

Processing–Mechanical Property Relationships in Injection Moldings of Polybutylene

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Synopsis

Two unfilled nonpigmented extrusion grades of polybutylene have been injection-molded into a tensile bar mold under a wide range of barrel and mold temperatures. The overall structure of the moldings has been determined and correlated with processing conditions. The short term tensile mechanical properties of the moldings have been ascertained and correlated with molding structure. For low mold temperatures, the Young's modulus and tensile strength of injection moldings of polybutylene are controlled by the extent of and structure within the highly oriented skin. Low barrel temperatures can give rise to highly crystalline thick skins that treble the Young's modulus and fracture stress, when compared to high barrel temperature moldings. Increasing the mold temperature introduces a brittle response in polybutylene injection moldings. Modulus is controlled, at the high mold temperatures, by the skin thickness and by the crystallinity of the material comprising the core of the molding.

INTRODUCTION

The injection molding of semicrystalline thermoplastics induces complicated rheological and thermal histories that lead to the development of complex morphologies and textures, as has been shown in studies on polyethylene,^{1,2} polypropylene,^{3,4} and polyoxymethylene.^{5,6} In these materials the structure of the moldings was layered, and three morphologically distinct regions were observed: a highly oriented crystalline surface layer, an equiaxed (crystallographically) spherulitic core, and a layer between these with a morphology intermediate between that of the core and the highly oriented skin. The mechanical properties of each layer can differ widely,⁷ from the soft ductile to the stiff brittle response, so that the mechanical properties of the overall molding depend on the relative abundance of the various structures within the molding.^{6,8}

Polybutylene (PB), a semicrystalline thermoplastic, was successfully polymerized from butene-1 as early as 1954.⁹ PB is polymorphic, with four observed crystalline modifications, of which two, labeled I and II, are commonly encountered in melt-processed material. Attention initially concentrated on this polymorphism, with little work being undertaken on the structure and properties of the processed material despite the outstanding environmental stress-cracking resistance, impact, and creep properties of PB. Despite this lack of published information in the academic literature, PB is now routinely extruded into film and pipe¹⁰ and injection-molded into, among other artifacts, fittings for pipeline

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systems operating at elevated (82°C) temperatures.^{11,12} However, it is known that preferred orientation can markedly change some of the properties of PB,¹³ and injection molding, as noted above, introduces significant preferred crystalline and macromolecular orientation. It is therefore pertinent to examine the mechanical behavior of PB injection moldings to identify the influence of the preferred orientation on properties.

EXPERIMENTAL

Materials

Isotactic PB is a linear semicrystalline polyolefin which has two common crystallographic modifications, I and II. Form I (PB-I) is stable at room temperature and has a hexagonal unit cell with $a = b = 17.7 \text{ \AA}$ and $c = 6.5 \text{ \AA}$.¹⁴ Form II (PB-II), which has a tetragonal unit cell with $a = b = 14.9 \text{ \AA}$ and $c = 20.7 \text{ \AA}$,¹⁵ forms first when a nonpressurized nonoriented melt cools. At temperatures below 80°C, PB-II transforms to PB-I,^{16,17} with the rate of transformation depending on temperature, pressure, and preferred chain axis orientation. In the absence of stress, the PB-II to PB-I transformation is essentially complete in about 2 weeks at room temperature.^{18,19}

Two grades of PB were injection molded, both supplied by Shell International Chemical Co., Ltd., and labeled 0100 and 0200. Both grades were unfilled, nonpigmented, and with low melt indices (0.4 and 1.8 g/10 min for the 0100 and 0200 grades, respectively). These grades are similar to those used in pipe and pipe fitting applications. The density of material compression-molded from these grades is given as 915 kg·m⁻³.

Sample Preparation—Compression Moulding

The main objective of this work was to investigate the properties of injection moldings. However, since this introduces significant preferred orientation, and a reference unoriented state is required for comparison, samples of both grades were compression-molded into 3 mm thick plaques. These were molded at 180°C, a temperature at which, for reasonable heating times, no significant changes in melt index occurred. Samples were held at this temperature for 5 min and then cooled at two rates, a slow cool, where the samples cooled in about 2 h (mean rate of cooling of 1.5°C/min), and fast cooling (5 min, 30°C/min), effected by circulating cold water through the heavy metal platens of the molder.

Sample Preparation—Injection Molding

The two grades of PB were injection-molded on a microprocessor controlled Sandretto Screw Injection Molder (Model 6 GV/50), into a 3 mm thick, 57 mm gauge length tensile bar mold, which conformed in dimensions to ASTM D 638 Type I. The recommended barrel and mold temperatures for PB are 180–200°C and 15–30°C, respectively.¹⁹ In this work a wider range of conditions were utilized. Specifically, (a) barrel temperature was extended from 180°C to 240°C for the 0100 grade and from 160°C to 240°C for the 0200 grade, and (b) mold

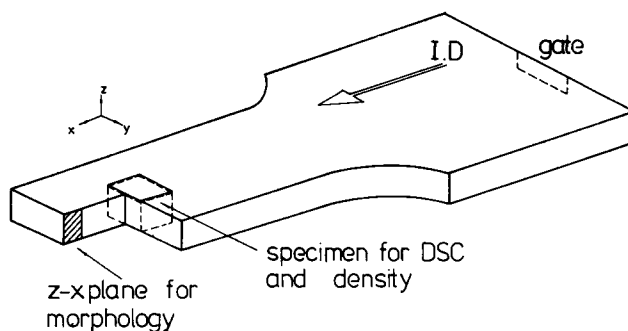


Fig. 1. Schematic presentation of the positions from within the molded tensile bars, from which samples were taken for morphology study, DSC analysis, and density measurement.

temperatures employed ranged from 20°C to 70°C for the 0100 grade and from 20°C to 55°C for the 0200 grade. The injection and packing pressure were identical and equal to 30% of the maximum pressure at the front of the screw, which is given as 1310 bar for the 40-mm screw. For all moldings the total cycle time was 50 s, of which 30 were for cooling and 7 for filling and packing.

In the transformation from PB-II to PB-I a measurable change in volume occurs.¹⁹ Since pressure and preferred orientation can accelerate this transformation, molding conditions may influence post-molding shrinkage. Therefore, the length and thickness of moldings were determined, using a screw micrometer, immediately after removal from the cavity, and 2 months later.

Optical Microscopy, Density Determination, and Differential Scanning Calorimetry

Thin ($\approx 5 \mu\text{m}$) sections for optical microscopy were microtomed off the z - x plane in the center of compression and injection moldings (see Fig. 1) using a Leitz sledge microtome. The sections were mounted in lens oil and contained between a glass slide and a cover slip. Optical photomicrographs were obtained from the thin sections by use of a Reichert Zetopan microscope using crossed polars.

Density was determined in a calibrated alcohol-water density gradient column, according to BS3715, at 25°C. The density of the total thickness of the compression and injection-molded material was determined. In addition, since the structure of the injection moldings was layered, rectangular samples were obtained from within the tensile bar moldings, at the position indicated in Figure 1, and at various depths. Thin ($\approx 30 \mu\text{m}$) sections parallel to the x - y plane were microtomed for analysis. Due to the elasticity of PB, the following formula was used to estimate the thickness (t) of each cut section,

$$t = W/A\rho$$

where A and W are respectively the measured area (x - y plane) and weight of the microtomed sample, and ρ is the density, taken as $920 \text{ kg}\cdot\text{m}^{-3}$ for the highly oriented skin.

The rectangular samples prepared for density determination were then used to obtain values for the melting temperature. Differential scanning calorimetry

TABLE I
Physical Properties of Compression-Molded Plaques of PB

	PB0200 grade Quickly cooled	PB0100 grade	
		Quickly cooled	Slowly cooled
Density ($\text{kg}\cdot\text{m}^{-3}$)	910	912	920
Yield strength (MPa)	15	17	15
Tensile modulus (GPa)	0.18	0.23	—
Ultimate tensile strength (MPa)	32	35	16
Elongation at break (%)	360	320	50
Melting point ($^{\circ}\text{C}$)	119	121	128
Diameter of spherulites (μm)	40	70	500

thermograms were obtained using a Perkin-Elmer DSC-2 calibrated with Indium metal. The heating rate was $5^{\circ}\text{C}/\text{min}$, the scanning range 5 mcal/s and the sample weight about 2 mg .

Tensile Tests

The stress-strain behavior of the injection-molded samples was determined as molded at room temperature using an Instron testing machine. The samples were aged for a minimum of 1 month before testing to ensure that the PB-II to PB-I transformation was complete. The crosshead speed employed was 5 mm/min to give an initial rate of strain of $1.5 \times 10^{-3} \text{ s}^{-1}$. Young's modulus was calculated from the initial slope of the load-extension curve.

Tensile samples were compression-molded directly with sample dimensions conforming to ASTM D 638 Type IV, and the samples were tested, after suitable ageing, at room temperature. The crosshead speed employed was 50 mm/min to give an initial rate of strain of 2.5×10^{-2} .

EXPERIMENTAL RESULTS

Compression-Molded Samples

Table I identifies the density, melting temperature, spherulite size, and mechanical properties of compression-molded samples of PB 0100 cooled at the two rates and PB 0200 cooled quickly. The cooling rate clearly influenced the properties in a manner similar to that observed by Weynant et al.²⁰ Slowly cooled PB had large spherulitic diameters and behaved in an essentially brittle fashion when compared to the quickly cooled material, which was ductile and possessed of small spherulites. The properties for the fast cooled compression molded PB recorded in Table I are similar to those given by the material manufacturers.

The Overall Structure of Injection Moldings

Figure 2 presents low magnification optical photographs of z - x cross section microtomed samples from three different PB 0100 moldings processed under the following conditions: 180-70, 180-20, and 240-20 (the first number refers

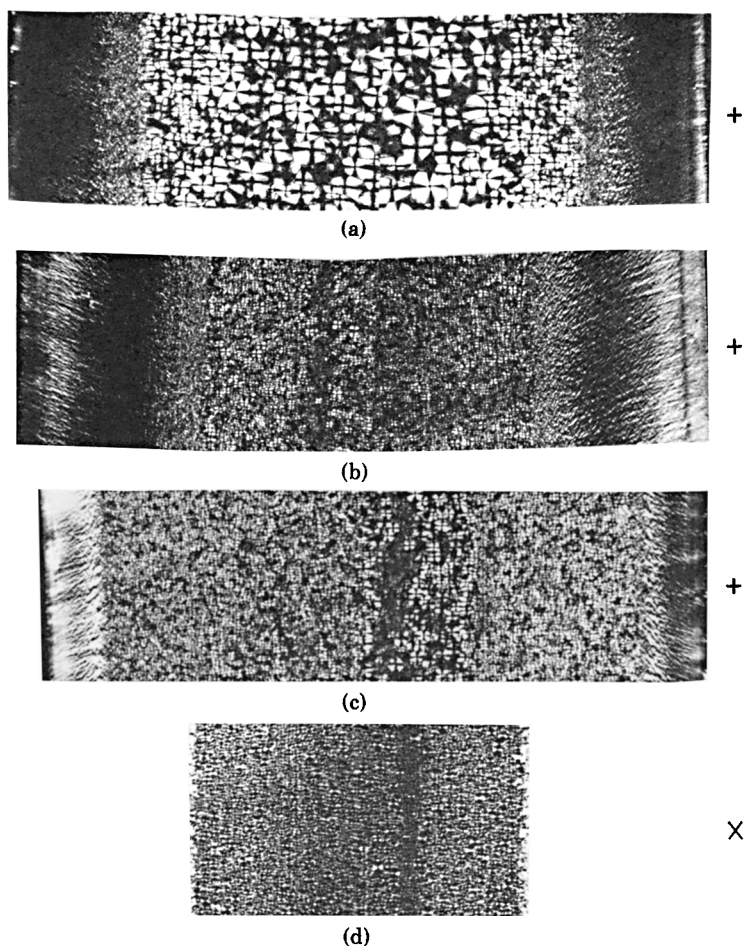


Fig. 2. Low magnification polarized optical micrographs of $z-x$ cross section microtomed from three different PB0100 moldings processed under different conditions (a) 180-70, (b) and (d) 180-20, and (c) 240-20 (the first number refers to barrel temperature, the second one to mold temperature). (+) Crossed polarizers parallel and perpendicular to flow direction; (X) crossed polarizers at 45° to flow direction.

to the barrel temperature, the second to the mold temperature). From Figure 2 it can be seen that:

(a) The morphology of the molding is symmetric about the center line of the molding, and similar in distribution for all three molding conditions.

(b) All injection moldings are composed of an essentially spherulitic core and a highly oriented and birefringent skin, the thickness of which can be measured when the polarizer and analyzer are rotated to 45° to the flow direction.

(c) When the polarizer and analyzer are at 0° and 90° to the flow direction, the morphology of the skin does not appear uniform.

DSC thermograms and density profiles through the thickness of moldings can be used to examine molding structure further. Figure 3 shows thermograms from selected layers of the 180-20 injection molding produced after the specimens had aged for at least 1 month, so that the possibility of multimelting peaks caused

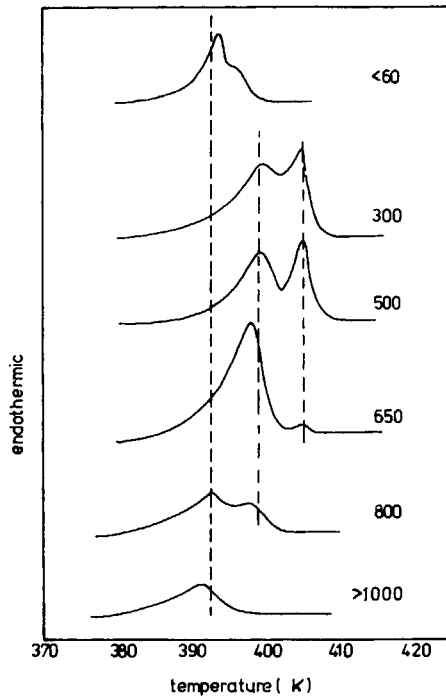


Fig. 3. DSC Thermograms from selected depths of an injection-molded PB0100 (180-20) molding. The number adjacent to the thermogram refers to the depth (μm) of the sample below the top (x - y) plane of the molding.

by polymorphism can be excluded. The spherulitic core material exhibits but a single melting peak, while in the center of the highly oriented skin there were two melting peaks, both of which were above that of the core material. The melting temperatures the various layers exhibit, and their relative abundance, are shown in Figure 4(b) for the 180-20 molding. The corresponding optical micrographs and density profiles are shown in Figures 4(a) and (c), respectively.

Figure 4, which is typical of other PB injection moldings in representing structure distribution, illustrates how the structure of these injection moldings changed through the thickness, and shows the density and material melting temperature of these moldings peaked just below the surface and then dropped and leveled off as the center of the molding was approached. The maxima in density and melting temperature therefore occurred in the highly oriented region of the molding.

Influence of Processing Conditions on Structure

Changes in either the barrel or mold temperature influenced the structure of moldings, as shown by Figure 2. This change in structure can be followed most simply by recording the overall, or average density of the whole molding (Fig. 5). In general, increasing the barrel temperature reduced the overall density of the molding, when the mold temperature was set at 20°C [Fig. 5(a)], while mold temperature increases had the reverse effect, increasing the overall density [Fig. 5(b)].

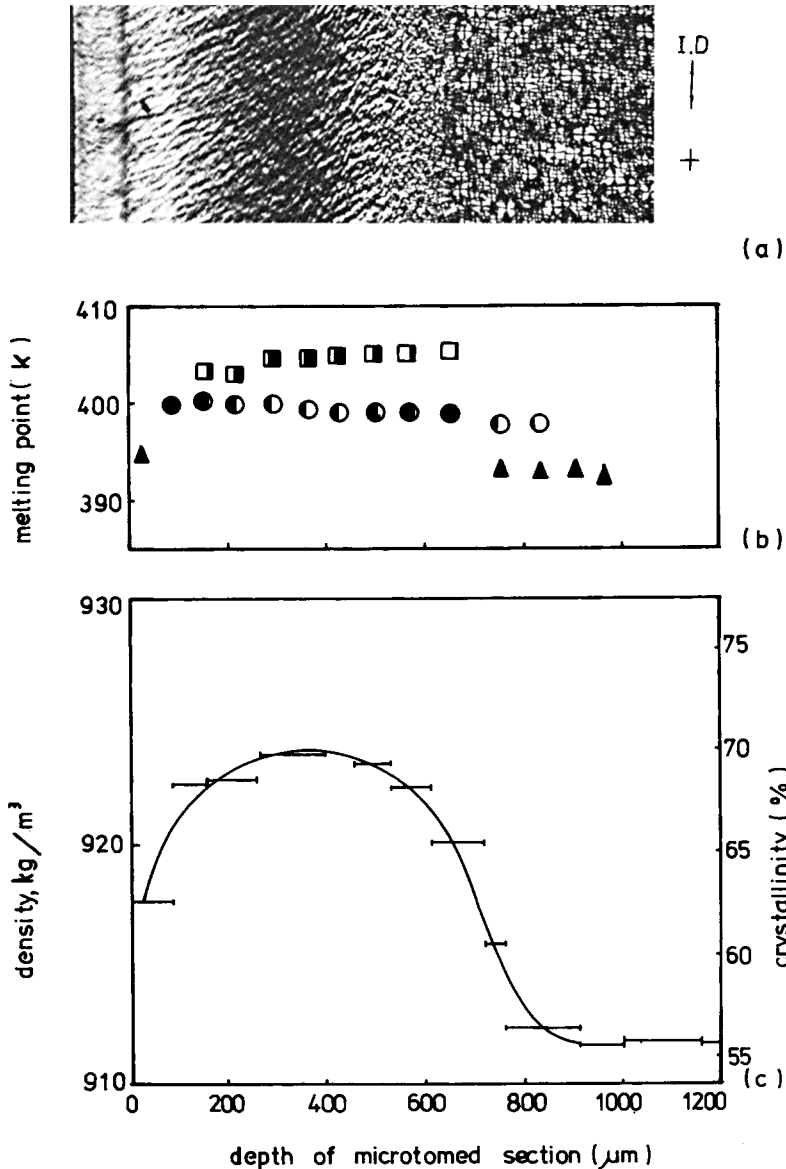


Fig. 4. Optical micrograph of z - x cross section of injection-molded PB0100 (180-20) (a); the corresponding through thickness melting temperatures and density profiles, (b) and (c), respectively. \blacktriangle , \bullet , \blacksquare refer to melting temperature at about 392 K, 399 K, and 405 K, respectively. \blacktriangle , \circ , \blacksquare represent the coexisting of double melting temperatures, and the black parts in them represent the fraction of the area under the melting curve at that temperature.

Figure 2 highlighted changes in structure which occurred as the barrel and mold temperature were varied. Increasing the barrel temperature reduced the extent of the highly oriented skin [Fig. 6(a)] and changed the through-the-thickness density profile. The density of material in the highly oriented skin decreased with increasing barrel temperature, while the density of the core material was relatively insensitive to barrel temperatures changes [Fig. 6(b)]. The average spherulite size in the core of the molding was relatively insensitive

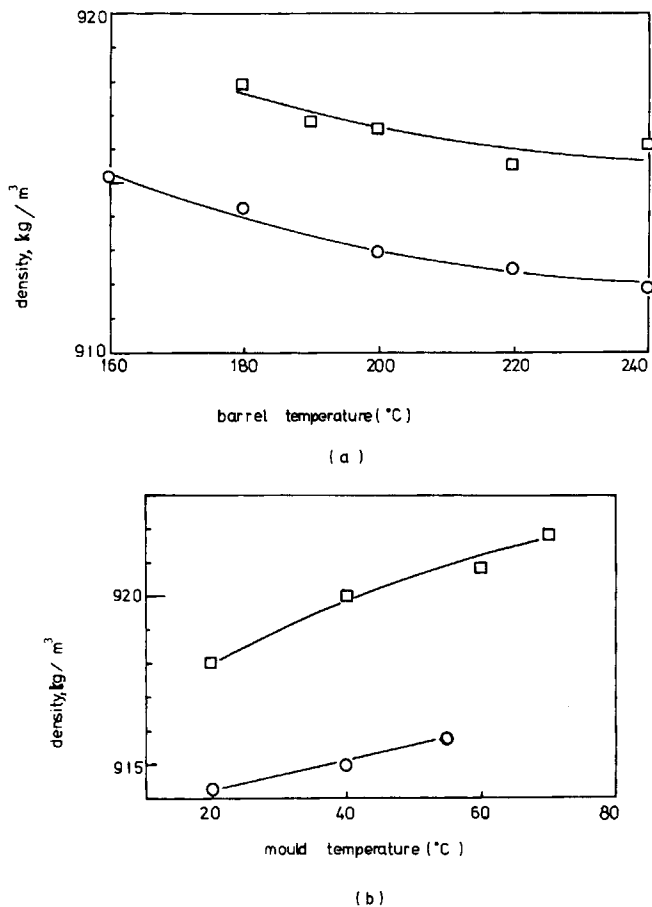


Fig. 5. Influence of processing conditions on average density of injection-molded bars: (□) PB0100; (○) PB0200. (a) The influence of barrel temperature at a constant mold temperature of 20°C; (b) the influence of mold temperature for a constant barrel temperature of 180°C.

to changes in the barrel temperature, remaining about 20–50 μm for both grades.

Mold temperature increases reduced skin thickness [Fig. 7(a)] but increased, markedly, the density of the polymer in the core of the molding [Fig. 7(b)]. Concomitant with the increase in core density with increasing mold temperature was the increase in spherulite size, from 20 to more than 150 μm for PB 0200 grade. Spherulite size changes with mold temperature were similar for the 0100 grade material.

It is appropriate to consider now post-molding shrinkage, which for PB is principally associated with the PB-II to PB-I transformation and subsequent crystallization.¹⁹ Figure 8 shows post-molding shrinkage correlated with the extent of the highly oriented skin. Data for both grades is included in Figure 8. Increasing skin thickness clearly reduced the shrinkage after molding.

Mechanical Properties of Moldings

The stress-strain behavior of the fast cooled compressed molded material differed markedly from the injection-molded tensile bars, the difference being

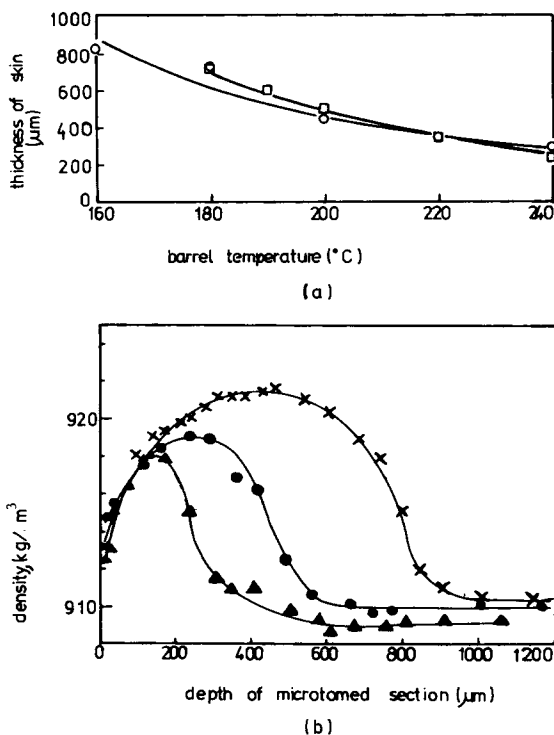


Fig. 6. Influence of barrel temperature on: (a) the extent of highly oriented skin of injection-molded bars [(\square) PB0100; (\circ) PB0200]; (b) the density profiles through thickness [(\times) PB0200 (160-20); (\bullet) PB0200 (200-20); (\blacktriangle) PB0200 (240-20)].

particularly marked for the low barrel temperature moldings (Fig. 9). In general, the injection-molded material failed at lower strains, yet was stiffer and stronger. Barrel temperature exerted an influence on the mechanical properties of the injection moldings (Fig. 10). For instance, for the 0200 grade, decreasing the barrel temperature from 240 $^{\circ}\text{C}$ to 160 $^{\circ}\text{C}$ resulted in a factor of three increase in both modulus and fracture stress.

The major influence of mold temperature was on the site of fracture, which changed from the narrow section of the molding (20 $^{\circ}\text{C}$ mold temperature) to the curved or gripped section (40 $^{\circ}\text{C}$ and above). This increased tendency to early brittle fracture was observed in both grades, and excluded any useful measurement of yield or fracture stress, so that only modulus changes were recorded, and for both grades these stayed fairly constant (Table II).

The site and cause of fracture of the injection-molded PB samples was investigated. The initiation of fracture in the gauge length of moldings was predominately confined to the highly oriented region (Fig. 11). The underlying skin-core structure of moldings can also be discerned in Figure 11. In addition, evidence of the fibrous nature of the material in the highly oriented skin could be clearly observed (Fig. 12), and these fibrous regions corresponded to the regions of high density and melting point. Since the melting point of a polymer indicates, to some extent, the underlying structure,²¹ and a high melting temperature is characteristic of a fibrous material,^{2,22} the fracture surface morphology observed was expected.

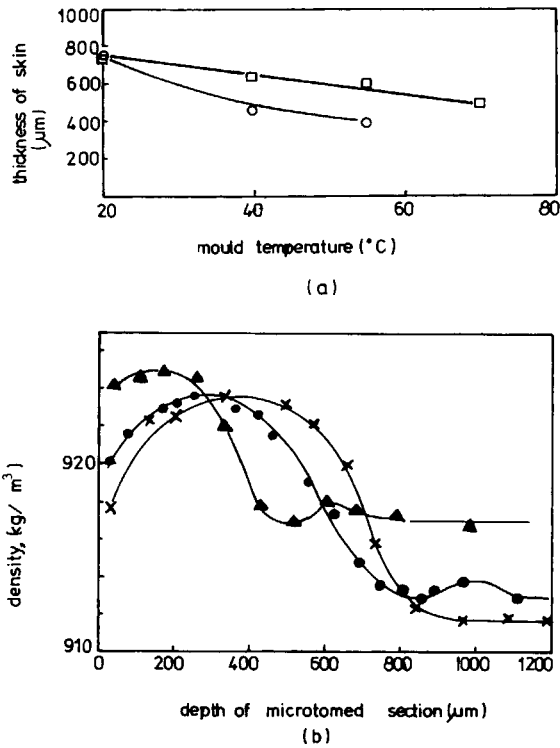


Fig. 7. Influence of mold temperature on: (a) the extent of highly oriented skin of injection molded bars [(□) PB0100; (○) PB0200]; (b) the density profiles through the thickness [(×) PB0100 (180-20), (●) PB0100 (180-40); (▲) PB0100 (180-70)].

At the site of the initiation of fracture an included particle was sometimes observed (see Fig. 13), and the majority of these particles, when analyzed, were found to be rich in iron. An analysis of the cause of failure of polyethylene pipes by one of us²³ has revealed discreet particles initiating fracture, some of which were iron-rich. The result here for PB is thus consistent with this other investigation.

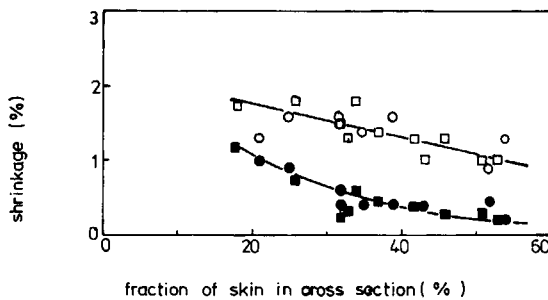


Fig. 8. The relationship between post molded shrinkage and fraction of skin in z-y cross section. The upper curve is for longitudinal shrinkage, the lower for width (y direction): (□, ■) PB0100; (○, ●) PB0200.

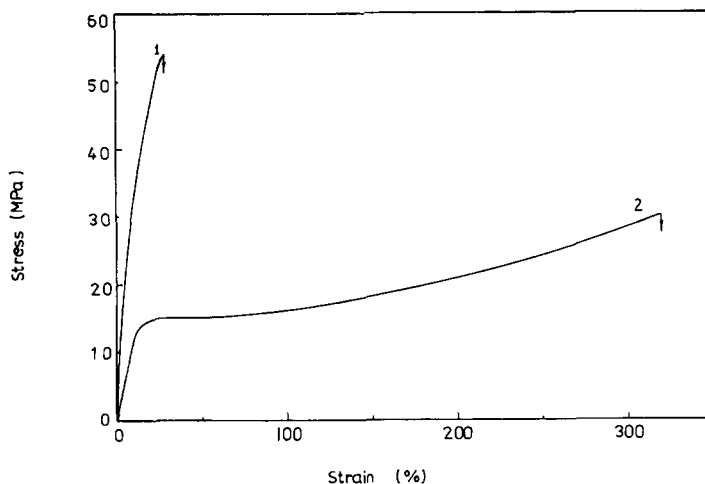


Fig. 9. A comparison of stress-strain behaviors of: (1) low barrel temperature injection-molded PB0200; (2) quickly cooled compression-molded PB0200.

DISCUSSION

Structure Distribution in Injection Moldings

The early studies of Spencer and Gilmore²⁴ on the process of injection molding clearly differentiated between melt flow behind the advancing front and the "forcing out" of melt onto the cold mold wall at the front. Tadmor²⁵ proposed

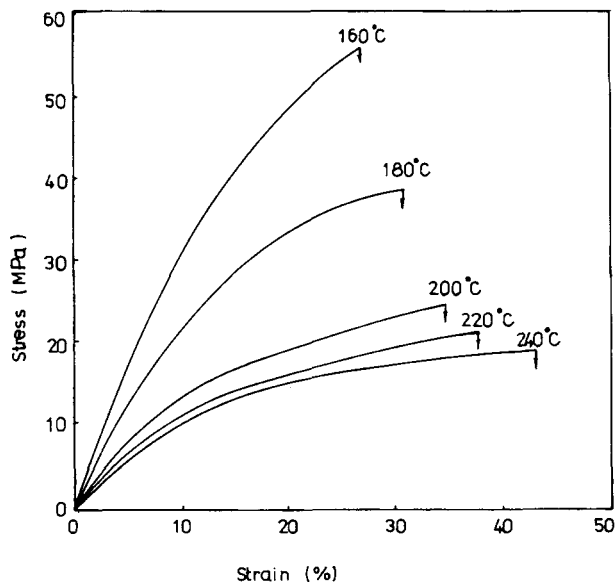


Fig. 10. Influence of barrel temperature on the stress-strain behavior of injection-molded PB0200, with mold temperature kept constant (20°C).

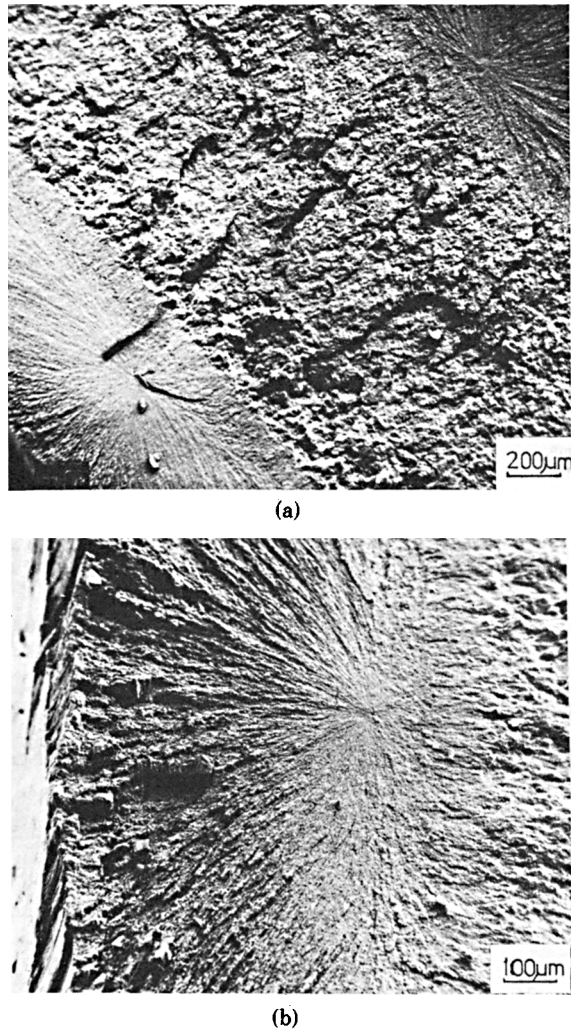


Fig. 11. (a) and (b) Scanning electron micrographs of the fracture surfaces of PB0100 180-20 moldings, showing the site for the initiation fracture.

a model that clearly distinguished between melt flow at the front and the flow of melt behind the front and between solidified layers. In the model of Tadmor the flow of the melt at the front is extensional in character, a mode of polymer flow capable of producing significant molecular uncoiling and extension²⁶ and crystallization in polyethylene melts at temperatures approaching the equilibrium melting temperature.²² This “molecularly extended” melt is shock cooled on contacting the cold mold wall to retain the orientation induced by the flow. In the core of the moldings the flow has a transverse velocity gradient and experiences a lower rate of cooling, allowing the relaxation of any shear flow induced molecular orientation.

The Tadmor model has been applied by Bowman⁶ to explain the texture and morphology present in injection moldings of a polyoxymethylene copolymer.

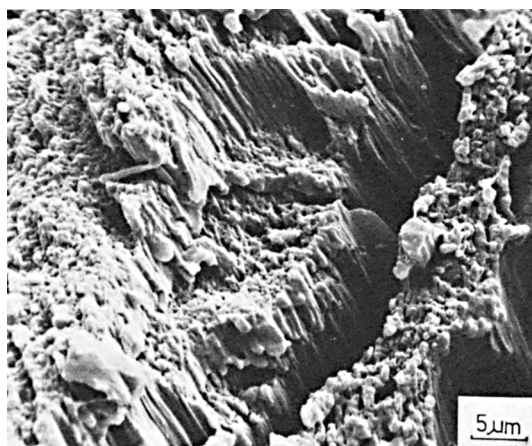


Fig. 12. The appearance of the fracture surface in the highly oriented area of a tensile fractured PB0100 injection molding (180-20).

It may similarly be applied to other injection moldings of semicrystalline polymers exhibiting an oriented skin-equiaxed core type of morphology.^{3-5,7}

Another approach to understanding structure in injection moldings is due to Schmidt,²⁷ who examined the distribution of coded polymer after it had been essentially extruded into a mold at rates at least between $\frac{1}{10}$ and $\frac{1}{100}$ of those typical of commercial injection molding. In an early publication^{27a} Schmidt recognized the existence of both extensional and shear flow in injection molding, but did not so clearly designate or accept extensional flow as the cause of the molecular orientation in the skin. Using the Schmidt model structure variations within the skin are more readily explained, but the low rates of extrusion into the cavity in the initial experimental work, and on which all analysis is based, induces a sense of caution in the application of this model for the explanation of structure in these PB moldings where mold filling was complete in a fraction of a second.

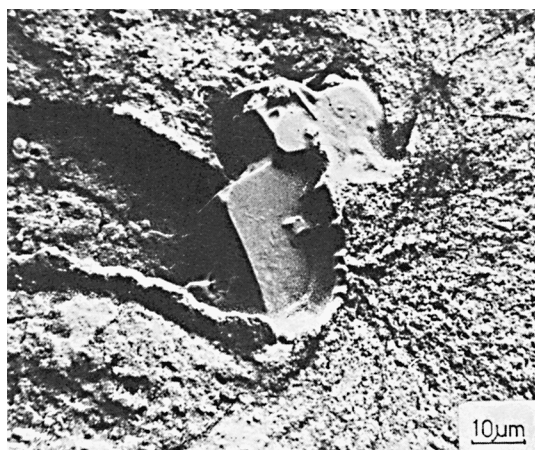


Fig. 13. A particle at the fracture initiation site in a PB0100 (240-20) injection molding.

For these PB injection moldings, there is clear evidence of a distinct skin core morphology (Fig. 4) and the presence of a high melting point phase in the skin (Figs. 3 and 4). It is proposed that the melt that constituted the skin of these moldings was uncoiled and extended by the flow process to give rise to the high melting point phase²² and this led to high crystallinities.²⁸ The peak in the melting temperature (and crystallinity) occurred not at the surface of the molding, as the Tadmor model would suggest, but in the middle of the skin. This may suggest that the Tadmor model is still applicable but that the material at the melt front itself cooled as it moved down the mold, the lower melt temperature inhibiting the process of molecular uncoiling at the immediate melt front.

Clearly, only part of the material in the skin was highly oriented (see the multiple melting peaks of Fig. 3). The authors have examined the structure within the skin in some detail and have observed a fibrous component, which, on heating, using a hot stage in a polarized light microscope, was observed to be the last phase to melt. The authors are preparing this work for publication.

Thus, the skin is complex in structure. The high melting point material in the fibrous form, formed from polymer molecularly extended by the extensional flow which both Tadmor²⁵ and Schmidt²⁷ propose to be present. This fibrous component was not present at the very surface of the molding, but in the middle of the skin, this probably being due to the cooling of the melt at the surface of the melt front as it moved in the cavity. The added crystalline fraction, which corresponded to the presence of the high melting point phase (Fig. 4), followed from the crystallization of an oriented PB melt.²⁸

The core of these PB moldings differed from the skin in having lower crystallinities and a single low melting temperature (Figs. 2, 4, 6, and 7). The core material during the filling stage experiences a transverse velocity gradient^{25,27} and is essentially insulated from possible shock cooling effects associated with the cold mold wall by the already stationary molding skin. This mode of flow induced little preferred molecular orientation. This, combined with the low rates of cooling, gave rise to the essentially equiaxed structure present in the core of these moldings; an equiaxed core morphology is a characteristic of most injection moldings²⁻⁷ and predicted by both Schmidt²⁷ and Tadmor.²⁵

Influence of Processing Condition on Structure Distribution

An examination of Figures 5, 6, and 7 leads to the following conclusions:

- (i) increasing the barrel temperature reduced the overall density of moldings,
- (ii) the thickness of the highly oriented skin decreased with increases in either the barrel or the mold temperature,
- (iii) the density of the core of the molding was controlled primarily by the mold temperature,
- (iv) the maximum density observed in the material comprising the skin of moldings was a function of both barrel temperature and molecular weight.

Consider first the influence of barrel temperature on structure distribution. Figure 6(a) highlights the fact that the extent of the highly oriented skin, as measured from the polarized light photomicrographs when the polarizer and analyzer were crossed and oriented at 45° to the injection direction (see Fig. 2), was a function of barrel temperature only. Change of grade, which is equivalent

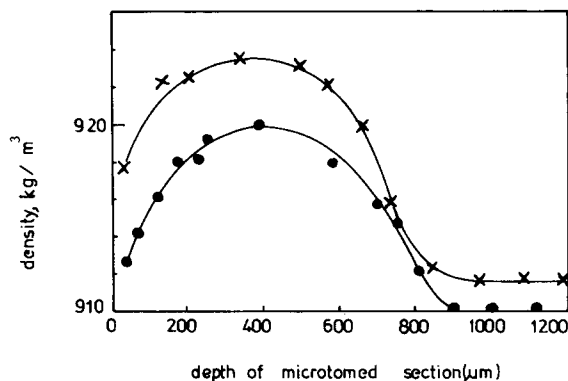


Fig. 14. The influence of polymer grade molecular weight on the shape of the through thickness density profile for the same barrel (180°C) and mold (20°C) temperature.

to a change in molecular weight (\bar{M}_w for 0100 is given 728,000, for 0200 as 573,000), had little influence.

However, when the density of the material comprising the skin of the injection moldings is examined, it can be seen clearly (Fig. 14) that molecular weight had a major influence. Increasing molecular weight increases relaxation times,²⁹ so that preferred orientation introduced by the extensional flow at the melt front^{24,25} was retained for longer periods in the high molecular weight material to allow crystallization and growth from oriented melts. Crystallization of oriented melts is greater than quiescent melts,^{28,30} so that the higher skin density in the lower melt index polymer, for the same barrel temperature, was due to the changes in relaxation times. For these two grades (molecular weights) of PB, the barrel temperature then controlled the volume of oriented material, while molecular weight clearly influenced the "structure" within.

Turning to the influence of mold temperature on structure distribution, it was observed that skin thickness decreased with increasing mold temperature. As the temperature gradient is reduced, so the rate of heat withdrawal decreases, and, consistent with the barrel temperature effect, the thickness of the skin decreased. The density distribution within the molding also changed as mold temperature was increased. First, the peak in the density profile in the skin material moved toward the mold wall, but the maximum density (and therefore crystallinity) remained at approximately the same value. The high density in the skin layer was a result of the flow-induced crystallization, which was clearly influenced little by mold temperature.

The other influence of mold temperature on the shape of the density profile was on the density, and spherulite size, of the core material. Weynant et al.²⁰ have shown that cooling rate has a profound influence on the final crystallinity of PB. The higher density in the core of the moldings at the higher mold temperatures reflects the reduced rate of cooling.

Post-Molding Shrinkage

Figure 8 indicates how post-molding shrinkage changed with structure, when the structural changes were induced by varying only the barrel temperature. It

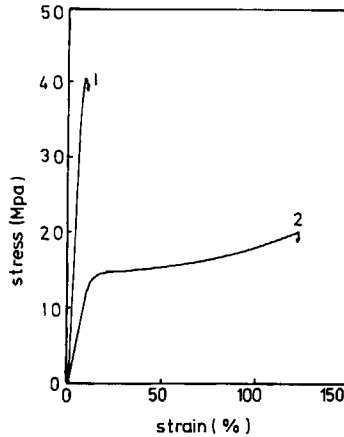


Fig. 15. The stress-strain behavior of tensile samples, machined from (1) the skin, (2) the core, of an injection-molded tensile bar [PB0100 (200-20)].

has been shown that for the same barrel temperature, the two grades of PB gave similar skin thicknesses [Fig. 6(a)] but radically different density profiles (Fig. 14). Since shrinkage correlates well with the extent of the highly oriented skin, it must be assumed that preferred orientation rapidly induces the PB-II to PB-I transformation to reduce post-molding shrinkage. Minimum post-molding shrinkage in PB injection moldings is therefore obtained by molding to induce preferred molecular orientation, that is, using low barrel temperatures. However, the use of these processing conditions to reduce post-molding shrinkage will lead to other changes, in the mechanical response and the level of internal stress. Therefore, a balance between these factors may have to be sought.

Stress-Strain Behavior of Injection Moldings

In this study, the barrel and mold temperatures have been varied, and both exerted a powerful influence on the stress-strain behavior of the moldings. At a fixed mold temperature of 20°C, increasing the barrel temperature reduced the Young's modulus and tensile strength of moldings, while increasing the strain to failure (Fig. 10). Increasing the mold temperature from 20°C to 40°C and above changed the modulus little (Table II), but induced a brittle response from the moldings. The features of the molding structure which controlled these changes in stress-strain behavior were different for those moldings produced at varying barrel temperatures but constant (20°C) mold temperature, from those moldings produced with varying mold temperatures but constant (180°C) barrel temperature. The influence of barrel and mold temperature variations are therefore discussed separately.

The Influence of Barrel Temperature

Consider first the response of moldings produced with the mold temperature constant at 20°C, but with varying barrel temperatures. The stress-strain behavior of these injection moldings differed markedly from the fast cooled com-

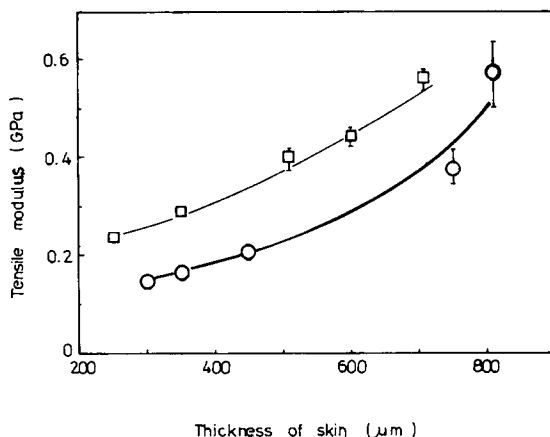


Fig. 16. A plot of tensile modulus as a function of skin thickness. Data for bars processed under different barrel temperature but at a constant mold temperature of 20°C: (\square) PB0100; (\circ) PB0200.

pression-molded tensile bars (Fig. 9). The injection moldings exhibited a "hard elastic response,"³¹⁻³³ while the quickly cooled compression moldings yielded at low stresses and cold drew to large strains. The compression moldings were structurally, through the thickness, homogeneous, while the injection-molded tensile bars were composed of, most simply, a highly oriented high density skin and an equiaxed medium density core. The behavior of these two layers may be expected to be different, so each of the two layers (skin and core) from a PB 0100 200-20 injection molding were examined separately (Fig. 15). As expected, the responses were different, the oriented skin being both considerably stiffer and stronger than the core material, while failing at lower strains. This behaviour accords with previous studies.^{2,7}

If now the response of the skin and core is examined (Fig. 15) and compared with both the response of a whole molding and a quickly cooled compression molding (Fig. 9), it can be seen that the response of the skin was typical of the whole molding, while the core behaved in a manner similar to that of the fast cooled compression-molded bars. Further, the density of the core material in the injection moldings (at all barrel temperatures) was similar to that of the quickly cooled compression moldings, and as will be shown later by extrapolation techniques, the mechanical properties of the core material were also similar to the compression-molded material. Varying the barrel temperature varied the extent and density of the skin material, and this was the reason for the changes in the stress-strain properties of PB injection moldings produced at various barrel temperatures. The skin structure and extent determined the mechanical properties of thin PB injection moldings (3 mm and less) produced at low (20°C) mold temperatures.

If the highly oriented skin determined the properties of the total molding, a relationship between the extent of the skin and the Young's modulus and tensile strength should be present (see Figs. 16 and 17). From these figures it can be seen that:

(a) for a given skin thickness, the 0100 grade polymer gave the stiffer and stronger moldings,

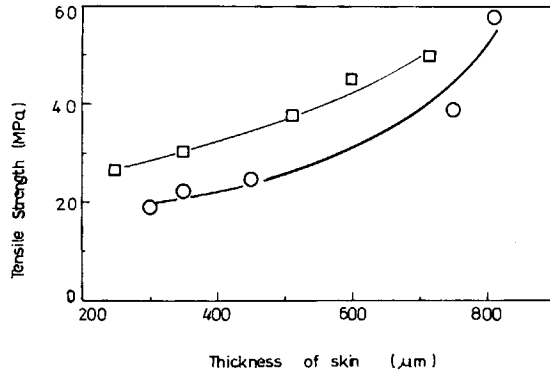


Fig. 17. A plot of tensile strength against skin thickness for injection-molded bars processed under different barrel temperature but at a constant mold temperature (20°C). Symbols as Figure 16.

(b) for a given grade, increasing skin thickness resulted in an increased value for both Young's modulus and yield/fracture stress,

(c) the data in Figure 16, when extrapolated to zero skin thickness, gave values for the Young's modulus of approximately 0.20 and 0.12 GPa for the 0100 and 0200 grades, respectively, values approximately 10% and 30% below those measured on the fast cooled compression-molded bars (see Table I),

(d) the curves for Figure 17, when likewise extrapolated, gave fracture stresses of approximately 18 and 15 MPa for the 0100 and 0200 grades, respectively, values close to the yield stresses of the fast cooled compression-molded tensile bars.

For these PB injection moldings produced with a mold temperature of 20°C, the extent of the oriented skin depended only on barrel temperature [Fig. 6(a)], and this skin thickness decreased as the barrel temperature was raised. However, skin thickness did not uniquely determine molding modulus and tensile strength (Figs. 16 and 17); the low melt index grade gave the stiffer and stronger moldings. This can be accounted for, in part, by the higher density of the skin of the moldings processed from the lower melt index grade material (see Fig. 14). The stress-strain properties of these PB injection moldings, parallel to the flow direction, then depended on both the extent of the highly oriented skin and the structure within that skin, which is in part reflected in the density of the material. The structure of the skin material can also vary in the fraction of fibrous material present and in other ways, not examined here. The density of the skin is one manifestation of the variations in skin structure between grades.

If the skin structure and extent determines the properties of the injection moldings processed at low (20°C) mold temperatures, it is reasonable to examine if a rule of mixtures approach may be applied. The Young's modulus of the molding (E_{tm}) is then given by

$$E_{tm} = E_s V_s + E_c (1 - V_s)$$

where V_s is the volume fraction of the highly oriented skin, E_c is the modulus of the core material, the value of which for each grade is obtained from the compression molded material [a reasonable value, see point (c) above], and E_s the modulus of the skin is to be calculated. If the rule of mixtures holds E_s

TABLE II
Influence of Mold Temperature on Modulus of Injection
Moldings^a

Mold temp (°C)	Modulus (GPa)	
	PBO200	PBO100
20	0.38	0.57
40	0.34	0.56
55	0.32	—
60	—	0.60
70	—	0.60

^a The barrel temperature was held constant at 180°C for both grades.

should be constant. Inserting values for V_s and E_{tm} from Figures 6(a) and 10, respectively, and using the value of E_c from Table I, the values for E_s were found to vary from 0.26 to 0.94 GPa for 0200 grade (for instance) as the barrel temperature was lowered from 240°C to 160°C. This variation implies that the rule of mixtures cannot be applied to these injection moldings, the reason for the differences in E_s being due to the changes in the structure of the skin (see Fig. 14). Similarly, for tensile strength, the rule of mixtures was not found to be applicable.

Finally, it should be noted that the properties of PB compression and injection moldings were very sensitive to processing conditions and that the increases in Young's modulus and tensile (fracture) stress, over the values for compression-molded material [see Table I and (20)] were dramatic. An increase in stress at yield/fracture from 15 to 55 MPa for the 0200 grade is a substantial change. Concomitant with the changes in stiffness and strength was the reduction in failure strain, from 300+% for some compression moldings to a figure of approximately 25% for some injection moldings. While this is a major reduction, a failure strain of 25% for other plastics materials (such as ABS or acetal) would not be considered exceptionally low. The figures for these PB injection moldings are then typical of a host of other polymers which are themselves not classed as brittle plastics.

The Influence of Mold Temperature

For PB injection moldings processed under a wide range of barrel temperatures but with a constant mold temperature of 20°C, the stress-strain behavior depended on the extent of and the structure within the highly oriented skin. Mold temperature increases also produced changes in the skin thickness [Fig. 7(a)], the extent of the skin decreasing in a manner similar to that observed when the barrel temperature was increased [see Fig. 6(a)]. However, when the Young's modulus of the moldings was determined and plotted as a function of mold temperature, it was observed that the stiffness was dependent upon the grade of the plastic, but relatively independent of the skin thickness (Fig. 18). An examination of density profiles through the thickness of these PB injection moldings produced at different mold temperatures revealed that increases in mold temperature changed the total density profile, and in particular increased the density of the material within the core of the moldings [Fig. 7(b)]. The rel-

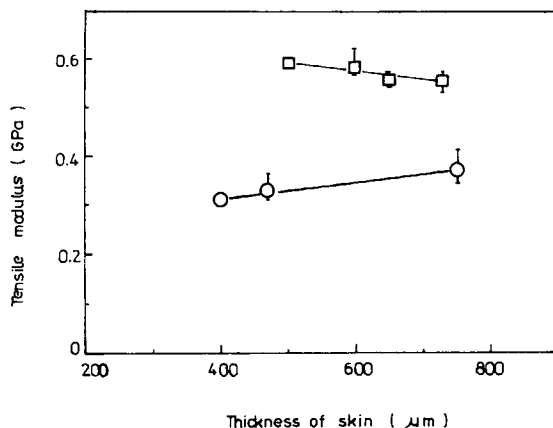


Fig. 18. A plot of tensile modulus against skin thickness of injection molded bars processed under different mold temperature but constant barrel temperature (180°C). Symbols as Figure 16.

ative insensitivity of molding modulus to changes in mold temperature and skin thickness can then be ascribed to the changes that occurred in the structure of the core material. Not only did the density of this core material increase substantially, but the size of the spherulites was also markedly increased (see Fig. 2).

The mechanical properties of these PB injection moldings produced with varying mold temperatures then depended on the structure of the whole molding, with the core material contributing significantly to the stiffness of the total molding. This behavior is different from those moldings produced under different barrel temperatures but with a constant mold temperature, where the stress-strain behavior depended mainly on the skin extent and structure.

Fracture of Injection Moldings

As was noted in the fourth subsection under Experimental Results, the fractures of injection-molded samples processed at high mold temperatures (40°C and above) were in the curved or gripped section of the tensile bar moldings. In contrast, those moldings produced at a mold temperature of 20°C , irrespective of barrel temperature, failed in the gauge length. The two cases are therefore considered separately.

Figures 11 and 15 demonstrate that the highly oriented region of the injection moldings was the site for the initiation of fracture, and that region of the molding behaved in an essentially brittle manner when tested alone. Isotropic PB may exhibit a ductile or essentially brittle response, depending on the crystallinity of the material.²⁰ Material of high crystallinity (density) and having large spherulites behaved in a brittle manner. Shock-cooled PB, on the other hand, behaved in a ductile manner.

The birefringent skin of the PB injection moldings had both a high density [see Fig. 6(b)] and was highly oriented, fracture surfaces clearly exhibiting a fibrous nature (Fig. 12). A limited amount of work was therefore undertaken on oriented low density ($910\text{ kg}\cdot\text{m}^{-3}$) PB, the material being oriented by cold rolling, reducing the thickness of the plaques to one quarter of the original value. When

tested parallel with the rolling direction, the material behaved in a manner similar to the skin of the injection moldings. The sample failed at low (25%) strains and very high (96 MPa) stresses. And the density of the rolled material was, allowing for experimental error, identical to the starting material. Therefore, from the work of Weynant et al.²⁰ and our own work on rolled PB, both the higher density and the preferred orientation could have contributed to the low ($\approx 25\text{--}35\%$) failure strains and earlier fracture that the PB injection moldings exhibited.

The site of the initiation of these fractures within the moldings was within the highly oriented skin, but towards the center of the molding. Many of the fractures initiated from included particles (see Fig. 13). The iron rich nature of many of these particles infers that the source of the particle may have been in some of the processing equipment used to either granulate the pellets or process the feedstock. Close to the initiating particle there was little evidence of local drawing of the material (Figs. 13 and 11). Further from the initiation site (which tended to be toward the center of the molding but within the highly oriented skin), the underlying fibrous nature of the material in the highly oriented skin was revealed (Fig. 12). The failure strains of the injection-molded bars, 20–40% imply some extension of this fibrous material. After fracture, most of the strains were recoverable, and the whitening phenomena present during extension would disappear immediately. Such long-range elasticity is termed "hard elastic"^{31–33} and is believed to be energetic instead of entropic, as in rubber elasticity. The hard elastic response is considered to be characteristic of an oriented structure. Figure 12 provides the evidence for this, where it can also be inferred that the fibers recovered significantly after fracture.

Consider now the influence of mold temperature changes. The tendency to premature brittle fracture in the curved or gripped section of those injection moldings processed at mold temperatures of 40°C and above may be associated with density increases in the skin and core material [see Fig. 7(b)]. Weynant et al.²⁰ have demonstrated that high crystallinities in PB compression moldings can lead to a low strain (<20%) fracture, and with large spherulites, which accompanied the high crystallinities, interspherulitic fracture. While increasing the mold temperature reduced skin thickness [Fig. 7(a)], it did not reduce the density of the skin or core material, rather it increased both. Since the rate of injection, the injection pressure, and the barrel temperature were maintained constant as the mold temperatures were varied, it is to be expected that the amount of fibrous material would not have changed significantly. The higher densities may then be associated with the lower rates of cooling, and these higher densities led to the brittle response.

CONCLUSIONS

The structure and mechanical properties of polybutylene injection moldings have been found to depend on the processing conditions employed and the grade (molecular weight) of plastic. The use of low barrel and mold temperatures, particularly for the high molecular weight 0100 grade, gave rise to moldings with a Young's modulus (≈ 0.9 GPa) and fracture stress (50–60 MPa) considerably above the values for the fast cooled compression-molded tensile bars (0.2 GPa for modulus, 15–18 MPa for yield stress, and 34 MPa for fracture stress). This change in behavior is related to the oriented skin material, which was induced by the flow and shock cooling of the polymer melt. The injection moldings also

failed at relatively low (>25%) strains, but strains above that for the glassy brittle plastics (4–8% typical values). The fracture initiated in the highly oriented region.

The use of high (40°C and above) mold temperatures induced major changes in the structure of the core material in moldings. Spherulite size and density increased to relatively high values. In addition, the material behaved in a brittle manner, failure occurring outside the gauge length in the curved or gripped section of the molding. High mold temperatures are therefore to be avoided.

The provision of financial support for one of use (M. G.) from the People's Republic of China is acknowledged. The authors wish also to acknowledge the supply of materials from Shell Chemicals Ltd., the provision of laboratory facilities by, and helpful discussions with, Professor M. Bevis, and the support of Hepworth Plastics, Ltd.

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Received March 26, 1982

Accepted February 7, 1983