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**EXPERIMENTAL STUDY OF POST-SHEAR CRYSTALLIZATION
OF POLYPROPYLENE MELTS**

by

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**A thesis submitted to the Faculty of Graduate Studies and
Research in partial fulfilment of the requirements of the degree of
Master of Engineering.**

October 1997

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ABSTRACT

The properties of plastics products are governed by their crystallinity and morphology. In order to study the effects of processing shear stresses on crystallization behavior, a fiber pullout technique was applied in conjunction with polarized light microscopy and a hot stage. The shear apparatus consists of a single glass fiber sandwiched between two layers of polypropylene films mounted on the hot stage. At the crystallization temperature, shearing was introduced by pulling the fiber at a constant velocity for a fixed period of time. Static crystallization of the polymer then ensues. Computerized data acquisition and image analysis were employed to observe the evolution of crystallinity, morphology, and growth rates of crystallites in various shear and temperature fields.

Two distinct morphological zones were produced upon fiber pullout: bulk spherulites and a shear-induced layer localized within the vicinity of the fiber surface. The two zones displayed similar kinetic behavior despite the difference in appearance. Comparison of growth behavior in the two zones revealed rates independent of the shear rate but strongly dependent on crystallization temperature. Such a behavior in the shear-induced layer suggests the existence of different growth regimes for a range of shear rates. Only when the critical shear rate is surpassed is there a substantial increase in the growth rate of the shear-induced layer.

SOMMAIRE

Les propriétés des pièces en matériau plastique sont déterminées par la cristallisation et la morphologie. Afin d'étudier l'effet des contraintes de cisaillement présentes lors des procédés de transformation, la technique d'écoulement en cisaillement autour d'une fibre a été utilisée. Cette technique a été employée en conjonction avec une plaque chauffante, ainsi qu'un microscope optique en lumière polarisée. Le dispositif de cisaillement consiste en une fibre de verre unique intercalée entre deux couches de films de polypropylène, et placé sur une plaque chauffante. A la température de cristallisation, le cisaillement est appliqué en tirant sur la fibre à vitesse constante pour un temps déterminé. La cristallisation du polymère en condition statique s'ensuit. L'acquisition de données par ordinateur et l'analyse d'images ont été utilisées afin d'observer l'évolution de la cristallisation, de la morphologie, ainsi que les taux de croissance des sphérulites sous diverses conditions de température et de cisaillement.

Deux zones morphologiques distinctes ont résultés du cisaillement imposé par le déplacement de la fibre: des sphérulites dans le volume et une structure cylindrique, causée par le cisaillement, au voisinage de la fibre de verre. Les deux zones ont présenté, d'un point de vue cinétique, des comportements semblables en dépit de leurs aspects différents. Pour chaque zone, l'analyse des résultats a révélé des taux de croissance indépendants du taux de cisaillement, ainsi qu'une dépendance avec l'inverse de la température de cristallisation. Une telle caractéristique suggère, pour la structure cylindrique, l'existence de différents régimes de croissance pour un intervalle des taux de cisaillement étudiés. Un changement est observé dans le taux de croissance de la structure cylindrique uniquement lorsque le taux de cisaillement critique est dépassé.

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1. INTRODUCTION

In the processing of crystallizable polymers, the mechanical properties of the final product are highly dependent on the microstructure of the material. The resultant crystallization kinetics and morphologies are easily altered by pressure, temperature and shear. Extensive studies performed on the dependence of polymer crystallization under various external parameters have elucidated the fundamental structures involved, beginning with the nucleus.

Primary nucleation is the process by which a small structural entity of a new phase, the nucleus, is initiated within the amorphous state of the polymer matrix. The nucleus gives rise to the formation of spherulites or growing crystals, which determine the final crystallinity of the product. A thermodynamic description of the crystallization process can be described by the Gibbs free energy equation:

$$\Delta G = G_{\text{crystal}} - G_{\text{melt}} \quad (1.1)$$

$$\Delta G = \Delta H - T\Delta S \quad (1.2)$$

or more precisely for polymeric systems^{1,2} as

$$\Delta G = \Delta G_c + \sum A\gamma \quad (1.3)$$

where ΔH is the enthalpy of crystallization, ΔS is the entropy of crystallization, ΔG_c is the free enthalpy of crystallization, γ is the specific surface free energy and A is the corresponding surface area. A schematic of the process is shown in Figure 1.1.

For temperatures below the melting temperature of the polymer, ΔG exhibits a maximum value corresponding to the critical nucleus size. Nuclei to the left are subcritical nuclei, while those to the right are called supercritical. Stable nuclei or small crystals are formed when ΔG is negative. However, in order to achieve the thermodynamically stable crystal, the primary nuclei must first pass the positive ΔG path. Therefore, the larger the required size of the nucleus, the longer the nucleation process will be. A change in pressure, crystallization temperature or shear will affect the formation of the critical nucleus and thus the mechanical properties of polymers.

Figure 1.1 Change in free enthalpy as a function of size illustrating the nucleation process.¹

Primary nucleation can be classified as homogeneous or heterogeneous. Homogeneous nucleation occurs due to the internal restructuring of molecular chains leading to the formation of nuclei. Heterogeneous nucleation occurs due to the presence of preformed nuclei or foreign surfaces which function to lower the critical nucleus size.

New layers on a crystal surface can be formed by secondary and tertiary nucleation processes which are similar to primary nucleation. The only difference is a lowering of the free energy barrier due to the creation of a smaller surface area. The results of secondary and tertiary crystallization processes are a reorganization of the crystalline regions, producing more perfectly formed crystallites.³

Hoffmann et al.⁴ described the rate of nucleation, N , in polymers as:

$$N = N_0 \exp\left(-\frac{U^*}{R(T - T_\infty)}\right) \exp\left(-\frac{\Delta G^*}{kT} f(\theta)\right) \quad (1.4)$$

with

$$T_\infty = T_g - 30K \quad (1.5)$$

$$\Delta G^* = \frac{\beta \sigma_e \sigma^2 T_m^2}{(\Delta h f(T))^2 \Delta T^2} \quad (1.6)$$

$$f(\theta) = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} \quad (1.7)$$

$$f(T) = \frac{2T}{T_m + T} \quad (1.8)$$

where N_0 is a pre-exponential factor, U^* is the activation energy for molecular transport from the melt to the crystal surface, R is the gas constant, T_∞ is the Gibbs-di Marcio equilibrium glass transition temperature and k is the Boltzmann constant. For ΔG^* , β is a geometric constant and equals 32, T_m is the melting temperature, Δh is the heat of fusion per unit volume, ΔT is the supercooling, σ and σ_e are the crystal growth and end face surface energies and the function $f(T)$ corrects for the change of the heat of fusion with supercooling. Under homogeneous nucleation, $f(\theta)$ assumes a value of 1 ($\theta=180^\circ$) whereas, for heterogeneous nucleation, $0 < f(\theta) < 1$ since the wetting contact angle is $0 < \theta < 180^\circ$.

The spherulite growth rate, G , is then given by

$$G = G_0 \exp\left(-\frac{U^*}{R(T - T_\infty)}\right) \exp\left(-\frac{\beta b \sigma \sigma_e T_m}{kT(\Delta h f(T))\Delta T}\right) \quad (1.9)$$

where the notations are the same as before except for b which is the thickness of the macromolecular segment deposited on the growth face and β which is a coefficient dependent on the growth regime present.

From the above equations, it is clear that the nucleation and growth rates are very sensitive to the crystallization temperature as shown in Figure 1.2.

Figure 1.2 Isotactic polystyrene spherulite radial growth rate as a function of the crystallization temperature.³

1.1. MORPHOLOGY

1.1.1. BIREFRINGENCE

Birefringence measures order in the axial direction and is defined by

$$\Delta n = n_1 - n_2 \quad (1.10)$$

where n_1 and n_2 are the refractive indices along two orthogonal directions.^{5,6} Although birefringence is a convenient index for orientation, its magnitude and sign may vary considerably from system to system due to differences in chemical nature and composition. A birefringent material may even inhibit the transmission of light in some cases. This optical extinction will occur if the thickness of the birefringent area is less than one wavelength; if the optical axis is parallel to the polarizer direction; or if the

direction of the light is parallel to the optic axis. There are three different types of birefringence.

1.1.1.1. Orientation Birefringence

Orientation birefringence arises when there is an alignment of optically anisotropic molecular chains. When the chains are randomly arranged, the net refractive index is the same for all directions in the material. However, under manufacturing processes such as drawing or extension, the randomness is disturbed by alignment of the chains. The refractive index of the material then varies with the material direction.

1.1.1.2. Deformation Birefringence

Deformation or strain birefringence occurs in materials under stress. The load per unit volume can alter the distance between the atoms of the material, changing the polarizability of the bonds in the direction of the applied stress. This effect can occur in isotropic and anisotropic materials.

1.1.1.3. Form Birefringence

Form birefringence occurs in a medium containing two or more separate phases with different refractive indices. It has been found in styrene-butadiene block copolymers. Form effects have also been shown to contribute to birefringence in simple semi-crystalline polymers such as polyethylene.

1.1.2. POLARIZED LIGHT MICROSCOPY

Polymeric structures can be characterized visually with the aid of microscopy due to their birefringent nature. The polarizing microscope is equipped with a pair of polarizing filters above and below the specimen. When the two polarizers are orthogonal, light is prohibited from passing through unless the specimen causes interference by splitting the beam. The specimen will appear bright against a dark background. This

occurs only if the molecules are optically anisotropic (Figure 1.3). A visual record of spherulite size density, distribution and growth pattern can be obtained.

Figure 1.3 Polarized light micrograph of LLDPE.⁷

1.1.3. SPHERULITES

Under quiescent conditions, semicrystalline polymer melts form regular birefringent structures with circular symmetry called spherulites. Spherulites are composed of fibrils which grow radially outward from the nucleus into the amorphous phase. Polymer chains are imbedded in the fibrils as a series of lamellar crystals winding helically along the growth direction (Figure 1.4). Consequently, the molecular chains lie at right angles to the fibril axis. As the fibrillar growth advances, a network is produced as branching occurs due to defects in fibril structure or unincorporated amorphous polymer.^{3,8-9}

Spherulite growth continues until impeded by neighboring spherulites, causing polygonized structure formation. This primary crystallization is highly temperature sensitive and is nucleation controlled.

Figure 1.4 Spherulite composed of chain folded lamellae and branching points.³

1.1.4. TRANSCRYSTALLIZATION

When a heterogeneous substance is present in a polymer melt, it can serve as a nucleating site, leading to a phenomenon known as transcrystallization. Transcrystallization occurs when nucleation at a foreign surface is so profuse as to inhibit three-dimensional growth due to adjacent growing nuclei.^{5,6,10} This results in morphology consisting of unidirectional lamellar growth of spherulites normal to the surface. An optical micrograph of a transcrystalline polyethylene growth induced by an aluminum surface is shown in Figure 1.5.

Transcrystallinity is most commonly observed in supercooled melts of composite materials. Many researchers have looked into the possible side effects or even benefits of the presence of such a layer. However, due to its strong dependence on substrate characteristics and crystallization parameters, the appearance of the layer is still unpredictable and its effects debatable.¹¹⁻¹⁷

Figure 1.5 Transcrystalline region in polyethylene grown in contact with an aluminum surface.¹⁰

1.2. STRESS EFFECTS ON CRYSTALLIZATION

1.2.1. THEORY OF FLOW INDUCED CRYSTALLIZATION

The polymer melt consists of coiled and intercoiled molecules in a random configuration at a state of maximum entropy. Melts undergoing processing exhibit an increased rate of crystallization when compared to quiescent melts. This phenomenon is termed flow induced crystallization and two mechanisms have been postulated to explain the observed behavior.

The first mechanism envisions a highly entangled mass of polymer molecules restricted in molecular movement. When process stress increases, molecular extension is generated through the orientation and slippage of polymer chains. Ultimately, this could lead to disentanglement. Orientation of the molecules is achieved by the formation of nucleation lines from which lamellae grow out radially, perpendicular to the flow. As the

chains become ordered, conformational entropy decreases, and the equilibrium melting temperature increases. Thus, crystallization of stressed polymers takes place at a higher temperature than under quiescent conditions.¹⁸⁻²⁵

The second mechanism suggests that heterogeneous particles in the melt may cause localized flow disturbances, which increase molecular stretching and enhance nucleation. This mechanism has been disputed, as some studies found that introduction of heterogeneous particles had no effect on either quiescent or stressed melts. Nucleating agents, however, did increase the rate of crystallization as interaction with polymer molecules increased nucleation density.^{19,26}

1.2.2. MORPHOLOGY

Investigation into the morphology of polymer samples has revealed a consistent shishkebob structure upon the introduction of shear stresses.²¹ Although most of these investigations are isolated studies, they can be translated to stresses experienced and morphology recorded in injection molded samples.

As shown in Figure 1.6, the kebobs are not lamellar overgrowth depositions but rather structures molecularly incorporated into the fiber backbone by a two-stage mechanism. Extended chain nuclei are first formed followed by the growth of the twisted or parallel lamellar crystals. The kebob size and diameter depends on the rate and temperature of the quench, or its thermal history.

Figure 1.6 Shishkebob morphology.²¹

Microscopy suggests a proportional increase in the number of crystalline structures formed with applied stress. Under high levels of shear stress, the crystalline structure can become so profuse that it is indiscernible under the microscope (Figure 1.7). In almost all cases, the time required for completion of radial growth of spherulites was much less than those under quiescent conditions.²⁶⁻²⁸

Figure 1.7 HMWLPE after crystallization at 120°C under various shear stresses. (a) quiescent conditions, (b) $\sigma = 1.36 \times 10^5$ dynes/cm³, (c) $\sigma = 2.71 \times 10^5$ dynes/cm³, (d) $\sigma = 5.42 \times 10^5$ dynes/cm³.²⁶

Upon close examination of injection molded polyethylene, Kamal and Tan²⁹ noted four distinct morphological zones across the longitudinal cross section. With increasing distance from the surface of the molded sample, the four structures are: nonspherulitic, small asymmetric spherulites, oblate asymmetric spherulites and randomly nucleated spherulites at the core. Fujiyama et al.³⁰ showed that injected molded polypropylene

displays a well-defined two-phase structure of skin and core. The skin layer is further distinguished by an outer oriented amorphous layer and an inner oriented crystalline layer.

1.3. SHEAR STRESS EXPERIMENTS

All plastics processing operations involve the application of heat and stress, often at high shear rates. As a result, the polymer is subjected to a myriad of deformational mechanisms. Due to this intrinsic complex nature, many isolated studies on the sole effects of shear stress on polymer melts have been performed with the intent of providing a basis for the observed phenomena.

1.3.1. COUETTE TYPE EXPERIMENTS

Studies of the effects of shear stress on polymer crystallization were first performed using Couette type viscometers. The polymer sample is placed in the annular region and is melted. As the sample is quenched to the crystallization temperature, one of the concentric cylinders is rotated inducing shear stress. The resultant transmitted stress and the viscosity of the polymer are measured as a function of time. A rapid increase in the viscosity function indicates the onset of crystallization.

Kobayashi and Nagasawa³¹ observed a rapid increase in the rate of crystallization and the rate of nucleation with the introduction of shear. Electron micrographs revealed lamellar crystals which grew perpendicular to the direction of flow. The thickness of the lamellae and the growth rate differ from those found in quiescent melts.

Fritzsche and Price¹⁸ modified the basic Couette viscometer by adding a dilatometer to the apparatus. The polymer sample occupies the top of the inner cylinder and the annular region while the bottom is filled with mercury. The polymer is first melted by an electrical resistance heater. Then it is quenched to the crystallization

temperature by a bath of circulating water. Measurement of the change in the height of mercury indicates the change in volume as shearing progresses. The resulting data are used to study the effect of shear on crystallization kinetics.

As shear rate increased, a corresponding increase in melting temperature, nucleation rate and orientation is observed. However, with an increase in crystallization temperature, the nucleation rate, growth rate, crystallization rate and viscosity decreased. They also noticed that crystallization occurs sooner and much more rapidly for high molecular weight materials than for low molecular weight materials.

One major disadvantage in using cylindrical rheometers is due to the viscous heating effects which produce significant temperature gradients within the melt. Moreover, the bulky size of the equipment presents a greater difficulty in cooling the melt and controlling the crystallization temperature with a short lag time. Parallel plate devices were employed to avoid the above problems.

1.3.2. SLIDING PLATE EXPERIMENTS

The rectilinear motion of one flat plate relative to another can generate simple shear flow. One technique often used is the placement of a thin polymer sample between glass slides and then deforming the sample in shear by applying a load to one of the glass slides. The crystallization process can be viewed and recorded simultaneously with a polarizing microscope, while a differential transformer allows measurement of the displacement of the glass slide with time.

Haas and Maxwell²⁶ developed a continuous test setup permitting melting and supercooling of the polymer sample in situ by means of moveable heating guns. Under high shear stresses, they observed a marked decrease in crystallization time, an earlier onset of crystallization with increased supercooling or with low molecular weight polymers, a large increase in the number of spherulites formed (see Figure 1.7 on page 10), and the development of oriented morphologies.

Lagasse and Maxwell¹⁹ further investigated the effects of shear on induction time of samples with different molecular weights. With low molecular weight polyethylene samples, there exists a critical shear rate, γ_c , above which shear accelerated crystallization occurs (Figure 1.8). Above γ_c , the typical lamellar structure is observed; below γ_c , an unoriented spherulite structure is obtained, similar to those derived from quiescent melts. High molecular weight PE samples, however, displayed accelerated crystallization at all levels of shear. They suggested that the critical condition is governed by disentanglements between polymer chains.

Figure 1.8 Polyethylene crystallization kinetics under various shear rates and crystallization temperatures.¹⁹

1.3.3. CAPILLARY EXPERIMENTS

Pressure driven flow through tubes occurs most often in melt processing, whether it is in an extrusion die or in the runners of an injection mould. As such, in an attempt to represent the injection molding process more accurately, capillary experiments were performed with the proviso that memory effects can be neglected. Most capillary rheometers operate on the basis of a constant velocity piston driving melted polymer from the reservoir to the capillary. Melt pressure can be measured by using a force transducer on the piston or a pressure transducer near the capillary entrance.

Titomanlio and Marrucci³² modified a typical capillary rheometer with a downstream reservoir to allow for higher pressures at the exit. Crystallization experiments analyzing changes in pressure against temperature showed a critical temperature at which pressure rises dramatically (Figure 1.9). This increase was interpreted as a result of flow induced crystallization. Larger effects were encountered when the flowrate, capillary length, and pressure drop were increased.

Figure 1.9 Typical curve of the pressure upstream of the main capillary as a function of temperature for HDPE.³²

Kim and Kim²⁷ believe that the profuseness of nuclei obtained from samples sheared through the capillary are due to microscopic, and not macroscopic, ordering. The observed increase of nuclei occurred only after an initial induction time required for the formation of stable nuclei. Under low shear rates, DSC exotherms indicate two separate peaks suggesting two different and independent crystallization mechanisms. The 'fast' process, as represented by the first peak, is due to the crystallization of the disentangled molecules while the 'slow' process arises from the crystallization of the highly entangled molecules. As the shear rate increases, the fast process dominates the overall crystallization process.

Figure 1.10 Change of isothermal crystallization exotherms at 120°C with shear rate.²⁷

Ness and Liang²⁴ observed the same patterns of behavior by monitoring the entry pressure drop with shear rate. At low test temperatures, the entry pressure drop displayed two peaks while at high test temperatures, only one peak was observed. They believe that the main factors affecting flow induced crystallization are: temperature, flow rate, and geometry. The onset of flow induced crystallization can be enhanced by lowering the operating temperature to values near the melting point of the material and by using a die with larger entry angles.

1.3.4. BICONICAL TYPE EXPERIMENTS

Tan and Gogos²⁰ used a biconical rheometer to evaluate shear stress responses directly during flow induced crystallization. A typical curve is shown in Figure 1.11 and can be explained by four regions of behavior. In the first region, a classic stress overshoot phenomenon is observed with all polymeric melts. Region two represents the steady flow response of the melt from which the viscosity of the material can be obtained. The transition between the second and third regions is the incubation time for phase transformation and is related to the rate of nucleation. Flow induced crystallization occurs in regions three and four as stress within the melt increases due to slippage of polymer molecules, leading to crystallization.

Figure 1.11 Typical stress response for flow induced crystallization.²⁰

Model simulations of crystallinity gradients developed in injection molded polymers were performed by Hsiung and Cakmak.²² Their structure-oriented model predicted an enhanced stress crystallized layer at lower injection flow rates and at lower mold temperatures.

1.3.5. FIBER PULLOUT EXPERIMENTS

The fiber pullout technique stems from a modification of the sliding plate experiment. The setups are equivalent, except that shear is generated by the axial movement of an imbedded fiber within the polymer matrix between two glass slides (Figure 1.12).

Figure 1.12 Schematic of the fiber pullout technique.

Early studies introduced shear by tugging the fiber manually at an unknown rate for a short period of time. The principle objective was to observe any distinct morphological changes derived from shear. Gray³³, Misra et al.¹³ and Devaux et al.³⁴ observed the appearance of a shear-induced layer, similar in appearance to a transcrystalline layer, around the fiber. They suggested that shear stresses produce molecular orientation along the axial direction, resulting in a reduction in entropy. The melting temperature and the degree of supercooling are thus enhanced, leading to an increase in crystallization rates.

As the technique was refined by implementing a constant pulling speed, the appearance and growth of the transcrystalline layer was evaluated. Thomason and Van Rooyen³⁵ observed that a low level of applied stress was sufficient to create a shear-induced layer for a Twaron aramid fiber/PP system. Tribout et al.³⁶ noted that growth rates were higher under shear than after the cessation of shear. Aside from the shear rate, other factors which have been considered are the shearing temperature,^{37,38} the cooling rate³⁵ and the crystallization temperature.³⁸

1.4. OBJECTIVES

The previous section outlined some of the techniques and problems associated with the study of shear induced crystallization. These methods are either bulky in terms of equipment size, require large sample sizes, involve significant viscous heating effects, have variable shear fields, or cannot be easily coupled with optical instruments for morphological observations. To avoid these problems, we propose the use of the fiber pullout technique.

In light of the above, the objectives of this research are:

- 1) To examine the effects of localized and long-range shear on crystallization of polymer melts by applying and refining the fiber pullout technique.
- 2) To evaluate the effects through morphological observations and kinetic measurements.

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2. EXPERIMENTAL

2.1. MATERIALS

2.1.1. POLYPROPYLENE

A general-purpose polypropylene (PP) homopolymer resin designed for injection molding was used for the experiments. Profax 6523, produced by Montell Polyolefins, shows high resistance to solvents and chemicals, high stiffness, good storage life and excellent resistance to environmental stress cracking. The PP resin complies with the U.S. Food and Drug Administration requirements and is typically used in the automotive and food industries. The physical properties of Profax 6523 are reported in Table 2.1 and the molecular weight distribution curve is shown in Figure 2.1. The ordinate, dRI, is the differential refractometer index measured in volts.

The melt flow index measures the mass of polymer that is extruded through the capillary in 10 minutes and is expressed as the flow rate/10 minutes. The shear thinning transition indicates the stress at which a further increase would result in a decreased resistance to fluid flow or shear thinning behavior.

Isotactic polypropylene is known to exist in four forms: monoclinic α , hexagonal β , triclinic γ and δ phases. The α monoclinic structure is the most common and best characterized. It crystallizes from the melt in the form of an ordered birefringent spherulite. [Section 1.1.3.] The β , γ and δ structures are metastable and are less understood in terms of formation. The presence of these structures elicited the careful consideration of the experimental conditions discussed in Section 2.2.4.1.

Table 2.1 Physical Properties of Profax 6523

Molecular Weights:

M_n (g/mol)	8.27×10^4
M_w (g/mol)	4.25×10^5
M_z (g/mol)	1.02×10^6
M_w/M_n	5.14

Processing:

Melt Temperature Range (°C)	228-274
Mold Temperature Range (°C)	21-49

Properties:

Melt Flow Rate (dg/min)	4
Density (g/cm ³)	0.9
Melt Density (g/cm ³)	0.746
Specific Heat (J/kg·°C)	2952
Melt Thermal Conductivity (J/m·s·°C)	0.139

Viscosity Model Constants:

Power Law Index, n	0.2937
Shear Thinning Transition, τ (kPa)	16.84

Mechanical Properties:

Tensile Strength at Yield (MPa)	34
Elongation at Yield (%)	12
Rockwell Hardness (R Scale)	85
Deflection Temperature (°C at 455 kPa)	97

Figure 2.1 Molecular weight distribution curve for Profax 6523.

2.1.2. FIBERS

Several fibers were considered for the application of the fiber-pull out technique. The first and foremost criterion used in the final selection was that the fiber should not induce transcrystallinity under quiescent conditions. The properties of the fibers considered in this work are listed in Table 2.2.

Fibers are most often treated with molecular additives or coupling agents to improve interfacial adhesion between the fiber and the polymer matrix. The coupling agents are designed to initiate a chemical reaction at the interface to promote chemical bonds. Other processing aids such as binder, lubricant, wetting agent and antistatic agent

are mixed with the coupling agent to produce the most compatible product for a specific application. The contribution of sizing to composite properties has been known to create an interphase surrounding the fiber whose properties may be different from those of the polymer matrix.¹ In terms of fiber processing, it has been shown that the sizing is not uniformly distributed. All these factors may affect the final properties of the composite.

Table 2.2 Fiber Properties

	DACRON® POLYESTER	DU PONT® NYLON	NOMEX® ARAMID	VETROTEX® GLASS FIBER
Breaking Strength (N)	1.84	1.63	1.3	-
Elongation at Break (%)	14.9	21.1	28	3.4
Average Filament Diameter (μm)	20	15	18	20

- Not given

Due to the proprietary status of the sizing formulation, most companies do not disclose details of the sizing composition. Of the fibers considered, the Vetrotex glass fiber is known to have a silane-type sizing that is most compatible with polyester, vinyl ester and epoxy resin systems. Information for the other fibers was not disclosed.

2.2. EXPERIMENTAL TECHNIQUES

2.2.1. APPARATUS

A schematic of the experimental setup is shown in Figure 2.2. The evolution of polymer crystallinity and morphology under static and shear conditions is observed with a Leitz Laborlux 12 Pol S polarized light microscope equipped with a hot stage and an

Figure 2.2 Experimental apparatus.

image recording system (Javelin Electronics Chromachip II camera, Model JE3462HR). Temperature readings are measured with a K-type thermocouple inserted within the hot stage [see Section 2.2.5.] and are recorded continuously with a computerized data acquisition system. A three-gear motor with a velocity range of 0.08 mm/s to 50 mm/s is used to shear the polymer samples.

Figure 2.3 shows a specially designed sample holder used to prevent movement of the polymer during shear. It is mounted on top of the hot stage and its extended arm is attached to the periphery of the microscope. The composite is placed in the center portion. To ensure uniform sample thickness throughout the experiment, bars on opposite sides of the holder glide over the top glass slide of the polymer sandwich. Thin slits along the diagonal of the holder allow controlled fiber placement and movement during shear. A glass cover is then placed over the sample holder to minimize heat loss.

Figure 2.3 Sample holder.

2.2.2. SAMPLE PREPARATION

PP films were first compression molded with a Carver Laboratory Press (model 2114). The compression molding cycle consists of three phases: melting, pressurization and quench. 2.5 g of PP pellets were spread evenly within a $150 \times 150 \times 0.100$ mm³ mold placed between two thin Mylar sheets. The above was inserted between two metal plates in the press and heated to its melting temperature of 220°C. As the polymer melts, it flows over the smooth inert Mylar surface to fill the entire mold. After five minutes have passed to ensure complete phase transformation, the melt is pressurized to 138 MPa (20 000 psi). Pressure and temperature were maintained for five minutes after which the melt was quenched with cold tap water. Once cooled, pressure was released and the mold was removed.

The compression molded films were then cut into $20 \times 20 \times 0.100$ mm³ samples to be used in the experiments. As optical resolution is highly dependent on film thickness, uniformity of the sample was verified by measuring thicknesses along the five positions shown in Figure 2.4. Emphasis was placed on the diagonal as the fiber occupies that area during shear.

Figure 2.4 Polymer film thickness measurement positions.

In order to obtain accurate and reproducible data, care must be taken to prevent heterogeneous nucleation. The probability of this phenomenon occurring is high when a heterogeneous substrate is present, due to the introduction of dust particles or imperfections along the surface. In these sets of experiments, there are two such substrates to contend with: the microscope slide and the fiber.

Microscope slides 1 mm thick were cut into 25x25 mm² pieces to enable a snug fit in the sample holder. Each slide was cleaned with acetone and wiped with a very fine cellulose lens paper to eliminate dust particles. An individual fiber was pulled out of a mesh of 50 to 200 identical fibers depending on the fiber used. Due to the delicate nature of the fibers and the presence of sizing, the fibers were wiped with ethanol instead of acetone to prevent etching.

To prepare the composite for melting, one fiber was placed between two PP films which itself was sandwiched between two glass slides. One end of the fiber was attached to the motor and the other end was attached to a small weight (~2 g) of putty. The putty, along with a fiber railing system, enables guided movement during shear. A schematic of the top and side view of the sample is shown in Figure 2.5. The initial distance between the two glass slides is 200 μm .

Figure 2.5 Top (a) and side (b) views of the prepared sample.

2.2.3. PROCEDURE

Each experiment consists of five steps summarized in Figure 2.6 below.

Figure 2.6 Experimental thermal cycle.

The PP-fiber sandwich is raised to its melting temperature of 220°C for 5 min to erase any thermal history. During the melting phase, a slight pressure was applied to the composite to prevent the entrapment of air bubbles. Once time has elapsed and no observable nuclei are present in the melt, the temperature was brought down at a constant cooling rate to its final crystallization temperature. At that moment, shearing is activated by the motor which pulls the fiber forward at a preset velocity. The shear is applied for a specific period of time and fiber pullout length. Shearing is then stopped and isothermal crystallization is observed under static conditions. To facilitate comparison, the reference time for all experiments, zero time (t_0) is taken as the moment at which the crystallization temperature is attained, regardless of the presence of shear.

At the end of the experiment, the glass slide/composite sandwich was quickly transferred to a 1L container of liquid nitrogen. The composite was removed from the slide and its final thickness was measured at the positions shown in Figure 2.4.

2.2.4. PARAMETERS

Two principle experimental parameters were investigated: crystallization temperature and shear rate. A third parameter, the cooling rate, was kept constant.

2.2.4.1. Temperature

The nucleation and growth rate equations [Equations 1.4 and 1.9] predict an exponential dependence on temperature. As such, temperature levels require careful consideration, for high crystallization temperatures entail extremely slow kinetics, while low crystallization temperatures may induce phase transformation that is too quick to observe.

Varga and Karger-Kocsis² found that at crystallization temperatures above 140°C, isotactic polypropylene (iPP) crystallized only in its α form, which has a melting temperature (T_m) of 165°C. There exists an upper ($T_{\beta\alpha}$) and lower ($T_{\alpha\beta}$) threshold temperature for which iPP crystallizes in the β form. The critical threshold temperatures were deduced to be from 140°C for $T_{\beta\alpha}$ and 100°C for $T_{\alpha\beta}$.³ The DSC enthalpy curve in Figure 2.7 performed on a Perkin-Elmer DSC 7 system, shows that the onset of melting of Profax 6523 occurs at 153.3°C while the peak melting temperature is 159.2°C.

In light of the above information, three temperature levels were investigated: 140°C, 145°C and 150°C. It is postulated that within this temperature range, iPP exists only in its α monoclinic phase; thus only one type of crystallization kinetics should be present.

Figure 2.7 DSC enthalpy curve of Profax 6523.

2.2.4.2. Shear Rate

All plastics manufacturing processes involve some level of shear, ranging from 0 s^{-1} to 80 s^{-1} depending on the process. To evaluate the influence of shear over a wide range, three shear rates were investigated: 10 s^{-1} , 25 s^{-1} and 50 s^{-1} . The effects were compared to a control experiment, where no shear was applied for the same crystallization temperature.

Mathematically, the shear rate ($\dot{\gamma}$) in the fiber pullout experiment is defined as the derivative of the fiber velocity (V_f) as a function of the radial distance (r):

$$\dot{\gamma} = -\frac{dV_f}{dr} \quad (2.1)$$

and the shear strain, γ :

$$\gamma = \int_0^t \dot{\gamma} dt = \dot{\gamma} t \quad (2.2)$$

The shear stress (τ), then, is a function of the viscosity (η) and the shear rate:

$$\tau = \eta \dot{\gamma} \quad (2.3)$$

For a polymer melt following the power law model,

$$\eta = m(T) \dot{\gamma}^{n-1} \quad (2.4)$$

with the boundary conditions that at the fiber surface (r_f), the velocity is a maximum (V_f) and at a radial distance far removed from the fiber (r_e), the velocity is zero. Here, $m(T)$ is a temperature dependent proportionality constant. The equation of motion, in combination with the above equations, can be solved to yield the following expression for the shear rate:

$$\dot{\gamma} = \frac{1-n}{n} \frac{1}{r^{1-n}} \left[\frac{1}{r_f^{1-1/n} - r_e^{1-1/n}} \right] V_f \quad (2.5)$$

and the shear stress,

$$\tau = \frac{m}{r} \left[\left(\frac{1-n}{n} \right) V_f \left(\frac{1}{r_f^{1-1/n} - r_e^{1-1/n}} \right) \right]^n \quad (2.6)$$

The above equations are the same as reported by Monasse.⁴

The shear rate equation predicts a rapid decrease in velocity in the direction perpendicular to the fiber surface as seen in Figure 2.8. Thus, the mathematical model, in the absence of slip, predicts a highly localized effect due to shear.

The shear experiments consist of pulling the fiber at a set velocity for 15 mm across the matrix. The length of shearing time is adjusted in order to allow for equal levels of total shear strain in all experiments. The final fiber pull velocity and pull time with the corresponding shear rate are listed in Table 2.3 for the experiments carried out in the present study.

Figure 2.8 Shear rate profile from fiber radius.

Table 2.3 Shear Variables		
Shear Rate (s^{-1})	Velocity ($\mu m/s$)	Shear Time (s)
10	35.4	425
25	88.1	170
50	176.2	85

2.2.4.3. Cooling Rate

As transcrystallization is a nucleation-controlled process, it depends strongly on thermodynamic conditions such as crystallization temperature and cooling rate. It has been suggested that upon cooling of the melt, stresses are generated at the fiber-melt interface, inducing nucleation sites responsible for transcrystallization. The stresses are

believed to be produced by a mismatch in thermal expansion coefficients between the fiber and matrix.

To test this hypothesis, Thomason and Van Rooyen⁵ evaluated three different types of fibers over a wide range of cooling rates. As the cooling rate is increased, the strain rate at the interface is increased. This in turn increases the probability of the appearance of a transcrystalline layer. For glass fibers, cooling rates above 100°C/min induced transcrystallization; the corresponding rates for carbon fibers were 50°C/min and for aramid fibers, 10°C/min.

Other researches into the glass fiber/PP system have revealed transcrystallization at much lower cooling rates. Wagner et al.⁶ reported transcrystalline growth at 10°C/min and Nagae et al.⁷ reported 5°C/min for acid-modified polypropylene coated glass fibers.

From these studies, it is clear that the cooling rate has an effect on transcrystallization, although the extent is arguable. Preliminary crystallization experiments under a cooling rate of 20°C/min showed transcrystalline growth around the glass fiber. The appearance of this transcrystalline layer, however, disappears upon lowering the cooling rate to 10°C/min. Under these circumstances, a constant cooling rate of 8°C/min was utilized in this study to minimize the occurrence of transcrystallinity.

2.2.5. POLYMER MELT TEMPERATURE

2.2.5.1. Temperature Calibration

Preliminary experiments exhibited a gross discrepancy between the temperature measurements and the observed kinetics. The thermocouple used was calibrated beforehand with various standards; thereby the errors seemed to emanate from other factors. To verify the actual temperature of the polymer above the hot plate, a calibrated

E-type thermocouple of diameter 127 μm (0.005 in) was sandwiched between two polymer films. A mock quiescent experiment was carried out with the thermocouple replacing the fiber. It was placed directly under the objective lens. The hot plate temperature and the polymer temperature were then recorded. This procedure was repeated five times over the entire range of investigation: from room temperature to 240°C in 10°C intervals.

Surprisingly, the polymer temperature recorded was consistently higher than the hot plate temperature, sometimes by as much as 15°C at elevated temperatures, down to 2°C at room temperature. Several factors can account for this variation, namely: conduction errors, heat loss and thermocouple placement.

Conduction errors are difficult to isolate and assign as that involves the inherent makeup of the stainless steel used for the hot plate. Impurities, imperfections and entrapment of air bubbles can all attribute to errors in the final temperature measurement. Of major importance is that convection is also present. The thermocouple is not fused with the hot plate but rather inserted into an opening on the lateral side of the plate. The fit is not perfect, allowing for heat loss through heat exchange as the gradient between the plate temperature and room temperature is greater as temperature increases.

Although these factors contribute to the discrepancy, the major culprit is the design of the hot plate. A schematic of the internal makeup of the hot plate is shown in Figure 2.9. Several design problems are apparent upon inspection. For one, the heating filament does not cover the whole area of interest, leading to nonuniform temperature distributions in some areas of the polymer sample. Secondly the presence of two slots in the gap between the filament produces a great amount of heat loss as one of the slots is secured by a screw and the other, by a removable thermocouple.

Due to these problems, the hot plate measurements were discarded and complete calibrations based on temperature readings from the inserted thermocouple between the polymer films were taken to be the correct reading.

Figure 2.9 Center cut-through of hot plate.

To prevent the design of the hot plate from affecting the experiments, several precautions were undertaken. Firstly, a sample size of $20 \times 20 \times 0.100 \text{ mm}^3$ (Section 2.2.2.) was used to minimize the volume of sample directly above the heater filament gap. Secondly, shearing occurred on the diagonal of the sample holder, with an axis at 90° from the center of the gap shown in Figure 2.9, thereby ensuring the experimental area is uniform in temperature. Lastly, temperature measurements were retaken to evaluate its stability. From these precautions, the errors in temperature estimation were minimized.

2.2.5.2. Temperature Measurement and Control

Temperature measurements during the experiment were continuously taken, using the thermocouple inserted into the hot plate. The resulting voltage was translated into two sets of readings: the hot plate temperature and the polymer temperature. The polymer temperature was obtained by converting the hot plate temperature to the actual temperature the thermocouple would have read if it were placed in the center of the

composite under the microscope. Calibration data were obtained using the procedure described in the previous section.

Unfortunately, the transformer controlling the power supply to the hot plate was a simple manual element. Exploratory experiments indicated a maximum deviation of $\pm 1.5^{\circ}\text{C}$.

2.3. IMAGE ANALYSIS

Figure 2.10 shows a typical optical image obtained from the polarized light microscope. Due to the thickness of the polymer sample, three-dimensional growth in multiple layers occurs within the sample. Label A shows the embedded fiber, B shows a growing spherulite in the same layer as the fiber while C shows a spherulite growing in a different layer.

Figure 2.10 Raw image of quiescent experiment at T_c of 145°C and an isothermal crystallization time of 60 minutes. A is the embedded fiber, B are same layer spherulites, C are spherulites growing in a different layer.

Although the sample thickness can be modified to reduce the disturbances seen here, there is a minimum required thickness defined by the shear rate equation. From Figure 2.8, the shear profile extends 40 μm beyond the fiber surface. Due to radial symmetry, the diameter of interest is 100 μm as shown in Figure 2.11.

Figure 2.11 Shear rate radial symmetry.

Some researchers have used sample thicknesses equal to the same diameter of the fiber.^{3,8} However, the main focus of their work was to study the transcrystalline layer under quiescent isothermal crystallization. In this study, emphasis is placed on shearing effects, thus such a thickness would not be useful.

A minimum thickness is required to exclude frictional forces between the glass slide and the fiber during shear, which can cause fiber damage and heat generation, affecting nucleation and crystallization. Another factor is the possibility of a nonuniform velocity distribution thereby affecting adjacent molecules. Although a minimum of 100 μm was calculated, a final thickness of ~ 200 μm for the composite was chosen to minimize or avoid the above problems and to reduce the effects of heat dissipation.

As in most circumstances, there is a tradeoff. In this case, thicker films produce poor image quality. The images obtained are difficult to assess qualitatively and quantitatively. Thus graphical modifications were performed on each image to extract data pertaining to the layer of interest. To accomplish this, several computer software programs were required. Raw images were imported into Lotus CorelPaint and converted into spherulitic outlines by eliminating background colors. Other impurities present in

the image, such as dark patches, were filtered manually. Due to the unbiased nature of the filtering process and the orientation of the spherulites, the contours are usually broken. In order for proper processing, care must be taken to ensure continuity of each spherulite by connecting the contour manually.

A typical initial image produced is shown in Figure 2.12. It is further modified by a software program called SKIZ by Mathematic Morphology, which eliminates all the haze and disturbance to render a skeletal image of the original picture (Figure 2.13). From this final image, qualitative observations are easily distinguished and quantitative measurements are facilitated by use of SigmaScan Pro from Jandel Scientific. This highly powerful software identifies the intensity of each pixel in the image and analyzes the coordinates, diameter, area, etc., defined by the object. Through calibration of the image size, the data are analyzed to produce the relevant information.

Figure 2.12 Initial processed image of a quiescent experiment performed at T_c of 145°C and an isothermal crystallization time of 60 minutes..

Figure 2.13 Final processed skeletal image of a quiescent experiment performed at T_c of 145°C and an isothermal crystallization time of 60 minutes.

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3. RESULTS AND DISCUSSION

This chapter describes the results obtained from the fiber pullout technique. Under the conditions employed in this study, stable nuclei formed at temperatures ranging from 160°C to 185°C upon cooling. However, no appreciable crystallization was observed during shear, as the nuclei density in the matrix remained constant. All the following observations regarding crystallinity and morphology were made after the cessation of shear. Thus, this research concentrates on post-shear crystallization.

3.1. FIBER INDUCED TRANSCRYSTALLIZATION

Preliminary experiments indicate the presence of a transcrystalline layer on the fiber surface in the absence of shear for three of the four fibers (Figure 3.1). The only fiber which did not induce heterogeneous nucleation on its surface was the glass fiber produced by Vetrotex as seen in Figure 3.2. This fiber was subsequently used for all experiments.

Although there have been many studies on the development of the transcrystalline layer, the mechanism is not fully understood. Some factors once believed to have a strong influence on nucleation have proved negligible. These include similarities of the chemical structure of the fiber and polymer matrix, crystallographic unit cell geometries, crystal lattice parameters and chain conformation.¹

Other studies have reported that wettability and surface energy of the substrates², stress-induced crystallinity³⁻⁵, epitaxial growth due to lattice matching⁶⁻⁷, residual stresses caused by differences in thermal expansion coefficients⁸ and the fiber material, topology and surface coating⁹ all affect transcrystallization.

Figure 3.1 DuPont nylon yarn composite under quiescent conditions at T_c of 140°C and isothermal crystallization time of 30 minutes.

Figure 3.2 Vetrotex fiber composite under quiescent conditions at T_c of 140°C and isothermal crystallization time of 30 minutes.

It is of interest to note that transcrystallization has never been observed in conjunction with uncoated glass fibers.¹⁰⁻¹² The apolar, inert polyolefins do not seem to interact with the polar amorphous glass fiber under quiescent conditions. Glass fibers coated with various types of sizing, however, have produced a transcrystalline layer, under certain conditions, as reported by Nagae et al.¹² Upon studying the nucleation behavior, under static conditions, of glass fibers with and without acid-modified polypropylene (AMPP) coating, they found that AMPP coated glass fibers induced transcrystallization. Bare glass fibers showed no signs of transcrystallization over a wide range of cooling rates.

Although a silane-type sizing is present on the surface of the Vetrotex glass fiber, it did not provoke transcrystallization under the experimental conditions of this study.

3.2. TEMPERATURE PROFILES

As discussed in Chapter 2, temperature control was implemented manually. Figure 3.3a shows a typical temperature profile of the five regions described in Section 2.2.3. This particular experiment was carried out under a crystallization temperature of 140°C and a shear rate of 10 s⁻¹. The hot plate temperature and the polymer temperature were both plotted to indicate the magnitude of error without calibration at high temperature levels.

The cooling rate is calculated by taking the slope of the cooling curve shown in Figure 3.3b. The start of cooling is taken at the moment power is lowered, and the end of cooling occurs when the crystallization temperature is reached. At t_0 , shearing is started. It is stopped at t_c according to the criteria described in section 2.2.4.2. (Figure 3.3c). This is accompanied and followed by observation and recording with the CCD camera for a long period.

Figure 3.3a Experimental temperature profile at a crystallization temperature of 140°C and a shear rate of 10 s^{-1} .

Figure 3.3b Experimental cooling curve at a crystallization temperature of 140°C and a shear rate of 10 s^{-1} .

Figure 3.3c Isothermal crystallization curve at a crystallization temperature of 140°C and a shear rate of 10 s⁻¹.

Although manual control was implemented, the crystallization temperature was maintained to within $\pm 1^\circ\text{C}$. Statistical data regarding temperature variability during the above experiment and the average ranges for all experiments in this study are listed in Table 3.1.

Table 3.1 Temperature measurement statistical averages		
	This Experiment	All Experiments
Mean Temperature (°C)	140.36	T_c to $T_c + 0.5$
Standard Deviation (°C)	0.38	0.3 to 1.0
Maximum Temperature (°C)	141.37	$T_c + 1.5$
Minimum Temperature (°C)	139.36	$T_c - 1.0$
Cooling Rate (°C/min)	7.55	8 ± 0.5

Care was taken to prevent the temperature from dropping below the crystallization temperature, as crystallization kinetics could be substantially changed by a small decrease in temperature. Therefore, the crystallization temperature was always slightly higher than the set point.

3.3. QUALITATIVE OBSERVATIONS

3.3.1. COMPARISON OF QUIESCENT AND SHEAR EXPERIMENTS

Two sets of experiments, both raw images and modified images are shown for the same temperature. Figure 3.4 depicts an experiment performed at 145°C under quiescent conditions while in Figure 3.5, a shear rate of 10 s⁻¹ was applied. The following observations can be made regarding the evolution of crystallization in the two cases.

1. A sheath enveloped the fiber in the case where shear was applied. It was not caused by the heterogeneous fiber substrate as seen by the absence of a transcrystalline layer under quiescent conditions, but rather through a rearranging of molecular orientations caused by shear.

The sheath corresponds to what Varga and Karger-Kocsis^{13,14} described as a shear-induced cylindritic layer. They demonstrated that in a sheared polymer melt under crystallization temperatures within the β -phase formation range ($T_c=130-140^\circ\text{C}$), a β transcrystalline-like layer appears. Upon further investigation, they found that the supermolecular structure actually consist of two separate layers: an α row-nucleated region in the vicinity of the fiber surface and β cylindrites growing selectively from the α nuclei. As the β form grows more rapidly than the α form, the resulting structure looks like a β transcrystalline layer due to the occlusion of the α -phase. This β - α bifurcation is the basis in differentiation between a transcrystalline layer from a shear induced layer

Figure 3.4 Quiescent isothermal experiment at 60 minutes under a T_c of 145°C.

Figure 3.5 Shear isothermal experiment at 60 minutes under a T_c of 145°C and a shear rate of 10 s^{-1} . Arrow indicates direction of fiber movement, R is the right side and L is the left side of the fiber.

(Figure 3.6). Transcrystallization is characterized by retaining the initial crystalline structure. In this case the α -phase should remain in the α form. They also observed that above the upper temperature limit for β modification ($T_{\beta\alpha}\approx 140^{\circ}\text{C}$), α cylindritic crystallization took place. Thus, the sheath seen in Figure 3.5 is produced by shear-induced α -cylindritic nucleation and growth.

Figure 3.6 Schematic diagram of (a) transcrystalline and (b) cylindritic crystallization.¹⁵

2. The crystallizing polymer matrix, beyond the shear induced layer, seems to be unaffected by the application of shear.
3. From the images, both the bulk spherulites and the shear-induced layer grow with time. The only limitation on growth is the available free volume within the matrix.
4. As the spherulites and shear induced layer grow, impingements occur in which the lateral movement along one or multiple sides are impeded or halted by an adjacent spherulite. The impingement halts growth along the interface. However, as it normally occurs along the growing extremities of a spherulite and not at the nucleus, radial growth in unimpeded sections grow undisturbed.

3.3.2. COMPARISON OF DIFFERENT SHEAR RATES

To evaluate the influence of different shear rates, Figure 3.5 is compared to Figure 3.7, in which a shear rate of 25 s^{-1} was applied. Qualitatively, it is difficult to distinguish between the two sets, as both the spherulites and the shear-induced layer appear to be quite similar.

The shear rate equation clearly shows the localized effect of shear. Consequently, the spherulites in the bulk matrix for the two experiments should display the same morphological behavior, as the crystallization temperatures were identical. However, at first glance, it is surprising that the shear induced layer seems to be unaffected by the magnitude of the shear. Several factors can account for this behavior.

Firstly, it should be remembered that, while the shear rates in the two experiments were different, the total shear strain [see equation 2.2] was the same for all experiments. Thus, the influence of shear on nucleation and crystallization may be primarily related to the total shear strain.

From previous studies with parallel-plate shearing of polymer melts,¹⁶⁻¹⁸ it is known that shear promotes nucleation. In the experiments performed here, preferential nucleation occurs along the fiber surface, however the degree of nucleation is difficult to ascertain. Assuming that shear affects nucleation and growth, the similarity of the results obtained with the two shear rates can be caused by saturation of the nucleation sites along the fiber. Thus, the smallest shear rate of 10 s^{-1} appears to be sufficient to completely cover the entire fiber surface area with nuclei. An increase in shear rate would then have no effect, as maximum nucleation is achieved.

On the other hand, there may exist a range of shear rates for which no appreciable differences are discernable. Kim and Kim¹⁶ observed two separate crystallization processes under different levels of shear rates. They concluded that these processes involve either crystallization of disentangled molecules or crystallization of highly

20 min

20 min

40 min

40 min

60 min

60 min

Figure 3.7 Shear isothermal experiment at 60 minutes under a T_c of 145°C and a shear rate of 25 s^{-1} .

entangled molecules. The existence of different regimes is observed in the DSC exotherm, in which two separate peaks are present for shear rates below 35 s^{-1} (Figure 3.8). Optical micrographs of the PET samples exposed to different shear rates (Figure 3.9) show no distinguishable morphological differences between shear rates of 11.7 s^{-1} and 35 s^{-1} and between 350 s^{-1} and 1168 s^{-1} . Lagasse and Maxwell¹⁹ also noted that for a given temperature, there is a critical shear rate above which crystallization is accelerated. The range of shear rates in the present study may not be sufficient to produce a second crystallization regime.

Figure 3.8 Change of isothermal crystallization exotherms at 120°C with shear rate.¹⁶

One other possibility suggested by many researchers is that shear affects only nucleation and not growth. Therefore, with an applied shear stress, nucleation is initiated on the fiber surface. As shear rate increases, the number of nuclei increases on the fiber surface since the nuclei are subject to the same environment, they will appear spontaneously and homogeneously. These nuclei will grow radially outward perpendicular to the fiber, as nuclei adjacent to it prevent movement in any other direction.

Figure 3.9 Optical micrographs (x300) of PET samples treated at the shear rate of (a) 11.7, (b) 35, (c) 350 and (d) 1168 s^{-1} and crystallized at 215°C from the melt.¹⁶

Slip along the fiber surface might be an important factor. Slip could reduce the effect of shear at the moment of disassociation between the surface and melt. This critical point may occur near the start of shearing or near the end. In either case, slippage exposes the melt to different velocity profiles, depending on the extent of slip.

Although it is difficult to evaluate slip with the setup in hand, careful observation of nuclei (formed during cooling) moving close to the fiber can establish the presence or absence of slip. Typical results are shown in Figure 3.10 for crystallization at 140°C and a shear rate of 50 s^{-1} . In this case, a block of nuclei along the fiber surface is followed as a function of time. After two seconds of shearing, the block has moved to the left as a group, indicating the absence of slip, as all the nuclei are traversing within the same

Figure 3.10 No slip profile for a crystallization temperature of 140°C and a shear rate of 50 s^{-1} at (a) 50 s after the beginning of shear and (b) 52 s after.

Figure 3.11 Slip profile for a crystallization temperature of 150°C and a shear rate of 50 s^{-1} at (a) 54 s after the beginning of shear and (b) 56 s after.

velocity field. Upon investigation of the experimental conditions, the above behavior was observed in all cases except one. Figure 3.11 depicts crystallization at 150°C with a shear rate of 50 s⁻¹. Two points along the fiber surface are followed as a function of time, points A and B. With a time lapse of two seconds, it can be seen that point B was retarded in flow compared to point A. At a longer time period, point A has moved beyond the screen while point B is still noticeably present.

The presence of slip inevitably affects the analysis. However, the extent of slip is not known. The fact that the majority of the polymer melt follows the velocity profile, even at high shear rates, indicates that slip is not the major factor influencing the final shear induced layer. What was taken to be slip might in fact be an error in judgement due to optical quality.

3.4. DATA ANALYSIS – BULK PROPERTIES

3.4.1. EVALUATION OF SPHERULITE RADIUS OVER DISTANCE

Based on the velocity profile calculated in section 2.2.4., shearing occurs beyond the fiber surface. To verify this, spherulite diameters as a function of the radial distance away from the fiber center were measured. The results are plotted in three-dimensional form in Figure 3.12. The x-y plane represents the layer of interest with zero on the y-axis denoting the fiber center. The z-axis marks each spherulite's radius along the plane.

The graphs reveal a uniform distribution of bulk spherulites in the matrix outside the shear zone. Nucleation is random and is a function of the crystallization temperature. The spherulites grow at approximately the same rate as the whole group moves together along the radius axis. To appreciate the uniformity of the spherulitic growth, the above graphs were replotted showing only the distance from the fiber center versus the

(a) 10 min

(b) 20 min

(c) 30 min

(d) 40 min

Figure 3.12 3D plot of the spherulite diameter along the plane of optical micrograph.

spherulite radius in Figure 3.13. Figure 3.14 plots the distance parallel to the fiber against the spherulite radius. These graphs clearly show a high concentration of spherulites within a radius range indicating uniform growth behavior. Although there is a distinct pattern, the scatter within the data is not lost in the interpretation. Four significant factors attribute to the scatter.

1. *Image Capture.* A rectangular section of the composite is magnified by the microscope and transmitted to the computer. Spherulites near the borders of the image are cut off and this corresponds to smaller data readings at the peripheries. This effect is more prominent as time progresses, as spherulites initially beyond the borders grow large enough to enter the image and vice versa.

2. *Fiber.* The fiber acts as a barrier to lateral movement, as does the shear induced layer, if present. In such a case, the spherulites close to the fiber will be impeded from growing. The image analysis software will register smaller radius measurements near the fiber center.

3. *Induction Time.* Induction time is defined as the length of time between the beginning of thermal equilibrium and the start of crystallization. For fast crystallizing polymers such as PP and PE, the induction time can be so short that it cannot be accurately determined. In many instances, nuclei are born at different times. As a result, those which appear earlier will have a head start on growth, causing the scatter among the data.

4. *Impingement.* The most significant contribution to scatter is due to spherulite impingement. This phenomenon is manifested as time progresses. As indicated in Section 3.1, with time, spherulite size increases and the matrix free volume decreases, leading to a greater probability of spherulite contact. The probability for impingement is also higher for lower crystallization temperatures, as the number of nuclei in the matrix is greater.

Figure 3.13 2D plots of the sphenulite radius against the distance from the fiber center for an experiment at 140°C and a shear rate of 10 s^{-1} at (a) 10 min, (b) 20 min, (c) 30 min and (d) 40 min.

Figure 3.14 2D plots of the spherulite radius against the distance parallel to the fiber for an experiment at 140°C and a shear rate of 10 s^{-1} at (a) 10 min, (b) 20 min, (c) 30 min and (d) 40 min.

There have not been many reports in the literature concerned with the variation of the bulk spherulites as a function of distance. Emphasis is usually placed on the appearance, growth and mechanical properties of the shear induced layer. From this analysis, it is clear that the bulk spherulites are evenly distributed in the matrix and that they have the same radii regardless of proximity to the fiber. The uniformity of the spherulite radii implies that shear has an extremely localized effect. The plots also suggest uniform growth rate for all spherulites, as indicated by group progression over time. However, as time progresses, spherulitic growth is impeded by the fiber, the shear induced layer or by other spherulites, as indicated by the larger scatter in the data.

3.4.2. EVALUATION OF GROWTH RATES

In order to obtain a more accurate evaluation of spherulite growth, individual spherulites, unimpeded in growth in all directions, were isolated and followed with time, regardless of position. Figure 3.15 plots the individual spherulite radius versus time at all shear rates, for a crystallization temperature of 140°C. Figure 3.16 plots the results for a crystallization temperature of 150°C. Up to eight unimpeded spherulites were followed until crystallization in the matrix has become so pronounced as to affect the resolution of the optical image. Each curve represents an individual spherulite.

The growth behavior of the spherulites is uniform with time and displays similar growth rates as indicated by the slope. The curves, however, do not superimpose on one another due to the difference in induction times of each spherulite.

In spite of the absence of impingement, there are still fluctuations within the data. Some of the errors are due to the experimental procedure and method of analysis. During the experiment, shearing often rotates the spherulites close to the fiber. The slight stress applied can change the polarizability of the bonds in the direction of the applied stress. This would create a difference in the refractive index between the stress direction and

Figure 3.15 Individual spherulite radius as a function of time at a crystallization temperature of 140°C and a shear rate of (a) 0 s^{-1} , static run, (b) 10 s^{-1} , (c) 25 s^{-1} and (d) 50 s^{-1} .

Figure 3.16 Individual spherulite radius as a function of time at a crystallization temperature of 150°C and a shear rate of (a) 0 s^{-1} , static run, (b) 10 s^{-1} , (c) 25 s^{-1} and (d) 50 s^{-1} .

directions perpendicular to it, leading to changes in birefringence. The appearance of the spherulite in the matrix would change and the identification of spherulite boundaries would be compromised.

Another uncontrollable factor is the crystallization process itself. As a polymer crystallizes, isotropic shrinkage occurs causing a decrease in thickness due to contraction, thereby changing the resolution of the image. Focus can be restored by altering the height of the sample, however, the original settings are lost.

Although these problems occur, all of the data follow a linear curve indicating a constant growth rate. A linear increase of spherulite radius with time has been reported frequently. For example, Incardona et al.²⁰ observed constant growth rates for isothermal crystallization with a J-1 polymer/carbon-fiber composite. Under static conditions, the carbon fiber induced transcrystallization. A plot of the resulting spherulite radius and transcrystalline layer thickness is shown in Figure 3.17.

Figure 3.17 Spherulite size during isothermal bulk crystallization and layer thickness of isothermal transcrystalline versus time of J-1 polymer at 275°C.¹⁹

The growth rates as a function of shear rate and temperature were calculated for the present experiments and are summarized in Table 3.2. Figure 3.18 plots the average growth rate as a function of the shear rate for the different crystallization temperatures. Allowing for experimental error, the growth rates are approximately the same for all shear rates. When comparisons are made between different shear rates, the growth rates lie within a narrow range for each crystallization temperature. This supports the observation that shear does not influence crystallization in the bulk, far from the fiber.

Table 3.2 Average growth rate in $\mu\text{m}/\text{min}$ of individual PP spherulites versus shear rate and temperature.

Shear Rate (s^{-1})	140°C	145°C	150°C
0	0.650 ± 0.039	0.250 ± 0.043	0.100 ± 0.007
10	0.505 ± 0.044	0.226 ± 0.031	0.105 ± 0.007
25	0.566 ± 0.043	0.272 ± 0.026	0.093 ± 0.011
50	0.670 ± 0.031	0.321 ± 0.032	0.099 ± 0.010

The average spherulite growth rate as a function of the crystallization temperature for each shear rate is plotted in Figure 3.19. The curves display a substantial decrease in the growth rate as temperature increases, and an exponential dependence is apparent for a shear rate of 10 s^{-1} and for quiescent conditions. This is expected, as the growth rate of spherulites follows an exponential dependence on the crystallization temperature [see Equation 1.9].

Figure 3.18 Average spherulite growth rate versus shear rate for various crystallization temperatures.

Figure 3.19 Average spherulite growth rate versus crystallization temperature for various shear rates.

3.5. DATA ANALYSIS – SHEAR INDUCED LAYER

Row-nucleated cylindritic crystallization caused by self-nucleation was observed only when shear was applied. The dense packing of nucleated sites, inhibiting growth in the lateral direction triggers unidirectional growth perpendicular to the fiber surface. Of direct interest is the preferential nucleation on the fiber surface.

Following the experience with the growth of isolated spherulites in the bulk, the analysis concerning the shear-induced layer was performed in the regions where no impingement with bulk spherulites occurred. In these regions, the thickness of the layer is rather consistent and forms a cylindrical shell around the fiber. The uniformity of the shear-induced layer indicates spontaneous nucleation at the moment of shear thereby eliciting synchronized growth.

Although most studies have used the differences in birefringence to evaluate the crystallinity of the polymer over time, this is not a feasible method in this work as outlined in Section 1.1.1. The shear-induced layer indeed becomes brighter as the experiment progresses, but the causes can be attributed to many factors. Thus, the only consistent measurable property of interest is the thickness of the layer and its growth over time.

Figures 3.20 to 3.22 show plots of the shear induced layer thickness as a function of time. Each graph depicts the thickness on the right and left-hand sides of the fiber as denoted by the positive and negative values respectively, with zero denoting the fiber surface.

There is a linear increase in thickness with time indicating a constant growth rate. This tendency is apparent for all experiments and has been reported by several authors.^{11,19,20}

Figure 3.20 Shear induced layer thickness as a function of time for various shear rates at a crystallization temperature of 140°C .

Figure 3.21 Shear induced layer thickness as a function of time for various shear rates at a crystallization temperature of 145°C .

Figure 3.22 Shear induced layer thickness as a function of time for various shear rates at a crystallization temperature of 150°C.

The discrepancies between the left and right shear induced layer thicknesses of the fiber are due to slight movements during shear. The abrupt motion of the fiber at the start of shear causes a temporary imbalance in the system, resulting in a slight shift of the fiber to the left side. This shift is quite small, usually between 2-4 μm . As the shift occurs at the beginning of the experiment, it is felt that the two sides or surface areas of the fiber are not nucleated at the same time. On the left side, the shift causes a slight compaction of the polymer matrix which is resolved through dispersion of the melt. Shearing nucleates the polymer melt adjacent to the fiber surface, and then crystallization continues to grow undisturbed. On the right side, because the shift is in the opposite direction, the viscosity of the film at the particular crystallization temperature is high enough to create a brief void between the polymer matrix and the fiber. Although a minute amount of time is needed before the melt flows to fill the void, the difference causes a time lapse in nucleation between the two sides. As such, it is due to this mechanism that causes the difference in side thicknesses. Although this imbalance creates a nonuniform shear

induced layer thickness on opposite sides, the growth rates for both sides are similar once nucleation is initiated, as listed in Table 3.3 and plotted in Figure 3.23.

Table 3.3 Growth rates in $\mu\text{m}/\text{min}$ of the shear induced layer versus shear rate and temperature.						
Shear Rate (s^{-1})	140°C		145°C		150°C	
	Right	Left	Right	Left	Right	Left
10	0.508	0.596	0.228	0.295	0.102	0.119
25	0.589	0.659	0.276	0.292	0.087	0.107
50	0.599	0.610	0.257	0.271	0.102	0.103

Figure 2.23 Shear induced layer growth rate as a function of shear rate at different crystallization temperatures.

As with individual spherulites, the growth rate of the shear induced layer decreases rapidly with increasing temperature (Figure 3.24). Under a semilog plot (Figure 3.24b), an exponential dependence is observed for shear rates of 10 s^{-1} and 50 s^{-1} .

Figure 3.24 Shear induced layer growth rate as a function of crystallization temperature for various shear rates.

Figure 3.24b Shear induced layer growth rate as a function of crystallization temperature for various shear rates for the left and right sides of the fiber under semilog plot.

Similar results have been reported by Jay²⁰ who also studied a PP/glass fiber composite system. Two crystallization temperatures (125°C and 130°C) and two shear rates (10 s⁻¹ and 78 s⁻¹) were used to produce the curves shown in Figure 3.25. From the results, there is a linear increase in the shear-induced layer with time. However, he also found that the growth rate increased dramatically at the higher shear rate of 78 s⁻¹. This increase is significant in comparison to the results obtained at 10 s⁻¹ (Figure 2.25c) in which the difference from static conditions is relatively small.

Figure 3.25 Experimental studies on PP/glass fiber composite by Jay under quiescent conditions and with velocities of 78 $\mu\text{m/s}$ and 350 $\mu\text{m/s}$ (10 s⁻¹ and 78 s⁻¹). (a), (b) Shear induced layer radius growth as a function of time under a crystallization temperature of 125°C and 130°C. (c) Comparison of growth rates under static and shear.²⁰

Such an appreciable difference in growth rates due to shear has not been observed in this study. Shear rates from 10 s^{-1} to 50 s^{-1} display the same tendencies in growth despite the increase in magnitude, indicating a nucleation controlled mechanism. A change in the growth kinetics of the system at 78 s^{-1} implies the existence of a threshold level for which a different crystallization mechanism is occurring. Kim and Kim¹⁵ have suggested the increase in nucleation and growth is due to the transformation of highly entangled molecular chains in addition to the disentangled chains. Another explanation for this behavior is a difference in nucleation processes. Upon melt shearing, row nuclei of the α -modification are generated first. If the crystallization temperature is below $T_{\beta\alpha}$, there is a high probability that the α -row nuclei is covered by closely packed β nuclei. The β nuclei induce β -cylindritic growth, which terminates growth of the α -cylindritic front. It is well accepted that below $T_{\beta\alpha}$, the growth rate of the β -phase is higher than that of the α -phase allowing for the $\alpha\beta$ transition. Shearing may produce local supercooling of the melt leading to a shift in the $\alpha\beta$ bifurcation transition interface. A decreased α -row nucleated front will have a greater growth rate as the β -modification grows faster than the α -modification. In this study, crystallization temperatures were above $T_{\beta\alpha}$, therefore only α -cylindritic growth took place.

In summary, for crystallization temperatures above $T_{\beta\alpha}$, the shear-induced layer is highly dependent on the crystallization temperature, but not on shear rate between 10 s^{-1} and 50 s^{-1} .

3.6. COMPARISON BETWEEN BULK SPHERULITES AND THE SHEAR INDUCED LAYER

Given the similarities of the two investigated regions, a comparison into their growth behavior was carried out. Figure 3.26 plots the growth rates for the individual

Figure 3.26 Comparison between individual spherulites and shear induced layer growth rates under different crystallization temperatures.

spherulites and the shear induced layer against the shear rate for all crystallization temperature levels. Figure 3.27 plots the growth rates as a function of crystallization temperature. The curves are almost overlapping each other indicating that the thickness of the shear-induced layer grows at the same rate as the radius of an α -spherulite growing in the bulk. This correlates strongly to the hypothesized evolution of crystallinity in the shear-induced layer as shown in Figure 3.28.

Figure 3.27 Comparison between individual spherulites and shear induced layer growth rates under shear rates of (a) 10 s^{-1} , (b) 25 s^{-1} , (c) 50 s^{-1} and (d) all the curves.

Figure 3.28 Evolution of (a) a spherulite and (b) the shear induced layer comprised of profuse spherulitic growth equivalent to the radial growth of an individual spherulite in the bulk.

Nucleation takes place due to the supercooling of the melt below its melting temperature range. At that moment, randomly distributed nuclei are visible in the bulk matrix and along the fiber surface. Under shear, the regions along the fiber experience a localized entropy change due to orientation of polymer molecules generated by the axial force. This drop in entropy decreases the activation energy barrier required to initiate nucleation. As shear progresses for a length of time, sites are nucleated along the fiber surface until it becomes so profuse as to almost saturate the entire surface area. Although the total number of nuclei is difficult to measure, the final result is to inhibit growth of the nuclei in all directions except radially outward perpendicular to the fiber surface. It is postulated that nucleation has stopped by the time shearing terminates as there is no longer an added driving force.

The reasoning behind this is that by the time shearing terminates, the medium has already achieved thermal steady state. Due to the similarities of the growth rates, it is assumed that the predominant form of crystallization in the shear-induced layer is the α phase. Qualitatively, nucleation in the bulk matrix is most apparent below 190°C and by the time the crystallization temperature is reached (at t_c), no new nuclei were observed from t_c onwards.

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4. CONCLUSIONS

The fiber pullout technique provides a useful and dependable approach for the study of the crystallization behavior of polymer melts in post-shearing experiments, especially in the vicinity of fibers. In this study, consistent and repeatable results were obtained with the technique. The principle observations from these experiments for the crystallization of isotactic polypropylene under crystallization temperatures of 140°C, 145°C and 150°C and shear rates of 0s⁻¹, 10s⁻¹, 25s⁻¹ and 50s⁻¹ are as follows.

1. There are two distinct morphologies in a melt undergoing shear: bulk spherulites and a shear-induced layer.
2. The bulk spherulites
 - i. are distributed randomly throughout the matrix.
 - ii. have the same growth rates for a particular crystallization temperature.
 - iii. are not affected by the presence of shear.
 - iv. display a substantial decrease in the growth rate as crystallization temperature increases.
3. The shear induced layer
 - i. is localized within the fiber vicinity created by spontaneous nucleation and synchronized growth upon shearing.
 - ii. grows linearly with time indicating a constant growth rate for each crystallization temperature.
 - iii. has the same growth rate for the same total shear strain despite the differences in the magnitude of the shear rate.
 - iv. growth rate decreases almost exponentially with increasing crystallization temperature.

4. Comparison of the bulk spherulites and the shear induced layer display identical growth rates typical of the α -spherulite modification.

From the results of these sets of experiments, it is postulated that different growth regimes exist for a range of shear rates. Only when the critical shear rate is surpassed is there a substantial increase in the growth rate of the shear-induced layer.

5. FUTURE WORK

One of the main observations of this study is the probable existence of stepwise growth regimes. An evaluation of the growth rate and morphological features of the shear induced layer above a shear rate of 50 s^{-1} should be undertaken. If the threshold exists over a narrow shear rate range, it will provide valuable additional information process applications.

Secondly, the higher is the shear rate, the greater will be the difficulty in analyzing the effects of shear on nucleation. It is well known that shear enhances nucleation, but the extent is unknown. If an extremely low shear rate was employed over a short distance, individual nuclei on the fiber surface could be produced and followed.

The bulk of the observations in this study have related to post-shearing crystallization. It would be interesting to conduct experiments involving continuous shearing and observation of the morphology to evaluate the direct effect of shear on crystallization behavior. Apart from continuous shear, experiments investigating the effects of different total shear strains or constant shear rates for different times.

Finally, this study and most others have only concentrated on uniaxial flow. In most processing systems, shearing can occur in multiple directions. Thus an analysis into the shear memory effects for a multishear system should be evaluated. This can be done by shearing along one direction and abruptly changing the axial angle while maintaining shear.

APPENDIX

APPENDIX

An unexpected result was observed several times during the course of the experimental study. Although the results were interesting, these experiments were not included in the analysis. Upon the application of shear, despite the guarded fiber railing system setup, the fiber shifted position by not 2-4 μm but by as much as 90-130 μm in a sliding motion during the length of shearing. Figures A.1 and A.2 show the pre-shearing and post-shearing positions of the fiber under a crystallization temperature of 145°C and a shear rate of 50 s^{-1} . The sliding shift of the fiber continued for the duration of shearing and stopped only when shearing stopped 95 μm away from its origin. Several important features were noted during these experiments.

1. *Right Side of the Fiber.* In the above experiment, as the fiber moves toward the right, spherulites on the right of the fiber are moved closer together and packed along the vicinity of the fiber surface. However, as shearing continues, the velocity of the fiber pulls the mass away and separates them through the velocity field. Most of the initial spherulites present have moved beyond the field of vision within the first three seconds. These spherulites are refreshed by others streaming in. By the end of shearing, the actual number of spherulites present to the right of the fiber remains relatively constant due to the movement of the fiber and the randomness of nucleation across the sample. In this manner, movement of the fiber does not cause any appreciable difference in morphology at the end of shearing.

2. *Left Side of the Fiber.* The images show clearly that the displaced areas to the left of the fiber are depleted of spherulites in the layer of interest. What is interesting to note is that the area remains depleted during and after shearing. Any nuclei present are due to the velocity gradient of the moving fiber, bringing in nuclei from other regions of the composite. Therefore, from these experiments alone, the results seem to contradict each other. On one level, shearing is supposed to enhance

Figure A.1 Pre-shearing position of fiber at a crystallization temperature of 145°C and a shear rate of 50 s^{-1} . The arrow indicates the direction of fiber movement, R and L are the right and left sides of the fiber.

Figure A.2 Post-shearing position of fiber at a crystallization temperature of 145°C and a shear rate of 50 s^{-1} .

nucleation, however, in the above images, that is not the case. The area remains void of spherulites despite the fact that shearing occurred in those areas. There are two possibilities that can account for this behavior:

- i. There is preferential nucleation on the fiber surface.
- ii. There exists a shearing threshold for nucleation.

The first possibility is supported by all the experiments performed, as nucleation and growth of the shear-induced layer occurs on the fiber surface. However, from the results, it was observed that the magnitude of the shear rate, under a constant shear strain, does not have an effect on the growth rate nor the final morphology. Thus, even a shear rate of 10 s^{-1} should be sufficient to nucleate the polymer matrix. The fact that this does not occur in the area from which the fiber moved suggests that a threshold level exist. This threshold is lowered by the presence of the fiber leading to preferential nucleation on its surface. The reasons for this occurrence are the same as those cited in Section 3.1.

Although shearing does not affect nucleation in the bulk matrix, it does leave a mark close to the fiber surface. A distinct line parallel to the fiber $\sim 20 \text{ }\mu\text{m}$ away can be seen after a time lapse of 5 minutes (Figure A.3). Within 10 minutes (Figure A.4), three equidistant separation lines in the zone were observed. The lines were quite prominent at 20 minutes (Figure A.5).

The separation lines are unmistakably derived from shear. However, the mechanism by which the first line appeared only $20 \text{ }\mu\text{m}$ away and not the full $95 \text{ }\mu\text{m}$ is unknown. One possibility is the length of time shearing occurred at that position. At the start of shear, the introduction of an axial force caused an abrupt disturbance in the composite. Rapid movement of the fiber to the right occurred for the first $40 \text{ }\mu\text{m}$ and then decreased in rate. The shear exposure time may not have been enough to nucleate the matrix, leaving the displaced portion bare. This reinforces the idea that a threshold

Figure A.3 5 minutes after isothermal temperature is reached at a crystallization temperature of 145°C and a shear rate of 50 s⁻¹. Arrow indicates a nucleation line caused by shear.

Figure A.4 10 minutes after isothermal temperature is reached at a crystallization temperature of 145°C and a shear rate of 50 s⁻¹.

Figure A.5 20 minutes after isothermal temperature is reached at a crystallization temperature of 145°C and a shear rate of 50 s⁻¹.

level exists for which both the shear rate, the length of time, or the total shear strain are integral variables.

In the region close to the fiber surface, shearing induced nucleation along three lines parallel to the fiber. Each line was nucleated homogeneously and grew synchronistically. Thomason and Van Rooyen¹ showed that the presence of a fiber surface after shearing was not necessary throughout isothermal crystallization for a shear-induced layer to appear. This is seen here for which the continued movement of the fiber left nucleated layers behind. Growth of the spherulites along the lines is bidirectional and is only limited in the lateral direction. As time progresses, adjacent α -row nucleated cylindrites impede growth of all layers except the α -cylindrites in the extremity.

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