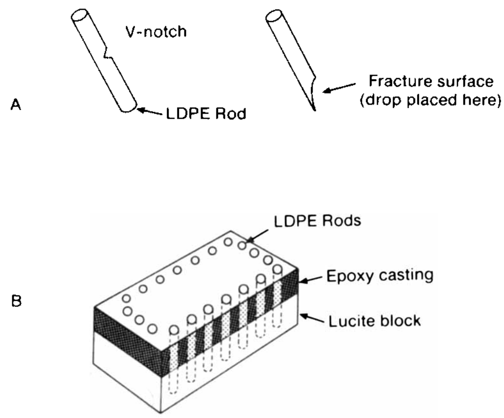

Fig. 1. Interior surface sample preparation: (a) fracture of v-notched rod exposing surface smooth enough for sessile drop measurement; (b) grinding of rods secured in a Lucite block and embedded in epoxy resin.

Sessile Drop

Sessile drop contact angles were measured with a horizontal travelling microscope with a cross-hair eyepiece attached to a goniometer (Spindler and Hoyer, Gottingen, F.R.G.). The cylindrical LDPE specimen was mounted on a wooden block or on an open adjustable stage without temperature control (Fig. 2). The stage was illuminated from behind at a sufficient distance to minimize heating of the drop by the light source.

A sewing needle that had been cleaned by heating in a bunsen burner until red hot was used to place a small drop of glycerol carefully onto the exterior surface of the cylindrical specimen. The drops were sufficiently small (0.3–0.4 mm diameter) to avoid gravitational distortion, yet were large enough to measure conveniently. Contact angle measurements were made quickly after

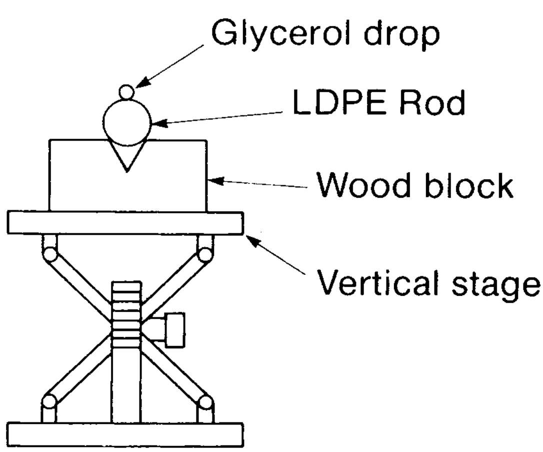

Fig. 2. Sessile drop measurement of contact angle on the exterior surface of cylindrical rod mounted on a wooden block.

drop formation. The variation of contact angle with drop size was not investigated but all drops were approximately the same size. Contact angles at both left and right sides of the drop were measured to determine symmetry. In all cases, three to five drops of glycerol at different points on the surface were measured and averaged. The precision was approximately $\pm 1°$. Glycerol forms a stable drop on these surfaces, making it possible to obtain very reproducable readings; no variation in angle was noted in the few minutes required for measurement.

Wilhelmy Plate

The Wilhelmy plate apparatus located in the Applied Surface Thermodynamics Laboratory of the Department of Mechanical Engineering, University of Toronto, was used (courtesy of Dr. A. W. Neumann). The LDPE rod was suspended from an electrobalance (Ventron R-100, Cahn Instruments, Cerritos, CA) and the balance was brought to the null point by counter-weights. The platform was moved up so that the surface of the liquid was approximately 1 mm below the lower edge of the LDPE rod and then raised by a motor drive (Model BSH-200, Bodine Electric Co., Evanston, IL) at 10 mm/min. The force exerted on the rod was measured by the Cahn balance as the sample continued to advance into the liquid. Receding contact angles were not measured because tilting of the sample took place inside the liquid.

The contact angle θ was measured from the force mg using

$$\cos\theta = \frac{mg}{P\gamma} + \frac{V\rho g}{P\gamma} \tag{1}$$

where m = apparent mass (g) as measured with electrobalance, g = local gravitational force = 979.3 dyn/g, P = perimeter of the sample (cm), γ = surface tension of glycerol = 63.4 dyn/cm,[6] V = volume of immersed sample at a particular depth, and ρ = density of the wetting liquid. The second term is a buoyancy factor whose contribution was found to be negligible.

Surface Energy

The contact angle was converted to surface tension using Neumann's equation of state[7]:

$$\cos\theta = \frac{(0.015\gamma_{LV} - 2.00)\sqrt{\gamma_{SV}\gamma_{LV}} + \gamma_{LV}}{\gamma_{LV}\left(0.015\sqrt{\gamma_{SV}\gamma_{LV}} - 1\right)} \tag{2}$$

where γ_{SV} is the solid–vapor surface tension and γ_{LV} is the liquid–vapor surface tension. The solid–vapor surface tension (γ_{SV}) was calculated by iteration.

Surface Characterization

The interior and exterior surfaces of two pellets were analyzed by ESCA at the Surface Science Laboratory of the University of Western Ontario. The

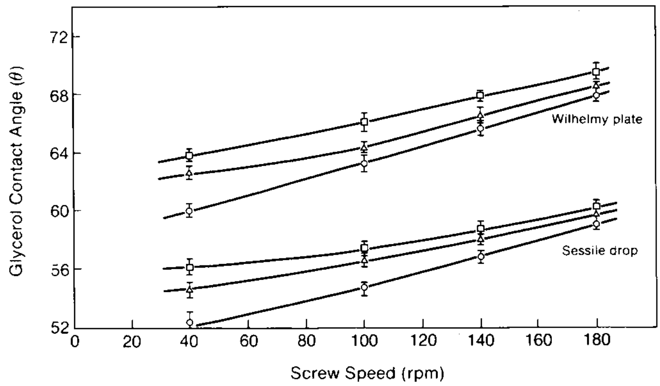

Fig. 3. Effect of screw speed on exterior surface contact angles measured by sessile drop and Wilhelmy plate methods. Extrusion temperatures (°C): (die pressures): (○) 110(3600– ≥ 6000); (△) 120(3120– ≥ 6000 psig); (□) 130(2800– ≥ 6000).

exterior surface was exposed by slicing the pellet in half with a scalpel immediately before analysis. One sample was extruded at a low screw speed/low pressure (35 rpm/2500 psig/130°C); the other was extruded at high speed (180 rpm/6000 psig/130°C). Both samples were analyzed long after (≥ 1 year) contact angle measurement on other pellets in the same batch; in the interim the pellets had been stored in a closed bottle in the laboratory.

RESULTS

Surface Measurement

The variation in the exterior surface contact angle of a rod extruded at different screw speeds (40–180 rpm) and temperatures (110–130°C) is shown in Figure 3. Regardless of the method of measurement (sessile drop or Wilhelmy plate), the mode of variation of the contact angle with the extrusion conditions was identical; both values increased with increasing screw speed. The difference in the two values was expected since the sessile drop method provides essentially only static angles while the advancing angle was obtained by the Wilhelmy method.

It can be seen that the contact angles measured on the surfaces of rods extruded at a particular temperature increased with increasing screw speed (Fig. 3). This suggested that the rods extruded at low speeds have a higher surface tension relative to those produced at higher screw speeds. The higher the extrusion temperature, the higher the contact angle and consequently the lower the surface tension.

Interior Surface

The interior of the same 4 mm diameter extruded rods was exposed by either fracture or grinding, and the contact angle was measured by the sessile drop technique on the exposed surface. The contact angles of glycerol on these interior surfaces also varied with the processing conditions (Fig. 4). The mode

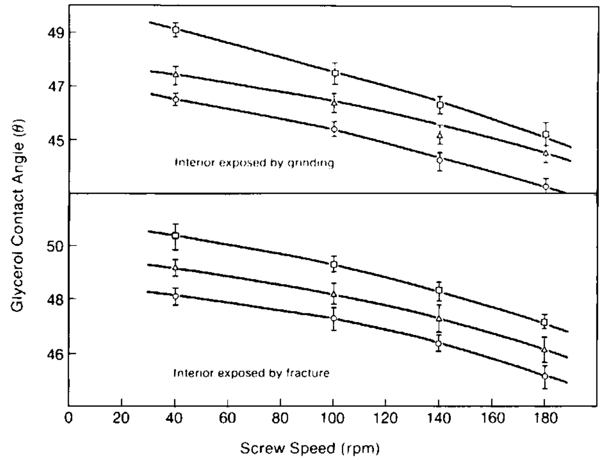

Fig. 4. Effect of screw speed on interior surface contact angles, with interior surface exposed by grinding or by fracture. Extrusion temperatures (°C): (○) 110; (△) 120; (□) 130.

of variation of the contact angle on surfaces exposed by either grinding or fracture was identical; the small difference in actual values was presumed related to the effect of the exposure method.

The interior contact angles decreased with an increase in screw speed. This indicated that a rod extruded at higher screw speed (and also correspondingly higher pressure) resulted in an interior with higher surface tension than the interior of a rod extruded at lower screw speed (or lower extrusion pressure). Comparison of contact angle values on interior surfaces of rods extruded at different temperatures indicated that higher temperatures resulted in interior surfaces with lower surface tension than that of rods extruded at lower extrusion temperatures.

The results obtained in Figures 3 and 4 are replotted in Figure 5 to compare exterior and interior contact angle values. The values of sessile drop contact angles on the exterior surface of the rods were always lower than those on the

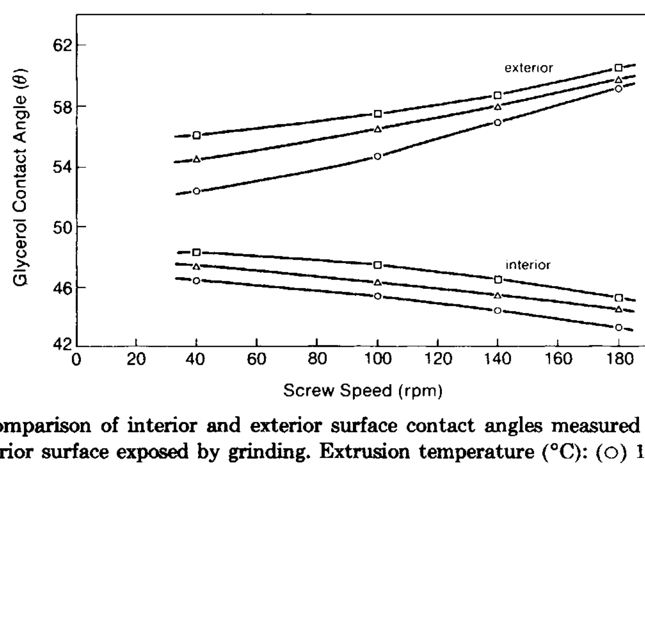

Fig. 5. Comparison of interior and exterior surface contact angles measured by sessile drop method. Interior surface exposed by grinding. Extrusion temperature (°C): (○) 110; (△) 120; (□) 130.

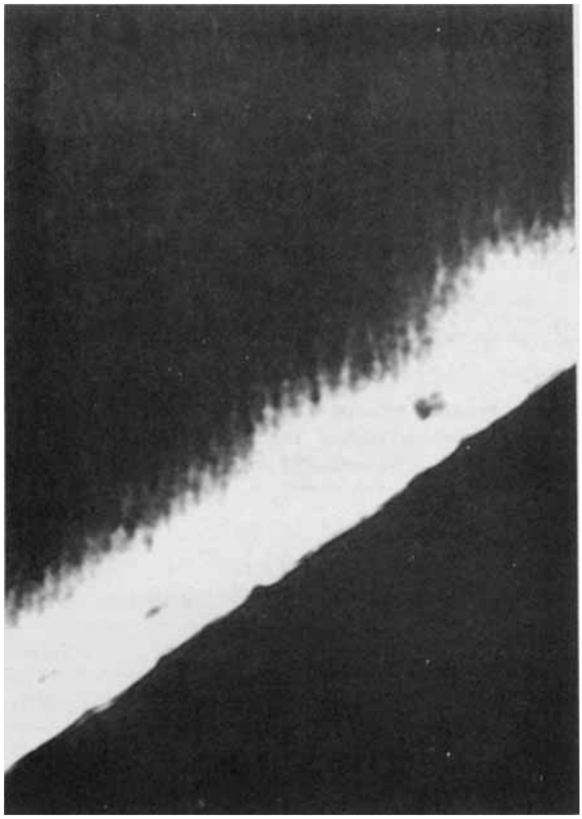

Fig. 6. Photomicrograph of surface of pellet extruded at 130°C, 40 rpm, 3800 psig, showing difference between surface and bulk morphologies. Pellet was cross-sectioned perpendicular to the extrusion direction by an ultramicrotonne and examined under polarizing light. Taken from Ref. 1.

interior at all extrusion conditions, suggesting that the exterior of the rods had a lower surface tension than the interior.

The effects of screw speed and extrusion pressure were isolated to a limited extent in Figures 6 and 7. Increasing the screw speed at nearly constant die pressure (3200–4200 psig) resulted in a significant increase in the exterior contact angle with an almost negligible effect on the interior contact angle (Fig. 6). Rods extruded with increasing extrusion pressure at constant screw speed resulted in a small variation in the exterior contact angles but a slightly larger variation in the interior angles (Fig. 7).

Surface Characterization

The ESCA results are summarized in Table I. Some silicon and oxygen was found in the exterior surface of both pellets and a small amount of silcon and oxygen was detected in the interior of the low screw speed pellet. No silicon was found in the interior of the other pellet. The silcon/oxygen ratio varied from approximately 1 : 2 to 2 : 1. Traces of sulfur were found on the exterior of the high screw speed sample. The carbon 1s binding energy was 278.4 ± 0.1 eV, indicative of the methylene groups of polyethylene.

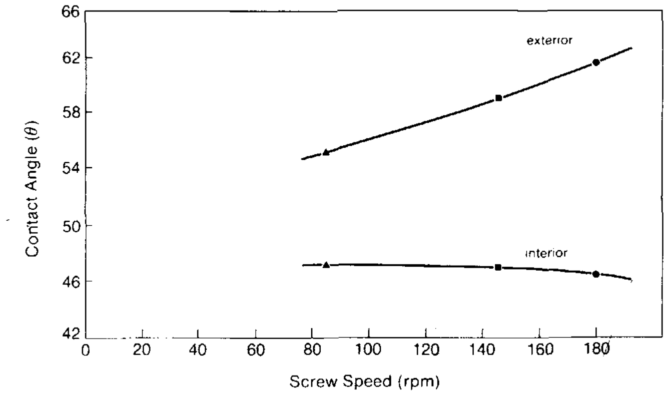

Fig. 7. Effect of screw speed on exterior and interior contact angle measured by sessile drop method. Interior surface exposed by grinding. Temperature adjusted to minimize accompanying variation in die pressure: (▲) 120°C, 85 rpm, 3200 psig; (■) 125°C, 145 rpm, 3700 psig; (●) 135°C, 180 rpm, 4200 psig.

TABLE I
ESCA Analysis of Extruded LDPE Pellets[a]

	Exterior surface (atom %)					Interior surface (atom %)		
	Cls	Ols	Si2p	S2p	Nls	Cls	Ols	Si2p
Low screw speed	65.6	16.8	17.6	—	—	96.7	1.1	2.2
35 rpm, 2500 psig		Cls (B.E.) = 278.3 eV				Cls (B.E.) = 278.4 eV		
		Si : O = 1.05				Si : O = 2.0		
High screw speed	78.6	11.2	5.5	0.8	1.4 (162.2 eV) 2.44 (159.2 eV)	100	—	—
180 rpm, 6000 psig		Cls (B.E.) = 278.6 eV				Cls (B.E.) = 278.3 eV		
		Si : O = 0.48						

[a] Extrusion temperature = 130°C.

DISCUSSION

Contact angles on the exterior surface obtained from Wilhelmy plate and sessile drop methods showed a similar variation with screw speed and extrusion temperature (Fig. 3), although the sessile drop method gave angles ~ 8–9°C lower than the advancing angle measured by the Wilhelmy plate method. A similar difference in the contact angle on a styrene–butadiene–styrene copolymer measured by these two methods was also observed by Smith et al.[8] This difference is related to the hysteresis effect causing a difference between receding and advancing contact angles. The receding contact angles obtained from the Wilhelmy plate method would be expected to correlate more closely with the static sessile drop contact angle, but receding values could not be measured here since tilting of the sample rods inside the liquid precluded such measurements.

Only the sessile drop method was used to measure the angles on the interior surfaces of the same rods. However, two techniques were used to expose the interior surfaces: grinding and fracture. The contact angles were greater (by ~ 2°) when the interior surface was exposed by fracture (Fig. 6) instead of grinding. Both sets of values displayed a similar variation with screw speed and temperature, however. Accordingly, the difference in absolute values is presumably related to the influence of sample preparation. Because the purpose of the study was to analyze the effects of extrusion processing conditions on surface and bulk morphology, the absolute value of contact angle was not considered essential for interpretation of the morphology; only the relative values were necessary.

Effect of Processing Conditions

The effect of processing conditions on contact angle was attributed to the effect of surface morphology (e.g., degree of crystallinity or density) on contact angle. Schonhorn reported a similar change in the surface density of polyethylene films melt crystallized against high energy surfaces that ultimately resulted in a dramatic change in wettability.[6] The decrease in contact angle from 48.2° to 45.2° on the interior surfaces (exposed by grinding) of the extrudate at 130°C with increasing screw speed (Fig. 5) suggested an increase in surface tension and crystallinity. Similar increases in surface tensions in the interior of the pellets produced at 120 and 110°C were also observed. These results are consistent with the increases in crystallinity and crystallite size, and decrease in DICUP diffusivity observed[1] in rods produced at increasing screw speed and correspondingly higher extrusion pressure. On the exterior surfaces of the extrudate at 130°C (Fig. 5) the contact angle increased from 55.5° to 60.0° (sessile drop method), suggesting that surface layers of decreasing surface tension and hence decreasing crystallinity were formed with the increase in screw speed. This was also true for the exterior surfaces of pellets extruded at 120°C and 110°C. However the previously described decrease in DICUP diffusivity[1] was attributed to an increase in surface crystallinity, rather than a decrease in crystallinity as observed here. This difference may be related to the difference in "surface" thicknesses under consideration. The contact angle is characteristic of the surface which is a few angstroms thick, whereas the optical photomicrographs indicate and dicumyl peroxide diffusivities reflect a surface region several microns thick. The higher crystallinity of the first few angstroms of surface would offer little additional resistance to diffusion and so would have limited impact on dicumyl peroxide diffusivity. Nevertheless, the difference between surface and bulk crystallinities apparent in the photomicrographs (Fig. 6) and the absorption kinetics of dicumyl peroxide were also present in the contact angle values.

Figures 7 and 8 show the effect of isolating the effects of screw speed and extrusion pressure. Increasing the screw speed from 85 to 180 rpm, at nearly constant pressure, resulted in an increase in exterior contact angle from 55.0° to 61.4° (Fig. 7) with only a small decrease (47.0° to 46.4°) in the interior contact angle. This suggested that screw speed affected the density of the outer surface more so than that of the interior, provided the extrusion pressure was not much changed. The slight variation observed in the contact

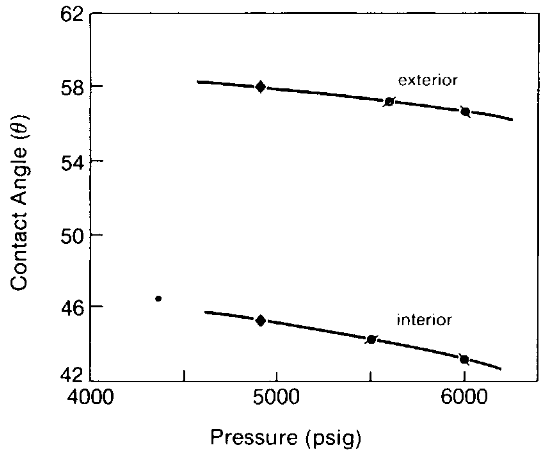

Fig. 8. Effect of die pressure on exterior and interior contact angle measured by sessile drop method. Interior surface exposed by grinding. Screw speed maintained constant at 125 rpm: (◆) 135°C, 4500 psig; (●) 125°C, 5600 psig; (●) 115°C, 6000 psig.

angles on the interior surfaces is presumed to be related to the effect of the unavoidable increase in pressure on bulk morphology.

The decrease in interior surface contact angle (Fig. 8) from 45.3° to 43.4° with increasing extrusion pressure (4900–6000 psig) at constant screw speed (125 rpm) is consistent with the conclusion that the bulk morphology of the extruded rods was dependent on extrusion pressure as was evident from the dicumyl peroxide absorption results.[1] It was expected that the outer surfaces of these rods would have had a constant contact angle since the crystallinity of the exterior surface was presumed to be unaffected by changes in die pressure.[1] However, the slight decrease in exterior contact angle (58.6° to 56.1°) makes it difficult to rule out an effect of extrusion pressure on the morphology of the first angstroms of the surface. Nevertheless, this effect in terms of contact angles was less significant when compared with the effect of screw speed (Fig. 7).

It was interesting to observe that the ratio of interior surface energy to exterior surface energy [calculated using eq. (2)] was linearly correlated with screw speed (Fig. 9) regardless of the temperature or pressure at which the extruder was operated, with the exception of the rods produced at the lowest screw speed (40 rpm). Extrapolation of the linear relationship to zero screw speed resulted in a Y-intercept of unity, corresponding to equal bulk and exterior energies (or densities), which is what would be expected for polymer cooled under quiescent conditions. Since the same linear relationship was observed for rods extruded at constant screw speed (varying temperature) and constant temperature (varying screw speed) (Fig. 9), it appears that the effect of pressure on surface and bulk morphology of the extrudate is essentially the same whether the pressure is increased by increasing the screw speed or by decreasing the temperature.

The deviation of the experimental values at 40 rpm from the linear correlation may be related to an effect of the die surface which provided opportunity for a greater degree of surface nucleation leading to an increase in

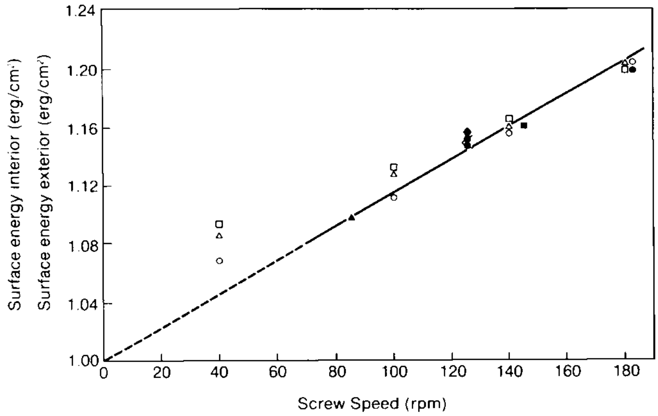

Fig. 9. Ratio of the surface energy of the exterior surface to that of the interior surface for rods extruded under various operating conditions. Symbols as in Figures 4–7.

nuclei density and the formation of transcrystallinity as observed in the photomicrographs.[1] Such additional nucleation alters the relationship between screw speed and the bulk/surface morphology ratio implicit in the linearity of the rest of the correlation.

Surface Chemistry Effects

This study has shown that contact angle measurements are sufficiently sensitive for characterizing changes in both the interior and exterior of 4 mm diameter rods produced under different extrusion conditions. However, the ESCA results indicate that, in addition to morphological effects, surface chemistry differences cannot be ruled out in intrepreting the results. The presence of significant silicon and oxygen on the pellet surfaces with a ratio consistent with silicone (at least in one sample) suggests that the pellet was contaminated with silicone. The higher amount of silicon on exterior surfaces than in interior surfaces was consistent with the higher contact angle on the former surfaces. On the other hand, the higher silicon content of the exterior surface of the pellet extruded at lower speed was inconsistent with its lower contact angle relative to pellet extruded at higher speed. Unfortunately, the source of the silicone cannot be determined. Since it is not an additive to this resin, the silicone presumably was a contaminant that adsorbed to the surface of already extruded pellets. Whether this happened before or after contact angle measurement is unknown, although the latter is more likely given the long time between contact angle and ESCA measurement. The only additive used in the resin is a sulfur containing antioidant which only appeared in one ESCA spectrum so that migration of this additive is unlikely to have had much impact on the contact angle measurements. Similarly the carbon 1s binding energy and peak shape did not support the presence of oxidized material or components other than polyethylene at the surface. Since the variation in contact angle values with the extrusion conditions parallelled the results obtained with DICUP diffusivity, these additives or contaminants were not considered important at least in interpreting the contact angles in a relative sense. Absolute use of the data would require quantification of the extent of additive migration or contamination under different processing conditions.

CONCLUSIONS

Contact angle measurements on the exterior and the interior surfaces (latter exposed by fracture or grinding) were used for the characterization of the surface and bulk morphology of the LDPE extrudate. The variation in contact angle values was related to the presence of a transcrystalline layer at low screw speeds and to an increased degree of crystallinity in the interior of the samples extruded at high pressure.

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