

Directional Solidification of Isotactic and Atactic Polypropylene Blends

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ABSTRACT: The directional solidification of polypropylene (PP) films results in an oriented semicrystalline microstructure and may offer a method to improve the properties of a product. The directional solidification of isotactic PP samples blended with 0% to 50% atactic PP, by mass, was therefore studied. The effects of composition and processing conditions were monitored to determine how they affect the quality and microstructure of the directionally solidified films. Difficulty was encountered in reproducing testable samples with a unidirectional crystal microstructure. Tensile testing of directionally solidified films was used to quantify the yield strength and elastic modulus of the films. These properties were compared with those of other PP films. The tensile test results do not support the hypothesis that enhanced mechanical properties were produced by directional solidification of the PP films. Improving the sample fabrication method and optimizing the processes involved may, however, lead to directionally solidified PP films with enhanced mechanical properties. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1516–1528, 2000

Key words: crystallization; polypropylene; spherulites; heat transfer

INTRODUCTION

The demand for materials with enhanced mechanical, chemical, and electrical properties for high-performance designs, or for specialized applications, is constantly increasing. Composite materials are often used for these high-performance applications. Polymeric materials that emulate a composite may also be developed by processing polymer blends in such a way that part of the microstructure is oriented in a preferred direction. The aligned microstructure of the polymer may then act as reinforcements for a surrounding weaker phase, e.g., an oriented crystalline phase in an amorphous phase.

The mechanical properties of thin polymer films are commonly altered through mechanical

means, but very little has been done to alter the properties of polymers using thermal means. This article reports an attempt at orienting the lamellae of polymer blends by using a thermal gradient and assessing the resulting mechanical properties of the samples. Because semicrystalline polymers are used in numerous engineering applications, we used a blend of a crystallizable and noncrystallizable polypropylene (PP).

Semicrystalline polymers, as their name indicates, do not crystallize completely and the final degree of crystallinity in a part depends upon the structure of the molecular chains and the processing conditions. Polymers with a unique way of coupling the monomers are typically called isotactic or syndiotactic, in contrast to atactic polymers in which an irregular arrangement of the monomers is found. For PP, the molecular chain can be viewed as consisting of a carbon chain with C and CH₃ side groups attached to them. The arrangement of these side groups determines whether or

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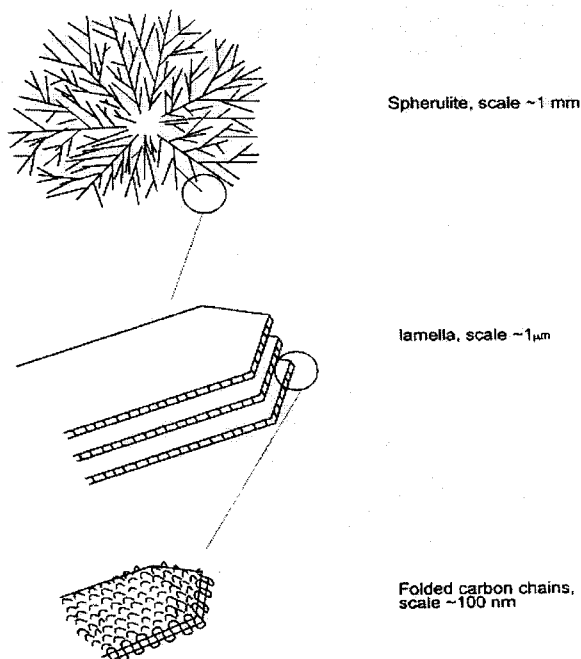


Figure 1 Illustration of the multiple scales encountered in a spherulite.²

not it is crystallizable. The isotactic structure results in a crystallizable molecule, where it is typical to represent one side of the carbon chain with only H atoms, whereas the other side alternates between H and CH₃ side groups. Atactic PP contains random placement of H and CH₃ side groups on both sides of the carbon chain. Thus it is unable to crystallize and remains amorphous.

When a semicrystalline polymer is raised above its melting point and then cooled down, nucleation occurs and crystal growth is initiated in form of lamellae. These lamellae grow radially and their growth rate is affected by various factors.^{1,2} Because the lamellae are found organized in the shape of spheres during their growth, they are referred to as "spherulites" and a number of attempts have been made at modeling the spherulitic growth in semicrystalline polymers.^{3,4} Spherulites are made of bundles or stacks of lamellae that branch out radially, and each lamella is a polymer crystal comprised of carbon chains arranged according to a chain-folding mechanism, as shown in Figure 1.

The shape of a spherulite may be altered by modifying the thermal conditions in which it cools. If PP is cooled by passing it through a sufficiently steep temperature gradient, an average spherulite takes on a quasi-parabolic shape,

shown by Figure 2. The purpose of this work is to explore the possibilities of using a temperature gradient to orient the spherulites resulting from the crystallization of isotactic PP and blends of isotactic/atactic PP, and thus enhance the properties of a polymer film.

EXPERIMENTAL

Various aspects of the experimental work carried out are presented and discussed below, namely, sample fabrication, the directional solidification apparatus, and testing.

In this work, a nearly two-dimensional spherulitic structure was studied by using a very thin (2–5 mils thick) polypropylene film. The thin film was comprised of primarily isotactic PP (melting point of 189°C, molecular weight of 280 000) combined with a smaller portion of atactic PP (softening point of 150°C, molecular weight of 23 000), situated on a microscope slide, heated above its melting temperature and pushed across a temperature gradient very slowly to cool or solidify. A schematic of the apparatus used for this process is shown in Figure 3. This solidification process is commonly referred to as directional solidification.

In preparation for the directional solidification, samples were fabricated very carefully. Initially the desired composition of atactic/isotactic PP was combined with Xylene in a flask, boiled to obtain a homogeneous solution, then removed from the heat and allowed to sit to allow the Xylene to evaporate. Next, the dry pieces of ho-

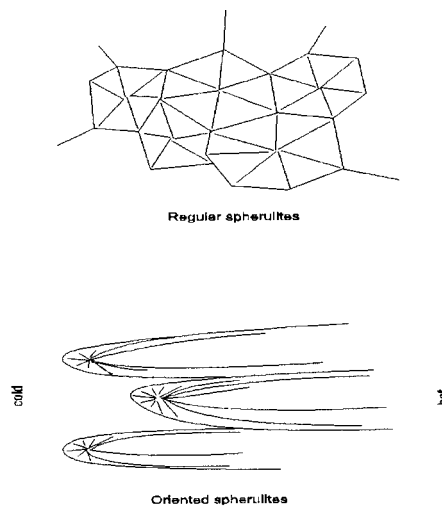


Figure 2 Schematic of the effects of directional solidification on the microstructure of polypropylene.²

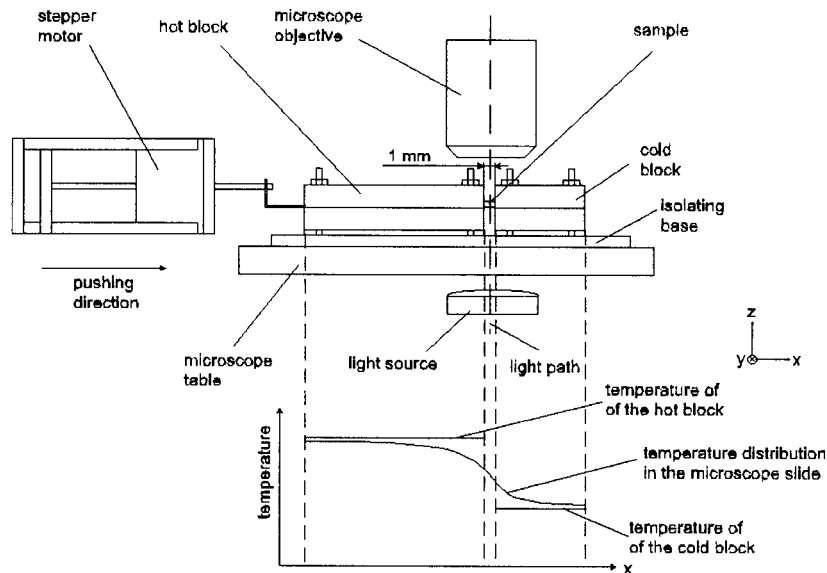


Figure 3 Illustration of the directional solidification apparatus used in this study.¹

mogeneous PP were placed on a 1" × 3" microscope slide that was heated above the PP melt temperature. A cover glass was then pressed onto the melted PP and the slide was removed from the heat. An epoxy glue was then used to seal the cover glass to the slide, creating a seal around the edges of the thin PP film.

In a blend of directionally solidified isotactic and atactic polypropylene, only one type of lamellar structure developed, which was the α -phase.¹ Because it was the only type of structure present in the blend, the α -phase descriptor is left out and here it is referred to only as a spherulite or lamellar structure. However, two different structures resulted from the directional solidification of 100% isotactic polypropylene and are distinguished by referring to them as α -phase or β -phase. These structure types are shown in Figure 4 and further described in the literature.⁵

A power supply was used in conjunction with a thermostat to heat the hot reservoir block with a temperature variation of $\pm 1.7^\circ\text{C}$ ($\pm 3\sigma$) where σ is the standard deviation. Temperature measurements were taken every 1–4 min, for both the hot and cold blocks, over the duration of the directional solidification (which typically lasted from 8 to 50 h). The temperatures of the hot and cold blocks were recorded to assure that temperatures were constant throughout the entire solidification process because experiments were often carried overnight. A stepper-motor controlled by a BASIC program was used to provide continuous pushing velocities ranging from 0.15 $\mu\text{m/s}$ to 10.0 $\mu\text{m/s}$.

Five different types of samples were tensile tested for comparison and the quantity of each type tested is shown in parenthesis:

1. PP packaging film, cross-direction (3)
2. PP packaging film, machine-direction (3)
3. Nondirectionally solidified 100/0, isotactic (6)
4. Nondirectionally solidified 95/5 (6)
5. Directionally solidified 95/5 (3)

A polypropylene film supplied by the Michigan State University (MSU) Packaging Department was tested in both the machine direction and

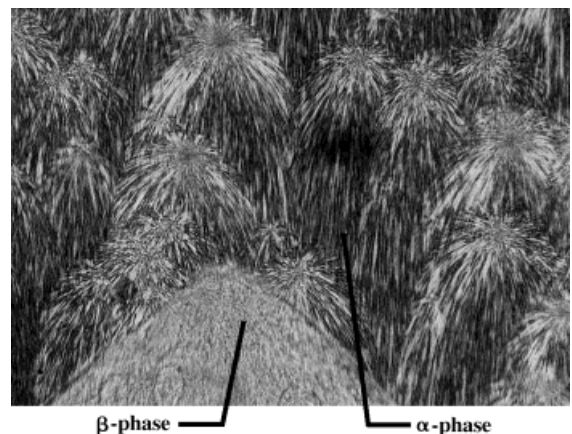


Figure 4 Diagram of the α -phase and β -phase crystal types (observed in an isotactic polypropylene sample, 1050 × 1600 μm).



Figure 5 Typical 50/50 directionally solidified sample with atactic interfaces (Sample 22, $1050 \times 1600 \mu\text{m}$).

cross-direction to allow for additional comparisons to be made. This film was manufactured by an extrusion process. As it comes out of the extruder, the film is cooled and rolled onto tubes. The direction in which it is extruded is referred to as the machine-direction, whereas the transverse direction is referred to as the cross-direction. The PP packaging film specimens were very easily prepared for tensile testing. A piece of 1 mil thick PP film was cut from the roll in the lab and then cut again by using the film cutters provided that can automatically cut strips of 1.0" width. This was done in both the machine and cross-directions. The machine-direction is the direction that results in weaker strength and elastic modulus, but provides much longer elongation before total failure.

The nondirectionally solidified samples that were used as specimens were fabricated using methods similar to compression molding techniques. To provide an adequate rectangular-shaped testing specimen, the rough edges were trimmed with scissors. Next, the specimen width was carefully measured and recorded with 0.001" accuracy using calipers. The specimen thickness also needed to be determined because the strength and elastic modulus are dependent upon the cross-sectional area. It proved to be very difficult to determine an accurate method of specifying the thickness because the thickness was not uniform.

The directionally solidified specimens used for mechanical testing exhibited some elongated or oriented texture. The spherulitic structure was very similar to the structure shown in Figure 5. Also, voids were randomly scattered throughout

the directionally solidified film. Thus, with a lack of unidirectionality and bubbles present in the directionally solidified specimens, a far from ideal specimen was used for tensile testing. For the directionally solidified specimens, a similar procedure to that of the nondirectionally solidified specimens was used. Unfortunately, a smaller region was directionally solidified, and only part of that directionally solidified region was removed intact from the cover glass, epoxy, and slide.

It was also very difficult to obtain samples of good quality for the mechanical tests. First removing the hardened epoxy bonding the cover glass to the glass slide was not easy. Once the epoxy was removed, though, it was an even more difficult process to remove the sample from the cover glass and slide. Often the adhesion between the PP sample and glass slide or cover glass was such that the sample would destroy during the removal process. Also, if the samples were less than 2 mils thick, they could not be removed from the slide, because the adhesion strength was greater than the strength of the sample. Often the sample edges were brittle and crumbled as the cover glass was being pried from the sample. Because only a region of the directionally solidified sample could be used, this reduced-size specimen forced deviations from the suggested testing specifications as described in Table I.

FACTORS AFFECTING SAMPLE QUALITY

Prior to the mechanical testing of specimens, over 40 samples were fabricated, directionally solidified, and analyzed, with the best samples used for mechanical testing.⁴ Many factors were found to affect the quality of a directionally solidified sample. The following are processing parameters and other variables that directly affect the sample quality, listed in decreasing order of importance on the directional solidification: composition (% isotactic, % atactic, by weight), homogeneity of the polypropylene blend, cooling rate for sample preparation, temperature of the hot reservoir block, temperature for sample preparation, temperature gradient, pushing velocity, distance sample starts from the leading edge, heating rate for the directional solidification, and hold time. The variables that have the greatest influence on the directional solidification are described below.

Four different compositions of polypropylene were studied: 50/50, 95/5, 98/2, and 100/0. The compositions that were chosen for the mechanical

Table I Deviations From the Suggested Testing Specifications for Various Specimen Types

Suggested Testing Specifications	Specifications Actually Used		
	PP Packaging Film (machine and cross-directions)	Nondirectionally Solidified Specimens (100/0 and 95/5)	Directionally Solidified 95/5 Specimens
Grip length > 2.0" Uniform specimen thickness throughout	Grip length = 0.340" Uniform specimen thickness (1 ml) throughout	Grip length = 0.274 Varying specimen thickness in both the length and width directions up to 100% of the recorded thickness within a single sample	Grip length = 0.274 Varying specimen thickness in both the length and width directions up to 50% of the recorded thickness within a single sample
Defect-free specimen	Defect-free specimen	Most specimens contained air bubbles	Specimens contained bubbles

tests were 95/5 and 100/0 because they were the easiest to manufacture.

Using a 95/5 blend of PP seemed to result in the best sample quality, though this quality was not attained consistently. It was possible to make directionally solidified samples without atactic interfaces or voids visible. Unfortunately, voids appeared in some cases, but could most likely be attributed to the sample preparation. Also, the sample preparation procedure was easy with the 95/5 blend. An example of a 95/5 blend of high quality is shown in Figure 6. The spherulite structure is only slightly unidirectional, but there are no voids or atactic interfaces to weaken the strength of the polypropylene film. Based on the high quality of the 95/5 directionally samples, it appears promising that thin PP films may be developed with a unidirectional spherulite crystal-

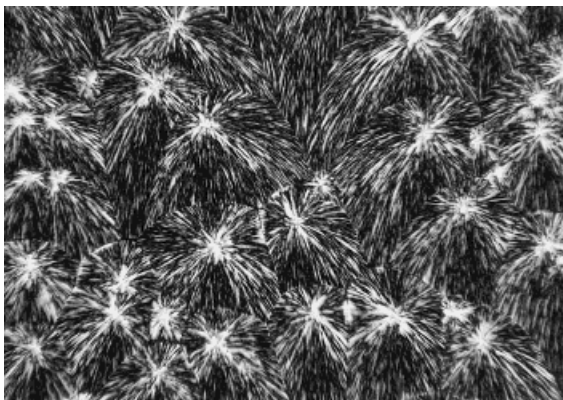


Figure 6 High-quality 95/5 blend (Sample 14, 1050 × 1600 μm).

line structure. Unfortunately, because the sample quality is so sensitive to processing conditions and very time consuming, it would be very difficult to manufacture these directionally solidified films in large volumes.

Pure isotactic samples, or 100/0 blends, were analyzed as well. Atactic interfaces did not exist because the samples did not contain any atactic PP (or only a negligible fraction). This held promise for developing mechanically testable samples because the samples would not be brittle due to the atactic interfaces. These 100/0 samples needed to be solidified at a higher temperature because they contained only isotactic PP that has a melting point of 189°C. Unfortunately, as the 100/0 samples were directionally solidified, voids (air bubbles) formed within the sample that were even larger than the ones in a 98/2 blend. Voids that were present prior to directional solidification grew approximately 10x in magnitude. Despite much effort to process the sample and directionally solidify it without any voids, not a single pure isotactic sample was directionally solidified without them. Even if samples did not contain voids prior to directional solidification, voids formed anyway. The most likely reason for this is that as a polymer crystallizes, it becomes denser, thus leaving air voids behind due to a reduction in volume of the polymer. Often when a 100/0, or pure isotactic, sample started to directionally solidify, an α -phase structure formed early on in the directional solidification for a very short period, as shown in Figure 7. Then, just prior to the transition to β -phase, the α -phase became highly oriented, as seen in Figure 4.



Figure 7 Unidirectional α -phase crystalline structure often present in early stages of directional solidification (Sample 27, $1050 \times 1600 \mu\text{m}$).

Once the β -phase structure formed, a few random α -phase spherulites still formed, shown in Figure 8, but the α -phase structure never reestablished itself as the predominant type. As found by previous researchers⁵ and confirmed by observations in this work, the β -phase crystalline structure is favored by slow growth rates, high temperature gradients, and large degrees of superheat in the melt, each of which tend to suppress nucleation. Thus, to prevent the β -phase from developing, the temperature of the hot reservoir block was reduced with hopes of increasing the growth rate and decreasing the temperature gradient and amount of superheat. When the temperature was reduced to the minimum temperature at which a crystalline structure still formed, the 100/0 samples did not directionally solidify with a typical unidirectional crystalline structure. Instead, the spherulites were very small and almost round, even at extremely slow pushing velocities, as seen in Figure 9a.

The PP blends that formed were also observed to be nonhomogeneous due to differences in the softening point of atactic PP versus the melting temperature of isotactic PP. The softening point of the atactic PP is 150°C , whereas the melting point of the isotactic PP is 189°C . Thus when a blended sample was being prepared, the temperature necessary to melt the sample had to be greater than 189°C . At this temperature, the atactic PP was subject to melting first and became less viscous than the isotactic PP. As the PP blend chips (obtained after evaporation of Xylene) were heated on the hot plate, it appeared that the atactic PP became very fluid, pooled around the edges, with the isotactic remaining in the center,

thus causing the sample to lose its homogeneity. Then, as the cover slide was gently pressed down to sandwich the PP sample, the atactic PP was squeezed outward to the sample edges and sometimes out of the sample completely onto the hot plate. This notion was also evidenced by noticing higher regions of atactic interfaces near the edges of some directionally solidified samples, whereas the center often had fewer atactic interfaces. It appeared that samples that remained on the hot plate longer, melted to a lower viscosity during sample fabrication that appeared to result in the separation of the two types of PP. A possible preventative measure is to sandwich the PP between the slide and cover glass as soon as possible, before the two types of PP have a chance to separate. Even though atactic PP melted first, puddled around the isotactic PP, and was then squeezed to the sample edges, there were noticeable differences between the different sample compositions, i.e., between the 100/0 and 98/2. Enough atactic material was hot melted and squeezed out of the sample, so the significant difference could be observed.

No significant effects of the sample cooling rate during sample preparation were observed. In most cases, the sample cooled within 5–10 s of removal from the hot plate by sliding the sample around on the lab table top. The microstructure was then analyzed and it was theorized that tiny spherulites had formed, but were basically too small to see even under the maximum power of the microscope. These small spherulites appeared as tiny specks as shown below in Figures 9b and 9c. Figure 9c shows the identical sample microstructure as seen in Figure 9b, only under a higher magnification.



Figure 8 β -phase crystal structure forming around a few α -phase crystals in a pure isotactic sample (Sample 27, $1050 \times 1600 \mu\text{m}$).

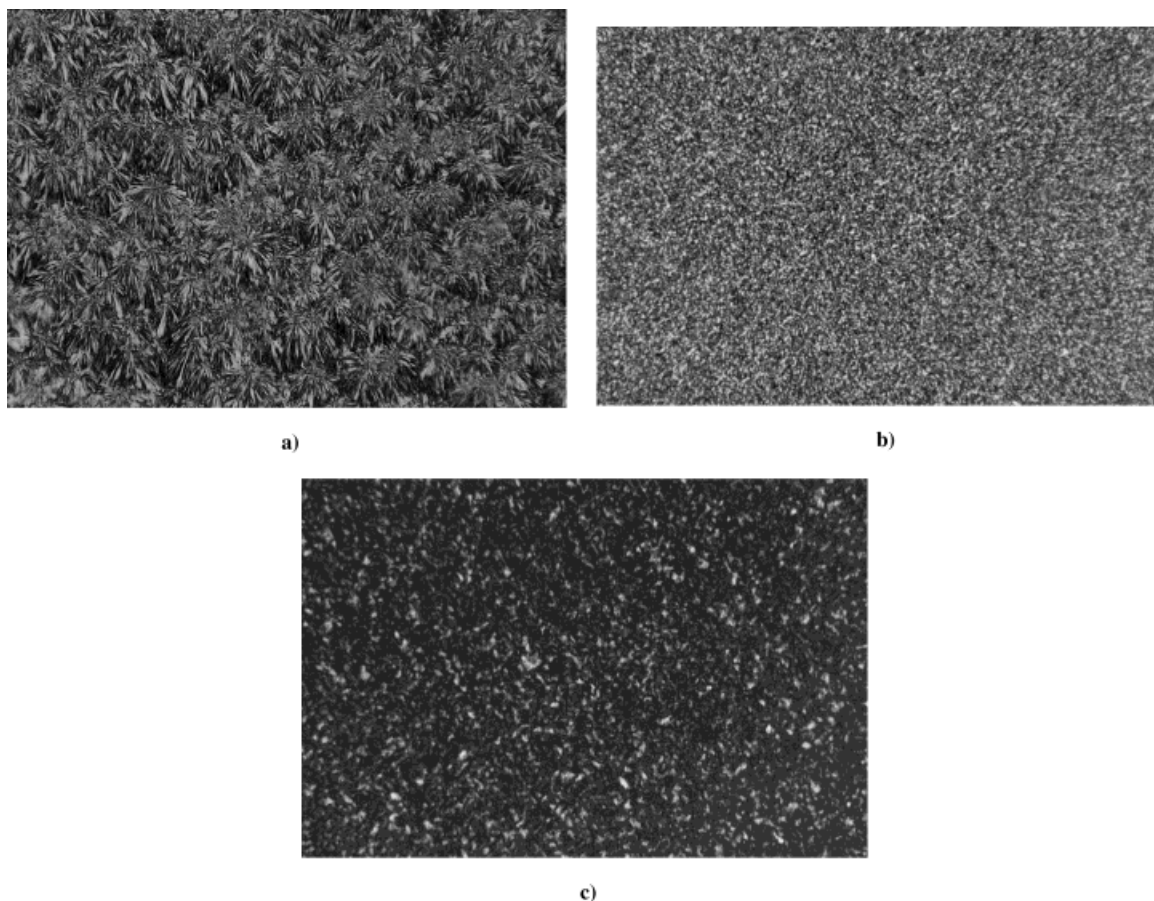


Figure 9 (a) Example of a pure isotactic α -phase crystalline structure (Sample 30, $1050 \times 1600 \mu\text{m}$); (b) 98/2 sample prior to DS ($1050 \times 1600 \mu\text{m}$); (c) Magnification of microstructure seen in (c) ($420 \times 620 \mu\text{m}$).

If the temperature of the hot reservoir block was not high enough, directional solidification did not take place. As the percentage of atactic PP decreased, the temperature necessary for directional solidification to occur decreased. Roughly speaking the minimum hot block temperature for DS to occur for 95/5 was 173°C , whereas it was 195°C for 100/0. The effect of superheating the sample was not analyzed in detail, but if the PP was heated to a temperature too high, then thermal degradation of the polymer would occur. The temperature at which degradation occurs was not determined because most samples were solidified just above the melting temperature.

The temperature of the hot plate used to prepare the sample was critical and probably played the most important role as far as sample quality is concerned. If the temperature was set too high, bubbles formed in the PP blend as the cover glass was pressed on. This issue could be minimized by

setting the temperature of the hot plate just above the melting point of the isotactic PP. Unfortunately, the hot plate used for sample preparation fluctuated in temperature more than was desirable. Also, it was very difficult to set the hot plate at a desired temperature due to the lack of precise control of the plate temperature. The hot plate temperature could change by as much as $\pm 30^\circ\text{C}$.

SIMPLE ANALYSIS OF DIRECTIONAL SOLIDIFICATION

As seen discussed previously, the temperature gradient is responsible for aligning the spherulites and suppressing nucleation in the melt. The temperature gradient applied in the apparatus was measured by embedding a thermocouple in the sample and measuring the temperature of the

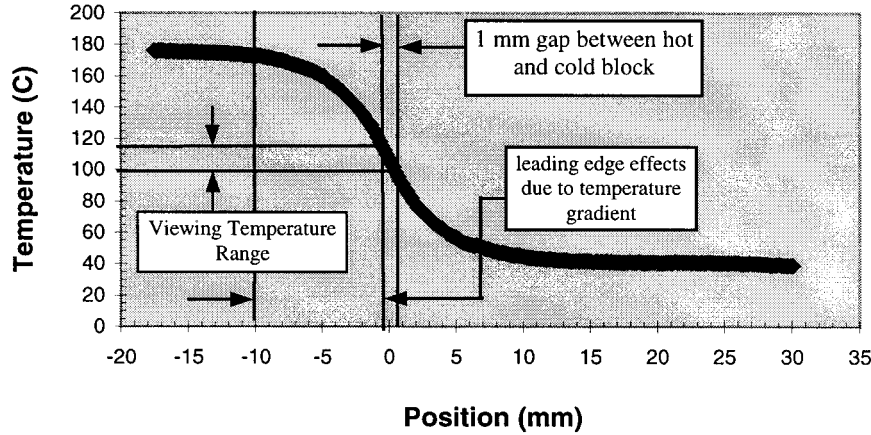


Figure 10 Temperature gradient “as seen” by the polypropylene on the slide.

sample as it was pushed across the device. Knowing the initial position of the thermocouple relative to the edge of the hot block and knowing the pushing velocity, it was possible to plot the temperature of the actual sample as a function of position on the directional solidification apparatus. This plot is shown in Figure 10.

The velocity at which a sample is pushed in the directional solidification apparatus is responsible for the orientation of the spherulites and generally speaking the slower the pushing velocity, the greater the orientation of the spherulites.

To obtain an uninterrupted growth front from a single nuclei, nucleation in the subcooled melt ahead of the front created by the growing lamella must be suppressed. An analysis presented by Lovinger and Gryte⁶ allows computation of the temperature gradient that may suppress nucleation in the directional solidification apparatus. This analysis is slightly modified and repeated below.

The number of spherulites that nucleates per unit time in a sample as it is pushed through a linear temperature gradient is given by

$$\dot{n}_T(T, x, t) = N(T)A \frac{dx}{dt} \quad (1)$$

where A is the cross-sectional area, dx/dt is the pushing velocity, and N is the total number of nuclei per unit volume that will appear at a given temperature. The total number of nuclei that will appear at a given temperature (assuming that the small volume considered, i.e., $A dx$, is roughly at a uniform temperature) can be obtained with

$$N(T) = N_r \exp[-\beta_N(T - T_r)] \quad (2)$$

where N_r and β_N are fitting parameters and T_r represents a reference temperature. This expression was found to give a satisfactory fit to experimental data for the nucleation of PP spherulites.⁷ The total number of nuclei can be found with

$$n_T = A \int_0^x N(T, x, t) dx = \frac{A}{T_G} \int_{T_m}^T N(T, x, t) dT \quad (3)$$

and substituting the value of N and carrying the integration, the following result is obtained

$$n_T = -\frac{N_r A}{T_G \beta_N} \{ \exp[-\beta_N(T - T_r)] - \exp[-\beta_N(T_m - T_r)] \} \quad (4)$$

where T_G is the temperature gradient applied. The conditions necessary to prevent the formation of new nuclei can be found by setting $n_T < 1$ or that

$$-\frac{N_r A}{T_G \beta_N} \{ \exp[-\beta_N(T - T_r)] - \exp[-\beta_N(T_m - T_r)] \} < 1 \quad (5)$$

In the above equation, the crystallization temperature is not known. However, in directional crystallization, the pushing velocity is adjusted so that the growing interface is located at a fixed

position and therefore at a fixed temperature. Numerous relationships are available to relate the growing interface to the crystallization temperature and one such expression is given by

$$G(T) = G_r \exp[-\beta_G(T - T_r)] \quad (6)$$

which can be used to simplify eq. (5) into

$$-\frac{AN_r}{\beta_N} \left\{ \left\{ \frac{G}{G_r} \right\}^{\beta_N/\beta_G} - \exp[-\beta_N(T_m - T_r)] \right\} < T_G \quad (7)$$

and values of all the constants and variables that appear in eq. (7) are needed. To estimate the value of the temperature gradient required to suppress nucleation if the growth velocity is 1 $\mu\text{m}/\text{sec}$, the following values were used:

$$N_r = 2 \times 10^9 \text{ m}^{-3}, \beta_G = 0.916 \text{ K}^{-1},$$

$$\beta_N = 0.18 \text{ K}^{-1}, G_r = 1.259 \times 10^{-6} \text{ m/s},$$

$$T_r = 115^\circ\text{C}.$$

In addition, a cross-sectional area of 10^{-6} m^2 and a melting point of 200°C were assumed. This allowed us to estimate that a temperature gradient of $110^\circ\text{C}/\text{mm}$ would suppress nucleation ahead of the growing interface. This temperature gradient is well above the gradients possible with our apparatus.

Furthermore, the pushing velocity V_p is related to the cooling rate by

$$\frac{\partial T}{\partial t} = V_p \frac{\partial T}{\partial x}$$

under steady operating conditions. For most cases, the temperature gradient observed was $20^\circ\text{C}/\text{mm}$, so a cooling rate was determined for various pushing velocities based on this gradient, as shown in Table II. The cooling rate affects the spherulites' growth rate and their nucleation. To better understand the effects of pushing velocity and cooling rate, samples were directionally solidified at various pushing velocities. First, an infinitely fast cooling rate was simulated by cooling the sample down virtually instantaneously by removing it from the 180°C hot reservoir block and sliding it around on a lab tabletop with the resulting microstructure in Figure 11a. This basically yielded the same microstructure as that of

Table II Cooling Rates, Given a Pushing Velocity and a Temperature Gradient of $20^\circ\text{C}/\text{mm}$

Pushing Velocity ($\mu\text{m}/\text{s}$)	Cooling Rate (degrees/minute)
10.00	12.00
5.00	6.00
1.00	1.20
0.80	0.96
0.60	0.72
0.40	0.48
0.15	0.18

the sample being cooled down during the fabrication of the sample, as shown in Figure 9b. Next, a slower cooling rate was observed by directionally solidifying a sample at pushing velocity of $10.0 \mu\text{m}/\text{s}$. At this pushing velocity, the formation of small crystalline structures became evident, but a random structure remains as evidenced by Figure 11b.

The next slower cooling rate observed was with a pushing velocity of $5.0 \mu\text{m}/\text{s}$ as shown in Figure 11c. With a decrease in pushing velocity comes a slightly more developed and organized crystalline structure, but yet still not slow enough to allow for the formation of distinct spherulites.

The majority of the samples were pushed at a velocity between 1.0 and $0.4 \mu\text{m}/\text{s}$ and the microstructure did not differ that drastically from one another. The microstructure consisted of spherulites that ranged in shape from round to elongated, with their orientation only slightly dependent on the pushing velocity. As the pushing velocity decreased, the crystalline microstructure became slightly more oriented, but other processing variables factored in, affecting the overall quality of the sample. Sometimes as the samples were pushed slower, atactic interfaces were more prevalent, as shown in Figure 11d, which seems to indicate that the cooling rate can determine the likelihood of atactic interfaces.

Finally, as each sample was prepared on the slide, its distance from the leading edge of the slide varied slightly. The distance from the leading edge refers to the distance from the leading edge of the slide to the point at which the sample is positioned on the slide. In the early samples it was positioned very close to the leading edge, but through experience it was found that positioning it approximately 10 mm from the leading edge negated leading edge effects. This distance can be

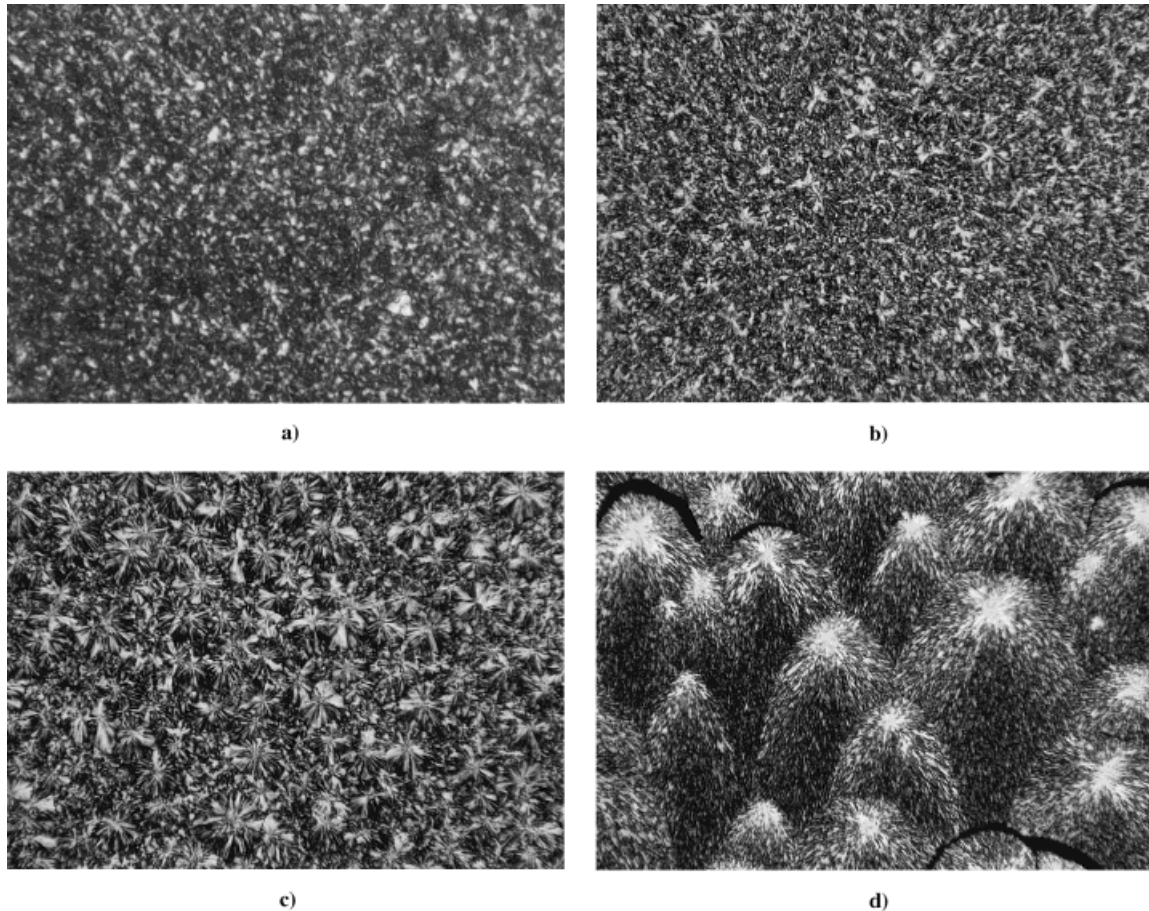


Figure 11 (a) “Instantaneous” cooling of a 95/5 sample after being held at 179.4° C for 1000 min or almost 17 h (Sample 18, 420 × 620 μm); (b) 95/5 sample pushed at 10.0 μm/s (Sample 12, 1050 × 1600 μm); (c) microstructure of a 95/5 sample pushed at 5.0 μm/s (Sample 33, 1050 × 1600 μm); (d) microstructure of a 95/5 sample pushed at 0.15 μm/s (Sample 33, 1050 × 1600 μm).

a significant factor because a temperature gradient exists in the slide while it is on the hot block. The temperature gradient that exists in the sample was obtained by placing an extremely small thermocouple within the sample and then directionally solidifying it. By knowing the initial position and velocity of the sample, the temperature as a function of time plot was converted to a temperature as a function of position plot, as seen in Figure 10. The position was calibrated with “0” being the center of the 1.0 mm gap between the hot and cold blocks. Notice the temperature gradient that exists in the sample when it is within 10 mm of the edge of the hot block. Thus, it was important to situate the sample approximately 10 mm from the leading edge, otherwise the entire sample would not reach a uniform temperature. These leading edge effects could result in an un-

desirable start to the directional solidification process.

RESULTS AND DISCUSSION

An Instron tensile tester was used to test the various specimens and the results are provided below. The testing procedure given by the American Society of Testing and Materials (ASTM D 882-90) was followed, except for the deviations given in Table I. A cross-head speed of 10 in./min was used for tensile testing. The output of the tensile testing machine included failure load and elongation, along with a plot of force as a function of cross-head extension. From this information the yield strength (σ_y) and elastic modulus (E) were computed. To determine whether or not the

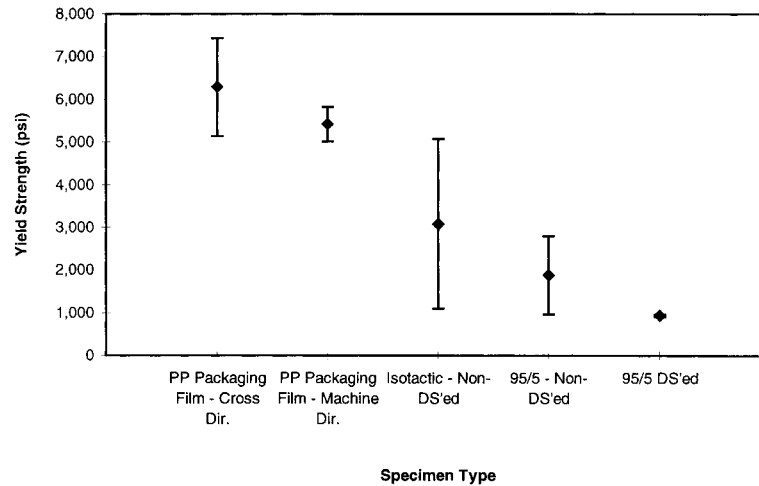


Figure 12 Yield strength of various specimens with 95% confidence regions.

mean values of yield strength and elastic modulus are significantly affected by the directional solidification process or can be attributed to random variations, a two sided Student's t-test was performed.⁸

Samples sufficiently large and ductile were fabricated and tested on an Instron tensile tester. Unfortunately, not all of them met the standards specified by ASTM. Deviations from these suggested specifications are listed in Table I for the various specimen types. The reason that specimens were smaller in width and that the grip length was shorter than recommended by the ASTM standard was due to the difficulty of processing samples sufficiently large to meet the ASTM size of 3" × 1". It was, however, much easier to fabricate the nondirectionally solidified

samples (100/0 and 95/5) than the directionally solidified samples.

The yield strength and elastic modulus were determined from the failure load and elongation given by the tensile tester, used in conjunction with the plot generated by the tensile test plotter. After making the necessary calculations, average values were computed with a confidence region of the standard deviations (2σ). A plus or minus 2σ range represents a 95.45% confidence region. The mean yield strength and elastic moduli with 95% (2σ) confidence are shown in Figures 12 and 13, respectively.

Unfortunately, it was determined that the directionally solidified specimens had the lowest yield strength of all samples tested, whereas the packaging film had the highest strength. Most

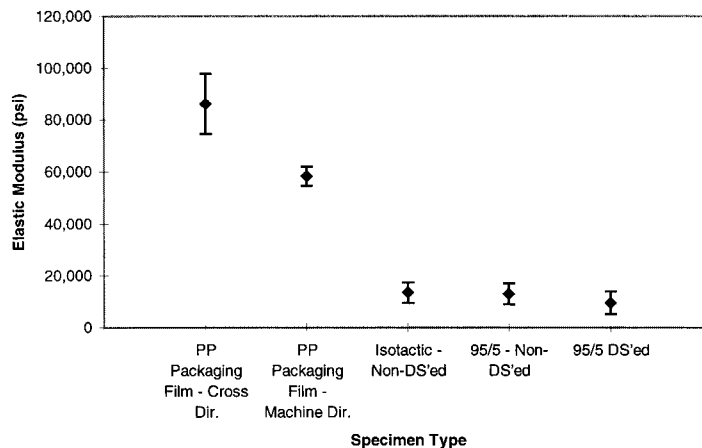


Figure 13 Elastic modulus of various specimens with 95% confidence regions.

Table III Two-Sided *t*-Test Between the Yield Strength of Various Specimens^a

	PP Packaging Film Cross- Direction	PP Packaging Film Machine Direction	Isotactic Nondirectionally	95/5 Nondirectionally	95/5 Directionally
PP packaging film cross-direction	*	2.49	6.13	11.61	16.22
PP packaging film machine direction	2.49	*	5.53	16.04	38.65
Isotactic nondirectionally	6.13	5.53	*	2.69	5.29
95/5 nondirectionally	11.61	16.04	2.69	*	5.04
95/5 directionally	16.22	38.65	5.29	5.04	*

^a For 95% confidence $t = 2.78$; For 98% Confidence $t = 3.75$.

likely the reason for this is that the packaging film is manufactured under very tight processing conditions, whereas the samples used here were manufactured with less expensive equipment. Therefore, an optimal manufacturing process was not achieved.

The large confidence region for the isotactic nondirectionally solidified specimens can be attributed to the inaccurate method used to measure its cross-sectional area. The method of determining the nondirectionally solidified specimen thickness could have possibly resulted in strengths recorded 50% larger than their actual strength, which might be a possible explanation for the average and confidence region to be larger than that of the 95/5 nondirectionally solidified and the 95/5 directionally solidified specimens. The confidence region of the 95/5 nondirectionally solidified specimens could also be improved by improving the method of determining their cross-sectional area. It is surprising that a larger confidence region in the packaging film's cross-direction resulted than in the machine direction. Because the testing method was conducted very carefully and no observable differences appeared, it is believed that the larger confidence region in the cross direction might be attributed to polymer chain arrangement during manufacturing.

The elastic moduli of the PP packaging films are significantly higher than the others, again most likely due to the perfected industrial manufacturing process. The 100/0 nondirectionally solidified, 95/5 nondirectionally solidified and the 95/5 directionally solidified specimens all have very similar elastic moduli. This similarity between them is further analyzed by conducting *t*-tests in the following section.

The computed value of "*t*" for each pair of specimens can then be compared to *t*-values of those provided for 95% and 98% confidence levels.⁸ These confidence level *t*-values are based on the most conservative estimates by using the minimum number of degrees of freedom encountered. To interpret these results, if the computed *t*-value for a pair of specimens is greater than that provided by the confidence level, then the arithmetic means can be considered significantly different, otherwise they are considered to be different only by random variation.

In Table III, it is seen that two combinations of compared specimens have a *t*-value that does not produce a 95% or 98% confidence of their means being significantly different. When comparing the mean yield strength of the 100/0 nondirectionally solidified specimens with 95/5 nondirectionally solidified specimens, there appears to be no significant difference in yield strength, as seen by a *t*-value of 2.69. Thus, it appears that adding atactic PP to pure isotactic PP has little effect on the strength of the PP. Also, the difference between the mean yield strength of the PP packaging film cross-direction and machine direction, is not significantly different as seen by a *t*-value of 2.49. Despite having very similar yield strengths, the cross- and machine direction of PP packaging films have very different elastic moduli, as seen in Table IV.

When comparing the average values of the elastic modulus, it appears that there are a few combinations of specimens that do not produce significantly different elastic moduli as seen in Table IV. When comparing the 100/0 nondirectionally solidified to the 95/5 nondirectionally solidified there is virtually no difference between

Table IV Two-Sided *t*-Test Between the Elastic Modulus of Various Specimens^a

	PP Packaging Film Cross- Direction	PP Packaging Film Machine Direction	Isotactic Nondirectionally	95/5 Nondirectionally	95/5 Directionally
PP packaging film cross direction	*	7.92	24.09	21.14	21.37
PP packaging film machine direction	7.92	*	33.86	33.65	29.65
Isotactic nondirectionally	24.09	33.86	*	0.39	2.65
95/5 nondirectionally	21.14	33.65	0.39	*	2.32
95/5 directionally	21.37	29.65	2.65	2.32	*

^a For 95% confidence $t = 2.78$; For 98% Confidence $t = 3.75$.

their elastic moduli as seen by a t -value of 0.39. Two other combinations of specimen elastic moduli comparisons do not meet 95% confidence of having significantly different elastic moduli means. When comparing the elastic modulus of the 95/5 directionally solidified specimen, to either the 95/5 nondirectionally solidified or 100/0 nondirectionally solidified specimens, it can be seen by their t -values that their elastic moduli are similar only by chance. Again it appears that the amount of atactic PP present in a specimen has little effect on its elastic modulus.

CONCLUSIONS

Directional solidification of PP using various compositions and processing conditions was performed, which yielded samples consisting of an oriented α -phase. Unfortunately, the sample quality was not very reproducible under nearly identical processing conditions. This lack of reproducibility most likely stems from the sample fabrication method in which the homogeneity and air entrapment within the sample were difficult to control. Also, in many samples there was only minimal orientation of the microstructure, including the specimens used for tensile testing. This is attributed to the insufficient temperature gradient used and this is supported by simple calculations.

Directionally solidified samples were tested in tension and compared to nondirectionally solidified samples and PP packaging films. It was found that mechanically testable directionally solidified

samples could be manufactured, but it was not possible to realize improved material properties, namely yield strength and elastic modulus, based on the results of three directionally solidified samples. However, it may be possible to improve and optimize the directional solidification of PP process enough to provide multiple, consistent samples with improved mechanical properties. A greater understanding is necessary to eliminate air bubble formation and to control the rejection of the atactic PP as the spherulites grow, forcing the atactic material to be pushed to the spherulites interfaces, thus resulting in weak interfaces.

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