

The Influence of Structure and Processing Conditions on Engineering Mechanical Properties in Bulk Crystallized Isotactic Polypropylene

J. H. REINSHAGEN* and R. W. DUNLAP, *Department of Metallurgy and Materials Science, Carnegie-Mellon University, Schenley Park, Pittsburgh, Pennsylvania 15213*

Synopsis

A study of the influence of processing conditions and structure on engineering mechanical properties was conducted in bulk isotactic polypropylene. The influence of one processing parameter, undercooling, defined so as to account for both pressure and temperature effects, was particularly studied.

Improved mechanical properties were found with increased undercooling. At low undercoolings, brittle failure without yield occurred, presumably the result of a sparsity of intercrystalline links under these conditions. As undercooling was increased, failure occurred after yielding as failure stress elevated dramatically, apparently because of greater link density. A modest improvement in yield stress with increased undercooling was attributed to the increasingly cross-hatched lamellar structure produced at higher undercoolings, a structural trend confirmed by electron microscopy.

Spherulite size, varied by altering melt history (melt temperature and time at melt temperature) at constant undercooling, was found to have no effect on engineering yield stress. This result indicates that apparent yield stress-spherulite size effects found by several earlier investigators were probably caused by structural variations other than spherulite size.

INTRODUCTION

This paper reports the results of a study of the influence of processing conditions (melt treatment, isothermal crystallization temperature, and constant crystallization pressure) and structure on engineering mechanical properties of bulk isotactic polypropylene. It is a companion study to a previously reported investigation¹ designed to determine the influence of processing conditions on crystallization kinetics and resultant structure in bulk crystallized polypropylene. That study showed undercooling, defined as the melting temperature minus the crystallization temperature, and calculated with the aid of the Clausius-Clapeyron equation, to be an excellent parameter for interrelating the influence of crystallization temperature and pressure on polymer crystallization and structure. The results presented here further con-

* Present address: Westinghouse Electric Corporation, Bettis Atomic Power Laboratory, P.O. Box 79, West Mifflin, Pennsylvania 15122

TABLE I
Summary of Experimental Conditions

| $T_x, ^\circ\text{C}$ | P, psi | $T_{mp}, ^\circ\text{C}$ | $\Delta T, ^\circ\text{C}$ |
|-----------------------|-----------------|--------------------------|----------------------------|
| 150 | 3768 | 198.2 | 48.2 |
| 145 | 3768 | 198.2 | 53.2 |
| 135 | 1641 | 190.4 | 55.4 |
| 140.9 | 3768 | 198.2 | 57.3 |
| 135 | 3171 | 196.1 | 61.1 |
| 135 | 3768 | 198.2 | 63.2 |
| 140.9 | 6273 | 206.6 | 65.7 |
| 132.5 | 3768 | 198.2 | 65.7 |
| 130 | 3768 | 198.2 | 68.2 |
| 135 | 5925 | 205.5 | 70.5 |
| 125 | 3768 | 198.2 | 73.2 |
| 135 | 8066 | 212.2 | 77.2 |
| 120 | 3768 | 198.2 | 78.2 |
| 140.9 | 12573 | 224.4 | 83.5 |

firm the importance of this parameter and elucidate its influence on both the characteristics of tensile deformation and engineering mechanical properties.

The influence of spherulite size, varied by variation of melt treatment (melt temperature and time at melt temperature) at constant undercooling, on engineering mechanical properties was also investigated. This portion of the study was prompted by the often conflicting results reported by previous investigators in various polymer systems.²⁻¹⁰

EXPERIMENTAL

Polymer

The polymer used in this study was Hercules Profax 6623, a commercially available, general-purpose, heat-stabilized polypropylene. The polymer was characterized by Hercules as having an $M_w = 418,000$, an $M_n = 61,000$, an intrinsic viscosity of 2.7 dl/g (Decalin 135°C), and a nonisotactic (Decalin solubles) content of about 3%.

Molding Conditions and Procedure

The constant pressure molding rig employed in this study was capable of pressures up to 13,000 psi. The rig was inserted in the melt bath (at a temperature between 190° and 220°C) for isothermal melt treatment. Pressure was then applied (and held constant for the remainder of the treatment cycle), and the rig was transferred to the crystallization bath for isothermal crystallization at a temperature between 120° and 150°C. The finished samples were in the form of rods about $\frac{5}{16}$ in. in diameter and $2\frac{1}{2}$ in. long. The molding rig and molding procedure employed in this study are more fully described elsewhere (see ref. 11).

Undercooling is defined as

$$\Delta T = T_{mp} - T_x,$$

where T_x is the crystallization temperature and T_{mp} is the equilibrium melting temperature. The effect of pressure on the melting temperature was de-

terminated from the Clausius-Clapeyron equation, as described previously.¹ Table I lists the undercoolings obtained for the crystallization temperature and pressure combinations employed in this study.

Spherulite diameter was varied by variation of melt treatment at constant undercooling, a procedure that does not result in variation of other entities of structure. The influence of melt history on spherulite diameter in the polypropylene used in this study has been previously described.^{1,11} Spherulite diameter was determined via lineal analysis,¹² using polished and heat-etched samples, by reflected light microscopy. The spherulite diameter thus determined is simply the inverse of the average number of spherulite boundaries intersected per unit length by random straight lines projected on the sample surface.

Mechanical Properties

Tensile samples were carefully cut on a lathe from the as-molded rods. Small cuts were employed to minimize sample heating, and samples were stored in a freezer when not being machined or tested to minimize any room-temperature aging effects.

Tensile tests were conducted at room temperature using an Instron Testing Machine and employing an initial strain rate of 11.1%/min.

Yield stress was determined as the load at yield (maximum on the load-elongation curve) divided by the original cross-sectional area in the gauge length at the region of yielding.

Failure stress was determined as the load at failure divided by the cross-sectional area of the fracture surface. This area was calculated from the average diameter of the fracture surface, measured with a micrometer following failure. In some cases the fracture surface was sufficiently nonuniform (e.g., failure occurred at an angle to the diametral plane, or the specimen failed by tearing) to make determination of failure area, and thus failure stress, impossible. Specimens which cold drew extensively and uniformly (100% elongation or more) were not tested to failure and were termed "Did not fail."

Elongation to failure was determined as the total sample elongation at failure divided by the original gauge length, expressed as a per cent. Total elongation to failure was determined by direct conversion of the load-crosshead chart output of the Instron. (This was possible because the samples were much less stiff than the Instron or the load-cell employed.) As such, this strain measure includes both elastic and plastic strain. No attempt was made to correct for this, since elongation to failure based on original gauge length is a rather gross indication of failure properties in any process that involves necking and cold drawing.

RESULTS AND DISCUSSION

Influence of Undercooling on the Characteristics of Tensile Deformation

Undercooling has a dramatic effect on the tensile deformation of polypropylene. Figure 1 illustrates load-elongation curves for three different undercoolings: 48.2°, 63.2°, and 78.2°C. These undercoolings are representative

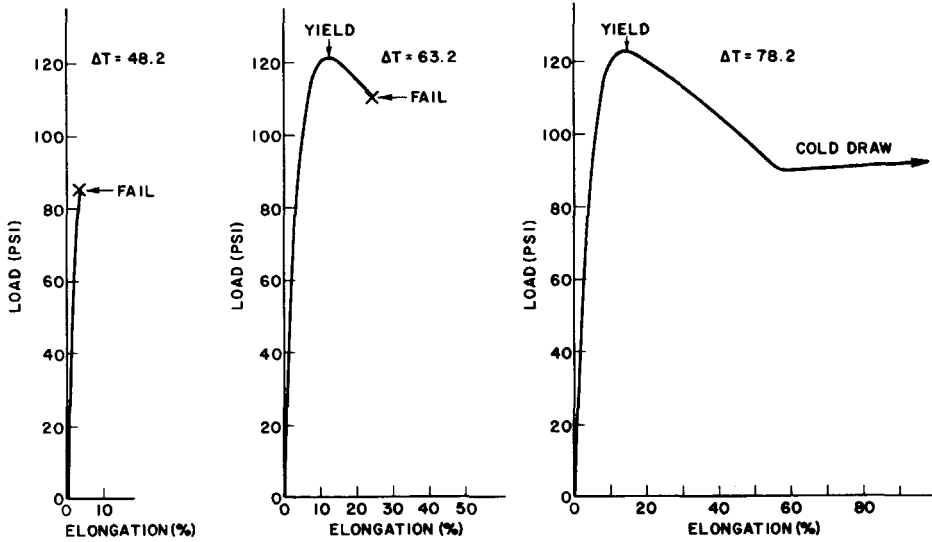


Fig. 1. Load-elongation curves for undercoolings of 48.2°, 63.2°, and 78.2°C. (Nominal initial sample diameter in gauge length 0.180 in.)

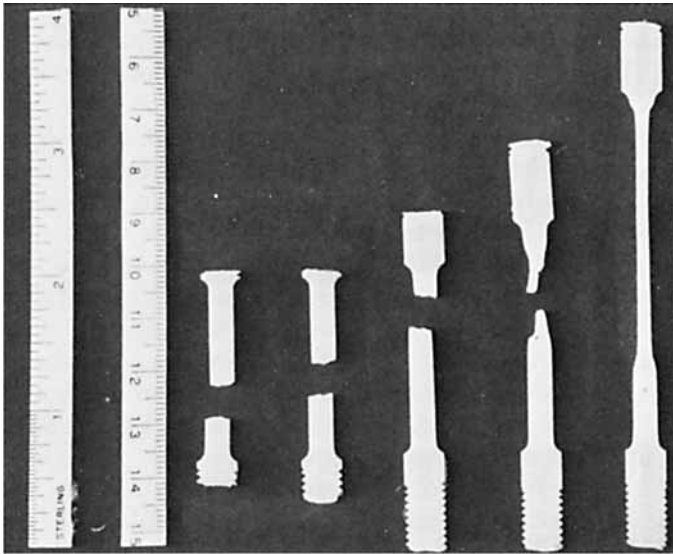
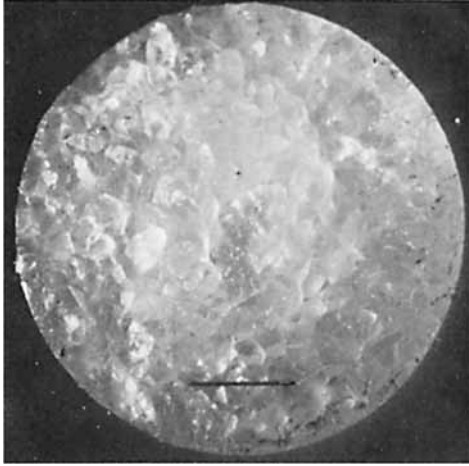
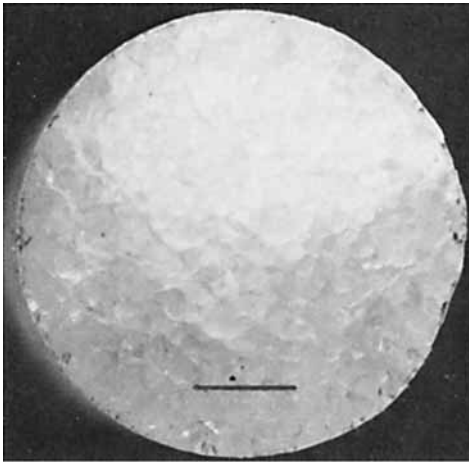


Fig. 2. Tensile test samples. Undercoolings from left to right: 48.2°C; 57.3°C; 63.2°C; 68.2°C; 78.2°C.

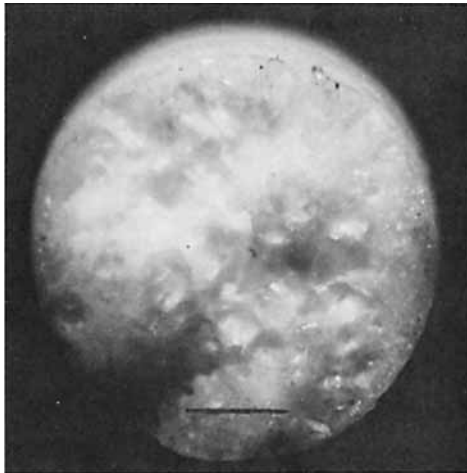
of the low, mean, and high undercoolings employed in this study. Figure 2 shows a photomicrograph of tensile samples crystallized at these three undercoolings, plus intermediate undercoolings of 57.3° and 68.2°C. Figure 3 illustrates fracture surfaces of the four samples illustrated in Figure 2 which failed during tensile testing. Although the behavior illustrated in these figures could be expected from the work of others,^{13,14} these results represent the first explicit documentation of the effect of undercooling on the characteristics of tensile deformation.



(a)

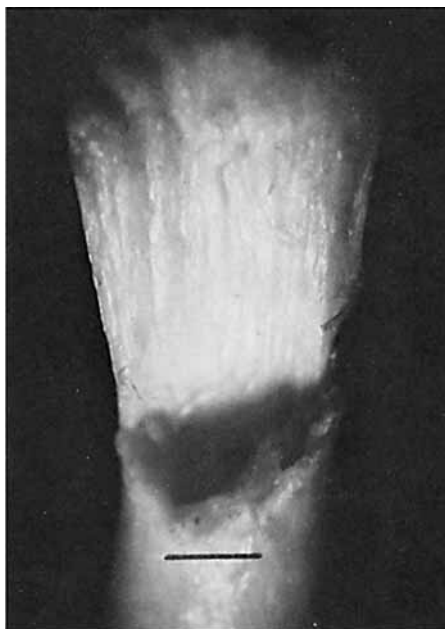


(b)



(c)

Fig. 3 (continued)



(d)

Fig. 3. Fracture surfaces of four tensile specimens crystallized at various undercoolings. Undercoolings: (a) 48.2°C; (b) 57.3°C; (c) 63.2°C; and (d) 68.2°C. (Marker length = 1 mm throughout.)

At the 48.2°C undercooling, the sample fails in a brittle manner, at low elongation, without yielding. Little or no "strain-whitening," believed caused by microvoid formation,¹³ is observed, although an apparent crack network develops in the sample prior to failure. (Formation of a crack network during tensile testing of annealed polypropylene has been previously reported.¹⁵) Failure occurs along spherulite boundaries, roughly in a plane perpendicular to the direction of application of tensile stress. Individual spherulites are easily discerned on the fracture surface [Fig. 3(a)].

At the 57.3°C undercooling, behavior is essentially identical to that for the 48.2°C undercooling, except that the sample fails at a somewhat higher load and slightly greater elongation [Figure 3(b)].

In the case of the 63.2°C undercooling, the sample strain-whitens to a limited extent uniformly throughout the gauge length prior to yielding. At the yield point, localized necking begins. The area around the neck increasingly strain-whitens and the load drops as the neck forms. In this case, the sample fails during necking with little or no cold drawing. No crack network is observed, and only a few spherulite boundaries are evident on the fracture surface [Figure 3(c)].

At the 68.2°C undercooling, behavior is identical to the 63.2°C undercooling, except that the neck is fully formed and failure ensues after limited cold drawing. Note that for the particular sample illustrated in Figure 2 and Figure 3(d), part of the fracture surface is parallel to the direction of drawing. Note the fibrous nature of this fracture surface as seen in Figure 3(d). Ob-

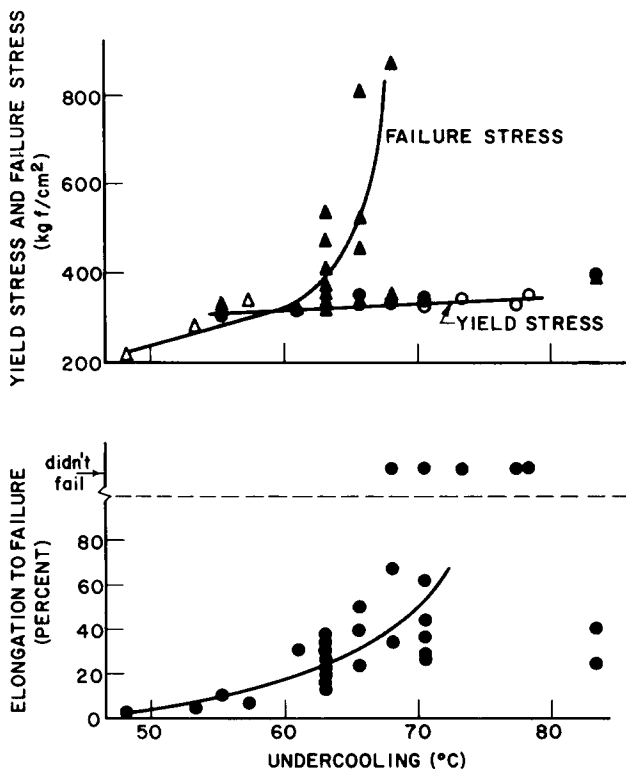


Fig. 4. Yield stress, failure stress, and elongation to failure vs. undercooling. Legend: (●) = yield stress for samples that fail; (○) = yield stress for samples that do not fail; (▲) = failure stress for samples that yield; (△) = failure stress for samples that do not yield; and (●) elongation to failure.

servation of such a structure is in agreement with the models for deformation behavior proposed by Samuels¹⁶ and Peterlin.¹⁷

For an undercooling of 78.2°C, the sample behaves the same as for an undercooling of 68.2°C, except that the neck stabilizes and full cold drawing ensues. This occurs when the material in the neck becomes sufficiently oriented so that less stress is required to draw the undrawn material than is required to further deform the drawn material. During cold drawing, the neck growth fronts propagate throughout the gauge length of the specimen at essentially constant load. The load would of course increase, after several hundred per cent elongation, when the growth fronts reached the shoulders of the specimen.

Influence of Undercooling on Mechanical Properties

The effect of undercooling on mechanical properties is now presented, both to get a measure of the range of mechanical properties obtained for the experimental conditions employed in this study, and to see how these properties vary with processing.

Figure 4 is a plot of yield stress, failure stress, and elongation to failure as

TABLE II
Summary of Results for Varied Undercooling

| ΔT , °C | No. of tensile samples | Mean engineering yield stress, ^a kgf/cm ² | Mean elongation to failure, ^a % | Mean failure stress, ^a kgf/cm ² |
|--------------------|------------------------------|---|--|---|
| 48.2 | 1 | Fail without yield | 2.3 | 216 |
| 53.2 | 1 | Fail without yield | 3.9 | 271 |
| 55.4 | 1 | 304 | 11.0 | 327 |
| 57.3 | 2 | Fail without yield | 7.0 ± 0.4 | 335 ± 1 |
| 61.1 | 1 | 317 | 30.1 | 319 |
| 63.2 | 20 | 330 ± 4 | 23.8 ± 5.6 | 367 ± 51 |
| 65.7 | 4 | 338 ± 7 | 37.8 ± 10.6 | 528 ± 171 |
| 68.2 | 3 | 337 ± 8 | (50.4 ± 23.4) ^b | (611 ± 362) ^b |
| 70.5 | 6 | 335 ± 5 | (38.8 ± 14.3) ^b | (c) |
| 73.2 | 1 | 340 | Did not fail | Did not fail |
| 77.2 | 4 | 334 ± 2 | Did not fail | Did not fail |
| 78.2 | 1 | 353 | Did not fail | Did not fail |
| 83.5 | 2 | 396 ± 4 | 32.0 ± 9.9 | 393 ± 2 |

^a Standard deviations are reported following the mean values for case of multiple samples.

^b Calculated excluding one sample that "Did not fail."

^c One sample did not fail; remaining five had sufficiently nonuniform fracture surfaces to make determination of failure area, and thus failure stress, impossible.

functions of undercooling. Data for this plot are summarized in Table II. The behavior shown here could be expected from the work of other investigators.^{13,14} However, these plots represent the first quantitative presentation of the effect of undercooling on the mechanical properties of polypropylene. Note that the two data points representing the highest undercooling (and highest pressure) employed exhibit anomalous behavior and are excluded from the present discussion.

At undercoolings less than about 55°C, all samples are seen to fail without yielding. As undercooling is increased above this level, some samples yield prior to failure. At undercoolings greater than about 58°C, all samples yield prior to failure, and yield stress shows a slight rise with increasing undercooling.

Failure stress is seen to rise at an increasing rate as undercooling is elevated. At undercoolings of about 70°C or greater, samples cold draw stably to more than 100% elongation and hence are not tested to failure. (Experience indicated that in such cases failure occurs once the entire gauge length has cold drawn and the deformation growth fronts are progressing into the shoulders of the tensile specimen. Failure occurs in a very ductile manner, and the cross-sectional area at the region of failure is impossible to determine accurately.) Note again that mode of failure also changes with undercooling, as illustrated by Figures 2 and 3. At low undercoolings, failure is brittle and interspherulitic. Spherulites are clearly visible on the fracture surface. As undercooling is increased, yielding occurs before failure, failure becomes more ductile, and identification of spherulites on the fracture surface by optical microscopy becomes impossible. As undercooling is further increased (to the highest undercoolings at which failure occurs without the entire gauge length of the specimen cold drawing), failure occurs in a very ductile manner, the

specimen often tearing. In this case, a fibrous structure running parallel to the direction of applied tensile stress is observed. Elongation to failure behaves in a manner quite similar to failure stress.

To help explain this behavior, elucidation of the work of other investigators is required. Way and Atkinson^{13,14} (although they do not provide quantitative mechanical property results), and also Way et al.,¹⁰ note in polypropylene that the (large) spherulites formed at high crystallization temperatures (low undercoolings) or slow cooling rates are inherently brittle at the spherulite boundaries, a result of the sparsity of interspherulitic links, void formation, and impurity segregation at the boundaries. (The decrease in intraspherulitic interlamellar links and the more pronounced decrease in interspherulitic interlamellar links with decreasing undercooling was first reported by Keith and co-workers¹⁸ in polyethylene. These experimenters also noted that decreasing molecular weight has an effect on link density similar to decreasing undercooling.)

In addition to the link effect, Way and Atkinson also note that the lamellar structure of polypropylene varies with undercooling in a manner not found in other polymers. For the polypropylene employed in their studies, they found that for crystallization temperatures less than about 140°C (molding pressure not specified, and thus undercooling not determinable), a crosshatched lamellar structure was present. In addition to the radial lamellae with tangentially oriented chains commonly found in semicrystalline polymers, they noted tangentially oriented lamellae. (This structure was investigated earlier by Padden and Keith.¹⁹) They attribute the formation of this structure to the similarity of lattice "a" and "c" dimensions at lower temperatures, which allows growth of the tangential lamellae from parent radial lamellae. The intraspherulitic structure thus obtained is stronger because of the physical interweaving of the radial and tangential lamellae. [These are the "Type I" polypropylene spherulites that Padden and Keith²⁰ determined predominate at crystallization temperatures below 134°C (atmospheric pressure; undercoolings greater than about 50°C).]

At crystallization temperatures above about 140°C, the lamellar structure develops a predominately radial texture, presumably because epitaxial misfit becomes too great for tangential lamellae to nucleate on the radial lamellae. (These are apparently the "Type III" spherulites Padden and Keith determined predominate at crystallization temperatures greater than 138°C.) The coarse, open structure associated with the radial lamellae formed at higher crystallization temperatures (lower undercoolings) produces a network that is physically less connected than the interwoven crosshatched structure produced at higher undercoolings, and is mechanically less strong.

Thus the structural reasons for the behavior of yield stress, failure stress, and elongation to failure with undercooling determined in the present study are at least qualitatively apparent. At low undercoolings, interspherulitic links are insufficient to transmit stress between spherulites and brittle failure without yielding occurs at the spherulite boundaries. This effect is also promoted by impurity segregation and void formation at the boundaries at low undercoolings. As undercooling increases, both interlamellar (i.e., intraspherulitic) and interspherulitic link density increase. Concomitant with the increase in link density, the internal spherulitic structure becomes more diffi-

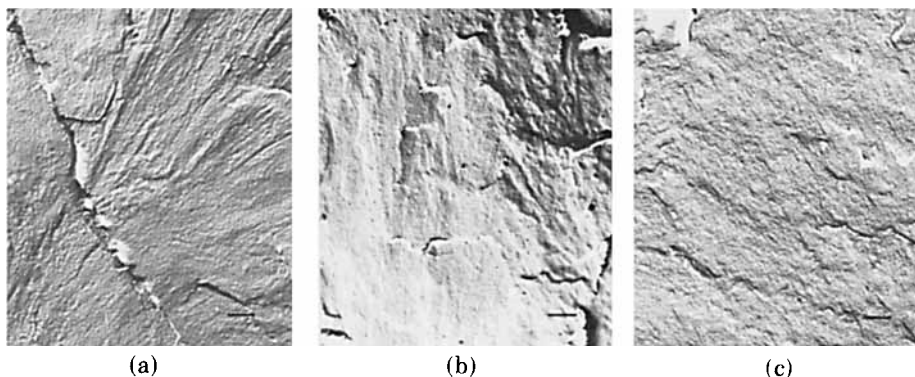


Fig. 5. Effect of undercooling on lamellar structure. Undercoolings: (a) 48.2°C (note the spherulite center); (b) 63.2°C; and (c) 83.5°C. Marker length = 1 mm.

cult to deform as the structure changes from predominantly radial lamellae to a more interwoven tangential/radial network. This point is illustrated by electron microscopy studies conducted to determine the lamellar character of representative areas of samples employed in this study. Figure 5 illustrates the fracture surfaces (from samples fractured at liquid nitrogen temperatures) of samples crystallized at undercoolings of 48.2°, 63.2°, and 83.5°C. [Note the center of the spherulite visible in the lower left of Figure 5(a).] All of these samples exhibit a crosshatched structure (in agreement with the work of Padden and Keith²⁰), but note that the radial component is more pronounced in the small undercooling sample [Fig. 5(a)]. Note in Figure 5(c) that the radial direction is indistinguishable from the tangential direction. (The highest undercooling samples exhibit anomalous mechanical property behavior, but the character of their lamellar structure follows the trend exhibited by the rest of the samples.)

Returning to the undercooling–mechanical property results (Fig. 4), as undercooling is increased above the lowest undercoolings, a point is reached where enough interspherulitic links are present to transmit stress between the spherulites so the intraspherulitic material yields. At this undercooling (about 58°C), macroscopic failure stress exceeds yield stress. As undercooling is further increased, the increase in link density and the trend for a more interwoven structure continues, resulting in both improved yield stress and failure stress. Yield stress increases slightly with increasing undercooling because of increasing difficulty in deforming the more interwoven lamellar network. Failure stress and elongation to failure show a dramatic increase, apparently because link density has increased sufficiently so that the applied stress is transmitted uniformly to the lamellae, allowing them to exhibit the full spectrum of deformation behavior.

Structure–Mechanical Property Relationships at Constant Undercooling

Varying undercooling causes variation in many entities of structure, including spherulite diameter, per cent crystallinity, and lamellar thickness.¹ In addition, link density and lamellar morphology are also varied, as described above. Thus quantitative determination of the effect of the different

morphological entities on mechanical properties is difficult when structure is varied by undercooling. To further investigate structure-mechanical property relationships, a series of 20 samples with varied melt treatments was crystallized at an undercooling of 63.2°C, representative of the middle of the range of undercoolings employed. Note that variation of melt treatment results in variation of spherulite diameter alone; other entities of structure are not affected. Data for these samples are provided in Table III.

Figure 6 is a plot of yield stress, failure stress, and elongation to failure as functions of spherulite diameter for crystallization at an undercooling of 63.2°C. Spherulite diameter was varied by varying melt treatment between 11 min at 190°C and 136 min at 220°C. It is apparent that the effect of spherulite size on yield stress is negligible; a line with zero slope fits the data adequately. (The yield-stress line shown on the figure is a least-squares fit.) A mean value of yield stress of 330 kgf/cm² (4700 psi) is obtained with a per cent standard deviation of 1.3%. Thus it may be concluded that the upper yield stress does not vary with spherulite size for the range of sizes considered and for the structures represented by this undercooling. Note that this does not rule out the possibility of a spherulite size effect at other undercoolings (presumably higher undercoolings, since failure occurs without yield at much lower undercoolings), where the structure is not the same.

Note that the above result is in conflict with the result of Way et al.,¹⁰ who investigated spherulite diameters in the same range as the present study and found that yield stress passed through a maximum with spherulite diameter. However, their method of variation of spherulite size (variation of cooling rate) results in variation of other entities of structure (e.g., per cent crystallinity, link density, impurity segregation, and void formation at spherulite boundaries). Apparently, it is the variation of these other entities of structure which seems to produce a spherulite size effect; if structural variations other than spherulite size are suppressed, no effect is noticed.

To illustrate this point, note that, for constant melt history, spherulite size decreases with increasing undercooling.¹ As seen in Figure 4, yield stress increases with increasing undercooling. Thus, if these results are combined to produce a plot of yield stress versus spherulite diameter varied by undercooling (for constant melt history), one reaches the erroneous conclusion that yield stress decreases with increasing spherulite size, as illustrated by Figure 7. In this figure, data for samples given a melt treatment of 30 min at 200°C are presented, and the line for spherulite size varied by melt history (Fig. 6) is illustrated for comparison. (Data for Figure 7 are presented in Table IV.) Figure 7 clearly demonstrates the problems associated with some earlier studies (ref. 4 and 5, for example): insufficient sample characterization can lead to fallacious conclusions concerning the structural parameters that influence mechanical properties.

At the 63.2°C undercooling, failure stress is relatively insensitive to variations in spherulite diameter for diameters greater than about 7.5×10^{-2} mm, as illustrated in Figure 6. (A least-squares analysis of the data for spherulite diameters greater than 7.5×10^{-2} mm yields a slope of -44 (kgf/cm²)/mm \pm 108%.) However, three of the four samples with spherulite diameters smaller than 7.5×10^{-2} mm (melt treatment of 11 min at 190°C) exhibit failure stresses considerably above the rest of the data. Electron microscopy reveals

TABLE III
Summary of Results for an Undercooling of 63.2°C

| Sample no. | Melt time, min | Melt temperature, °C | Spherulite diameter, ^a mm × 10 ² | Engineering yield stress, ^a kgf/cm ² | Elongation to failure, ^a % | Failure stress, ^a kgf/cm ² |
|-------------------|-------------------|----------------------------|---|--|---|---|
| 116 | 11 | 190 | 4.57 | 335.1 | 17.1 | 346.9 |
| 114 | 11 | 190 | 4.65 | 327.3 | 30.7 | 405.4 |
| 129 | 11 | 190 | 6.76 | 329.1 | 34.0 | 538.3 |
| 128 | 11 | 190 | 7.29 | 330.3 | 31.0 | 470.8 |
| Mean | 11 | 190 | 5.82 ± 1.40 | 330.5 ± 3.3 | 28.2 ± 7.6 | 440.4 ± 83.7 |
| 131 | 11 | 195 | 7.80 | 329.7 | 22.0 | 349.9 |
| 132 | 11 | 195 | 8.31 | 335.1 | 25.7 | 356.2 |
| Mean | 11 | 195 | 8.06 ± 0.35 | 332.4 ± 3.7 | 23.9 ± 2.6 | 353.1 ± 4.6 |
| 135 | 11 | 200 | 8.79 | 330.9 | 25.5 | 367.2 |
| 111 | 11 | 200 | 8.99 | 322.0 | 28.3 | 333.0 |
| Mean | 11 | 200 | 8.89 ± 0.14 | 326.5 ± 6.2 | 26.9 ± 2.0 | 353.1 ± 24.4 |
| 113 | 30 | 200 | 9.22 | 320.4 | 32.2 | 346.8 |
| 126 | 30 | 200 | 10.77 | 334.4 | 24.4 | 350.1 |
| 125 | 30 | 200 | 10.95 | 332.6 | 23.4 | 354.3 |
| 119 | 30 | 200 | 11.02 | 335.4 | 17.0 | 342.6 |
| Mean | 30 | 200 | 10.49 ± 0.85 | 330.7 ± 6.9 | 24.3 ± 6.6 | 348.5 ± 4.9 |
| 115 | 120 | 200 | 12.34 | 334.2 | 16.6 | 355.1 |
| 134 | 120 | 200 | 13.82 | 331.8 | 23.8 | 346.2 |
| Mean | 120 | 200 | 13.08 ± 1.05 | 333.0 ± 1.7 | 20.2 ± 5.1 | 350.7 ± 1.1 |
| 117 | 60 | 220 | 16.05 | 331.7 | 17.8 | 350.9 |
| 133 | 60 | 220 | 16.74 | 329.2 | 23.9 | 356.3 |
| Mean | 60 | 220 | 16.40 ± 0.49 | 330.5 ± 1.7 | 20.9 ± 4.4 | 353.6 ± 3.9 |
| 110 | 136 | 220 | 17.78 | 324.1 | 26.7 | 337.6 |
| 130 | 120 | 220 | 18.11 | 336.3 | 18.3 | 338.2 |
| 118 | 120 | 220 | 20.90 | 328.7 | 15.6 | 346.8 |
| 127 | 120 | 220 | 21.01 | 332.0 | 22.2 | 348.7 |
| Mean ^b | 124 | 220 | 19.45 ± 1.75 | 330.3 ± 5.3 | 20.7 ± 4.8 | 342.8 ± 5.8 |

^a Standard deviations are reported following mean values.

^b Values calculated including Sample 110.

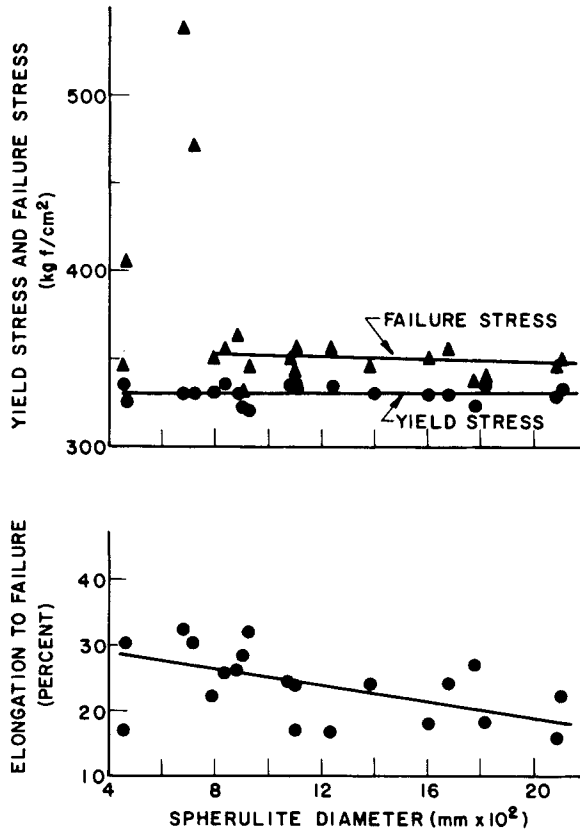


Fig. 6. Yield stress (●), failure stress (▲), and elongation to failure (●) vs. spherulite diameter for an undercooling of 63.2°C.

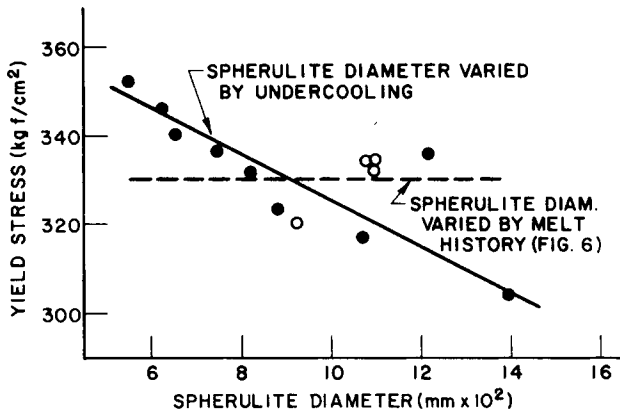


Fig. 7. Yield stress vs. spherulite diameter varied by undercooling illustrating apparent, but erroneous, spherulite size effect. Melt treatment: 30 min at 200°C. (Open circles denote points that also appear in Fig. 6.)

no structural differences between the three samples exhibiting the high failure stress and the fourth with the lower failure stress. The other methods of structural characterization employed in this and the companion study¹ also

TABLE IV
Data for Varied Undercooling at a Constant Melt Treatment of 30 min at 200°C

| Sample no. | Undercooling, °C | Engineering yield stress, kgf/cm ² | Spherulite diameter, mm × 10 ² |
|------------|---------------------|---|--|
| 108 | 54.4 | 303.9 | 13.94 |
| 112 | 61.1 | 317.2 | 10.69 |
| 113 | 63.2 | 320.4 | 9.22 |
| 126 | 63.2 | 334.4 | 10.77 |
| 125 | 63.2 | 332.6 | 10.95 |
| 119 | 63.2 | 335.4 | 11.02 |
| 97 | 65.7 | 332.1 | 8.20 |
| 91 | 68.2 | 346.4 | 6.22 |
| 107 | 70.5 | 323.9 | 8.79 |
| 124 | 70.5 | 336.1 | 12.14 |
| 94 | 73.2 | 340.3 | 6.50 |
| 96 | 77.2 | 336.4 | 7.44 |
| 92 | 78.2 | 352.9 | 4.95 |

reveal no clues concerning the reasons for this behavior. The apparent effect remains unexplained.

There is an apparent trend for decreased elongation to failure with increasing spherulite size, in agreement with the work of Kargin et al.² mentioned previously. As pointed out previously, samples crystallized at this 63.2°C undercooling fail following the onset of yielding and necking (as opposed to uniform deformation). These samples exhibit a correlation between increased elongation to failure and increased severity of necking, as reflected by increased reduction in area.

To see if degradation might be playing a role in these results (particularly for elongation to failure and failure stress), intrinsic viscosity measurements were conducted (by Hercules, Inc.) on samples given varying melt treatments. In addition, the intrinsic viscosity of a sample crystallized at a higher undercooling was measured, and the intrinsic viscosity of the original as-supplied pellets was remeasured. The results are presented in Table V. No trend for decreased intrinsic viscosity with increased severity of treatment is noted; the intrinsic viscosities fall about within the 0.1 dl/g accuracy quoted by Hercules. Thus little, if any, measurable degradation has occurred.

CONCLUSIONS

This study has presented quantitative illustration of the influence of undercooling on engineering mechanical properties in bulk crystallized polypropylene. At low undercoolings brittle failure without yield occurs, presumably the result of a sparsity of intercrystalline links under these conditions. As undercooling is increased, failure occurs after yielding as failure stress dramatically rises with increased undercooling, apparently because of increased link density. The modest improvement in yield stress with increased undercooling is attributed to the increasingly crosshatched structure produced at higher undercooling. Photographic documentation of the transition from brittle interspherulitic failure at low undercoolings to ductile fibrous failure at higher undercoolings has not been previously presented.

TABLE V
Intrinsic Viscosities of Selected Samples

| Sample | Sample description | Melt time, min | Melt temperature, °C | Undercooling, °C | Intrinsic viscosity, dl/g-Decalin 135°C |
|--------|-------------------------|----------------|----------------------|------------------|---|
| — | As received | — | — | — | 2.83 ^a |
| 131 | Moderate melt treatment | 11 | 195 | 63.2 | 2.70 |
| 58 | Moderate melt treatment | 11 | 195 | 57.3 | 2.95 |
| 113 | Moderate melt treatment | 30 | 200 | 63.2 | 2.73 |
| 118 | Severe melt treatment | 120 | 220 | 63.2 | 2.75 |

^a Compares with 2.7 dl/g originally quoted with pellets when furnished by Hercules.

Documentation of the lack of an intrinsic yield stress–spherulite size relationship (at a constant 63.2°C undercooling) is a significant result, particularly in view of the confusing, and often conflicting, results reported by other investigators in various polymer systems. In the present study, spherulite size was varied by variation of melt history. The results presented here show that the apparent yield stress–spherulite size effects found by several earlier investigators were probably caused by structural variations other than spherulite size; these structural effects were brought about by methods used to vary spherulite size in those studies (e.g., variation of crystallization temperature or cooling rate) and were masked by insufficient structural characterization.

Failure stress is apparently influenced by spherulite size in polypropylene under certain conditions at constant undercooling; the existence of improved failure stress at small spherulite diameters found at the 63.2°C undercooling remains unexplained. Also unexplained is the apparent deterioration of failure properties for the two samples crystallized at the highest undercooling (and highest pressure) employed in this study.

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