

The Skin-Core Morphology and Structure-Property Relationships in Injection-Molded Polypropylene

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Synopsis

Tensile bars of an isotactic propylene homopolymer and an ethylene-propylene copolymer were prepared by injection molding under a variety of melt temperatures and injection pressures. The effects of these processing variables on morphology and crystalline orientation were studied using optical microscopy and x-ray diffraction. Microscopy of microtomed thin sections of the tensile bars revealed the presence of three distinct crystalline zones, namely, a highly oriented nonspherulitic skin, a row or shear-nucleated spherulitic intermediate layer, and a typically spherulitic core. The thickness of the oriented skin layer is a function of the polymer melt temperature and varies inversely with temperature. The thickness of the intermediate layer varies with injection pressure, but in a complex manner. Preferred crystallite orientation in the skin and intermediate layers exerts profound effects on mechanical properties. Tensile yield strength, impact strength, and shrinkage increase with increasing combined thickness of the two oriented outer layers.

INTRODUCTION

Injection molding is one of the most commercially important fabrication processes for molding a broad spectrum of thermoplastics. A great deal of attention has been given to defining the engineering aspects of the operation for maximizing production rates and for controlling part strength, brittleness, shrinkage, and appearance characteristics.^{1,2} In spite of the advances made in understanding the process flow mechanics, and many of the factors influencing strength, moldability, and appearance, the injection molding of articles having consistent mechanical properties still involves a surprising amount of art. Moldability has been studied extensively for the commercially important polymers, yet for a given thermoplastic it is often found that apparently constant molding conditions do not necessarily yield moldings having equivalent mechanical properties. This can be explained partly by variations in processing equipment and variations in control of operating conditions. However, one of the most vital considerations is the nature of the polymer itself. One may expect that the more flexible the molding process and the more complex the mold geometry, the more dom-

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inant is the role played by the intrinsic properties of polymer.^{3,4} Properties such as softening or melting ranges, heats of fusion, temperature variation of viscosity, chemical stability, etc., are well known for most polymers. Unfortunately, little work has been done in attempting to relate the polymer properties to the actual setup or crystallization characteristics of the molding under the complex temperature and pressure environment of the mold.

It is generally recognized that the final properties of injection moldings are strongly dependent on morphology, orientation, and stress.^{1,3,5,6} Studies of various polymers have demonstrated that injection moldings have a skin made up of molecules that are highly oriented in the flow direction and an essentially nonoriented central bulk region, or core. This morphology has been observed in both glassy and semicrystalline polymers. The high degree of molecular orientation in the skin has been observed in certain instances to cause warpage, shrinkage, and premature fracture under impact and flexure.⁷⁻⁹

This paper describes the effect of polymer melt temperature and injection pressure on the overall morphology and consequent properties of an impact-modified ethylene-propylene copolymer and an extended heat resistant isotactic propylene homopolymer. We will not discuss the flow processes in the mold or the temperature gradients that give to the skin-core effect since these topics are adequately described elsewhere.^{3,9,10,11}

EXPERIMENTAL

Injection Molding

Standard ASTM tensile bar specimens were molded using a Van Dorn 200 ton-6 ounce reciprocating-screw injection molding machine having a pump pressure of 1250 psi and a cylinder pressure/pump pressure ratio of 10. Molding was carried out at melt temperatures of 190°, 218°, 233°, and 275°C under injection pressures ranging from 400 to 1300 psi. The copolymer was molded at a constant overall cycle time of 25 sec while the homopolymer was molded at cycle times ranging from 25 to 28 sec; longer cycles were used at higher melt temperatures. The mold temperature was held at 30°C for both materials.

Physical Testing

The tensile yield strength and Izod impact strength were determined according to ASTM D 638-64T and D 256-56, respectively. Shrinkage was evaluated for each specimen as the difference (mils/in.) between the mold cavity length and the tensile bar length 48 hr after molding.

Morphology

Tensile bars were sectioned using an A. O. Spencer Model 820 rotary microtome. Thin sections, 5-10 microns in thickness, were cut from the

midpoint of the bars perpendicular to and parallel to the flow direction. The microtomed specimens were immersed in Nujol and observed between crossed polarizers using a Leitz Ortholux microscope. A first-order red compensator was used to discriminate between positively and negatively birefringent spherulites and to examine the nonspherulitic skin morphology in detail. The photomicrographs displayed in this paper were taken at a magnification of $63\times$ using polarized light, but without the compensator. Thickness and area fractions of morphologic zones were measured directly from the photomicrographs.

X-Ray diffraction (flat plate) photographs were obtained using a Siemens Kristalloflex II generator equipped with a 1200-watt fine focus tube (Ni filtered CuK_α radiation) and Polaroid cassette. This technique was used for making qualitative comparisons of the degree of preferred orientation between the homopolymer tensile bars that were molded at 190° and 275°C and in adjacent regions of the same bar molded at 190°C . As in the case of microscopy, all x-ray work was confined to the midpoints of the tensile bars.

Materials

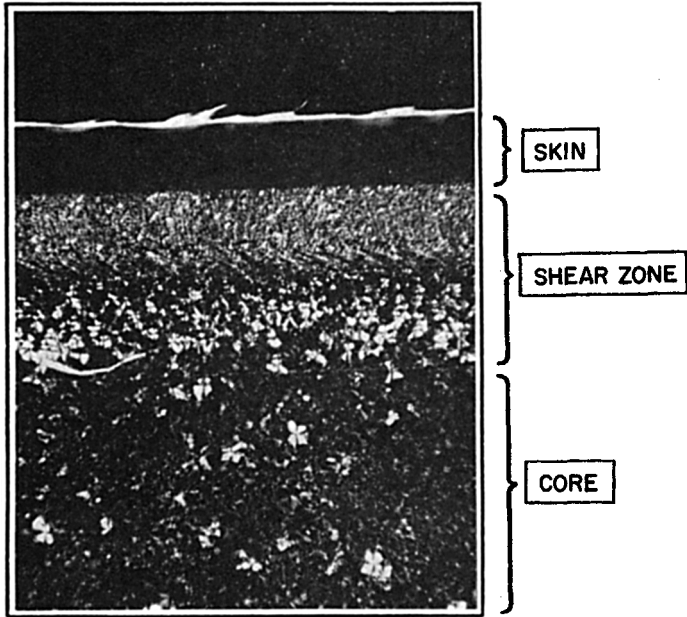
Two commercially available polymers were molded for this study: (1) Shell Polypropylene 5550 homopolymer having a melt flow of 5.3 g/10 min (ASTM D 1238L). (2) Shell Polypropylene 7526, a polyolefin copolymer; the melt flow of this grade is 3.5 g/10 min.

RESULTS AND DISCUSSION

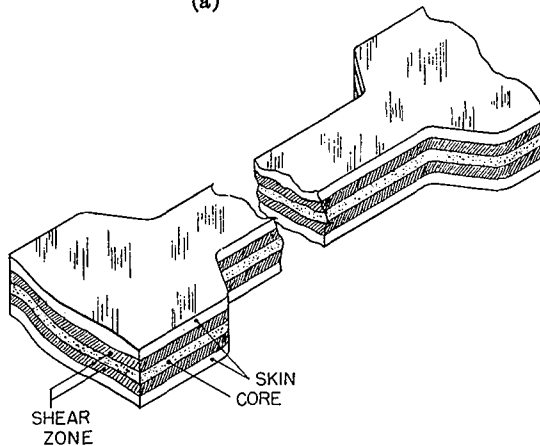
Optical microscopy showed that all of the tensile bars molded over the range of conditions mentioned above displayed the skin-core morphology as is characteristic of polypropylene. When observed in cross section, the boundary between the nonspherulitic skin and spherulitic core appears quite sharp in the case of the homopolymer but slightly diffuse for the copolymer. The corresponding areas observed parallel to the flow direction, however, were found to contain a layer between the skin and core that was not readily apparent in the cross sections. This intermediate layer, or what will be called the shear zone, is spherulitic, but the morphology differs from that in the core in that the spherulites (or sheaves) in the shear zone are row nucleated while those in the core are randomly nucleated. The shear zone is not easily observed in the cross sections because the birefringence of the row-nucleated spherulites viewed perpendicular to the cylindrical axes of the rows differs little from that of the core spherulites. The appearance of the three zones in a longitudinal thin section are illustrated in Figure 1a. This photomicrograph shows the morphology from the surface to approximately half the thickness (60 mils) of the tensile bar. The bright serrated edge on the surface of the skin is a cutting artifact. It should be borne in mind for the subsequent discussion that each tensile bar is made up of a core and almost identical shear and skin zones on each of the

two large surfaces. The manner in which these zones are distributed is illustrated schematically in Figure 1b.

Microscopical observation of the skin between crossed polarizers reveals no perceptible crystalline development except in certain instances where one sees a very shallow transcrystalline layer at the surface. The mole-



(a)



(b)

Fig. 1(a). The three morphologic zones in an injection-molded polypropylene tensile bar viewed in longitudinal section. The large bright spherulites are the type III variety. (b) Tensile bar (schematic) showing the arrangement of the morphologic zones illustrated in part (a).

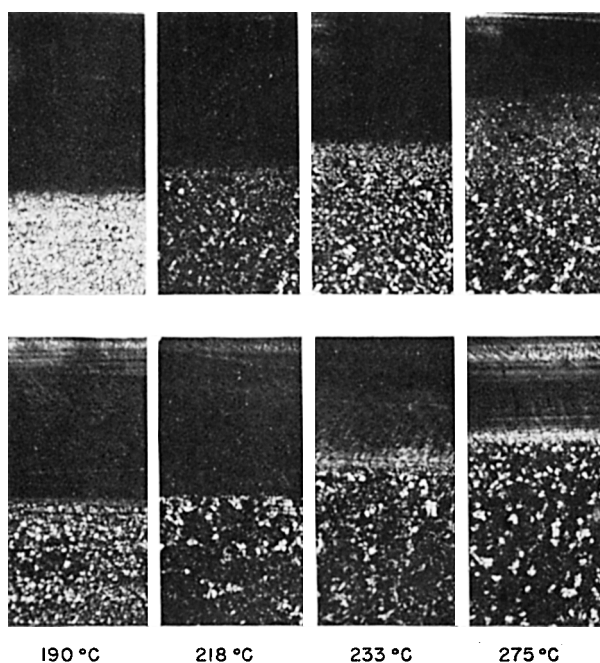


Fig. 2. Polypropylene homopolymer thin sections microtomed perpendicular (upper) and longitudinal (lower) to the flow direction in tensile bars molded at 800 psi and the temperatures indicated.

cules in the skin are highly oriented with the flow direction, as evidenced by relatively high birefringence and uniform extinction of the first-order white polarization color as the specimen is rotated in plane on the microscope stage. The spherulites in the shear zone are bunched tightly together along thin, negatively birefringent rows. The spherulites that were nucleated from each row are nearly identical in size and shape; their size increases with increasing distance from the skin-shear zone boundary much as the grains in a metal casting. The majority of the spherulites in this region are the negatively birefringent type III variety, characteristic of the metastable hexagonal crystal form.^{12,13} The presence of this polymorph is verified by the (111) reflections observed in the x-ray patterns to be discussed later. The core, which usually makes up the bulk of the volume in injection moldings, contains larger but randomly sized spherulites. With the exception of occasional type III spherulites, the spherulites in this zone are the positively birefringent type I variety which is characteristic of the stable, monoclinic polymorph.^{12,13}

One of the principal findings of this study is that the area fraction of skin (A_s) in both the homo- and copolymer specimens increases markedly with decreasing melt temperature. The same effect was reported by Clark¹⁴ for a polyacetal resin that was maintained at constant extrusion temperature but injected into molds at various temperatures. The variation in A_s for

the two polymers molded at 800 psi and four melt temperatures is illustrated in the photomicrographs of cross and longitudinal sections in Figures 2 and 3. Injection pressure affects A_s only slightly, if at all. It does, however, cause noticeable differences in spherulite appearance and in the

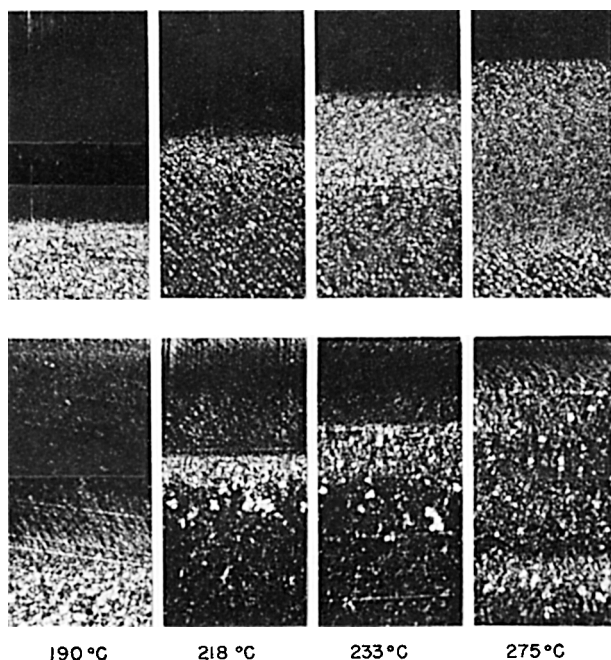


Fig. 3. Polypropylene copolymer thin sections microtomed and viewed as in the preceding figure.

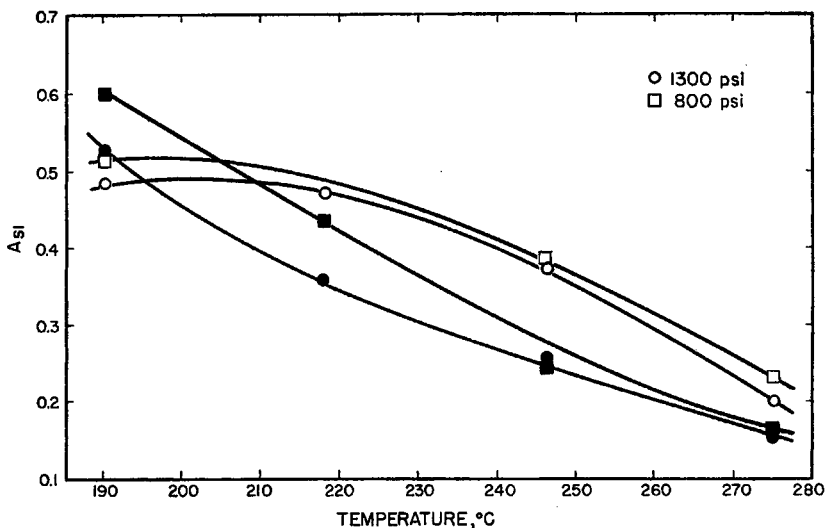


Fig. 4. Variation of skin area fraction (A_s) with molding temperature for the homopolymer (open figures) and copolymer (filled figures).

area fraction of the shear zone (A_s). The variation in A_s with melt temperature at injection pressures of 800 and 1300 psi for the two polymers are given in Figure 4. In addition to observing that the mode of variation is quite different for the two polymers, A_s for the copolymer is more sensitive

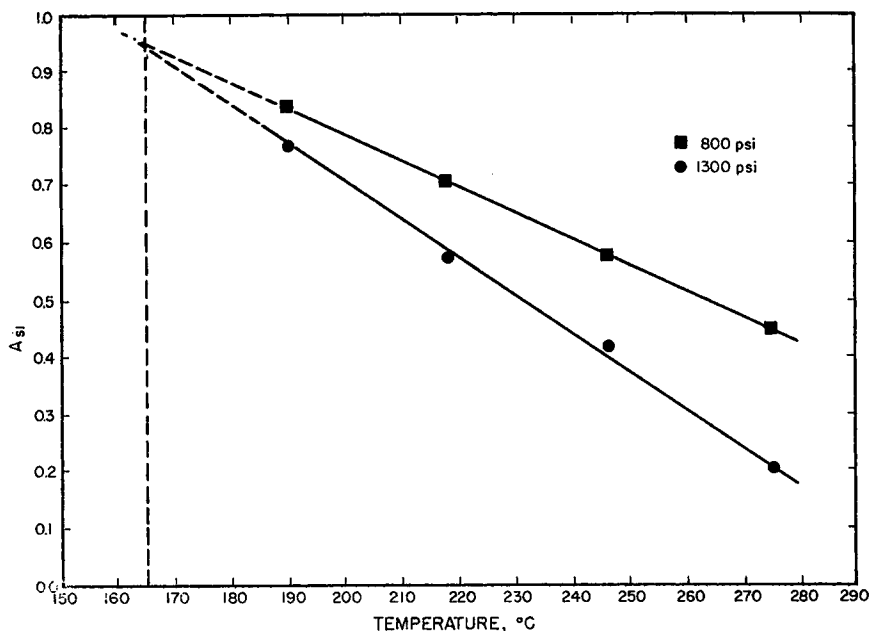


Fig. 5. Variation of the combined area fractions (A_{SI}) of skin and shear zones in the homopolymer with melt temperature and pressure. Note that the data predict the attainment of a completely oriented structure by molding at the melting point ($\approx 165^\circ\text{C}$).

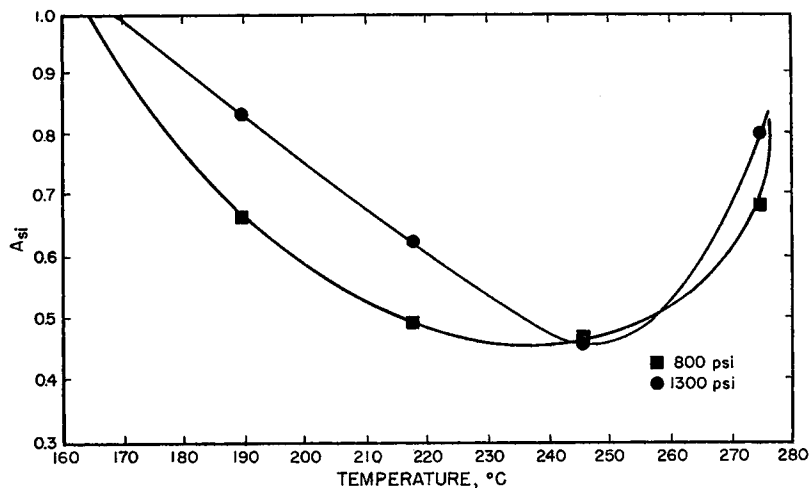


Fig. 6. Variation of A_{SI} for the copolymer as discussed in the preceding figure. Not only is this mode of variation more complex than shown for the homopolymer, but the effect of injection pressure is reversed.

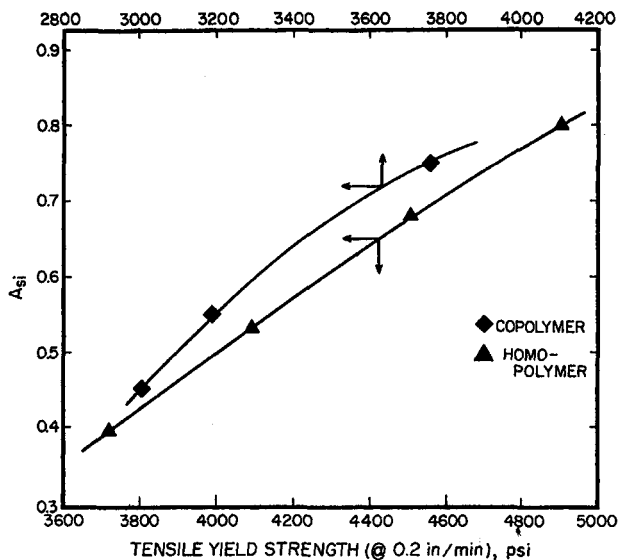


Fig. 7. Yield strength as a function of A_{SI} . Data are averaged values of A_{SI} and yield strength for tensile bars molded at 800 and 1300 psi.

to variations in melt temperature than is the homopolymer. Moreover, the injection pressure affects the area fraction of the shear zone much more in the case of the copolymer. Figure 5 shows that combining the area fractions of the skin and shear zones as A_{SI} for the homopolymer leads to a linear variation of the oriented portion of the specimens with temperature. In addition, the pressure effect stands out more clearly than suggested in Figure 4.

Applying the same treatment of data for the copolymer, as shown in Figure 6, also reveals the effect of pressure more clearly, but it complicates the effect of melt temperature. Owing to what may be a poorly understood rheological melt transition,¹⁵ the flow behavior of the copolymer changes abruptly in the temperature interval between 233° and 275°C to give very large values of A_I . The data also show another noteworthy difference in the behavior of the two polymers; namely, where the lower injection pressure gives the larger A_{SI} for the homopolymer, the opposite is observed for the copolymer. Extrapolating the data in Figures 5 and 6 to lower melt temperature leads to intersection of the curves at $A_{SI} \approx 1$, i.e., an oriented structure throughout the tensile bars. The temperature at which intersection occurs is about 165°C, the practical melting point of the homo- and copolymer. In other words, these results suggest that molding tensile bars at or close to the melting point would lead to the crystallization of a highly oriented film-like morphology throughout the specimen.

In examining the physical test data for the variously molded specimens, A_{SI} was found to vary smoothly with tensile yield strength, notched Izod impact strength, and shrinkage. Figure 7 illustrates the approximately linear increase in tensile yield strength with increasing A_{SI} for both poly-

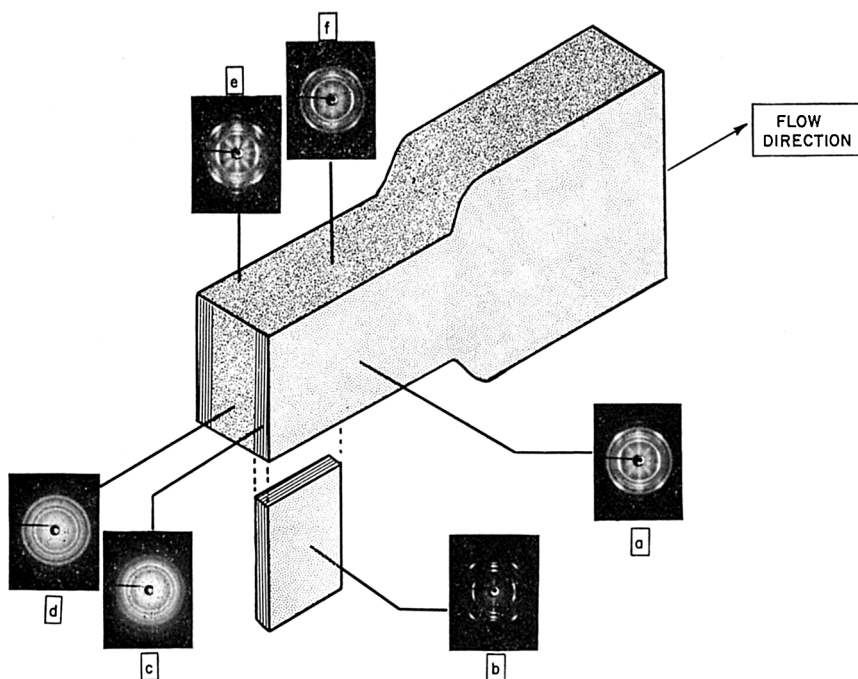


Fig. 8. Distribution of preferred crystallite orientation in a tensile bar molded at 190°C and 1000 psi.

mers. The reason for this correlation is clarified by the x-ray diffraction patterns of adjacent portions of the central region of the tensile specimen. The crystallites in the core are only slightly oriented with the direction of flow, while the skin is not only highly crystalline, but the crystallites are so aligned in the flow direction that the skin appears to have fiber texture.

Differences in crystallite orientation in various regions of a specimen molded at 190°C and 1000 psi are illustrated in Figure 8. The x-ray patterns arranged around the schematic tensile bar were obtained at normal incidence to the directions indicated on the figure. Pattern (b) shows what appears to be complete fiber orientation in a section of skin that was sliced from the tensile bar for this exposure. Pattern (c), of the same region but obtained parallel to the flow direction, indicates that, rather than pure uniaxial orientation the skin contains biaxially oriented crystallites. This interpretation is consistent with work done on biaxially oriented polypropylene film by Uejo and Hoshino.¹⁶ In pattern (f), one sees that the crystallites in the core possess some degree of preferred orientation. Patterns (a) and (c) are composites that result from superposition of the regions that gives the degree of orientation indicated by patterns (b) and (f). The crystallites in the core are randomly oriented about the flow axis as illustrated in pattern (d).

Even though a limited number of tensile bars was studied using x-ray diffraction, one sees qualitative differences in orientation in specimens

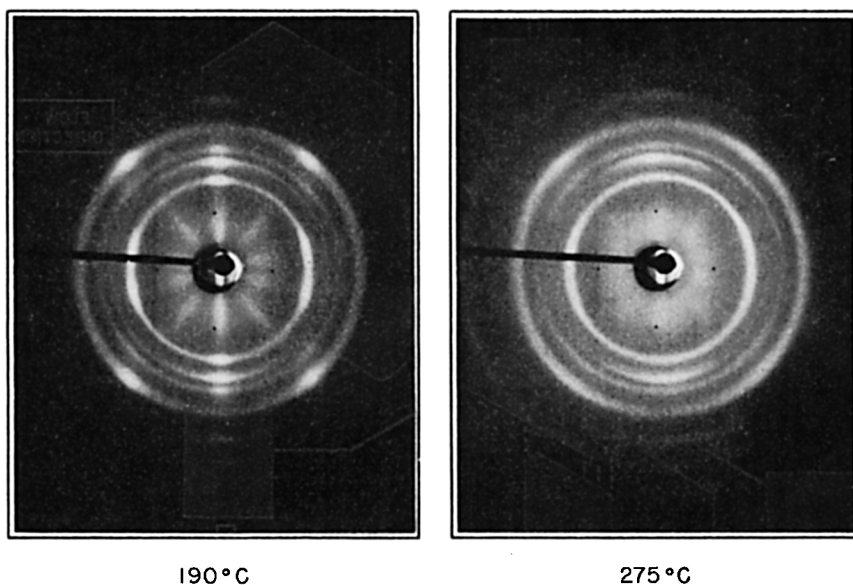


Fig. 9. X-Ray diffraction patterns illustrating the higher average degree of preferred crystallite orientation in tensile bars molded at lower temperatures. Transmission photographs obtained at normal incidence to the three morphological zones.

molded at different temperatures. Figure 9 demonstrates that the overall degree of preferred crystallite orientation in the bar molded from the homopolymer melt at 190°C is considerably higher than that in the bar molded from the melt at 275°C. The observation of fiber-like orientation in the nonspherulitic skin combined with the microscopical observation of the row-nucleated shear zone and the randomly nucleated and slightly oriented core suggests that an injection-molded tensile bar, or any other injection molding for that matter, should be considered as a composite material having a laminate structure. Since it is known that Young's modulus increases with orientation (along the tensile axis), it can be expected that the tensile yield strength measured along the flow axis should increase with increasing A_{SI} .

Figure 10 shows how shrinkage varies with A_{SI} at 800 and 1300 psi for the homopolymer. These data are consistent with the x-ray diffraction results discussed above, and the generally accepted macroscopic observations of others, that shrinkage increases with increasing molecular and crystalline orientation.^{7,9,16}

The variation in notched Izod impact strength with A_{SI} for the homopolymer is shown in Figure 11. The increased impact strength with increasing fraction of oriented crystallites appears reasonable from the standpoint that the skin is basically a film structure having a biaxial component of orientation. Owing to the complex nature of the Izod impact test, it is difficult at this point to judge whether the apparent minima in impact strength at intermediate values of A_{SI} are real or experimental artifacts.

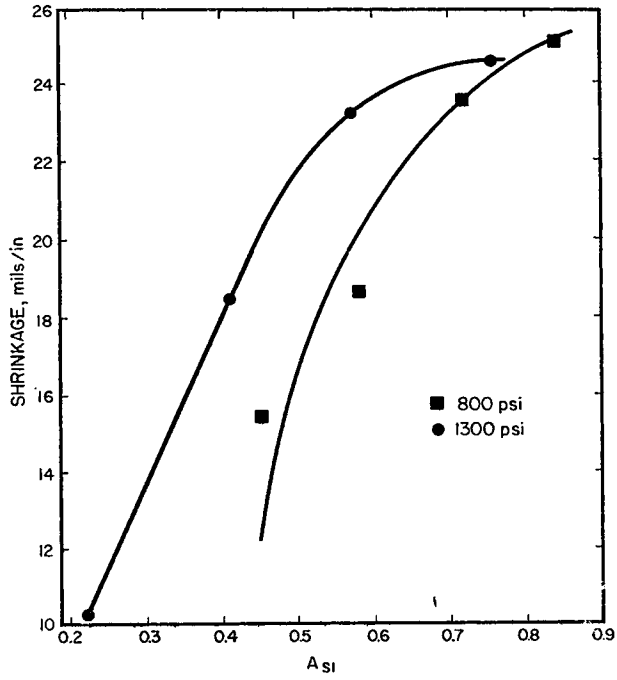


Fig. 10. Shrinkage of homopolymer tensile bars as a function of A_{SI} .

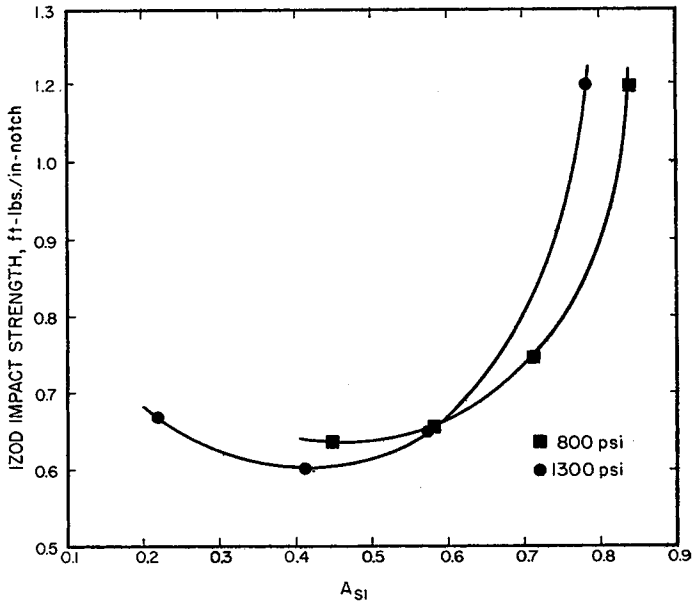


Fig. 11. Variation of homopolymer impact strength with A_{SI} .

CONCLUSIONS

This study has shown that polypropylene melt temperature and the injection pressure in injection molding exert profound influences on morphology. Furthermore, molecular properties such as MW, MWD, and degree of isotacticity remaining constant, preferred crystallite orientation is the principal parameter governing tensile strength, impact strength, and shrinkage. It is expected that other properties such as shear and flexural moduli, hardness, and chemical resistance to oxidizing agents and solvents are also related to the morphology and to the kind and degree of preferred orientation in the skin in polypropylene injection moldings. Although the structure-property correlations presented in this paper are limited in scope, it is evident that such correlations can be found in relatively large, bulk-crystallized specimens just as such correlations have been made by Samuels for polypropylene films and fibers.¹⁷ Two logical implications of this work are (1) that one should know the morphologic state of the polymer to assure that mechanical test data are meaningful and (2) that a detailed knowledge of the structure may permit fabrication of injection-molded articles having tailored mechanical properties.

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