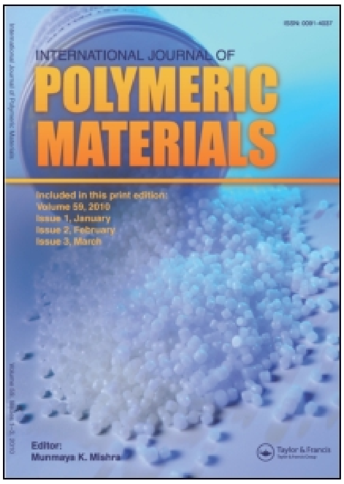

**International Journal of Polymeric Materials**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

# The Effects of Melt Processing Variables on the Morphology and Properties of Injection Molded Polypropylene

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**To cite this Article** Kantz, Melvin R.(1974) 'The Effects of Melt Processing Variables on the Morphology and Properties of Injection Molded Polypropylene', International Journal of Polymeric Materials, 3: 3, 245 — 258
**To link to this Article: DOI:** 10.1080/00914037408072355
**URL:** http://dx.doi.org/10.1080/00914037408072355

*Intern. J. Polymeric Mater.*, 1974, Vol. 3, pp. 245–258
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Printed in Reading, England

# The Effects of Melt Processing Variables on the Morphology and Properties of Injection Molded Polypropylene†

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(*Received May 3, 1974*)

Controlled variations in melt temperature and injection pressure during the injection molding of isotactic polypropylene tensile bars have been correlated with differences in the skin-core morphology and preferred orientation as observed using optical microscopy and X-ray diffraction. The molding anisotropy has, in turn, been related to systematic variations in tensile yield strength, notched Izod impact strength, and longitudinal shrinkage. The correlation between processing variables and morphology was used to construct a qualitative model for the origin of the skin-core morphology during the filling and packing stages of injection molding.

## INTRODUCTION

The engineering properties of injection molded polypropylene test specimens and end-use articles are critically dependent on morphology and orientation. A number of studies of crystalline and glassy thermoplastics have demonstrated how morphology and orientation and how mechanical properties can be controlled, or tailored by precise control of melt processing conditions.[1–5] However, detailed studies that link morphology and orientation with molding conditions on the one hand and with resultant properties on the other have yet to be presented. The objectives of this paper are twofold. One is to discuss the origins of the skin-core morphology and molding anisotropy in qualitative

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† Based on a paper published originally in *J. Appl. Polym. Sci.* **16**, 1249 (1972).

terms, while the second is to review the results of an earlier study[6] illustrating the variation of anisotropy in injection molded polypropylene with molding conditions and the correlation of selected properties with anisotropy. Microstructural details of molecular and crystalline orientation will not be discussed here as they are treated in papers by Clark,[7] Garber and Clark,[8] and Keller and Machin.[9]

The importance of anisotropy with respect to orientation and morphology in an injection molded article cannot be overemphasized. Large variations in physical and chemical properties with direction can lead to significant, and sometimes expensive, consequences. In the laboratory, unrecognized anisotropy may manifest itself as unacceptable variability in properties such as tensile and impact strength where these properties may relate to quality control and product development activities. Another major consequence may be observed as weakness or brittleness in only certain locations of the molding. High degrees of molecular and crystalline orientation are essential in fibers and other types of thin extruded materials, but unintentional anisotropy in an injection molding can be accompanied by sufficiently large residual stresses to cause warpage, shrinkage, and impaired toughness.[10–13] Hence, it is necessary to recognize and characterize anisotropy in test specimens to assure that mechanical test data are meaningful.

## EXPERIMENTAL METHODS

Type I ASTM tensile bars of Shell 5550 polypropylene having a melt flow of 5.3 g/10 min (ASTM D1238L) were molded using a 200-ton, 6-ounce Van Dorn reciprocating screw injection molding machine. Molding was carried out at melt temperatures of 190°, 218°, 233°, and 275°C under injection pressures ranging from 4,000 to 13,000 psi. Mold fill time and mold temperature were held constant at 10 sec and 30°C, respectively.

Tensile yield strength and notched Izod impact strength were determined according to ASTM conditions D638-64T and D256-56, respectively. Shrinkage was determined for each tensile bar as the difference (mils/in) between the mold cavity length and the specimen length 48 hours after molding.

Thin sections, 5–10 microns in thickness, were microtomed perpendicular and parallel to the flow direction at distances of 0.5, 4.0, and 7.5 inches from the gate. Thin sections were immersed in Nujol and observed between crossed polarizers on a Leitz Ortholux microscope. A first order red compensator was used to discriminate between positively and negatively birefringent spherulites. The thickness and area fractions of discrete morphological layers were determined from the photomicrographs of the thin sections that were obtained 4 inches from the gate. X-ray diffraction (flat plate) photographs were obtained using a Siemens Kristalloflex II system equipped with a 1200 watt fine focus tube (Ni filtered CuK$\alpha$). Diffraction patterns were made at half-inch intervals along the axis of the tensile bars.

## RESULTS AND DISCUSSION

### The effect of processing variables on properties

The injection molding of end-use articles is a rather pragmatic business. The molder's major concern in production is to maximize the number of units produced by using low melt temperatures, low mold temperatures, and high injection pressures to minimize cycle time. However, the lower limits or ranges through which these and many other variables can be varied are determined by the intrinsic properties of the polymer grade. The more important of these intrinsic properties include: melting temperature, heat of fusion, temperature and shear rate dependence of viscosity, and processing stability.

The rational approach to optimization is through the use of the mold area diagram which is a two-dimensional contour map that shows the lower limit of moldability (short-shot) and the upper limit (flash point) as effected by processing temperatures and pressures. While molding may be carried out within the area set by these limits, one still has to define that region of the area that leads to the production of consistently acceptable parts. For example, the criterion of acceptability may be 5000 psi tensile strength and shrinkage of no more than 14 mils/in in the longitudinal direction. The mold area study may show, however, that one or the other is attainable, but not both. The mold area diagrams in this section were included as a starting point to illustrate the macroscopic aspects of processing and behavior. The effects of injection pressure and melt temperature on tensile yield strength, shrinkage, and notched Izod impact strength are shown graphically by the mold area diagrams in Figures 1–3, respectively. Figure 1 shows that the yield strength increases primarily with decreasing melt temperature, and to a much lesser extent, with increasing pressure. Figures 2 and 3 show that shrinkage and impact strength also increase with decreasing melt temperature. The effect of injection pressure on these properties is much more pronounced than in the case of the yield strength; moreover the effect of pressure in the case of shrinkage is rather complex. As discussed in the following sections, the effect of processing on the morphology of the specimens from which the above data were collected will illustrate the relationships between processing, morphology, and properties.

### The effect of processing variables on morphology and orientation

The morphology illustrated in Figures 4a and b is typical of the skin-core morphology observed in the gauge section of polypropylene tensile bars when

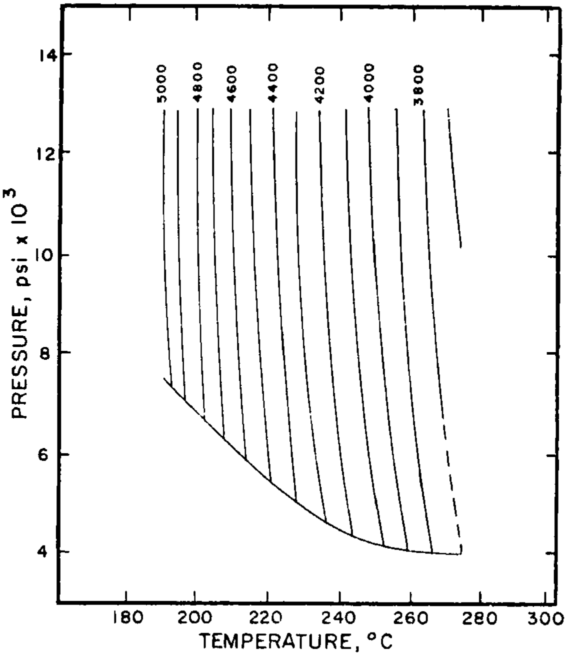


FIGURE 1 Mold area diagram showing the effect of melt temperature and injection pressure on tensile yield strength, (psi).

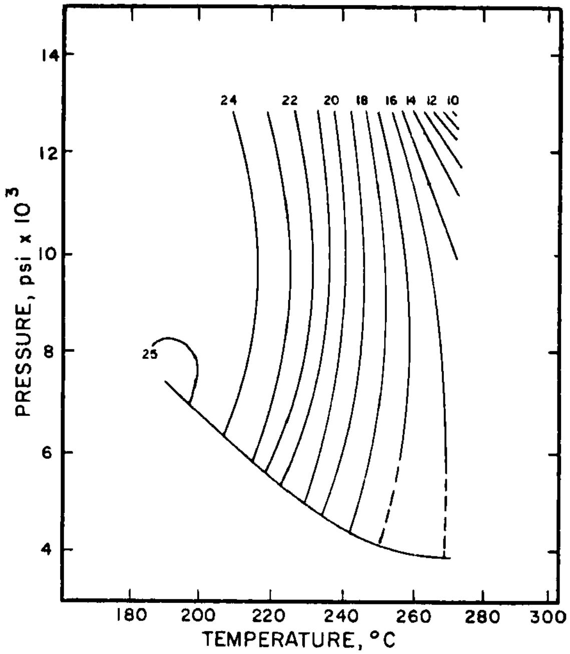


FIGURE 2 Mold area diagram showing the effect of melt temperature and injection pressure on longitudinal shrinkage, (mil/in).

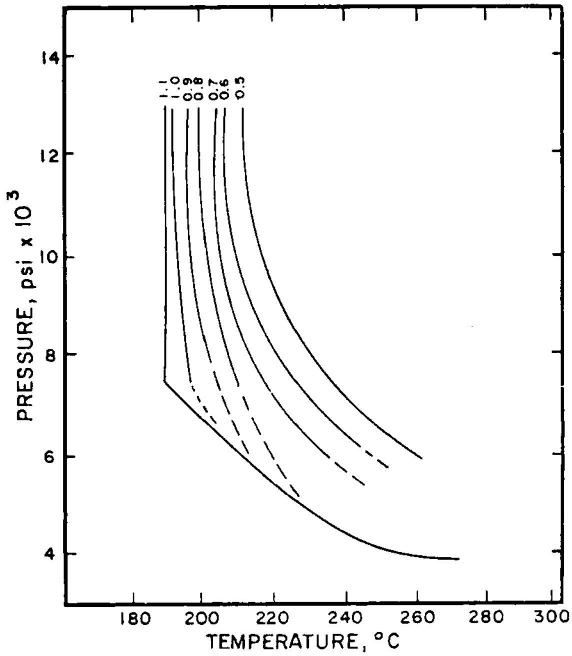
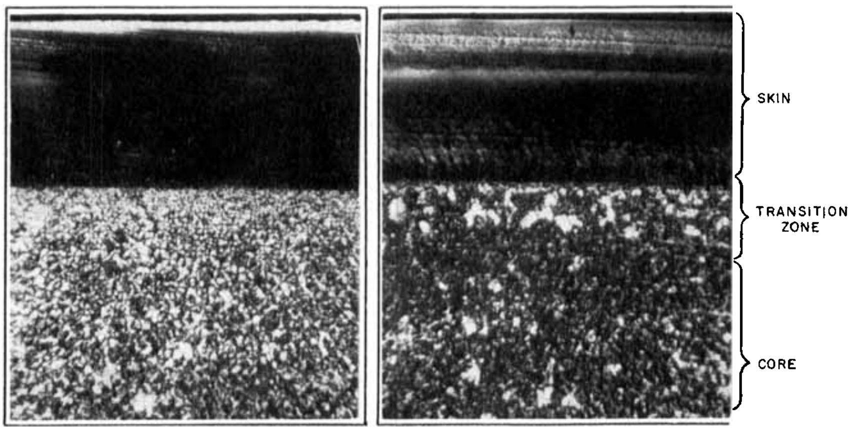


FIGURE 3 Mold area diagram showing the effect of melt temperature and injection pressure on notched Izod impact strength, (ft-lb/in-notch).



PERPENDICULAR TO FLOW

A

PARALLEL TO FLOW

B

FIGURE 4 Typical skin-core morphology of polypropylene viewed perpendicular (A) and parallel (B) to the flow direction—63 × magnification.

viewed perpendicular and parallel to the direction of flow. The designation skin-core implies the existence of two discrete phases or morphological layers in the cross-section of the molding. This, however, is not really the case. Figure 4b shows that the cross-section consists of three to four separate layers or macrophases. The presence of three of these layers was discussed in an earlier paper.[6] The morphology and texture of four layers in an injection molded plaque of polypropylene have recently been described in detail by Fitchmun and Mencik.[14,15] The layer between the non-spherulitic skin and the spherulitic core as shown in Figure 4b and subsequent photomicrographs will be called the intermediate zone. Other morphological features of importance and the origin of this morphology will be discussed in a later section of this paper.

Although the skin layer appears featureless or "amorphous" between crossed polarizers, birefringence values between 10 and $20 \times 10^{-3}$ and parallel extinction of polarization color show that this layer is highly oriented. X-ray diffraction shows that the skin is highly crystalline and possesses a fiber texture. Diffraction patterns b and c in Figure 5 illustrate this texture clearly for a

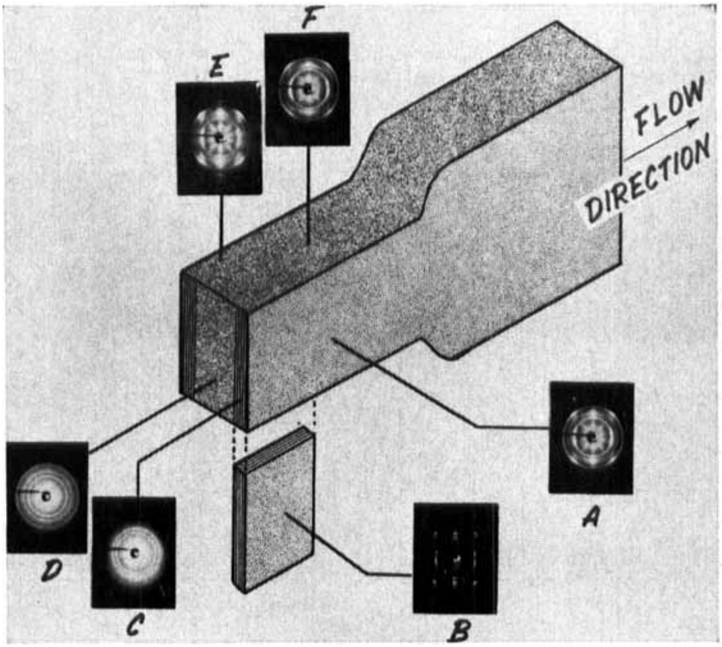


FIGURE 5 Distribution of preferred crystallite orientation in a tensile bar molded at 190°C and 10,000 psi.

tensile bar that was molded under conditions (190°C, 10,000 psi) that produced a sufficiently thick skin for study by X-ray diffraction. Pattern c indicates that there is a biaxial component of orientation within the layer. Pattern d obtained for the core spherulites shows completely random orientation. The remaining patterns arranged around the schematic tensile bar illustrate the superposition of oriented layers on the unoriented core as the X-ray beam was allowed to pass through the intact specimen.

The effect of varying the melt temperature at a constant injection pressure of 8,000 psi on morphology is illustrated by the sequence of photomicrographs in Figure 6. The micrographs show that skin thickness decreases markedly with decreasing melt temperature. Much the same result was obtained by Fitchmun and Mencik[14] in their work with polypropylene and by Clark[7] for polyacetal

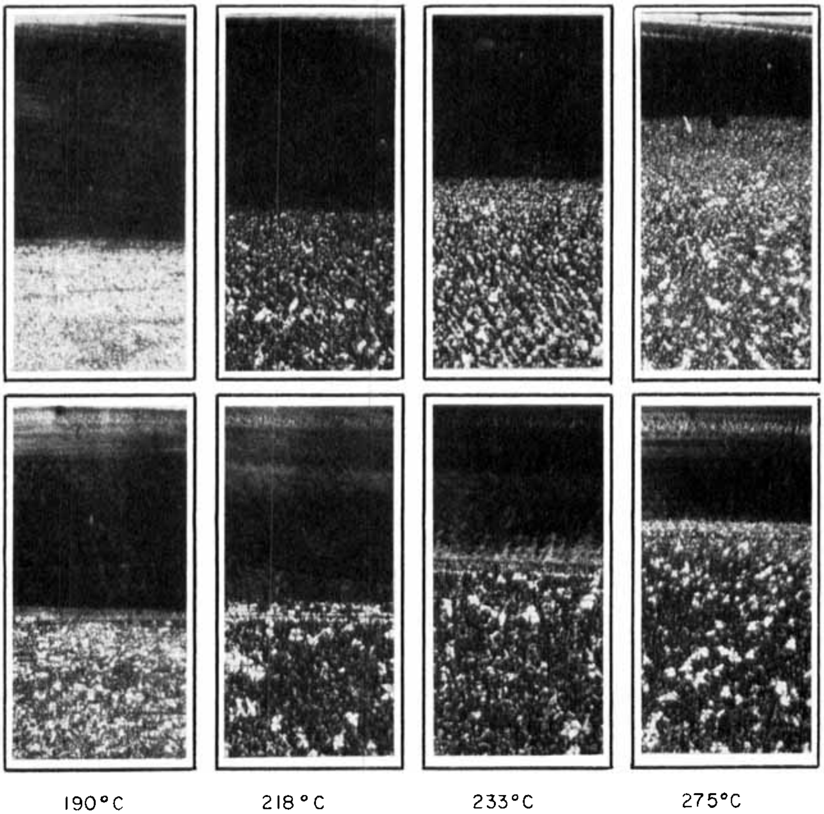


FIGURE 6 Polypropylene thin sections microtomed perpendicular (upper) and parallel (lower) to the flow direction in tensile bars molded at 8,000 psi and at the indicated temperatures—63 × magnification.

that was molded at constant melt temperature into molds of varying temperature. The effect of injection pressure on skin thickness is relatively small as demonstrated in Figure 7. On the other hand, pressure was observed to exert a profound influence on the thickness of the intermediate layer. When the thicknesses of the skin and intermediate layer are combined and converted to the area fraction of oriented phase, $A_0$, one finds an inverse linear variation of $A_0$ with melt temperature. This relationship is given in Figure 8. Comparison

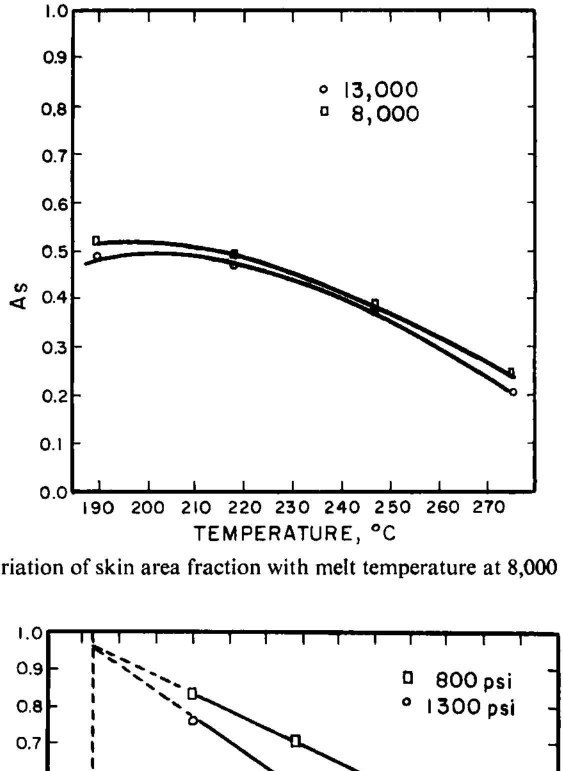


FIGURE 7 Variation of skin area fraction with melt temperature at 8,000 and 13,000 psi.

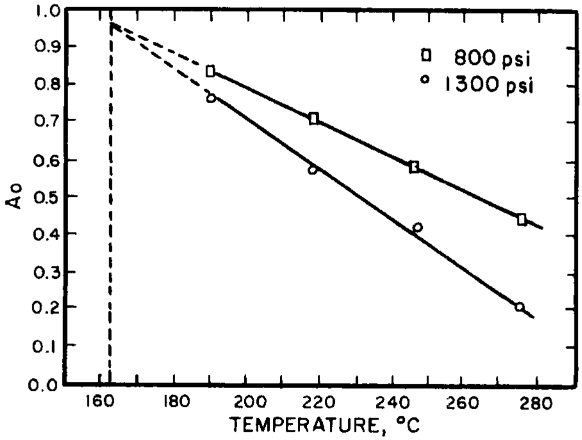


FIGURE 8 Variation of $A_0$ with melt temperature at 8,000 and 13,000 psi.

of the data given in Figures 7 and 8 show that $A_0$ is larger at low injection pressure than at high pressure for all temperatures. This result can be explained on the basis of shear-thinning, i.e., reduction in viscosity with increasing shear rate. Although the shear rates are not known, they do increase with increasing injection pressure. The lower viscosity at 13,000 psi than at 8,000 psi permits more rapid molecular relaxation so that less orientation is retained in the crystallized state. The data in Figure 8 are also interesting in that extrapolation to lower temperature suggests that a spherulite-free film structure would result were it possible to carry out injection molding at the melting point of 165°C.

## Correlation of morphology and properties

The tensile yield strength varies almost linearly with $A_0$ as shown in Figure 9. Here the specimen can be viewed as a two-phase composite material consisting of an unoriented core of spherulitic polypropylene sandwiched between two layers of highly oriented polypropylene. The modulus and yield strength of the oriented layer are greater than those of the core. Since the adhesion between the phases is considered to be perfect, the properties of the two phases are additive to yield linear or rule of mixtures composite behavior. Kwei, *et al.*[16] demonstrated a similar dependence of the sonic modulus on the thickness of the transcrystalline layer in compression molded films of polypropylene and polyethylene.

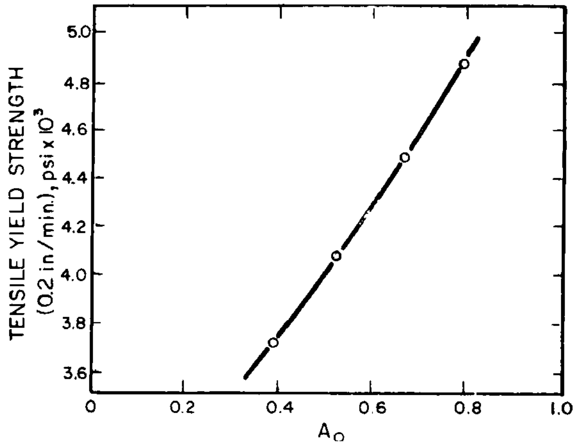


FIGURE 9 Tensile yield strength as a function of $A_0$.

Figure 10 shows the relatively smooth increase in shrinkage with increasing

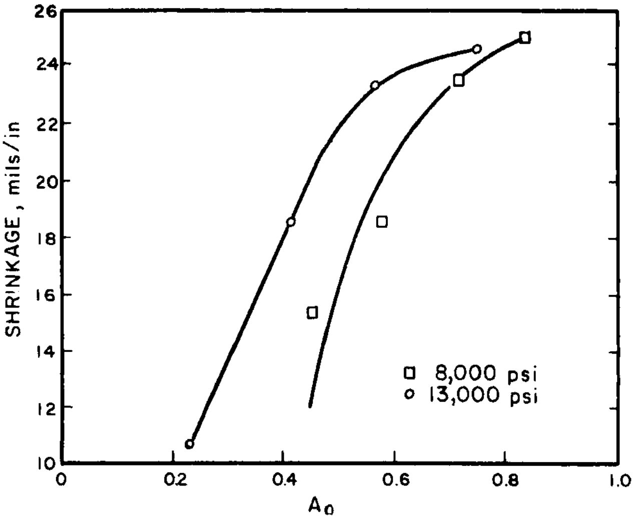


FIGURE 10 Longitudinal shrinkage as a function of $A_0$.

orientation, or $A_0$. These data are consistent with the observations of others[10,12,17] for both crystalline and glassy thermoplastics. The reason for the decline in the rate of shrinkage for samples having the highest amount of orientation is not known. The non-linear behavior may be an experimental artifact from insufficient time taken to observe the shrinkage.

The increasing impact strength for tensile bars molded at 8,000 and 13,000 psi with $A_0$ shown in Figure 11 is to be expected from the standpoint that the

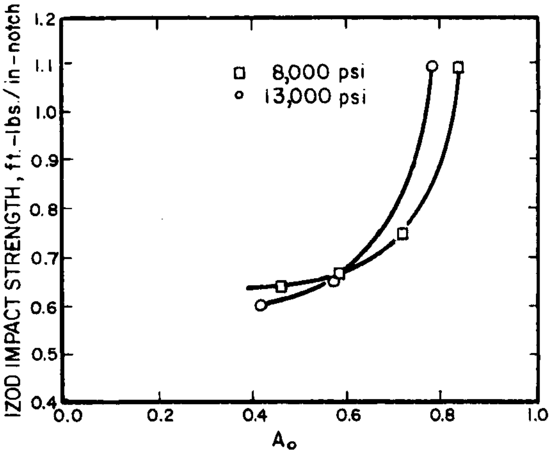


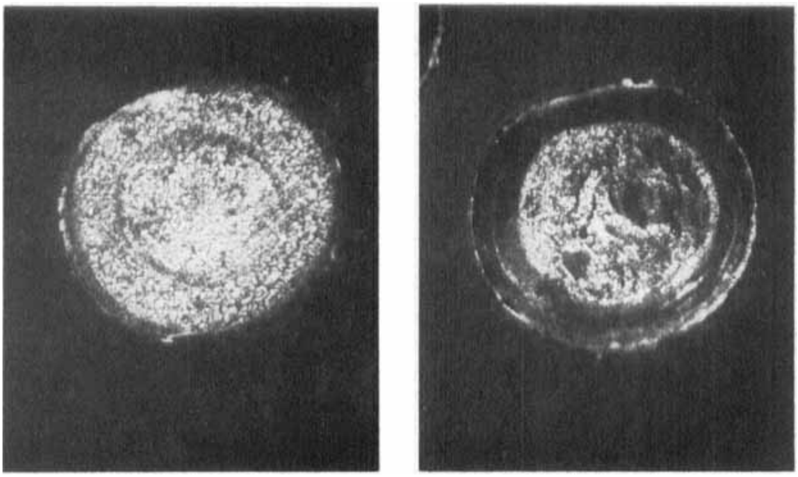
FIGURE 11 Notched Izod impact strength as a function of $A_0$.

molecules in the oriented layers are aligned, for the most part, perpendicular to the direction of crack propagation. As in the case of the yield strength vs $A_0$ it is probably correct to view the impact specimen as a composite material. Limited studies of the impact behavior of dart drop weight impact specimens have shown that impact strength and ductility increase with $A_0$.

## The origin of molding anisotropy

Molding anisotropy of the type described in this paper arises when a viscous, elastic, high molecular weight material at some elevated temperature is forced to flow through a channel or cavity whose walls are maintained at a temperature much lower than the melt temperature. As the polymer fills the mold four important gradients develop; namely, temperature, pressure, and shear and tensile (extensional) stresses. Considering only the temperature and shear stress gradients, that portion of polymer in contact with the cold mold wall cools more rapidly and experiences higher shear than the polymer in the interior of the mold. The shear stress at the wall disentangles and orients the previously coiled molecules in the direction of flow while the rapid temperature decline causes the viscosity of this oriented layer to increase by five to six orders of magnitude to $10^8$–$10^9$ poise. Thus, the orientation of these molecules is preserved. Just how thick the oriented skin layer becomes under the imposed molding conditions is expected to depend chiefly on the thermal conductivity, the molecular weight parameters, molecular configuration, and chain segment mobility. These characteristics govern the molecular relaxation times, crystallizability, and the sensitivity of melt viscosity to shear rate or shear stress. The low thermal conductivity of polypropylene allows the interior polymer to remain molten over most or all of the flow path so that molecular randomizacan occur prior to and during the packing portion of the cycle. Moreover, the flow front of the molten interior is relatively blunt, and the shear stress gradient is small so that nucleation occurs in an essentially quiescent state to permit the growth of typical spherulites.

It is now necessary to point out that the existence of a steep temperature gradient is not essential to the formation of the skin-core morphology. High wall shear stress and a shear gradient are quite sufficient as illustrated in Figure 12. The two photomicrographs in this figure show the morphology in cross-sections of polypropylene that was removed from the capillary of an Instron viscometer after slow cooling from 175°C to room temperature. Extrudate a, which was extruded below the critical shear stress for flow instability (ca. $1.5 \times 10^6$ dynes/cm$^2$), exhibits a transcrystalline layer but no skin. Extrudate b was extruded above the critical shear stress and shows the typical skin-core morphology found in injection molded polypropylene. With this example, the origin of the intermediate layer shown in Figure 1b becomes



$< T_{CRIT}$ $> T_{CRIT}$

FIGURE 12 Thin sections viewed perpendicular to flow that were microtomed from capillary viscometer extrudates cooled slowly to room temperature from 175°C—63 × magnification.

clearer by demonstrating the role played by both temperature and pressure. The intermediate layer is viewed as a transition region in which the melt viscosity is low enough for molecular relaxation processes and chain folding to occur and thus, to permit the nucleation and growth of crystallites. However, unlike the crystallites in the core spherulites, the crystallites in the transition region appear to be nucleated epitaxially on bundles of molecules oriented (and possibly extended) along shear stream lines or shear bands. The nucleation density along the length of the shear bands is so high that crystallites are constrained to grow predominantly in one direction, namely, perpendicular to the flow direction. This interior transcrystalline morphology is illustrated in greater detail in Figure 13. The crystallites in the sheaves along a given shear band increase in length with increasing distance from the skin owing to the lower nucleation density. The crystallites in the intermediate layer are predominantly the hexagonal crystal structure in contrast to the monoclinic structure that comprises the core spherulites. The growth of the hexagonal polymorph is known to be stimulated by pressure;[18] however, it is a thermodynamically metastable form with respect to the monoclinic form at ambient pressure. It is therefore not surprising that the crystallites in the intermediate region are less resistant to oxidizing agents as shown in the work of Fitchmun and Mencik.[14]

Returning to the origin of the skin, it can be argued that this layer was

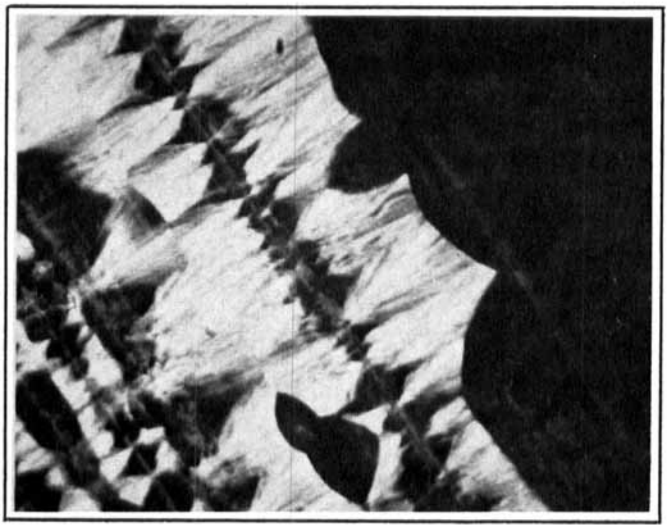


FIGURE 13 Crystallites nucleated from shear bands in the intermediate zone—720× magnification.

"quenched" to the paracrystalline form to account for the lack of apparent crystalline character. On the other hand, pressure and shear stress are known to alter the crystallization process drastically. At one atm, and depending on the heterogeneous nucleation density and thermal history, isotactic polypropylene crystallizes between 110° and 140°C. Under hydrostatic pressure of 5,000 atm Morrow[19] reported crystallization at 245°C. Taking a recently reported value for the melting temperature dependence on pressure of 0.083°C/atm for polypropylene,[20] one would expect melting under 5,000 atm to occur at approximately 600°C. Such a difference between the melting and crystallization temperatures corresponds to an enormous driving force for crystallization. The work of van der Vegt and Smit[21] and Sieglaff and O'Leary[22] based on capillary viscometry indicates that under readily attainable pressures corresponding to shear stresses of 1 to $2 \times 10^6$ dynes/cm$^2$ shear orientation-induced crystallization occurs at temperatures as high as 200°C.

X-ray diffraction patterns that were taken at half-inch intervals along the flow axis of the tensile bars revealed virtually identical degrees of orientation throughout the two-inch gauge length. Hence, it is concluded that the thickness of the three layers under the conditions studied are the same as those determined from the microtomed midsections of the bars. Further microscopical observations of thin sections taken 0.5 and 7.5 in from the gate, i.e., in the grip ends, showed that values of $A_0$ in the former were slightly lower than in the gauge section and significantly lower in the latter. These observations together with the skin-core morphology previously described were used to infer the fill or flow pattern in the tensile bar mold and to further illustrate the formation of the three morphological zones. As the melt enters the tensile bar gauge section from the constricted neck, the velocity of the center stream lines increases faster than the layer of melt cooling against the cold mold walls. The reduction in the cross-sectional area of the channel causes normal stresses to develop which means that the melt must accommodate elastic strain energy in addition to extensional and shear strain energy. While some of the elastic strain energy is stored, a large fraction of it is believed to be dissipated as Reynolds-like turbulence adjacent to the semi-solid skin layer. This finite region of secondary flow breaks up the flow front into a central plug and two satellite shoulders. As the melt enters the enlarged cross-section on the side opposite the gate, the velocity is reduced and the bulk of the stored elastic strain energy is relieved by elastic recovery, or what is called die swell in extrusion. The retention of relatively high orientation in the intermediate layer can be understood from the standpoint that molecular relaxation processes involving the large molecules are slower than the rate of injection of polymer into the mold. For example, mold filling is complete in approximately 0.8–1 second while it can be shown using the theory of Bueche[23] that the maximum molecular relaxation time is approximately 7 seconds at the melting point of polypropylene having weight and z-average molecular weights of $5.5 \times 10^5$ and $3 \times 10^6$, respectively.

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