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on Blown High Molecular Weight High Density
Polyethylene Films: A Composite Theory Approach

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Modeling the Effects of Solid State Orientation on Blown High Molecular Weight High Density Polyethylene Films: A Composite Theory Approach

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For Stacey and Kaitlyn
ABSTRACT

Polyethylene films are a major component in today’s flexible packaging and are made with the most widely used polymer in the world. The selection of polyethylene films is the direct result of their balance of cost, processing, and physical properties. To take full advantage of this balance, the effects of the operating parameters of the film fabrication process must be understood in an effort to optimize the relationship between processing and physical properties. Of particular interest to the design of most packages is controlling the degree of molecular orientation in a film. This characteristic is generally determined by selecting the proper polymer, film fabrication process (e.g. cast vs. blown), and the ideal operating conditions (cast quench rate, blown high stalk, blown in-the-pocket, etc.) to produce a film with the desired degree of orientation. For the case where extremely high degrees of uniaxial orientation are required, the fabricated film is typically oriented in a “solid state” drawing process, where the quenched film is stretched in a given direction at temperatures below that of the melting point of the polymer. During this process, the stacked lamellae that form during the film fabrication process are transformed into rigid, long fiber-like structures. The presence of these rigid structures produce films with significantly enhanced moduli, break strengths, and optical properties. The goal of this program is to characterize the films with the intent of modeling the transformation of lamellae into fibers and predicting the previously mentioned physical properties. By doing so, a connection can be formed between the polymer’s characteristics and the final film properties, resulting in the fabrication of films that are unique to the industry.
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1. INTRODUCTION

1.1. GENERAL

Polyolefins, which include polyethylenes and polypropylenes, are the most widely used polymers for producing films for flexible packaging. These applications include stand-up pouches, T-shirt bags, and can liner bags, all which have stringent demands for stiffness and tensile yield and break strengths. For the case of stand-up pouches, a very stiff film is needed to prevent the package from collapsing when it is stacked on a retailer’s shelf. Stand-up pouches are commonly used for fruit drink pouches and snack foods. T-shirt bags, most commonly used for carrying groceries, are produced with films that have high tensile strength, which prevents the bag from breaking upon loading. A stiff film is also beneficial in this application, making the filling of the bag easier for the user. Films for can liners, which are also called refuse or garbage bags, require both high yield and break strengths to prevent the bag from stretching and failing after being filled.

Of specific interest for these packages is the use of high molecular weight high density polyethylene (HMW-HDPE) for blown thick film that will later be uniaxially oriented in the solid state. These polymers, which have been the incumbents for many high strength thin film applications, such as T-shirt bags, provide unique physical properties after uniaxial orientation. In addition, these HMW-HDPE grades provide a much broader operating window for post orientation than typical Ziegler-Natta or chromium catalyzed monomodal HDPE grades. The combination of these two characteristics ignited a new, innovative, and interesting program to blow thick
HMW-HDPE films, uniaxial orient, and then model the enhancements seen in the films’ physical properties. Of specific interest are the machine and transverse direction moduli, the machine direction break stress and strain, and optical properties. Traditionally, inadequacies in these properties have opened doors for more costly engineering polymers, such as PET, to be used in either adhesive or extrusion laminations for flexible packaging. This work will show that through uniaxial orientation, HMW-HDPE films can be used in applications that are typical of engineering plastic films, thus significantly reducing both material and fabrication costs.

1.2. AN OVERVIEW OF POLYETHYLENE SYNTHESIS AND CHARACTERISTICS

Relative to many other polymers, films produced with polyethylene are easily processed, light weight, tough and tear resistant, flexible at both ambient and low temperatures, provide excellent chemical resistance, and most importantly, are low cost. Another critical characteristic that contributes to polyethylene’s success in the film industry is that it can be tailored to fit a specific packaging need. Changes in the polymer architecture, such as branching, branch density, molecular weight, molecular weight distribution, and bimodality of the molecular weight distribution play significant parts in designing a polyethylene for a specific application and control the polymer’s density. In addition, additives such as antiblock, slip, antistats, UV inhibitors, peroxides, tacifiers, pigments, and antioxidants can be easily added to the polymer to improve processing and/or enhance film performance.
There are several categories of polyethylene, which are typically defined by their density. They include low density (ranging from 0.916 to 0.925 g/cm³), medium density (ranging from 0.926-0.940 g/cm³), and high density (ranging from 0.941 to 0.965 g/cm³). Each of these categories can be further divided, depending on the reactor process used to synthesize the polymer.

For low density polyethylene (LDPE), high pressure autoclaves or tubes are used to polymerize ethylene through free radical initiation of a peroxide. Unsaturated hydrocarbons are used to control the polymer density. The high pressure autoclave, which operates between 18,000 to 30,000 psig, was the first process developed for polymerizing ethylene. Its invention, while serendipitous when an ICI scientist noticed a white residue in a high pressure ethylene vessel in 1933, revolutionized the world of materials science. The main disadvantage of the LDPE autoclave process is the high costs associated with maintaining high pressure equipment, such a compressors, reactor seals, and additive and initiator pumps. The process is also a victim to the low ethylene conversion efficiency of the free radical polymerization. Typically, 10 to 20 percent of the ethylene introduced into the reactor becomes polyethylene. The remainder is vented off in a series of disengaging vessels and recovered and recompressed from approximately 10 psig to the reactor pressure of 30,000 psig. This recovery and recompression process also adds significantly to the cost of the process.
Later technology incorporated a high pressure tubular reactor process that addressed some of the issues with operational costs. Typically, the tubular reactors have more favorable production economics because they can run at higher production rates and can use air or oxygen in the first stage of reaction initiation instead of a more costly peroxide. In both the autoclave and the tube, the polymer is molten as it exits the reactor process and is pelletized in a downstream extruder. The main reason why tubes have not replaced autoclaves is the unique architectural characteristics the autoclave produces in the polymer. The autoclave is a constantly stirred reactor, meaning it has a large stirrer that continuously agitates the contents of the reactor, creating extensive back mixing. This recirculation significantly increases the residence time of any given polymer chain within the reactor, increasing the likelihood of the removal of a hydrogen molecule from the backbone of a polymer chain, forming a free radical. This newly generated site serves as a location for monomer units to begin to polymerize, forming a long chain branch. The combination of the back mixing and the free radial generation by the initiators makes the autoclave the only process that can produce significant amounts of long chain branching. This characteristic is critical to certain applications, such as extrusion coating, extrusion lamination, and some cast film products.

In the 1970’s, linear low density polyethylene (LLDPE) was developed as a substitute to the more costly LDPE process. The key production advantage of LLDPE is that it can be produced on a reactor at much lower pressures and temperatures and much higher ethylene conversion percentages. Typically, this process is known as a “gas-
phase” process because the polyethylene powder is fluidized in a bed of ethylene feed gas. Due to its catalyst system and operating conditions, this process more closely resembles a high density polyethylene reactor than a low density polyethylene reactor. LLDPE is typically synthesized with Ziegler-Natta or metallocene catalysts, and not organic initiators. To adjust the density of the polymer, monomers such as butene and hexene are incorporated into the process.¹

Of all the polyolefins, high density polyethylene (HDPE) has the most flexibility in its reactor processes. Several exist, such as the vertical slurry loop, the horizontal slurry loop, the solution multi-reactor, and bimodal multi-reactor. The key differences between the HDPE and the LDPE (high pressure) processes are that the HDPE processes operate at much lower pressures and temperatures and the reaction is propagated by a catalyst, not an initiator. In the case where an initiator, such as organic peroxide, is used, the molecule is consumed by the reaction and becomes incorporated into the polymer chain. A catalyst merely serves to provide an active site for polymerization and is not consumed by the reaction. It typically consists of a charged component, such as chromium, on a support material, such as silica. This means residual material will be present in the catalyzed polymer. For all of the systems, a catalyst, such as a chromium or Ziegler-Natta type, is used to efficiently react ethylene and any comonomer incorporated into the process. A comonomer, such as hexene, is used to control the polymer density. Also, the ethylene conversion percentage is approximately 95 to 98 percent, thus significantly improving the economics of the process relative to the LDPE reactors. In addition, the HDPE
process operates at much lower pressures (500 to 600 psig) and lower temperatures than the LDPE process, again significantly reducing the economics associated with producing the polymer. In the case of the slurry reactors, ethylene gas, catalyst, and comonomer are injected into a medium of isobutane. Upon reaction, the polymer molecule settles at the bottom of a loop and is discharged into a degassing vessel. From the degassing vessel, the powder is dried and compounded into pellets. The solution multi-reactor process is the most flexible of all the HDPE processes, with its capability to quickly transition between products as its greatest asset. In the case of this particular technology, the polyethylene is polymerized in a hexane solution in multiple reactors in either a parallel or series arrangement. After the polymer is formed, the catalyst is removed in a stage downstream from the reactor. The polymer is then recovered from the solution in the form of a powder and pelletized. The bimodal multi-reactor process is similar to the solution multi-reactor process, only that the polymer is in a slurry and not a solution. In a slurry process, the polymer molecules fall out of suspension in a transfer medium, where the polymer actually precipitates out of a solvent in the solution process. The multiple reactors in this process can be operated in either a parallel or series mode, and can produce a robust range of polymers. As with the other HDPE processes, unsaturated hydrocarbons (such as butene, hexene, etc.) are used to control the product density. The primary products made in these reactors are high molecular weight high density polyethylenes (HMW-HDPEs), which are used to blow high strength, high modulus films. These polymers have a bimodal molecular weight distribution, meaning there are two Gaussian distributions seen in the molecular weight distribution of the polymer. This
property makes the polymers easier to process, lending their use to a wide range of applications, which include blown film, pipe, sheet, injection molding, and blow molding.

1.3. AN OVERVIEW OF THE BLOWN FILM PROCESS

Blowing film is one of the most common polymer conversion processes in the world. The majority of the commodity films used by consumers are produced by this method. The key attribute of blown film is the ability to balance machine and transverse direction properties by controlling molecular orientation through operating parameters. A typical blown film line consists of one to nine extruders, die, air ring, iris or bubble cage, collapsing frame, and a winder. The following figure displays a typical blown film line.

Figure 1. A typical blown film line. Image courtesy of Lung Meng Machinery Co., Ltd. (http://www.lung-meng.com).
The typical film blowing process for polyethylenes consists of a series of stages, including extrusion, blowing, collapsing, and winding. The polyethylene pellets are fed to an extruder that melts the polymer and meters the flow to the die. For LDPE and LLDPE, the extruder length to diameter ratio can range from 18:1 to 32:1, but is typically 24:1. Due to the lower melt viscosities of the lower density polyethylenes, the compression ratios of the screws are typically high, around 4.5. A mixer is incorporated into the end of the extruder screw, which provides additional shear to eliminate unmelted globules and creates a homogeneous melt. Upon exiting the extruder, the melt flows through a heated adapter into an annular die, which has a gap ranging from 1,500 to 3,000 microns. The molten polymer, now in tubular form, exits the die and passes through the cooling air ring. Typically, these air rings have multiple “lips” or exits for the air to maximize the cooling rate of the film. This air ring blows air, typically at ambient temperature, onto the surface of the film to solidify the melt. At the same time, the bubble is expanded in the transverse direction to the ratio of 1.5 to 4 times the diameter of the molten tube.

At this point, a frost line is evident, indicating the crystallization of the polymer melt. By decreasing the frost line height, the machine direction orientation of the molecules is increased and the percent crystallinity is decreased. The quicker quench rate associated with producing film at a lower frost line height results in less time for the polymer chain to relax after exiting the die, locking the molecular orientation in the machine direction. This faster quench rate also limits the time available for the
molecules to form well ordered lamellae stacks, reducing the total amount of crystallinity in the film. The process where the film is immediately quenched above the air ring is referred to as “conventional” or “in-the-pocket” extrusion within the industry, as shown in Figure 2.

**Figure 2.** The die, air ring, and expanded bubble of a conventional blown film process.

A similar extrusion process can be used for LLDPE and monomodal HDPE, keeping in mind that these polymers typically have a higher melt viscosity than the LDPE. Relative to a LDPE blown film line, higher horsepower motors, lower screw compression ratios, and modifying the die to lower the head pressure may be necessary. The main concern with processing LLDPE on a LDPE blown film line is the occurrence of melt fracture or “shark skin.” This is evident with a rough appearance on the surface of the film, which is the direct result of the polymer exposed to high shear rates as it exits the die. Slightly increasing the die gap will help remedy this issue.
For HMW-HDPE, different equipment and a different technique must be used to produce a film with the balance of properties that are acceptable for the industry. Due to the high molecular weight of the polymer, special extruders must be used to process the viscous material. An extruder with an intensively cooled, groove feed section is used instead of the conventional smooth bore barrel. This design reduces the melt residence time, which lowers the melt temperature, reduces degradation, and increases the extruder’s output. The extruders used for HMW-HDPE processing may also have a slightly larger length to diameter ratio, giving the molten polymer more time to homogenize. The dies of HMW-HDPE blown film lines typically have a much smaller die gap than LDPE/LLDPE blown film lines. The narrow gap is used to provide back pressure at the die exit to “reweld” the polymer as it exits from the spiral channels of the die. For HMW-HDPE, the die gap typically ranges from 800 to 1,200 microns. The key uniqueness when comparing the fabrication of HMW-HDPE films relative to any other PE film is the quenching process. Due to their high molecular weight, the HMW-HDPE chains have a much longer relaxation time than their lower molecular weight counterparts. If the film was immediately quenched as it exited the die, the molecules would be highly oriented in the machine direction, producing a film with highly anisotropic properties. To balance the orientation, the molten tube is “high stalked”, or extended to a specified height; typically 6 to 8 die diameters above the exit of the die. This process is shown in Figure 3.
Figure 3. The die, air ring, and expanded bubble of a high stalk blown film process.

The cooling of the molten neck is much slower with the high stalk process, and is typically controlled with a single lip air ring. This gives the molten polymer time to relax and crystallize into a more isotropic film. Above the specified neck height, the film is blown in the transverse direction approximately 3 to 4 times the diameter of the die, inducing transverse direction orientation upon the quenching of the film.

1.4. LITERATURE REVIEW

1.4.1. AN OVERVIEW OF MEASURED CHARACTERISTICS OF POLYETHYLENE AND HOW THEY AFFECT THE FINAL PROPERTIES OF BLOWN FILM

When discussing polyethylenes, the three key characteristics of the polymer that are commonly discussed are the percent crystallinity, molecular weight, and molecular weight distribution. These characteristics are defined by the
catalyst/initiator system, the reactor process, and the conditions used to manufacture the polymer.

Polyethylene is a semi-crystalline polymer, meaning it has both crystalline and amorphous regions. In the crystalline region, well ordered structures are formed, producing areas of high density. In the amorphous region, the polymer chains are randomly arranged, most likely due to branching from copolymers and/or imperfections in the crystallization process. The combination of these two phases gives the semi-crystalline polymer unique properties relative to other materials. The amorphous regions provide flexibility and processing ease while the crystalline regions provide strength and stiffness. In general, HDPEs are 60-85 % crystalline, LLDPEs are 35-60 % crystalline, and LDPEs are 35-55 % crystalline.\(^1\)

The density of the polymer significantly changes the final properties of the film. By increasing the polymer density, the stiffness, barrier, tensile strength, dart impact, abrasion resistance, and chemical resistance increase, while the tear resistance and optical properties decrease.\(^3\)

There are several molecular weights used to describe the average size of a polyethylene chain. Typically the weight average molecular weight (\(M_w\)) is used, with others including the number (\(M_n\)), z (\(M_z\)), and \(z+1\) (\(M_{z+1}\)) averages. To characterize the different groups of polyethylenes, we begin with the very low molecular weight grades, which have a \(M_w\) below 1,000. These products are typically used as waxes or greases as additives in lubrication applications. Low
molecular weight polyethylenes have a \( M_w \) ranging from 1,000 to 100,000 and are used in high flow injection molding applications. Medium molecular weigh polyethylenes have a \( M_w \) ranging from 100,000 to 150,000, and are typically used in blown film, injection molding, and blow molding applications. Finally, high molecular weight polyethylenes have a \( M_w \) ranging from 150,000 to 750,000 and are used in high strength blown film, large part blow molding, and selected profile extrusions. Very high and ultra high molecular weight polyethylenes are also produced, and can have a \( M_w \) above 3,000,000! These polymers are nearly impossible to process with conventional extruders and often require expensive solution processing. These specialty grades are used in film, fiber, and forging applications. In general, increasing the molecular weight of a polyethylene will increase the melt viscosity, optical properties, melt strength, toughness, dart impact resistance, abrasion resistance, and tensile properties of the film at the cost of processability. 

The final polymer characteristic used to describe polyethylene is the molecular weight distribution. This parameter provides a means for expressing the breadth of the molecular weight distribution of the polymer chains. Commonly, the ratio of \( M_w/M_n \) is used to measure the breadth of this distribution for monomodal polyethylenes. For bimodal high molecular weight polyethylenes, the ratio of \( M_z/M_w \) is often reported.
Rheology can also be used to approximate the breadth of the high molecular weight tail of the molecular weight distribution.\textsuperscript{4} For convenience, an empirical measure of the distribution of the long branch content, $E_T$, has been developed.\textsuperscript{4} This parameter is calculated from the reciprocal of the complex modulus of the melt, and will be used later to propose a correlation between the breadth of the high molecular weight tail of the molecular weight distribution and the rate at which micro-fiber structures are formed upon uniaxial drawing. In general, broadening the molecular weight distribution of a HDPE polymer increases processability, melt strength, and bubble stability at the cost of film toughness and tensile properties.

1.4.2. MODELING THE CHANGES IN PHYSICAL PROPERTIES AS A RESULT OF UNIAXIAL ORIENTATION

Traditionally, the study of the orientation of polyethylenes has focused on the effects of drawing a polymer in either the melt, in solution, or in a solid state over a varying gap. Limited work has focused on solid state deformation in a fixed, narrow gap. Additionally, past work was directed towards modeling the fiber drawing process, with the goal of explaining the enhancements in physical properties, such as modulus and tensile strengths and stresses. In general, little work has been directed towards studying the solid state orientation of HMW-HDPE films in a narrow gap drawing process.
While previous work may not exactly describe the effects of solid state orientation on the properties of HMW-HDPE film, the general concepts derived by past models can serve as valuable tools that can be applied to understanding the phenomena evident in the films. The following section will discuss the past work in modeling the enhancements in physical properties of polyethylene films and fibers after uniaxial orientation. The sources cited cover a range of fabrication and orientation processes of polyethylene films and fibers. All correlate the enhancements in physical properties to changes in the microstructure of the polymer.

Semi-crystalline polymer films can be oriented to improve physical properties, namely the modulus and tensile yield and break strengths. Several approaches have been proposed to explain the molecular transitions that enhance these properties, but none are related to the inherent properties of the polymer. To fully understand the structure property relationship of oriented films, any adequate model must incorporate the molecular transition that is occurring during the drawing process. A transitional model that relates the inherent properties of the polymer to the structural changes that are shown in Figure 4 would be valuable for developing new polymer films that have unique physical properties when oriented in a commercial process. Such a model would be beneficial to a fundamental understanding of structure property relationships and for use in polymer development for producing oriented films with improved properties.
Figure 4. Stress-Strain curve for drawn high molecular weight high density polyethylene films. Included are AFM, optical micrographs (50x magnification), small and wide angle x-ray scattering images, and pole figures from the wide angle x-ray scattering patterns for a set of polyethylene films at various elongations. The undrawn sample (0%) has randomly oriented stacks of lamellae. Upon drawing, the stacks begin to arrange in the drawing direction. Beyond the yield point, the stacks begin to transform into fiber-like entities (piled lamellae with long range order and/or packing of extended chains), highly oriented in the drawing direction. The sample quickly fails at an extremely high tensile stress (~10x of the undrawn film’s break strength) after the crystalline region has been completely transformed into fibers.
Several approaches have been used to explain the enhancements in the physical properties, namely the moduli, of semi-crystalline polymers when they are uniaxially oriented. The first step in generating a model is to define the various phases of the polymer. From the micrographs in Figure 4, it is obvious that some type of fibrillar structure forms. This has been noted in the literature.\textsuperscript{5-8} The original matrix is semi-crystalline with both amorphous and non-fibrous crystalline components. A model for oriented films should include at a minimum, fibers in a matrix, with more complicated composite morphologies possible. A general structural model should be based on experimental observations of the film. The evidence of highly anisotropic crystalline regions of large length/width ratios (aspect ratios) aligned in the drawing direction from various microscopy techniques\textsuperscript{5-8} supports the use of a modified version of the infinitely long fiber composite model as a foundation for explaining the mechanical enhancements of the films. In some cases, transitional models were developed to explain the changes in the crystalline structure upon orientation, i.e. fiber formation. The various transitional models\textsuperscript{9-11} differ on numerous accounts, including the geometry and structure of the fiber, the mechanism by which the fiber is formed, and how the matrix’s contribution to the overall composite’s physical properties is incorporated. None of the past models include a transition of the matrix phase. Literature models also fail to incorporate easily measured polymer characteristics, and none are easily applicable to commercial processes. Table 1 lists the attributes of the various models which will be discussed in this review.
Table 1. A tabulation of the attributes of the various models for oriented semi-crystalline polymer films. The Breese-Beaucage model is the only one that satisfies every category. MD refers to machine direction (orientation direction) and TD refers to transverse direction (perpendicular to orientation and normal directions).

The models in Table 1 range from simple empirical models loosely related to the composite morphology, to extravagant micro- and macro-structural designs that have little practical use, but provide insight for determining the boundary conditions for simpler empirical models. A practical model that explains the transitions caused by the drawing process and that incorporates easily measured characteristics of a given polymer is needed, but none of the previously proposed theories satisfy this request. A commonality in all of the methods is the presence of fiber-like structures reinforcing a less rigid matrix. Figure 5 shows the schematic drawings of the molecular structure of each model.
(a) Infinitely Long Fiber Composite\textsuperscript{12} (b) Short Fiber Composite\textsuperscript{13} (c) Peterlin\textsuperscript{9} (d) Barham and Arridge\textsuperscript{10} (e) Gibson, Davies, and Ward\textsuperscript{11}

**Figure 5.** Schematic drawings of the molecular structure evident in each model. (a) The infinitely long fiber composite\textsuperscript{12} consists of infinitely long, rigid fibers extending uniaxially through a softer matrix. (b) The short fiber composite\textsuperscript{13} is similar to the infinitely long fiber composite, except that the reinforcing fibers have a finite aspect ratio (length/diameter ratio). (c) The Peterlin\textsuperscript{9} model consists of spherulitic lamellae prior to orientation, with the formation of parallel mosaic fibrils (micro-fibrous) that intertwine to form macro-scale packs. Imperfections, such as vacancies from chain ends, chain ends in the amorphous region, boundary layer between mosaic crystalline blocks, and inter- and intra-microfibrillar tie molecules are shown. (d) the Barham and Arridge\textsuperscript{10} model consists of cylindrical components composed of crystalline material that deforms upon orientation to produce fibers with relatively large aspect ratios. The enhancement in the composite stiffness is the result of the increasing aspect ratio of the fiber and not an increase in volume fraction of fibers. (e) The Gibson, Davies, and Ward\textsuperscript{11} model consists of fiber-like structures that are composed of parallel crystalline blocks connected by rigid tie molecules that pass through the inter-crystalline amorphous regions. As the polymer is oriented, more tie molecules are pulled taunt, creating more fiber-like structures consisting of ordered crystalline blocks at higher levels of orientation. The enhancement in the composite’s stiffness is the result of increasing the volume fraction of fibers, not increasing the aspect ratio of the fiber. In all diagrams except for (c) Peterlin i.), the fiber direction corresponds to the machine direction (MD) and is vertical in the drawing. For the case of (c) Peterlin i.), the spherulitic growth direction is indicated as vertical in the drawing.

The infinitely long fiber composite (ILFC)\textsuperscript{12} is the simplest model. It assumes a uniform stress distribution throughout the system. The ILFC model consists of perfectly oriented rigid fibers that extend infinitely through a flexible matrix, as shown in Figure 5 (a). For the ILFC model, the physical properties of the
composite are not dependent on the geometry of the fiber. The moduli and break strength are merely the additive sum of the various components of a uniform axially strained system, as indicated in Equations (1) - (3). The composite’s elongation at break is equivalent to that of the strongest, most rigid component, the fiber, as indicated in Equation (4). The following set of equations is used to calculate the moduli, machine (fiber) direction break strength, and machine (fiber) direction elongation at break for the composite.

\[ E_{C, MD} = \sum_{i=1}^{n} E_i V_i \]  \hspace{1cm} (1)

\[ E_{C, TD} = \frac{1}{\sum_{i=1}^{n} \frac{V_i}{E_i}} \]  \hspace{1cm} (2)

\[ \sigma_{C, MD} = \sum_{i=1}^{n} \sigma_i V_i \]  \hspace{1cm} (3)

\[ \varepsilon_{C, MD} = \varepsilon_F \]  \hspace{1cm} (4)

\( E_{C, MD} \) is the composite modulus in the machine (fiber) direction, \( E_{C, TD} \) is the composite modulus in the transverse (normal to fiber) direction, \( E_i \) is the modulus of the \( i^{th} \) component, \( V_i \) is the volume fraction of the \( i^{th} \) component, \( \sigma_{C, MD} \) is the machine (fiber) direction break strength of the composite, \( \sigma_i \) is the machine (fiber) direction break strength of the \( i^{th} \) component, and \( \varepsilon_i \) is the machine (fiber) direction break elongation.

Due to its simplicity, the infinitely long fiber theory is often used to approximate the properties of composites. Its shortcoming is that it does not take into consideration the actual structure of the fiber or surrounding matrix and any
transformation of those phases that is occurring as a result of the deformation. It also assumes perfect adhesion between the matrix and the fiber. Characteristics of semi-crystalline polymers, such as chain branching, entanglements, glass transition temperature, polarity of side branches, and lamellar thickening from annealing are also not incorporated in this simple model. For these reasons, this model is not used in its basic form to explain strained polymer systems, but it does serve as a foundation for building more inclusive approaches. This model is best suited for systems where the fiber has a relatively large aspect ratio (length/diameter ratio > 10^3), such as epoxy reinforced with long glass fibers.

The short fiber composite (SFC) model proposed by Halpin and Tsai adds a level of complexity by incorporating the effects of the geometry of a fiber, namely the aspect ratio (l/d: the ratio of the length of the fiber to the diameter of the fiber) into the determination of the composite’s physical properties, as shown in Figure 5 (b). The following set of equations is used to calculate the moduli of the composite from the individual properties of each component of the composite.

\[
\frac{E_L}{E_m} = 1 + \left( \frac{2}{d} \right) \eta_f V_f \frac{E_f}{E_m} \left( 1 - \eta_f V_f \right) \quad (5)
\]

\[
\eta_f = \left( \frac{E_f}{E_m} \right)^{-1} \quad (6)
\]

\[
\frac{E_T}{E_m} = 1 + 2\eta_f V_f \frac{E_f}{E_m} \left( 1 - \eta_f V_f \right) \quad (7)
\]
\[ \eta_r = \left( \frac{E_T}{E_m} \right)^{-1} + 2 \] 

\[ (8) \]

\( E_L \) is the composite modulus in the machine (fiber) direction, \( E_T \) is the composite modulus in the transverse (normal to fiber) direction, \( E_f \) is the modulus of the fiber, \( E_m \) is the modulus of the matrix, \( V_f \) is the volume fraction of fibers, and \((l/d)\) is the aspect ratio of the fibers.

The Halpin-Tsai theory\(^{13}\) is well known in composite engineering and relates both the microstructure (in terms of aspect ratio) and the volume fraction of fibers to the mechanical properties of the composite.

The short fiber composite theory makes similar assumptions as the infinitely long fiber theory, such as perfect adhesion between components. The key issue with applying the Halpin-Tsai equation to semi-crystalline polymer systems is that the various parameters of the theory, namely the fiber aspect ratio and the moduli and volume fraction of each component, are typically estimates which cause a significant variation in predicted properties.\(^{14,15}\) This theory could be more effectively used in lower molecular weight, lower density polymers where the amorphous phase is known to be continuous.\(^{11}\) The Halpin-Tsai theory effectively predicts the composite properties for systems where the fiber and matrix properties are well known and do not change upon deformation, such as epoxy reinforced with short glass fibers\(^{12}\) or rubber strips within a lower modulus matrix.\(^{14}\)
A critical shortcoming of applying both the infinitely long and short fiber theories to drawn polymer systems is that they are not transitional models, meaning they do not predict changes in the composite properties that are the result of structural transformations caused by drawing. Neither theory relates the properties of the composite to those characteristics inherent to the polymer, namely molecular weight, molecular weight distribution, and zero-shear viscosity. Some transitional models\textsuperscript{9-11} have been reported that attempted to bridge the gap between transformations in the crystalline phase and enhanced physical properties resulting from orientation. None of these models relate such enhancements to the inherent characteristics of the polymer and are not easily applicable to commercial processes.

Peterlin\textsuperscript{9} proposed one of the foremost models that explains the molecular structure of drawn fibers. From the basic concept that a polymer consists of two phases; lamellae and amorphous regions (consisting of folds, chain ends, and tie molecules), he claims that upon drawing, microfibrils are formed that consist of crystalline material arranged in series with amorphous material. Passing through this intermediate amorphous region are tie molecules, some of which may be relatively taunt. Electron microscopy and IR dichroism were used to substantiate the claims that the fiber-like components are the basic structure of the oriented sample and the orientation of the amorphous region changes with both strain and annealing. Figure 5 (c) shows a schematic on the molecular scale of the
crystalline and amorphous regions in i.) spherulitic and ii.) micro-fibrous material. As shown in Figure 5 (c iii.), Peterlin claims that these lamellar microfibrils are grouped together by van der Waal forces into larger bodies; known as fibers, with the crystalline and amorphous regions of neighboring microfibrils lining up with one another. The microfibril clusters appear to intertwine at some fixed angle relative to the orientation direction and to weave yet larger fiber structures.

Peterlin claims the interconnectivity of tie molecules between the crystalline and amorphous phases within the microfibril affects the properties of the amorphous phase during orientation, thus significantly changing the overall properties of the oriented structure. In other words, the amorphous region is no longer a soft phase independent of the crystalline region, but contributes to the total structure of the composite. Peterlin concludes that the presence of strong microfibrils, which are the result of the numerous taut tie molecule that pass through the amorphous region and connect the crystalline blocks, cause the significant increases in tensile and modulus properties and any enhancement in properties is not the result of the orientation or transformation of the crystalline component.

On a larger scale, few tie molecules exist between neighboring fibrils, so according to Peterlin, the enhancements in strength and stiffness are seen as a result of the auto-adhesion from van der Waal forces between the long, narrow microfibrils within the macro-fiber packs. It is most unlikely that the microfibrils
are held together by van der Waal forces, primarily due to the length scale on which these forces act. The microfibrils, which likely have the approximate width of a lamellae, are of the order of thousands of Angstroms, and are two orders of magnitude greater than the scale with which van der Waal forces influence.\textsuperscript{16} The clusters of microfibrils are most likely held together by forces generated from surface energy effects and packing constraints, both of which increase as microfibrils are formed in the orientation process.

Peterlin’s model is the most complicated of all of those mentioned, with multiple variables that make it nearly unusable for predicting properties. This is evident with the theory’s lack of structure-property relationships, whether empirical or derived from first principles. A key uncertainty with the discussed model is its complete dependence on the orientation of tie molecules within the amorphous region, which can not be measured by current analytical techniques. Peterlin used IR dichroism to characterize the orientation of the amorphous phase and implied this was indicative of the orientation of the tie molecules. Stating that the enhancements in the properties of the oriented samples are directly related to the amount of taunt tie molecules insinuates that a lower density polymer would have better properties than a more crystalline polymer when oriented. This is definitely not the case, with significant improvements seen in moduli and tensile properties in higher density polymers when they are oriented.\textsuperscript{17,18} While at low strain values, the tie molecules may play a role in the overall properties of the composite, their contribution is drastically suppressed by the transformation of the crystalline
region into oriented lamellae stacks and eventually into extended chains at high strain values.

Micrographs of oriented films reveal narrow, crystalline rod-like structures having significantly large aspect ratios. The presence of such a crystalline region proposes a continuity of covalently bonded molecules in the orientation direction that are significantly stiffer and stronger than any reinforced amorphous region. Further strengthening the oriented crystalline region are the surface energy forces and packing constraints that hinder the slipping of the long, narrow fibrils past each other.

Peterlin also comments that the Herman’s orientation functions ($f_c$) measured by x-ray scattering techniques are not a valid means for predicting the enhancements in physical properties due to the tie/amorphous phase’s dominance. Extensive research has shown significant changes in the Herman’s orientation function determined by various techniques that correlate to changes in the polymer upon drawing. The crystallography techniques also show a parallel alignment, and eventual tilt to 34.4 degrees of the lamellae normal (SAXS: $f_c$~0.521), resulting form the near perfect alignment of the unit cell’s c-axis parallel to the orientation direction (WAXS: $f_c$>0.920). This indicates the c-axis of the unit cell aligns in the machine direction during the orientation process.
Peterlin attributes the enhancements in physical properties of the systems oriented at elevated drawing temperatures to the additional mobility of the softer amorphous region, similar to that seen in a swollen polymer matrix. Koenig, et al.\textsuperscript{8} contradicts Peterlin’s statement by using IR dichroism to show that while the amount of orientation in the crystalline phase is independent of the orientation temperature, the degree of orientation in the amorphous region slightly decreases with increasing orientation temperature. This decrease in orientation is likely the result of greater mobility of the chains in the less viscous amorphous phase at higher temperatures. Koenig, et al.\textsuperscript{8}, did comment that the amount of orientation in the crystalline region, regardless of temperature, was significantly higher than that of the amorphous phase.

Peterlin claims that annealing drives the oriented polymer’s properties back to those of the unoriented sample by relaxing the taut, amorphous reinforcing tie molecules. This conclusion is based on an analysis using IR dichroism, which showed significant changes in the orientation of the amorphous phase and little change in the crystalline region upon annealing. This regression of properties to those of an unoriented polymer may be typical for oriented systems that were drawn to low draw ratios and annealed out of tension for a relatively long time and/or at temperatures near the melting point of the polymer. The research by Koenig, et al.\textsuperscript{8}, showed no change in the orientation of the crystalline region and only a slight decrease in the orientation of the amorphous region upon annealing.
In addition, the amorphous orientation was significantly lower than that of the crystalline phase.

In the context of the crystalline transformation into fibers, one should consider the difference in melting temperatures \((T_m)\) between the fibers (higher \(T_m\)) and crystalline lamella (lower \(T_m\)). When fibers are formed, the entropy of the crystalline region decreases, causing an increase in the Gibbs free energy, and resulting in a higher melting temperature for the fibers relative to the crystalline lamellae. This change in melting temperature has a great effect on the annealing of the polymer. At relatively low annealing temperatures, only the amorphous region is softened. As the annealing temperature is increased, crystalline lamellae of increasing size begin to melt, softening the non-fibrous crystalline region of the matrix. Because of this increased melting temperature of the ordered fiber, annealing would only affect the fibrillar crystalline regions at temperatures closer to that of the infinitely large crystal \((T_\infty)\). Such temperatures are well above the average melting temperature of the bulk crystalline region, in effect making the system a melt and not a solid film. Since the fibrous component of the composite is the main contributor to the physical properties and it is not greatly affected by typical annealing conditions, which must be less than the average melting temperature of the crystalline region, the properties would likely have remained close to their oriented values.\(^6\)\(^,\)\(^7\) This means that typical annealing conditions are not conducive to full molecular relaxation of the fibrillar crystalline region to its pre-oriented state.
Bassett and Carder\textsuperscript{7} did observe a brief decrease in modulus at a specified annealing temperature between the lamellae and extended chain melting temperatures. This was due to a temporary melting of the crystalline region resulting from the conversion of chain folds into extended chains. After this transformation is complete, the increase of the modulus resumes under continuous strain. It could be possible that Peterlin only examined annealing conditions that were within this narrow time and temperature window and did not characterize the entire annealing process. While any changes are certainly a function of annealing conditions, commercial oriented films of both linear and slightly branched high molecular weight polyethylenes have been produced that retain their enhanced physical properties after annealing at 5 °C below the differential scanning calorimetry (DSC) peak melting temperature of the polymer.\textsuperscript{17, 18}

While there are significant problems with applying Peterlin’s theory to oriented linear polymers, there are several concepts that can be of use to a general model for drawn semi-crystalline polymers. Of greatest significance is the fact that fiber-like structures are formed when a polymer is oriented, likely the result of some type of transformation in the matrix component. In addition, these fiber structures are generated on multiple length scales in a hierarchical morphology. Individual lamella stacks, and if present, extended chains, align to form microfibers which are bound together in larger macro-scale fibers. Peterlin also described how the lamellar stacks align with their normal parallel to the machine
direction at low draw ratios, and then tilt to a specific angle upon further orientation, indicated by a four-point SAXS pattern described by Bassett. This pattern is associated with the chain tilt of lamella crystals as discussed below (Figure 6).

Barham and Arridge\(^{10}\) explain the enhancements in physical properties of oriented samples with a simpler proposal which suggests that a uniaxial draw of a semi-crystalline polymer leads to fiber structures with large aspect ratios. Barham and Arridge propose that this increase in fiber aspect ratio, which is the direct result of the homogeneous deformation of the structure, increases the reinforcing efficiency of the fibrils and is responsible for the increase in tensile modulus, as indicated in Figure 5 (d.) The following set of equations is used to calculate the machine (fiber) direction modulus of the composite.

\[
E_{\text{Composite}} = \Phi E_{\text{fiber}} V_{\text{fiber}} + E_{\text{matrix}} V_{\text{matrix}} \quad (9)
\]

\[
\Phi = 1 - \left[ \frac{L_f}{r_f} \left( \frac{G_m}{E_f \ln \left( \frac{2\pi}{\sqrt{3} V_f} \right)} \right)^\frac{1}{2} \right] \tanh \left[ \frac{L_f}{r_f} \left( \frac{G_m}{E_f \ln \left( \frac{2\pi}{\sqrt{3} V_f} \right)} \right)^\frac{1}{2} \right] \quad (10)
\]

\[
E_{f,\text{XRD}} = \left( 1 - \frac{1}{\cosh(\Phi)} \right) E_{\text{composite, tensile}} \quad (11)
\]

\(E_{\text{Composite}}\) is the composite modulus in the machine (fiber) direction, \(\Phi\) is the shear lag factor calculated from the x-ray and tensile elongations, \(E_{\text{fiber}}\) is the modulus
of the fiber, $E_{\text{matrix}}$ is the modulus of the matrix, $V_{\text{fiber}}$ is the volume fraction of fibers, $V_{\text{matrix}}$ is the volume fraction of the matrix, $\varepsilon_{\text{f, XRD}}$ is the elongation of the crystalline region determined from x-ray diffraction, $\varepsilon_{\text{composite, tensile}}$ is the macroscopic elongation of the specimen that is measured during elongation, $(L_f/r_f)$ is the ratio of the fiber length to the fiber radius (aspect ratio), and $G_m$ is the shear modulus of the matrix.

Based on this concept, the oriented polymer system was approximated as an infinitely long fiber reinforced composite that is corrected with Cox’s shear lag theory. Cox’s theory attempts to account for inefficiencies in the transfer of stress from the matrix to the fiber, which is associated with slippage at the interface between components. To make the stress transfer correction, the fiber portion of the infinitely long fiber composite theory is multiplied by the shear lag factor ($\Phi$), which is a relative measure of the adhesion between the matrix and the fibers. Doing so lowers the contribution of the fiber component to the composite modulus. The shear lag factor ($\Phi$) is related to the shear modulus of the matrix material ($G_{\text{matrix}}$), the aspect ratio of the fiber ($L_f/r_f$), the modulus of the fibers ($E_f$), and the volume fraction of the fibers ($V_f$) (Equation (10)). If there is perfect adhesion between the matrix and the fiber, stress is efficiently transferred from the matrix to the fiber and $\Phi$ is equal to unity, making Barham and Arridge’s model identical to the infinitely long fiber composite theory. The shear lag theory is an approximation and does not account for normal stresses, tensile stress on the fiber ends, or anisotropy in the fibers. For these reasons, the prediction of failure
mechanisms requires a more detailed approach, since the tips of the fibers are locations where composite failure typically is initiated.

X-ray diffraction was used by Barham and Arridge to measure the crystalline fiber strain ($\varepsilon_{f,XRD}$), and when compared with the strain of the composite measured during the orientation process ($\varepsilon_{\text{composite, tensile}}$), the shear lag factor ($\Phi$) can be determined (Equation (11)). Assuming that the modulus of the matrix ($E_m$) is significantly less than the modulus of the fiber ($E_f$), $E_m$ can be neglected and the volume fraction of fibers ($V_f$) can be calculated from the shear lag equation for the composite modulus ($E_{\text{Composite}}$) (Equation (9)). For the specific polyethylene studied by Barham and Arridge, this procedure resulted in a shear lag factor of 0.343, indicating a significant inefficiency of the fibrils as reinforcing agents relative to the infinitely long fiber composite theory, which has a shear lag factor of unity. This procedure also serves as a technique for determining the aspect ratio of the fiber if the tensile modulus of the fiber and the shear modulus of the matrix are well known (Equation (10)).

Barham and Arridge showed that the relationship between the increase in the composite modulus and the extent of which it was drawn could be very well explained with their model. They elaborated on their assumptions, which may be reasonable, depending on the system being studied. They assumed that the fibers have near perfect crystalline properties and they do not change when deformed. They also assume that the crystalline fibrils retain their shape, size, and properties.
throughout the annealing and self hardening process, which was supported by Koenig, et al.\textsuperscript{8} and Peterlin.\textsuperscript{9} At the time of their publication, they had little experimental evidence to support these claims.

Barham and Arridge proposed that the high modulus of the fiber is obtained as a result of a transformation of the crystalline phase from a cylindrical structure with a small aspect ratio to a fiber with extremely large aspect ratio, making it a more effective reinforcing component as the draw ratio increased by increasing its aspect ratio. While this assumption seems to be adequate for their approximate model, it does not effectively describe the transformation of a stack of orthorhombic lamellae into an extended chain fiber, likely by the long order alignment of stacked lamellae and the eventual extension of chains. Barham and Arridge did limit their model to linear polyethylene, whose Poisson ratio is 0.46, indicating it is highly incompressible, which adds some validity to their incompressible cylinder approach. Next, Barham and Arridge claim that the shear modulus of the amorphous and non-fibril crystalline material between fibrils is relatively small ($\sim10^3$ times less) in comparison to the fiber, contributes little to the physical properties of the composite, and does not change significantly with draw ratio. This concept contradicts that of Peterlin\textsuperscript{9}, which states that the tightening of the tie molecules within the amorphous component is the reason for the improvement in physical properties. They do agree with Peterlin’s model by suggesting that upon heating, this medium between the fibrils relaxes (and possibly melts), with its modulus dropping an order of magnitude, but disagree
with Peterlin’s model by stating that upon cooling, the medium begins to recrystallize and the modulus approaches its original value.

One of the key omissions in the Barham and Arridge model is that it does not account for transformations that are occurring in the matrix as a result of the deformation of non-fiber crystalline regions. In other words, they do not consider any enhancements that are possibly occurring as a result of the transformation of the crystalline component of the matrix into fibers, the stiffening of the amorphous region from taunt tie molecules, or effects of an anisotropic bulk amorphous region. It is expected that while the contribution of the matrix is small, relative to that of the fiber, it is changing as the material is strained. While accounting for the matrix’s contribution to the stiffening of the composite may not be critical for linear polymers of high molecular weight and crystallinity, it does play a more substantial role in branched polymers of lower crystallinity and molecular weight and can not be completely disregarded.

Gibson, Davies, and Ward\textsuperscript{11} proposed the concept of using x-ray data to statistically link the mechanical properties of an oriented film made from linear polyethylene to the crystalline structure of the material. Their model is analogous to the generalized infinitely long fiber composite theory, with the apparent fiber concentration being determined at each stage of the deformation. They define a fiber as a sequence of two or more crystalline lamellae linked together by inter-crystalline bridges. The fiber concentration is quantified by characterizing the
number of inter-crystalline bridges that link the crystallites, as shown in Figure 5 (e). The following set of equations is used to calculate the machine (fiber) direction modulus of the composite.

\[ p = \frac{D_{002} - L}{D_{002} + L} \]  
\[ E = V_f E_f \Phi' + V_m E_m \]  
\[ \frac{E}{E_f} = V_f \Phi' = \chi p(2 - p) \Phi' \]

\(D_{002}\) is the crystalline block thickness determined from the (002) wide angle x-ray scattering intensity, \(L\) is the long period (crystalline block thickness and inter-block amorphous region) determined from small angle x-ray scattering, \(p\) is the probability that a certain number of crystal blocks are linked together, \(E\) is the composite modulus in the machine (fiber) direction, \(\Phi'\) is the shear lag factor, \(E_f\) is the modulus of the fiber, \(E_m\) is the modulus of the matrix, \(V_f\) is the volume fraction of fibers, \(V_m\) is the volume fraction of the matrix, and \(\chi\) is the volume fraction of crystallinity.

While Gibson, Davies, and Ward\textsuperscript{11} acknowledge the presence of taught tie molecules, or bridges, and even use them to quantify the fiber concentration, they attribute the significant increases in mechanical stiffness to the crystalline continuity in the drawing direction. This concept supports Peterlin’s ideas that fiber-like structures are formed by the crystalline region and tie molecules are pulled taunt during drawing. Gibson, Davies, and Ward argue Peterlin’s concept that the formation of these taunt tie molecules and thus, an oriented amorphous
region, are the reason for the enhancements in stiffness seen through orientation. Gibson, Davies, and Ward’s study did not show evidence of extended chain crystals. They proposed a model consisting of lamellae linked by fiber bridges, with the amount of crystalline bridges increasing with increasing draw ratio. Gibson, Davies, and Ward claim that these sequences of linkages of two or more adjacent crystal blocks can be regarded as the fibers in a fiber composite. Such a description is contrary to previous definitions of a fiber, which include interconnected mosaic lamellae stacks or clusters of extended chains along a common axis in the draw direction, but do not include inter-fibrillar tie molecules. According to Gibson, Davies, and Ward’s depiction of their composite system (Figure 5 (e)), the fibers are actually linked together through a synergistic sharing of lamellae, more closely resembling a networked system and not a collection of individual fibers.

Gibson, Davies, and Ward used this idea of joined lamellae stacks to propose a statistical analysis of the probability that a certain number of crystal blocks are linked together, forming a large rigid structure. This probability is determined from the (002) WAXS intensity (D_{002}) and the long period (L) from SAXS (Equation (12)). For a polymer of given crystallinity (\chi), the ratio of composite modulus to fiber modulus (E/E_f) was plotted vs. the probability that a certain number of crystal blocks are linked together (p). The modulus of the fiber (E_f) is assumed to be equivalent to that of a perfect polyethylene crystal (~250-300 GPa), which may not be applicable if extended chains are not present. The slope of the
resulting linear plot is determined through linear regression, and is used to
determine the shear lag factor ($\Phi'$), as indicated in Equation (14). This technique
provides a relationship between the efficiency of the fiber as a reinforcing agent
as a function of the crystallinity of the polymer, which can be incorporated into an
equation similar to that of the shear lag modified infinitely long fiber model. This
model tends to the general fiber composite theory when the fibers consist of
relatively large amounts of crystalline blocks linked by inter-crystalline bridges.
While both this model and the one proposed by Barham and Arridge\textsuperscript{10} use the
shear lag theory, their transitions differ in that Barham and Arridge predict
enhancements as a result of the fiber’s increasing aspect ratio, while Gibson et al.
state the improvements are the direct result in the increase in the volume fraction
of fibers.

Gibson, Davies, and Ward’s model supports the eventual simplification to a
uniform stress fiber composite model, but omit several considerations that are
critical to polymer systems. The key issue with their statistical derivation of the
bridge probability is that they based their model on the observed anomaly that
$D_{002}$ is always greater than $L$. This is a physical impossibility, since the lamellar
thickness can not be greater than the long period, where the long period ($L$) is the
sum of the lamellae thickness ($D_{002}$) and the thickness of the amorphous region ($A$)
between lamellae ($L = D_{002} + A$) (Figure 6). To address this issue, the authors
created a physical structure that consisted of bridges extending between crystals,
with the presence of these bridges generating a larger value for $D_{002}$ than expected.
For this to be the case, a substantial fraction of bridges would need to be present to generate the scattering effect. A more reasonable assumption would be to incorporate the tilting of the c-axis of the unit cell relative to the lamellae normal (34.4°) of linear polyethylene, as shown in Figure 6.25 This tilting could explain why the authors saw D_{002} values (from WAXS) greater than L (from SAXS).

![Figure 6. Schematic drawings of the tilted c-axis of the unit cell within the lamella. The c-axis of the unit cell is aligned with the machine direction, while the lamellae normal is 34.4 degrees relative to the machine direction. The tilting of the c-axis results in the perception of a larger value of D_{002}, explaining why L was observed to be less than D_{002}.](image)

A thermal boundary condition imposed by Gibson, Davies, and Ward for the empirical derivation of the average shear lag factor (Φ’) at -50 °C hinders the applicability of the model. By fixing the model at this temperature, which is the halfway point between the onsets of the γ (glass transition) and α (melting) transitions, Gibson, Davies, and Ward felt they could safely assume the material is elastic, allowing them to disregard the viscoelastic nature of the polymer. While this simplifies the modeling process by making the shear lag factor dependent primarily on the volume fraction of crystallinity (χ), it renders the model inapplicable to commercial orientation processes, which typically operate near the α (melting) transition temperature of the polymer.17, 18 An average shear
lag factor that is not only dependent on the volume fraction of crystallinity ($\chi$) but also on the temperature of the process could improve the Gibson, Davies, and Ward model. One would expect the average shear lag factor to decrease with respect to increasing temperature, caused by a less efficient transfer of stress to the fibers as a result of the lower matrix shear modulus.

Another key issue, which seems to be recurring in most models, is the lack of incorporation of the dynamics of the matrix transformations caused by drawing. Gibson, Davies, and Ward simply ignore the contribution of the matrix (both amorphous and crystalline portions) to the modulus of the composite by stating that $E_{\text{matrix}} \ll E_{\text{fiber}}$. This simplification may be acceptable when the properties of the matrix and the fiber are known. This simplification may not be reasonable in semi-crystalline polymer fiber composites because the matrix includes crystalline portions that have yet to be transformed into fiber-like structures via the drawing process. This simplification can be further misleading, as in the case of Gibson, Davies, and Ward\textsuperscript{11} and Barham and Arridge\textsuperscript{10}, the modulus of the fiber is estimated to be equivalent to that of a perfectly elongated chain (perfect crystal $\sim 250$-$300$ GPa). In reality, the modulus of the fiber will be significantly less than that of a perfect crystal, primarily due to defects and non-perfect alignment and extension of chains, and thus narrowing the gap between the fiber and matrix moduli. In addition, a lower fiber modulus results in a higher shear lag factor ($\Phi'$) when the shear modulus of the matrix is significantly less than the tensile modulus of the fiber, indicating a more efficient transfer of stress to the fiber from
the matrix. This means that the simplification of utilizing the uniform stress model (infinitely long fiber) may provide acceptable methods for estimating the composite’s properties.

One documented work that is associated with commercial solid-state orientation of high density polyethylene film was conducted by Hatfield et al.\textsuperscript{17}, which saw significant enhancements in the moduli and tensile properties of medium molecular weight high density polyethylene (MMW-HDPE) films. Duckwall\textsuperscript{18} et al. completed similar work, but utilized a much higher molecular weight high density polyethylene and saw an increase in machine direction modulus greater than twice that of the undrawn film at a machine direction draw ratio of only 4.5:1. Neither set of authors disclosed a mechanism, whether empirical or theoretical, to explain the enhancements seen in the physical properties.

Weeks and Porter\textsuperscript{15} built upon these ideas and applied general composite theory to predicting the modulus of an oriented fiber extruded through a capillary die. Their model consisted of a composite of (1) a core region of extended chain crystals and (2) a sheath region surrounding the core that consists of highly oriented crystals, with the core region composing nearly 10 percent of the volume of the strand. This concept of having dissimilar crystalline phases is of interest, but does not address the fundamental issue with polymer microstructural composite theory, that being the determination of the continuous phase. In fact, Weeks and Porter point out that one of the shortcomings of their work, and the
work of others is that there is no evidence of long range order in the sheath.\textsuperscript{15}
This theory was one of the first that proposed treating an extended chain as a reinforcing rod, having a very large aspect ratio in a polymer structure. They found an excellent correlation between the experimentally measured modulus and that calculated from the composite theory. The shortcoming of their simplified model is that it does not account for the morphology changes in the sheath, which constitutes the majority of the volume of the sample. These variations were likely effected by the non-uniform crystallization of the molten polymer as it exited the capillary die.

1.4.3. CHARACTERIZATION OF ORIENTATION IN POLYMER FILMS

Extensive work has been conducted over the past sixty-plus years in technique development for measuring the average molecular orientation in a polymer film.\textsuperscript{19,27-65} The typical techniques used by today’s researchers include wide angle x-ray scattering (WAXS), small angle x-ray scattering (SAXS), birefringence, microscopy, and FT-IR dichroism. These techniques quantify the average molecular orientation of the film at various length scales, and can be characteristic of various phases present in the film. The following table lists those techniques, their pertinent length scale, and the phase(s) they observe.
<table>
<thead>
<tr>
<th>Technique</th>
<th>WAXS</th>
<th>SAXS</th>
<th>IR Dichroism</th>
<th>Birefringence</th>
<th>Optical Microscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characterizes</td>
<td>Unit Cell (1-10 Angstroms)</td>
<td>Lamellae (50-1000 Angstroms)</td>
<td>Bond Vibration under Cross Polarization at Specific Wavenumbers (1-2 Angstroms)</td>
<td>Refractive Indices of Polarized Chain Backbone (~10 Angstroms)</td>
<td>Optical Index Differences (1-100 µm)</td>
</tr>
<tr>
<td>Phase</td>
<td>Crystalline</td>
<td>Crystallite</td>
<td>Bonds in the Crystalline and Amorphous</td>
<td>Combination of Crystalline, Amorphous, and Interface</td>
<td>Crystalline Fibers</td>
</tr>
</tbody>
</table>

**Table 2.** Various analytical characterization techniques, pertinent length scales, and phase(s) they observe.

The end result of these techniques is the calculation of an orientation function, which is representative of the average molecular orientation of the sample. Past researchers, such as Ward et al.\textsuperscript{20}, Bassett et al.\textsuperscript{7, 25}, Porter et al.\textsuperscript{21}, Matsuo et al.\textsuperscript{22}, Crist\textsuperscript{24}, and Wilkes et al.\textsuperscript{23} used these techniques to correlate the changes in the polymer morphology to enhancements in physical properties.

Early work by Roe\textsuperscript{37, 38}, Stein and his colleagues\textsuperscript{27, 30, 31, 33, 39}, and Wilchinsky\textsuperscript{34-36, 40} led to the development of scattering techniques still used by today’s researchers. The x-ray techniques are used to measure the orientation of the crystalline structure at the various length scales of the unit cell and lamellae.
The following relationship can be used to determine the value of $\langle \cos^2 \Theta \rangle$ for uniaxially oriented systems by measuring the intensity of the diffraction peak for a selected crystal plane relative to the film’s machine direction.

$$
\left\langle \cos^2 \Theta \right\rangle = \frac{\int_{0}^{\pi/2} I(\phi) \cos^2 \phi \sin \phi d\phi}{\int_{0}^{\pi/2} I(\phi) \sin \phi d\phi} \quad (15)
$$

The fibrillar orientation is characterized by $\Theta$, which is the angle between an inter-structural direction (fiber axis) and a macroscopic direction (draw direction).

Once the average orientation of a plane normal term, $\langle \cos^2 \Theta \rangle$, is determined, the uniaxial Herman’s orientation function is simply:

$$
f = \frac{3\left\langle \cos^2 \Theta \right\rangle - 1}{2} \quad (16)
$$

For biaxially or three-dimensionally oriented systems, a more complex set of functions are needed.

Birefringence measurements can be used to calculate the Herman’s orientation function for the polymer chain backbone from the differences in the refractive indices of the film under cross polarization. Such a measurement includes
contributions of a length scale of 10-20 Angstroms and from the crystalline, the amorphous, and the interface between the phases. The intrinsic birefringence, $\Delta n_o$, is related to the measured birefringence, $\Delta n$, by the following relationship. $\Delta n_o$, is calculated from the molecular structure.\textsuperscript{66}

$$\Delta n = \Delta n_o \times f \quad (17)$$

In the case of biaxial orientation, determining the orientation functions becomes more complex. The following relationships are used to determine the biaxial average orientation of a plane normal term from measured birefringence data.\textsuperscript{64} These equations were derived from the work originally conducted by Desper and Stein.\textsuperscript{39}

$$\Delta_{MN} = \Delta n_o \left( \frac{3 \cos^2 \Phi - 1}{2} - \frac{\sin^2 \Phi \cos 2\Theta}{2} \right) + \Delta n_f \quad (18)$$

$$\Delta_{MT} = \Delta n_o \left( \frac{3 \cos^2 \Phi - 1}{2} + \frac{\sin^2 \Phi \cos 2\Theta}{2} \right) + \Delta n_f \quad (19)$$

$$\Delta_{TN} = \Delta n_o \sin^2 \Phi \cos 2\Theta + \Delta n_f \quad (20)$$

Where: $\Delta_{ij}$ = birefringence between the $i^{th}$ and $j^{th}$ axis

$\Delta n_o$ = intrinsic birefringence

$\Delta n_f$ = form birefringence
\[ \Phi = \text{angle between the axis of the structural unit (e.g. the local direction of the molecular backbone axis within a polymer repeat unit) and the machine direction of the film} \]

\[ \Theta = \text{angle between the projection of the chain backbone of the structural unit upon the transverse-normal plane with the transverse axis of the film} \]

The following figure shows the relationship between the axis of the molecular backbone, \( \Phi \), \( \Theta \), and the film axes.

**Figure 7.** Schematic of the relationship between the axis of the molecular backbone, \( \Phi \), \( \Theta \), and the film axes.
The following equations from Stein\textsuperscript{65} are used to calculate the biaxial orientation functions relative to both the machine direction axis ($\Phi$) and the transverse direction axis ($\Theta$) from the birefringence analysis.

\begin{align*}
    f_{\Phi} &= \frac{3\langle \cos^2 \Phi \rangle - 1}{2} \quad (21) \\
    f_{\Theta} &= 2\langle \cos^2 \Theta \rangle - 1 \quad (22)
\end{align*}

For the case of any polymer film, even those “uniaxially” oriented by a MDO machine, the biaxial orientation equations should be used. This is due to the fact that asymmetrical changes occur in the transverse and normal directions as a result of the MDO process. The uniaxial model may be applicable for the case of filament drawing, where the sample is symmetrical about the core and only changes in two dimensions (longitudinally and radially). Typically, birefringence is used in conjunction with a crystallographic technique, such as WAXS and/or SAXS, to provide a robust picture of the molecular orientation of the sample.

Past researchers, such as Stein\textsuperscript{28,29,32}, Hoshino and Stein\textsuperscript{33}, Chambon and Srinivas\textsuperscript{52}, Choi, White, and Spruiell\textsuperscript{44}, and Wedgewood and Seferis\textsuperscript{54} have proposed methods for combining these techniques to calculate the elusive amorphous orientation function. Holmes and Palmer\textsuperscript{49} coupled birefringence with X-ray diffraction to elaborate upon the work of Keller\textsuperscript{67}, proposing two types of molecular orientation in blown polyethylene film.
Infrared dichroism is another technique used in conjunction with crystallography to gain a better understanding of the molecular orientation of a polymer sample. This technique involves measuring the infrared absorbance of a sample at quantized wavenumbers under cross polarization. The polarizers are set 90 degrees apart, generally parallel and perpendicular to the stretching direction. From the absorbencies (A), the dichroic ratio (D) can be calculated.

\[ D = \frac{A_\|}{A_\perp} \quad (23) \]

Once the dichroic ratio is known, the uniaxial Herman’s orientation function for the band attributed to a given bond can be calculated by:

\[ f = \left( \frac{D - 1}{D + 2} \right) \left( \frac{D_0 + 2}{D_0 - 1} \right) \quad (24) \]

Where \( D_0 \) is given by:

\[ D_0 = 2 \cot^2 \Psi \quad (25) \]

\( \Psi \) is the angle between the chain axis and the transition moment direction for the vibrational mode responsible for the infrared absorption and is constant for a given bond in a molecule. Read and Stein\(^{46}\) carefully documented a wide variety of bonds that are characteristic of the unit cell axes and amorphous regions of
polyethylene. Koenig et al.\textsuperscript{8} used IR dichroism to measure the changes in orientation of uniaxially drawn polyethylene. Kissin\textsuperscript{57, 58} coupled dichroism with x-ray diffraction to measure the orientation of polyolefin films and fibers and discusses the relevancy to various models for crystalline orientation. Tetsuya, et al.\textsuperscript{59} utilized dichroism with x-ray diffraction to study deuterated molecules in biaxially oriented UHMW-HDPE films, with the intent of characterizing the orientation of the amorphous region. Wedgewood and Seferis\textsuperscript{48} used IR dichroism to study the effects of polymer density on the orientation characteristics of linear polyethylene.

Microscopic techniques, such as optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM), have been used to qualitatively characterize the microstructure and molecular orientation of polymer films. These techniques give the researcher a picture of how the microstructure changes upon orientation and relative length scales of the various phases present in the sample. Du\textsuperscript{60}, et al., used microscopic techniques to study the orientation of the lamellae structure in oriented melt-drawn HDPE. When this technique is coupled with software that can calculate the Fourier Transform of the images, orientation functions can be determined via a similar technique as x-ray diffraction. Such a methodology is rarely noted in the literature, but can serve as a quick, inexpensive method for comparing the degree of orientation between samples on a 10-200 μm scale (e.g. macro-fiber orientation).
Other techniques, such as Raman scattering and nuclear magnetic resonance (NMR) have been used by researchers to characterize oriented films. Capaccio, et al. used Raman scattering in conjunction with x-ray scattering to determine the distribution of crystal sizes in oriented linear polyethylene. Roe described a technique that uses wide-line NMR and fluorescence polarization to acquire information for determining a complete crystalline orientation distribution function. Schmidt-Rohr et al utilized two-dimensional NMR to investigate the molecular order of polymers, and showed its analogies with WAXS pole figure analysis. They also investigated the crystallinity, domain size, and characteristics of the amorphous phase of ultradrawn polyethylene fibers with solid-state NMR. Mowery and Schmidt-Rohr also used various NMR techniques to characterize the morphological composition of cold-drawn HDPE. They describe the existence of a major microstructural component (~30 % of the bulk mass) that has characteristics that are intermediate to the crystalline and amorphous domains.
2. ENHANCEMENTS IN THE PHYSICAL PROPERTIES OF MONOLAYER FILMS AS A RESULT OF UNIAXIAL SOLID STATE DRAWING

2.1. MATERIALS

Monolayer blown films were studied that were produced with Equistar’s Alathon® high molecular weight high density polyethylene (HMW-HDPE) grades that are typically used in high tensile strength films applications. The same catalysis and reactor process was used to polymerize all the products within the scope of this program. The products selected cover a much broader density range than most HMW-HDPE families, reaching in density from a homopolymer of 0.959 g/cc to a hexene copolymer of 0.938 g/cc. In addition, a much broader range of molecular weights are included, with melt indices values ranging from 0.05 g/10 minutes to 0.10 g/10 minutes. These two characteristics of the polymer are independent from each other, and are controlled by the independent conditions with which the polymerization occurs. Density (Figure 8, Table 3) is typically controlled by varying the amount of comonomer added to the reactor, while the molecular weight is determined by the reactor temperature and the amount of hydrogen added to the process.
Figure 8. Display of product densities and MI values for the HMW-HDPEs studied.

<table>
<thead>
<tr>
<th>Density (g/cc)</th>
<th>MI (g/10 minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HD 1</td>
<td>0.959</td>
</tr>
<tr>
<td>HD 2</td>
<td>0.949</td>
</tr>
<tr>
<td>HD 3</td>
<td>0.949</td>
</tr>
<tr>
<td>HD 4</td>
<td>0.940</td>
</tr>
<tr>
<td>HD 5</td>
<td>0.938</td>
</tr>
</tbody>
</table>

Table 3. Density and MI values for the HMW-HDPE grades studied.

The molecular weight distributions of these products are bimodal, and are represented in Figure 9. This characteristic of the polymer is unique to the reactor process and catalyst used to produce these resins and is atypical of most HDPE grades produced by other reactor technologies.
The following figures represent the molecular weight distribution of each of the polymers in the study. The $M_n$, $M_w$, $M_z$, and $M_{z+1}$ are obtained by gel permeation chromatography (GPC) on a Waters GPC2000CV high temperature instrument equipped with a mixed bed GPC column (Polymer Labs mixed B-LS) and 1,2,4-trichlorobenzene (TCB) as the mobile phase. The mobile phase is used at a nominal flow rate of 1.0 mL/min and a temperature of 145 °C. No antioxidant is added to the mobile phase, but 800 ppm butylated hydroxytoluene (BHT) is added to the solvent used for sample dissolution. Polymer samples are heated at 175 °C for two hours with gentle agitation every 30 minutes. The injection volume is 100 microliters. The molecular weights are calculated using the cumulative matching percent calibration procedure employed by the Waters Millennium 4.0 software. This involves first generating a calibration curve using narrow polystyrene standards (PSS, products of Waters Corporation), then developing a polyethylene calibration by the Universal Calibration procedure.

**Figure 9.** GPC curves for HD 1, HD 2, HD 3, HD 4, and HD 5
HD 1 has the most equal balance between the two modes in the molecular weight distribution and has the second broadest overall molecular weight distribution. HD 2 has a molecular weight distribution of similar bimodal distribution to HD 1, but has a slightly narrower overall molecular weight distribution. HD 3’s molecular weight distribution has a significantly different shape than that of HD 1 and HD 2, with the larger fraction of the molecular weight distribution in the lower molecular weight mode. HD 3 also has the broadest overall molecular weight distribution. The bimodal distributions of HD 4 and HD 5 are similar to each other, but significantly different than those of HD1, HD 2, and HD 3. The molecular weight distributions of HD 4 and HD 5 are less bimodal, meaning that the polymer molecular weights are more uniformly spread throughout the entire distribution. They also have the narrowest overall molecular weight distributions.

The values for $<M_n>$, $<M_w>$, $<M_z>$, and $<M_{z+1}>$ are presented in Table 4.

<table>
<thead>
<tr>
<th></th>
<th>$&lt;M_n&gt;$</th>
<th>$&lt;M_w&gt;$</th>
<th>$&lt;M_z&gt;$</th>
<th>$&lt;M_{z+1}&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HD 1</td>
<td>12,866</td>
<td>207,278</td>
<td>817,939</td>
<td>1,428,226</td>
</tr>
<tr>
<td>HD 2</td>
<td>14,317</td>
<td>194,693</td>
<td>762,993</td>
<td>1,280,440</td>
</tr>
<tr>
<td>HD 3</td>
<td>12,636</td>
<td>212,449</td>
<td>944,481</td>
<td>1,660,713</td>
</tr>
<tr>
<td>HD 4</td>
<td>16,051</td>
<td>175,481</td>
<td>680,489</td>
<td>1,142,594</td>
</tr>
<tr>
<td>HD 5</td>
<td>18,320</td>
<td>209,140</td>
<td>800,932</td>
<td>1,384,594</td>
</tr>
</tbody>
</table>

Table 4. $<M_n>$, $<M_w>$, $<M_z>$, and $<M_{z+1}>$ values for the HMW-HDPE grades studied.
A gradient column of distilled water and isopropyl alcohol was used to verify the densities of the polymer pellets per ASTM D 1505, with values reported in Table 5.

<table>
<thead>
<tr>
<th>Pellet Density (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HD 1</td>
</tr>
<tr>
<td>0.9538</td>
</tr>
<tr>
<td>HD 2</td>
</tr>
<tr>
<td>0.9451</td>
</tr>
<tr>
<td>HD 3</td>
</tr>
<tr>
<td>0.9463</td>
</tr>
<tr>
<td>HD 4</td>
</tr>
<tr>
<td>0.9371</td>
</tr>
<tr>
<td>HD 5</td>
</tr>
<tr>
<td>0.9359</td>
</tr>
</tbody>
</table>

**Table 5.** Gradient column densities for the base HMW-HDPE polymers.

Differential Scanning Calorimetry (DSC) was conducted on a TA Instruments DSC 2910 Autosampler per ASTM E 793 to determine the melting temperature for each of the five films to be oriented. Table 6 reports the second heat melting temperatures, enthalpies of fusion, volume fractions of crystallinity from DSC, densities from DSC, and the densities from the gradient column for the five unoriented films. The second heat DSC curves are included in the appendix. The following equation was used to calculate the volume fraction of crystallinity from the heat of fusion data obtained by DSC:\(^{64}\)

\[
V_{c,DSC} = \frac{\Delta H_f}{\Delta H_f^o} \quad (26)
\]

Where: \(\Delta H_f = \) Enthalpy of Fusion from DSC
$\Delta H_f^o$= Enthalpy of Fusion of a completely crystalline polyethylene sample (277.2 J/g)$^{66}$

The film density was calculated from the DSC data with the following equation:$^{64}$

$$\rho_{DSC} = \left[ V_{C,DSC} \left( \frac{1}{\rho_c} - \frac{1}{\rho_a} \right) + \frac{1}{\rho_a} \right]^{-1} \quad (27)$$

Where:

- $\rho_{DSC}$ = density of the film calculated from DSC data
- $V_{C,DSC}$ = percent crystallinity of the film obtained from DSC data
- $\rho_a$ = density of the amorphous polymer (0.885 g/cc)$^{66}$
- $\rho_c$ = density of the crystalline polymer (1.00 g/cc)$^{66}$

<table>
<thead>
<tr>
<th></th>
<th>$T_m$ ($^\circ$C)</th>
<th>$\Delta H_f$ (J/g)</th>
<th>$V_{C,DSC}$ (DSC)</th>
<th>Unoriented Film $\rho$ (DSC) (g/cc)</th>
<th>Unoriented Film $\rho$ (Column) (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HD 1</td>
<td>133.7</td>
<td>211.5</td>
<td>76.3</td>
<td>0.9614</td>
<td>0.9593</td>
</tr>
<tr>
<td>HD 2</td>
<td>129.9</td>
<td>183.5</td>
<td>66.2</td>
<td>0.9458</td>
<td>0.9487</td>
</tr>
<tr>
<td>HD 3</td>
<td>129.8</td>
<td>184.7</td>
<td>66.6</td>
<td>0.9464</td>
<td>0.9486</td>
</tr>
<tr>
<td>HD 4</td>
<td>125.9</td>
<td>138.4</td>
<td>49.9</td>
<td>0.9217</td>
<td>0.9385</td>
</tr>
<tr>
<td>HD 5</td>
<td>126.7</td>
<td>153.8</td>
<td>55.5</td>
<td>0.9298</td>
<td>0.9376</td>
</tr>
</tbody>
</table>

*Table 6.* DSC melting temperatures, enthalpies of fusion, calculated volume fractions of crystallinity, calculated density from DSC, and the measured density from the density gradient column for the five unoriented films.
The viscosity profiles for each of the polymers were obtained through DORS (Dynamic Oscillatory Rate Sweep) testing on an ARES II Rheometer per ASTM D4440 and are shown in Figure 10. DORS testing was conducted at 190 °C.

![Viscosity curves from DORS testing for the HMW-HDPE grades studied.](image)

**Figure 10.** Viscosity curves from DORS testing for the HMW-HDPE grades studied.

The zero shear viscosity, which is indicative of the viscosity at a zero shear rate, can be used in a range of models to predict certain characteristics of the polymer, such as its polydispersity.4

The polydispersity term, $E_T$, is an empirical measure of the breadth of the high molecular weight end of the molecular weight distribution.4 $E_T$ is a unitless parameter that has been shown to correlate with the steady state compliance4, which is independent of molecular weight but depends strongly on molecular weight distribution, particularly the high molecular weight tail.68
The Cross model was used to calculate the zero shear viscosity values.

\[
\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \left[ 1 + (\lambda \gamma)^m \right]^{-1} 
\]

(28)

Where:

- \( \eta \) = viscosity
- \( \eta_\infty \) = viscosity at infinite shear rate
- \( \eta_0 \) = viscosity at zero shear rate
- \( \gamma \) = shear rate
- \( \lambda \) = time constant = \( 1/\gamma_\text{power law} \)

\( \gamma_\text{power law} \) = shear rate where the fluid changes from constant shear rate behavior to power law behavior

\( m \) = Cross law exponent = \( 1-n \)

\( n \) = power law exponent = slope of the viscosity curve in the power law region

\( E_T \) is calculated by:

\[
E_T = \frac{C_2}{\left[ G'^2 + G''^2 \right]^{0.5}} \mid_{\text{at } \tan \delta = C_3} = \frac{C_2}{1.8 \ast G'} \mid_{\text{at } \tan \delta = C_3} \quad (29)
\]

Where:

- \( C_2 \) = Constant = 106 dyn/cm²
- \( C_3 \) = Constant = 1.5
- \( G' \) = Storage Modulus
- \( G'' \) = Loss Modulus = tan\( \delta \)\( \ast G' \)
The calculation and use of $E_T$ is only valid for polymers with very high molecular weights and/or extremely broad molecular weight distributions.\textsuperscript{4}

Table 7 shows the values for the calculated zero shear viscosity ($\eta_0$) and $E_T$ values for each resin.

<table>
<thead>
<tr>
<th></th>
<th>$\eta_0$ (Poise)</th>
<th>$E_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HD 1</td>
<td>$2.20 \times 10^6$</td>
<td>12.7</td>
</tr>
<tr>
<td>HD 2</td>
<td>$1.67 \times 10^6$</td>
<td>13.4</td>
</tr>
<tr>
<td>HD 3</td>
<td>$1.51 \times 10^6$</td>
<td>1.42</td>
</tr>
<tr>
<td>HD 4</td>
<td>$9.34 \times 10^5$</td>
<td>5.94</td>
</tr>
<tr>
<td>HD 5</td>
<td>$1.74 \times 10^6$</td>
<td>9.99</td>
</tr>
</tbody>
</table>

Table 7. Rheological data from DORS testing for the HMW-HDPE grades studied.

2.2. FILM BLOWING AND ORIENTATING PROCESSES

The base films used in this study were blown using typical conditions and techniques for producing HMW-HDPE film, which are known throughout the industry.

Monolayer base films that were 150 $\mu$m (6 mil) thick were blown on a three layer Hosokawa-Alpine blown film line. The line consisted of three extruders with grooved feed sections and length to diameter ratios of 24:1. Spiral grooves are machined in the feed section of the barrel to provide additional shear, which homogenizes the molten polymer. The die gap was set at 2000 $\mu$m. The film was “high stalked” (as explained in Section 1.3) by utilizing a single lip air ring to maximize the degree of isotropic molecular orientation within the film. By extending
the cooling time of the hot extrudate exiting the die, the polymer chains are given more time to relax and randomize. The air entrapped within the bubble was not cooled, since doing so would increase the cooling rate and reduce the randomness of the molecular orientation. The film was stalked such that the blow up begins at a height equivalent to eight die diameters above the die lip. A blow up ratio of 4:1 was used to further enhance the biaxial orientation of the film.

The films were oriented off-line, meaning the blowing and post-orientation steps were not conducted in series with one another. The following figure is a schematic of the two processes:

**Figure 11.** Schematic of commercial blown film and MDO units.
The 150 µm base films were oriented at an initial draw ratio of 2:1, then the draw ratio was incrementally increased until the maximum draw ratio for each grade was reached. In the cases of HD 2-5, the maximum draw ratio was determined when the films broke. For the case of HD 1, the maximum off-line draw ratio was predetermined by the limitations of the orientation equipment. The HD 1 film would not break at the machine’s highest drawing ratio of 11.6:1.

The MDO unit used to stretch the films consisted of various sections, including:

- **Unwind**
  - Heavy gauge film is unwound for orientation.

- **Preheat**
  - The thick film is uniformly preheated to 5 to 10 °C below the peak DSC melting temperature of that particular polymer.

- **Drawing**
  - The thick film is drawn between a narrow gap of two rolls turning at different speeds. The difference in roller speeds determines the draw ratio.

- **Annealing**
  - The film passes over additional rollers set at 5 to 10 °C below the DSC melting temperature. Annealing at this temperature reduces the amount of film shrinkage during the heat sealing of the downstream package forming process.

- **Cooling**
- Chilled water passing through idlers that cool the film to ambient temperature.

- Rewind

  - The thin, oriented film is rewound.

**Figure 12.** Schematic of a commercial MDO unit.

As the film is unwound, it passes over preheating rollers which warm the film to a temperature of 5 to 10°C below the DSC melting point. The heated film then passes between the drawing rollers, which consist of an infeed roller turning at the same speed as the preheat rollers, and an outfeed roller turning at a higher speed. The ratio of the two rollers’ speeds is indicative of the draw ratio of the oriented film. The gap between the two rollers in the draw section was minimized to reduce the amount of shrinkage in the transverse direction. Typically, the distance between the drawing rollers is of the order of 80 to 100 mm. Immediately after orientation, the film passes
through the annealing section, which conditions the film at the same temperature as that of the preheat section. The films were annealed at this temperature to minimize the amount of shrinkage during the downstream package fabrication and filling process. After annealing, the film is cooled to ambient conditions and rewound on a roll.

2.3. MEASUREMENT OF PHYSICAL PROPERTIES

All of the physical testing was conducted per the following ASTM specifications (as noted in the Appendix):

- Moduli: E 111
- Yield and Break Strengths: D 882
- Haze: D 1003
- Gloss: D 2457

All of the films were conditioned at 23 °C and 50 % relative humidity for 40 hours per ASTM specifications prior to testing. All tensile and modulus testing was conducted on an ISO certified Sintech 1/S unit manufactured by MTS. Haze measurements were collected on an ISO certified BYK (Gardner) Hazegard Plus unit. Gloss measurements were collected at 45 degrees on an ISO certified BYK micro-gloss unit.

2.4. DISCUSSION OF THE FORMATION OF FIBER STRUCTURES

During the film fabrication and post orientation processes, a range of molecular morphologies are evident. In the film blowing process, the polymer melt is extruded
through a narrow gap while being uniaxially drawn in the machine direction, inducing a high degree of machine direction orientation. During the crystallization process, the film is blown in the transverse direction in an attempt to balance the orientation between the machine and transverse direction. In the high stalk film blowing process, the stalk is allowed to cool for a longer time prior to the film being blown up in the transverse direction. This extended cooling rate allows for more relaxation and the formation of larger lamellae stacks that are more randomly orientated. In contrast, when a film is blown in a more conventional “in-the-pocket” fashion, the polymer is immediately blown up above the air ring. This technique results in a rapid crystallization, generating smaller lamellae that are more highly oriented in the machine direction. The difference in the two techniques is obvious when studying the properties of the films. For example, films blown with the high stalk technique typically have higher machine direction tear strengths than those blown in-the-pocket. For this reason, commercial films made with high molecular weight high density polyethylene (HWM-HDPE) are typically blown with the high stalk technique.

The next sections will discuss changes in the morphology of the crystalline region during the orientation process and are the result of collaborative work by Breese, McFaddin, Beaucage, Mirabella, and Bafna.69

Randomization of the lamellae through high stalk blown film

After the film is blown, the crystalline microstructure consists of a series of stacked lamellae of the order of $10^2$ to $10^3$ angstroms in thicknesses that are randomly
oriented relative to the machine direction. This is later supported by Figure 26, the plot of the Herman’s orientation function derived from SAXS analysis, which shows the trend to nearly random orientation functions of the lamellae normal for low characteristic draw ratios (< 2:1). These randomly oriented stacks are clustered together into groups with very large aspect ratios of the micron scale in width which are also randomly oriented.

Figure 13 is a schematic drawing of the randomized lamellae structures. All schematic drawings depict only the ordered crystalline region of the polymer structure. The amorphous region is not shown.

![Diagram](image)

**Figure 13.** Model for randomly oriented polyethylene lamellae clusters and stacks in the unoriented film. (a) Micro-scale, (b) Colloidal scale, (c) Nano-scale

The left portion of the figure represents clusters of micron scale widths that consist of randomly oriented lamellae stacks. These clusters have little preferential orientation
relative to the machine direction of the film. The middle image is a magnification of
a section of a randomly oriented cluster, showing randomly oriented stacks of
lamellae. These stacks are on the order of hundreds to thousands of angstroms and
can consist of a few to tens of lamellae. Often joining these stacks are tie molecules
or molecular entanglements due to imperfections occurring during the crystallization
process. Further magnification exposes the lamellae unit cells of the order of
angstroms, which are also randomly oriented relative to the machine direction of the
film.

The following image, which is a micrograph (50 X magnification) of a film blown
utilizing the high stalk technique, shows the presence of randomly oriented lamellae
clusters.

Figure 14. Optical microscopic photo of blown film made by high stalking HD 1
(50x magnification). The micrograph shows the micro-scale structures of the model
displayed in Figure 13 (a). Machine direction in vertical.
Figure 15 shows the corresponding (110) and (200) pole figures acquired with WAXS for the unit cell described in the nano-scale structure of Figure 13 (c).

![Figure 15](image)

**Figure 15.** (110) and (200) pole figures (from WAXS) for the unit cell described in the nano-scale drawing of Figure 13 (c) for unoriented HD 1 film. (Draw ratio of 1:1)

The technique described by Alexander\(^ 19 \) and Roe\(^ 42 \) was used to calculate the Herman’s orientation functions of the films. The broadness and divergence in the bands along the equators of the figures indicate a relatively low degree of machine direction orientation. This correlates with the relatively low degree of machine direction orientation when compared with other oriented films.

**Orientation of the lamellae clusters and stacks**

After the film is blown, it is oriented in the machine direction via the previously described MDO process (Section 2.2). As the film is preheated, the thinner lamellae
melt, rearranging and eventually recrystallizing in the form of relatively small fibers oriented in the machine direction. From the first heat DSC curves of the unoriented films, we can estimate that this fraction is approximately 20 to 25% of the total amount of crystalline material. These low molecular weight crystallites are captured in the volume fraction of fibers later calculated, but are not subject to the upcoming discussion of lamellae tilting and unraveling. Future work should be conducted, possibly with dynamic DSC, to further understand the crystallization kinetics of the preheating, drawing, and annealing processes. Additional thermal analysis should also be conducted to better understand the changes in both the crystalline and amorphous phases of the oriented films.70

At low draw ratios, the large lamellae clusters begin to orient in the machine direction and is depicted in Figure 16.

Figure 16. Oriented lamellae clusters and stacks seen at low draw ratios.
During this process, the normal of the lamellae stacks are briefly aligned in the machine direction at very low draw ratios (~2:1-3:1). In addition, intra-stack tie molecules and entanglements are pulled taunt.

When picturing this orientation process, one must realize that the c-axis of the polyethylene unit cell is directed at an angle of 34.4° relative to the normal of the lamellae. It is this tilted c-axis that is driven to align with the machine direction of the film, resulting in a lamellar orientation equivalent to 34.4° prior to the unraveling of the lamellae. The film will eventually reach a critical draw ratio where the c-axis of the unit cell is oriented perfectly with the machine direction, as shown in Figure 17.

At moderate draw ratios, the large scale lamellae clusters continue to orient in the machine direction. The lamellae stacks, whose normal was previously oriented in the machine direction, are now tilted to the critical angle of 34.4° with the machine direction. This rotation is due to the c-axis of the unit cells aligning in the drawing direction.
Figure 17. Oriented lamellae clusters and stacks at moderate draw ratios.

Based on the presented data, this typically occurs at a draw ratio between 2:1 and 6:1 for HD 1. For the case where the polyethylene unit cell \( (a = 7.42 \text{ Angstroms}, b = 4.95 \text{ Angstroms}, c = 2.55 \text{ Angstroms}) \) is oriented at 34.4 ° to the machine direction, the intensity of the scattering from the (110) pole and (200) pole would be concentrated relative to the equator at 15.4 ° and 34.4 °, respectively. Any formation of fibers, which likely would have occurred, would contribute to the scattering intensity about the equator, thus giving the appearance of a single intensity that extends from those generated by the unit cells in the (110) pole figure and a
concentration of intensity in the center of the figure in the (200) pole figure. Figure 18 (a) shows these described and pole figures. Unfortunately, a film sample was not produced in the HD 1 set that displayed these pole figures. This is due to the lack of samples collected at low to moderate draw ratios for the HD 1 film set. The pole figures seen in Figure 18 (a) would be indicative of a film produced at a low to moderate draw ratios, likely between 2:1 and 6:1. Figure 18 (b), which is the (110) and (200) pole figures for the HD 1 film oriented to a draw ratio of 2:1 most closely resembles the theoretical pole figures in Figure 18 (a). Evidence of the separate lobes in the (110) pole figure is present, with a distinct concentration of intensity in the center of the (200) pole figure.

**Figure 18 (a).** (110) and (200) pole figures for polyethylene unit cells tilted at exactly 34.4° relative to the machine direction. The intensity bands connecting the lobes (110) and in the center (200) are the results of scattering from small fibers that have been generated by the orientation process.
Figure 18 (b). (110) and (200) pole figures for HD 1 films oriented to a draw ratio of 2.1:1. At this draw ratio, the c-axes of the polyethylene unit cells are nearly tilted to 34.4° relative to the machine direction. The presence of the four lobes in the (110) pole figure and a concentration of intensity in the center (200) pole figure closely resemble the patterns predicted in Figure 18 (a).

Figure 19 shows the Herman’s orientation function of the c-axis of the unit cell relative to the machine direction of the film vs. the characteristic draw ratio at which the film was oriented for the HD 1 data set. This data was collected in transmission mode using a Bruker D8 Discover XRD unit with GADDS software. The XRD used a CuK$_\alpha$ source at 40 kV and 40 mA.

Figure 19. Plot of Herman’s orientation function from WAXS for the HD 1 film set vs. Characteristic Draw Ratio.
The figure clearly shows that at draw ratios above 6:1, the c-axis orientation does not significantly change, while the physical properties of the film continue to do so. Also, at these high draw ratios, the c-axis orientation is nearly unity, indicating nearly perfect alignment in the machine direction. Similar results are reported by Gibson, Davies, and Ward\textsuperscript{11}, but at draw ratios above 10:1. This supports the concept that the principle orientation mechanism prior to a critical draw ratio involves the tilting of the lamellae structure until the c-axis is aligned in the machine direction. Figure 20. is a micrograph of the HD 1 film drawn 6:1.

\textbf{Figure 20.} Optical microscopic photo of machine direction drawn HD 1 (6:1 draw ratio) (50x magnification) machine direction is vertical.

From the micrograph, an apparent alignment is occurring in the larger scale fibers.
The corresponding (110) and (200) pole figures acquired through transmission WAXS for the high stalked HD 1 film drawn 6:1 are shown in Figure 21.

**Figure 21.** (110) and (200) pole figures (from WAXS) for HD 1. (Draw ratio of 6:1)

The appearance of bright lobes in the (110) pole figure and the concentration of intensity in the core of the (200) pole figure indicate a high degree of c-axis orientation in the machine direction. The calculated Herman’s orientation function for the c-axis relative to the machine direction is 0.920.

**Unraveling of the lamellae to form fibers**

Once the critical draw ratio is reached, a new mechanism dominates the orientation process and results in the unraveling of the lamellae structures, possibly similar to the
mechanism proposed by Matsumoto. At this point, all of the lamella are aligned with their normals at 34.4° to the machine direction, with some lamellae possibly beginning to unzip and form long, rigid fibers oriented in the machine direction, as indicated in Figure 22. The large lamellae clusters appear as long rods which are made up of the smaller scale fibers. The smaller fiber structures consist of highly oriented stacks of lamella and possibly some extended chains with extremely large aspect ratios, their formation a result of the unraveling of the lamellae stacks.

**Figure 22.** The formation of polyethylene fiber structures at high draw ratios.

At this point in the drawing process, no changes in the orientation function obtained from WAXS would be evident, since the c-axis of the fiber also correlates with the c-axis of the lamellae. The orientation function obtained from WAXS would be nearly that of a perfectly oriented crystal, a value of 1.00. The crystalline phase is, for all practical purposes, continuous in the c-direction, with the degree of continuity increasing with the characteristic draw ratio. The orientation function derived from
SAXS will approach an asymptotical value of 0.521, indicating a lamellae normal orientation of 34.4° to the machine direction.

Figure 23 is a micrograph at 50 X magnification that shows the presence of the large rod-like structures that are highly oriented in the machine direction at the maximum draw ratio.

![Figure 23. Optical microscopic photo of machine direction drawn HD 1 (11.6:1 draw ratio) (50 X magnification) machine direction is vertical.](image)

The corresponding (110) and (200) pole figures acquired through transmission WAXS for the high stalked HD 1 film drawn 11.5:1 are shown in Figure 23.
Figure 24. (110) and (200) pole figures (from WAXS) for HD 1. (Draw ratio of 11.6:1)

The appearance of the bright lobes and center point in the (110) pole figure and the concentration of intensity in the center with an equatorial band in the (200) pole figure indicates a high degree of c-axis orientation in the machine direction, as well as uniform interplaner orientation. This type of pattern is indicative of a tightly packed cluster of uniaxially oriented fiber structures. The calculated Herman’s orientation function from WAXS for the c-axis relative to the machine direction is 0.957.

Two other techniques were utilized to better understand the orientation mechanism that was occurring during the orientation process. SAXS was conducted on the HD 1
film set to study the orientation of the lamellar structures. Since the films are very thin (12 – 150 µm), the samples were prepared by stacking the film to a final thickness of approximately 600 µm. Great care was taken to assure that the machine, transverse, and normal directions of each layer were properly aligned within the stack. The following figures show the SAXS scattering pattern for HD 1 at draw ratios of 1:1, 6:1, and 11.6:1.

Figure 25. SAXS scattering patterns for HD 1 at draw ratios of 1:1, 6:1, and 11.6:1. The machine direction of the film is directed up. Below each SAXS pattern is a schematic displaying the lamellae clusters and stacks at each characteristic draw ratio.
In the undrawn sample (characteristic draw ratio of 1:1), a random scattering pattern is evident, indicating a low degree of lamella orientation relative to the machine direction. As the film is draw to higher characteristic draw ratios, two pronounced lobes become evident in the scattering pattern, as indicated in the pattern for the characteristic draw ratio of 6:1. The formation of such lobes is indicative of the uniaxial orientation of lamellae in the machine direction. At high draw ratios, the scattering intensity significantly decreases, indicating the disappearance of stack lamellae, which is due to the transformation of the crystalline region into fiber-like structures. Faint lobes are still present, indicating the presence of a small amount of oriented lamella stacks.

Herman’s orientation functions were also determined from the SAXS data and are shown in the following figure.

**Figure 26.** Herman’s orientation function determined by SAXS.
From the SAXS data, a maximum orientation function of 0.512 is obtained, which correlates to a $\Phi$ value of $34.7^\circ$. This corresponds very closely to the theoretical $\Phi$ value of $34.4^\circ$ (i.e. $f = 0.521$), proposed by numerous researchers.\textsuperscript{25, 50, 71-73} These data support the previous work that the c-axis of the polyethylene unit cell is tilted at an angle of $34.4^\circ$ to the normal of the lamellae and that the orientation of the a lamellae at high draw ratios is at $34.4^\circ$ to the machine direction. When this crystal lamellar tilt relative to the machine direction is satisfied, the chains that compose the lamellae can begin to unravel and form extended chains.\textsuperscript{6}

A third technique is used that obtains an orientation function from micrographs of the films taken at a 50x magnification. By using these micrographs, the orientation on a larger length scale can be determined and used to characterize the orientation of the large fiber structures. To obtain an orientation function, the Fourier Transform of the micrographs was obtained using Image J software.\textsuperscript{75} The micrograph and corresponding Fourier Transform for the undrawn (1:1), 6:1, and 11.6:1 HD 1 samples are shown in Figure 27.
Figure 27. Micrograph and corresponding Fourier Transform of HD 1 drawn 1:1, 6:1, and 11.6:1.

From the micrograph images, the orientation of lamellae clusters and the formation of fiber structures are evident. The corresponding images of the Fourier Transform support such a statement, with the Fourier Transform of the undrawn film closely resembling that of a SAXS or SALS pattern, indicating randomness to the lamellae
cluster arrangement. As the draw ratio increases, the intensity of the Fourier Transform image begins to concentrate about the equator, indicating an increasing amount of orientation in the machine direction. At the highest draw ratio, the intensity of the Fourier Transform image is heavily concentrated along the equator, indicating a high degree of uniaxial orientation.

The Fourier Transform was then analyzed with the same software code that calculated the Herman’s orientation function for the SAXS scattering pattern. The plot of the Herman’s orientation functions for the micrograph images are plotted with respect to the characteristic draw ratio, and is shown in the following figure.

![Figure 28](image_url)

**Figure 28.** Herman’s orientation function obtained from 50 X micrographs vs. characteristic draw ratio.
The orientation functions begin to increase significantly above a characteristic draw ratio of 6:1, due to the unraveling and the alignment of the large cluster structures in the machine direction.

Surface imperfections are the likely cause for error in this technique, which may be significant. The surface roughness that obviously exists at these length scales can be eliminated by collecting the images using the technique described by Bafna et al. They suggest using benzyl alcohol to wet the surface of the films, removing the artifacts associated with the topography of the surface. By doing so, a direct image of the bulk of the sample is obtained and the errors associated with the surface imperfections of the film are addressed. Future work is planned to use this technique to collect additional micrographs, determine the Fourier Transform, and calculate Herman’s orientation functions.

To further quantify and understand the molecular orientation of the film, techniques that characterize different length scales (such as birefringence, light scattering, and microscopy) should be incorporated. This concept is supported by Figure 29, which shows the Herman’s orientation function for the polymer chain’s backbone relative to the machine direction of the film determined with birefringence vs. the characteristic draw ratio. Birefringence was used to characterize the average overall orientation of the HD 1 set of films. The refractive indices of the films were collected using an internally developed procedure and a Metricon 2010 refractometer. To accurately measure the refractive indices, the film sample was mounted in the apparatus with
glycerol between the prism and the film surface. The glycerol wets the surface of the film and reduces the effects of surface roughness on the refractive index measurement. This significantly improves the signal to noise ratio of the measurement. The scan rate of the apparatus was also slowed to its lowest set point. This further enhanced the knee of the intensity curve, providing a more accurate measurement of the refractive indices. When slowing the scan rate of the apparatus, the manufacturer warns of additional sensitivities to ambient light of the room. To address this issue, the entire device was covered with a thick, black felt tarp that sealed the testing cell from the ambient light. Once the scanning spectrum was collected, the raw data was analyzed with JMP software. The refractive index of the film was determined from the minimum point of this second derivative of the fitted curve. Measurements of the refractive indices relative to the machine, transverse, and normal axes were collected. This process was repeated five times for each sample, with the average standard deviation between the sets ranging from 0.05 % to 0.16 %, with the average standard deviation equal to 0.08 %.

Once the refractive indices were obtained, a least squares routine was used to calculate the value of $\cos^2\Phi$, $\sin^2\Phi$, $\cos(2\Theta)$, and $\Delta n_f$ utilizing Equations (4), (5) and (6). Through birefringence, an average orientation function in relation to the polymer chain backbone is obtained that includes all regimes, namely the fibers, lamellae, and amorphous regions. The orientation of the polymer chain relative to the machine
direction can be expressed by $f_{\Phi}$, while the orientation of the projection of the polymer chain on the transverse-normal plane is represented by $f_{\Theta}$. Figure 29 displays this relationship as a function of characteristic draw ratio where characteristic draw ratio is defined as the ratio of the undrawn film gauge to the drawn film gauge.

**Figure 29.** Plot of the biaxial orientation functions obtained from birefringence analysis for the HD 1 film set vs. Characteristic Draw Ratio.

The orientation of the polymer chains relative to the machine direction linearly increases with respect to draw ratio as predicted by the stress-optical relationship. This relationship is shown by the increasing trend of $f_{\Phi}$, with an initial value of 0.347 for a film drawn to a characteristic ratio of 2:1 to the highest value of 0.791 achieved at the orientation equipment’s operational limit. The orientation of the projection of the chain axis upon the transverse-normal plane is nearly isotropic at low draw ratios, indicated by an initial $f_{\Theta}$ value of -0.0346 at a characteristic draw ratio of 2:1. This
means that the projection of the chain is just as likely to be oriented in the transverse direction as it would be in the normal direction. Upon drawing, this orientation function decreases significantly, indicating that the average angle between the projection of the chain axis and the transverse axis is increasing. This implies that on average, the projection of the polymer chains is becoming more highly oriented in the normal direction. The minimum value of -0.308 occurred at a characteristic draw ratio of 10.5:1. Upon further orientation, \( f_\Theta \) begins to increase, trending again to a more random balance between the transverse and normal directions. This is due to the continuous formation of fiber-like structures, where for a perfectly crystalline, perfectly fiber-like structure, \( f_\Theta \) has a value of zero and \( f_\Phi \) has a value of 1. These conditions would never be obtainable for a film of semi-crystalline polymers, even at infinitely high draw ratios where all the crystalline material has been converted from lamellae stacks to fibers. This is due to the contribution of the amorphous regions to the measurement of the birefringence data, and the likelihood for some degree of randomness in this phase.

To summarize the analytical work that supports the previously described model of lamellae clusters, stacks, and macro- and micro-scale fibers, the orientation functions derived from the various techniques are included in the following figure.
Figure 30. Plot of the orientation functions acquired through various techniques vs. characteristic draw ratio. Comments are included that describe the orientation of lamellae groups, the unraveling oriented lamellae, and the formation of fiber structures.

At low draw ratios, the orientation functions derived from all of the techniques are relatively low. Upon orientation, it is proposed that the orientation from SAXS will quickly spike, indicating the orientation of the lamellae stack normals in the machine direction. This spike will peak at a draw ratio where the average orientation function from WAXS is equal to 0.521, indicating an average angle of 34.4° between the machine direction and the c-axis of the unit cell. Unfortunately, data at these draw ratios in the HD 1 film set is unavailable, but future work is planned to validate this concept. Upon further drawing, the SAXS orientation function decreases, due to the tilting of the lamellae stacks caused by the alignment of the c-axis of the unit cell towards the machine direction. Drawing to higher ratios drives the SAXS and WAXS orientation functions to their asymptotic values of 0.521 for SAXS and 1.00 for WAXS. These orientation functions are indicative of the perfect alignment of the
c-axis of the unit cell in the machine direction and the normal of the lamellae at 34.4° to the machine direction. At a draw ratio of approximately 6:1, the orientation function derived from the optical microscopy technique begins to drastically increase, indicating the formation of large, rod-like structures highly oriented in the machine direction. At high draw ratios, this orientation function quickly approaches the asymptotic value of 1.00, indicating a high degree of machine direction orientation at the largest length scale studied. As expected from the stress-optical relationship, the orientation function derived from birefringence linearly increases throughout the drawing process. This shows that regardless of the molecular architecture of the various domains in the film, the polymer chain is continuously aligning in the machine direction.

The changes in microstructure presented are indicative of the formation of the fiber structures likely consisting of a combination of ordered, aligned lamellae stacks, with the possibility for some extended chains. This observation is the basis for this work predicting the enhancements in physical properties as a function of the volume fraction of fiber-like structures present in the films. The following sections will discuss the improvements in machine and transverse direction moduli, machine direction break stress and strain, haze, and gloss with reference to increasing volume fractions of fibers present in the film.
2.4.1. STIFFNESS: MACHINE AND TRANSVERSE DIRECTION MODULI

The stiffness of a polymer film is a critical attribute that must be considered when selecting a material for a packaging application. In some cases, the stiffness of a film will affect package design, filling operations, and overall package performance. For the case of stand up pouches, a stiff film is necessary to maintain the “billboard effect” incorporated in the overall package design. In other cases, such as confection wrap, stiff films are necessary for good “dead fold,” and thus effect both packaging operations as well as the overall performance of the package. The machine and transverse direction moduli are direct measurements of the stiffness of a film relative to the respective directions of the film sample. The 1 % secant modulus, which is the slope of the stress-strain curve as it passes through the 1 % strain point, is commonly reported throughout the polymer films industry as the “modulus” of the film.

Derivation of Machine Direction Modulus as a Function of Fiber Volume Fraction

For the films of this study, a three-component system is proposed which consists of fibers and a matrix of both amorphous and non-fiber crystallites. The non-fiber crystalline phase consists of lamellae stacks with poor long range order and contains no extended chains. The fiber portion consists of both lamellae stacks with high long range order and those lamellae that have unraveled to form extended chains. The components of the fiber portion have a very large aspect ratio relative to those components of the non-fiber crystalline portion. The sum of
the percents of the non-fiber crystalline and fiber components is equivalent to the percent crystallinity of the polymer film, which is calculated by the following equation:

$$V_c = \frac{1}{\rho} - \frac{1}{\rho_a} - \frac{1}{\rho_c}$$  (30)

Where:  

$V_c$ = percent crystallinity of the film  

$\rho$ = density of the film measured in a gradient column  

$\rho_a$ = density of the amorphous polymer (0.885 g/cc)$^{66}$  

$\rho_c$ = density of the crystalline polymer (1.00 g/cc)$^{66}$

Figure 31 shows the volume fraction of crystallinity for each set of films at their respective draw ratios. From this data, it is apparent that the orientation process has little effect on the total crystallinity of the film.
Based on the previous statement that only the polymer chains from the crystalline region construct the non-fiber crystalline and fiber components:

\[
V_C = V_F + V_{NF} \quad (31)
\]

Where: 
- \(V_F\) = volume fraction of fiber components 
- \(V_{NF}\) = volume fraction of non-fiber crystalline components

The following relationship is used to calculate the machine direction modulus of an infinitely long fiber composite system:\textsuperscript{12}

\[
E_{C,MD} = \sum_{i=1}^{n} E_i V_i \quad (32)
\]
Where:  
\[ E_{C,MD} = \text{machine direction modulus of the composite} \]
\[ E_i = \text{modulus of the } i^{\text{th}} \text{ component} \]
\[ V_i = \text{volume fraction of the } i^{\text{th}} \text{ component} \]

Equation (32) is valid for systems with fibers that are perfectly oriented in the machine direction, have an extremely large aspect ratio, and when no slippage occurs at the interface of the various phases of the composite. For the case where the fiber aspect ratio is relatively small or interfacial slippage occurs, short fiber composite techniques such as the Halpin-Tsai\textsuperscript{13}, Halpin-Kardos\textsuperscript{14}, and shear-lag\textsuperscript{10},\textsuperscript{11} theories should be considered.

The fundamental issues with applying any type of fiber composite theory to semi-crystalline polymers is distinguishing which phase is the “fiber” and which is the “matrix.” The simplest approach would be to attribute the crystalline region to the “fiber” and the amorphous region as the “matrix.” While such a model can be used with some success for oriented samples of low crystalline polymers, this model quickly degrades when polymers of higher crystallinity are studied. This is largely due to the fact that in highly drawn, high crystalline polymers, the crystalline phase is continuous throughout the sample, with the amorphous phase merely “filling in the imperfections.” Due to this discontinuity and the very low modulus of amorphous polyethylene relative to crystalline polyethylene, the contribution of the amorphous component in the composite can be omitted to greatly simplify the model to a two component system consisting of fibers and
non-fibrous crystallites. This type of system was described by Gibson\cite{Gibson1} in the following schematic:

![Figure 32. Gibson’s assumed mechanical model for fiber, lamellar, and amorphous phases of highly oriented linear polyethylene.](image)

For the case of this work’s proposed model, the contribution of the amorphous region to the physical properties of the composite will be neglected. This simplification is the result of the significant differences in moduli between the crystalline and amorphous regions of the polymer and the fact that the volume fraction of fibers derived by this model is based directly on the moduli theory and data. Moduli values between 240-345 GPa have been reported for the extended polyethylene chain.\cite{Moduli1, Moduli2, Moduli3, Moduli4, Moduli5} Moduli values reported in the literature for the amorphous region are of two to three orders of magnitude lower than that of the extended chain, and range from 0.1-1 GPa.\cite{Moduli1, Moduli2} This means that at the elevated temperatures at which the drawing is taking place, the amorphous region serves merely as a flexible medium, allowing the transformation of non-fiber crystallites
Regardless, the concept of an oriented amorphous region is of great interest. Unfortunately, a simple, direct technique for determining the orientation of the amorphous region of thin polymer films has yet to be established. Of specific interest are the measurements of the orientation of the interlamellar, interfacial, and interfibrillar/sphuerilite amorphous regions through polarized microscopy and IR dichroism, both of which can be difficult to conduct with thin films. Future work is planned to research this area, focusing heavily on sample preparation and technique development.

Neglecting the amorphous region, Equation (32) then becomes:

$$E_{C,MD} = V_F E_F + V_{NF} E_{NF} \quad (33)$$

Substituting Equation (31) into Equation (33) provides:

$$E_{C,MD} = V_F E_F + E_{NF}(V_C - V_F) \quad (34)$$

A boundary condition present in four of the five films studied occurred at the ultimate characteristic draw ratio. At this condition, all of the non-fiber crystalline region has been converted into fibers, resulting in the highest practically obtainable moduli of the film. Beyond this condition, the fibers fail and cause the film to break. At this state, we assume no non-fiber crystallites exist and the volume fraction of fibers is equivalent to the crystalline volume
fraction. Such a concept is supported by Peterlin\textsuperscript{9}, stating that the fracture of the drawn sample in constant rate tensile experiments occurs almost instantaneously as soon as the necking has transformed the whole sample into a fibrous structure.

At this limiting condition, Equation (32) becomes:

$$E_{c,MD,MAX} = V_F E_F \equiv V_C E_F$$  \hspace{1cm} (35)$$

This relationship provides a calculation of the modulus of the fiber, $E_F$, for a given polymer, which does not change with draw ratio.\textsuperscript{10}

Substituting the $E_F$ calculated in Equation (35) into Equation (34), we obtain the following relationship between the machine direction modulus of a non-fiber crystalline/fiber composite with respect to the fiber volume fraction.

$$E_{c,MD} = V_F \left( \frac{E_{c,MD,MAX}}{V_C} \right) + E_{NF} (V_C - V_F)$$ \hspace{1cm} (36)$$

Derivation of Transverse Direction Modulus as a Function of Fiber Composition

From the infinitely long fiber composite theory\textsuperscript{12}, the following relationship is used to calculate the transverse direction modulus of a composite system:
Where: \( E_{C,TD} \) = transverse direction modulus of the composite
\( E_i \) = modulus of the \( i^{th} \) component
\( V_i \) = volume fraction of the \( i^{th} \) component

Utilizing Equations (31) and (37), an equation for the two component system of fibers and non-fiber crystallites is generated for the transverse direction modulus.

\[
E_{C,TD} = \frac{1}{\frac{\sum_{i=1}^{n} V_i}{E_i}} \quad (37)
\]

\[
E_{C,TD} = \frac{1}{\frac{V_F}{E_F} + \frac{(V_C - V_F)}{E_{NF}}} \quad (38)
\]

Based on the same boundary condition argument that supports Equation (35), the fiber modulus can be calculated by the following equation.

\[
E_{C,TD,MAX} = \frac{1}{\frac{V_F}{E_F}} = \frac{1}{\frac{V_C}{E_C}} \quad (39)
\]

Substituting the \( E_F \) calculated in Equation (39) into Equation (38), the following relationship between the transverse direction modulus of a non-fiber crystallite/fiber composite with respect to the fiber volume fraction is derived.
The characteristic draw ratio can be defined by the following equation:

\[ \frac{1}{E_{C,TD}} = \frac{V_F}{V_C E_{C,TD \text{ MAX}}} + \frac{(V_C - V_F)}{E_{NF}} \] (40)

Relating Fiber Composite Theory and Experimental Data to Determine \( V_F \)

The characteristic draw ratio can be defined by the following equation:

\[
\text{Characteristic Draw Ratio} = \frac{\text{Undrawn Film Thickness}}{\text{Drawn Film Thickness}} \quad (41)
\]

In the case of the polymer films studied, an exponential relationship was observed between the machine direction modulus and the characteristic draw ratio, represented in Figure 33.

![Figure 33. Plot of Machine Direction 1% Secant Modulus vs. Characteristic Draw Ratio.](image)

Such a relationship can be empirically represented by the following equation:
\[ E_{C,MD} = M_M \times \exp(B_M \times DR) \]  \hspace{1cm} (42)

Where \( M_M \) and \( B_M \) are constants that are specific to the polymer used to produce the film.

Linearizing the data is done by plotting the machine direction modulus versus the exponential of the product of a constant specific to a given polymer (noted as \( B_M \)) and the draw ratio. Figure 34 shows this relationship.

**Figure 34.** Plot of Machine Direction 1\% Secant Modulus vs. the exponential of \( B_M \times \)Characteristic Draw Ratio.

From Figure 34, we can see the direct correlation between percent crystallinity and the machine direction modulus. The films with the highest machine direction moduli at a given characteristic draw ratio were obtained with the highest percent crystallinity polymer, HD 1. The trend continues with HD 2 and HD 3, both having identical densities, which are slightly lower than that of HD 1. Finally,
HD 4 and HD 5, both having identical percent crystallinity, which is the lowest of the study, had the lowest machine direction moduli values at a specified characteristic draw ratio. From the trends generated for two polymers of the same percent crystallinity and different molecular weights, slight changes in molecular weight do not appear to greatly affect the slope of the trends of the moduli of the oriented films. It is evident that polymers with higher number average molecular weights do allow for slightly higher draw ratios, resulting in films with higher moduli values prior to the breaking of the film in the drawing process. This is evident when comparing HD 2 to HD 3 and HD 4 to HD 5. The reason why the higher molecular weight polymers can be drawn to higher ratios is likely due to the higher number of chain entanglements and the fewer number of chain ends present in the composite. The likelihood of the occurrence of a chain entanglement increases with molecular weight, which increases the probability of two chains becoming intertwined and unable to detangle. Chain ends serve as a site for the initiation of the catastrophic failure of the composite. The effects of the chain ends on the maximum draw ratio is amplified further in polymers with lower percent crystallinity. In other words, the difference between the maximum draw ratios of polymers with the same densities, but different number average molecular weights, increases with respect to decreasing polymer percent crystallinity.

For the case of the transverse direction modulus, a logarithmic relationship is observed with reference to the characteristic draw ratio, illustrated in Figure 35.
Figure 35. Plot of Transverse Direction 1% Secant Modulus vs. Characteristic Draw Ratio.

This relationship can be represented by the following empirical equation:

\[ E_{C,TD} = M_T \ln(DR) + B_T \]  (43)

Where \( M_T \) and \( B_T \) are constants that are specific to the polymer used to produce the film.

Linearizing the data is done by plotting the transverse direction modulus vs. the natural log of the characteristic draw ratio. Figure 36 shows this relationship.
Figure 36. Plot of Transverse Direction 1% Secant Modulus vs. Ln (Characteristic Draw Ratio).

Correlations between the polymers’ percent crystallinity and the transverse direction moduli can be seen that are similar to those discussed for the machine direction moduli. The polymer with the highest percent crystallinity (HD 1) obtained the highest transverse direction moduli. Following are HD 2 and HD 3, both having identical percent crystallinity, which is lower than that of HD 1. Finally, the lowest percent crystallinity set of polymers, HD 4 and HD 5 had the lowest moduli values. From the trends generated by the data for two polymers of the same percent crystallinity and different molecular weights, slight changes in molecular weight do not appear to significantly affect the slopes of the trends of the moduli of the oriented films. Again, it is evident that polymers with higher number average molecular weights do allow for achieving higher draw ratios, resulting in films with higher moduli values prior to the breaking of the film in the drawing process. This is evident when comparing HD 2 to HD 3 and HD 4 to HD
5 and is supported by the theory that the decrease in chain entanglements and the increase in the quantity of fiber ends limit the extent to which a film can be drawn.

When comparing the machine and transverse direction moduli, we see a crossover in magnitude similar to that reported by Ward.\textsuperscript{56} Below a specific draw ratio, the transverse direction modulus is greater than the machine direction modulus. Ward reported this draw ratio to be approximately 3:1. The following figure shows that this value varies from 3.5:1 to 5.5:1, depending on the polymer chosen.

![Figure 37. Plot of Machine and Transverse Direction Moduli vs. Characteristic Draw Ratio.](image-url)

Ward\textsuperscript{56} explained these surprising results with a model that regarded the polymer as an aggregate of anisotropic elastic units which are gradually aligned as the polymer is stretched.
A series of steps were utilized to determine the volume fraction of fibers present for each film at a given draw ratio. First, the theoretical equations for both the machine and transverse direction moduli were combined with the experimentally derived correlations to generate an equation for the modulus of the non-fiber crystalline component of the composite.

For the machine direction, Equations (36) and (42) are combined to yield:

$$E_{NF} = \frac{M_M \exp(B_M \cdot DR) - \left(\frac{V_F}{V_C}\right) E_{C,M,MAX}}{V_C - V_F}$$  \hspace{1cm} (44)

For the transverse direction modulus, Equations (40) and (43) are combined to yield:

$$E_{NF} = \frac{(V_C - V_F)}{\left[\frac{1}{\left(M_F \cdot \ln(DR) + B_T\right)} - \left(\frac{V_F}{V_C \cdot E_{C,TD,MAX}}\right)\right]}$$  \hspace{1cm} (45)

Equations (44) and (45) are then set equal to each other and the equation is solved for the fiber volume fraction in the composite.

This technique is similar to the one used by Weeks and Porter\textsuperscript{15} and Gibson\textsuperscript{11} (which utilized Cox’s shear lag theory\textsuperscript{26}), but is improved in the fact that the
effects of the drawing on the modulus of the non-fiber crystalline component is incorporated into the model. In the case of Weeks and Porter’s sheath and core model\textsuperscript{15}, they neglect any changes in the morphology of the sheath. When compared to the shear lag theory or the Halpin-Kardos\textsuperscript{14} theory, knowledge of a finite aspect ratio of the fibers is necessary, while changes in the “matrix” of the composite are ignored. It is proven that in the case of high molecular weight linear polymers, the aspect ratio of the fibers is so large that the infinitely long fiber composite theory can be utilized as an approximation to model the fiber portion of the composite. In addition, once the fibers are formed, further drawing does little to enhance that fiber’s contribution to the composite.\textsuperscript{14} The additional enhancements in composite properties are the direct result of both the increase in the volume fraction of fibers and the enhancements in the properties of the continuous phase. This is a result of the process of forming additional fibers through the transformation of non-fiber crystallites into fibers. Where previous methods have shortcomings is their neglect of changes in the matrix during the orientation process that significantly contributes to the physical properties of the composite. By solving the two equations for the non-fiber crystalline modulus derived from the machine and transverse direction moduli data simultaneously (Equations (44) and (45)), this transitional orientation of the matrix (non-fiber crystallites) can be captured. This stiffening is the result of the transformation of the less rigid, non-fiber crystallites into fiber structures at low draw ratios, which leaves the stiffer non-fiber crystallites in the continuous phase and results in a matrix with an overall higher modulus.
The following figure shows the increase in the modulus of the non-fiber crystalline phase and the decrease in volume fraction of non-fiber crystallites with respect to the characteristic draw ratio.

**Figure 38.** Plot of the non-fiber crystalline phase’s contribution to the composite moduli with respect to draw ratio.

It is obvious that as the films are oriented (indicated by higher characteristic draw ratios), the amount of non-fiber crystallites decrease due to their transformation into fibers, leaving the stiffer non-fiber crystallites that are more resistant to transformation. At low characteristic draw ratios, the less rigid non-fiber crystallites are easily converted to fibers, while extremely high characteristic draw ratios are needed to transform the stiffest of non-fiber crystallites into fiber structures.
A relationship similar to that predicted by Barham and Arridge\textsuperscript{10} is observed with the modulus of the non-fiber crystallites increasing with the characteristic draw ratio to a certain power. For the case of the higher density films, this power is approximately 0.27. For the lower density films, this power is much larger and of the order of 0.40 to 0.55. This could likely be the result of the limited amount of data available for the lower density films, relative to the higher density films. The lack of information for the lower density films at higher draw ratios misleadingly weighs the data of the correlation towards that of the lower draw ratios, which is also the area where the coefficient of the power relationship is highest. Future work should be conducted to include films produced with lower density, higher molecular weight polymers. Doing so would provide a film that could be drawn to higher draw ratios, possibly indicating a power relationship more closely matching the 0.27 value of the higher density films. In addition, any future work should also focus on relating the correlation of both the coefficients of the power relationships and the undrawn non-fiber crystallite modulus values to the polymer characteristics.

While changes in the moduli of the transforming non-fiber crystallites are of definite interest, a deeper understanding of how the fibers are formed with respect to the changing draw ratios is of more importance. These fiber structures have significantly higher moduli values, and play a larger role in the contribution to the physical properties of the film as the draw ratio increases. The following figure
shows the plot of the volume fraction of fibers in the composite versus the characteristic draw ratio.

**Figure 39.** Plot of $V_F$ vs. Characteristic Draw Ratio.

This correlation between the volume fraction of fibers and the characteristic draw ratio can be expressed by the following equation:

$$V_F = C \cdot \exp\left(B \cdot (DR - 1)\right) \quad (46)$$

Where:
- $C$ = amount of fibers present in the undrawn film
- $B$ = rate constant for the fiber formation process

The exponential relationship between the formation of the fiber structure in the film relative to the characteristic draw ratio is similar to the activated relationship that relates the rate at which a reaction occurs to the temperature of the system. This relationship is given by the following:
\[ k = A \exp\left(\frac{-E_a}{RT}\right) \] (47)

Where:

\[ k = \text{reaction rate coefficient} \]
\[ A = \text{constant} \]
\[ E_a = \text{activation energy} \]
\[ R = \text{ideal gas constant} \]
\[ T = \text{temperature of the process} \]

As one may expect, increasing the system temperature and decreasing the activation energy increase the reaction rate coefficient.

Now comparing Equation (46) to Equation (47), we can make the correlation between the activation energy and the constants A, B, C.

The true value in such an analysis is to correlate values for B and C to the characteristics of the polymers. Based on the proposed fiber composite model, the rate of fiber formation is heavily influenced by the highest portion of the molecular weight distribution, namely the breadth of the distribution and size of the higher molecular weight polymer chains. Increasing the zero shear viscosity of the polymer will decreases the volume fraction of fibers at a given draw ratio as a result of molecular mobility restrictions imparted by the higher viscosity and narrower molecular weight distribution. For these same reasons, films produced with polymers of higher zero shear viscosity will have lower volume fractions of
fibers in an undrawn film. As the molecules begin to align during the drawing process, the rate at which the fibers form will be greater for films with a higher zero shear viscosity, largely due to the longer average relaxation time of the molecules. Increasing $M_{z+1}$ increases the volume fraction of fibers at a given draw ratio and increases the volume fraction of fibers in an undrawn film. This characteristic is the direct result of the extremely long relaxation time and increased potential for entanglements of high molecular weight polymer chains. During both the film blowing and post orientation processes, these chains retain more of the uniaxial orientation induced by the film line’s die. The large lamellae formed by these high molecular weight molecules are also less likely to melt at the elevated orientation temperature, resulting in a more immediate unraveling to form fibers. In addition, increasing the breadth of the relaxation time spectrum by increasing the breadth of the high end of the molecular weight distribution decreases the volume fraction of fibers at a given draw ratio and decreases the rate at which the fibers are formed throughout the drawing process.

The values of the constants for each polymer, B and C, were compared with the previously mentioned characteristics of the polymers obtained by rheology (Dynamic Oscillatory Rate Sweep) and Gel Permeation Chromatography data. As previously described, the influence of the highest portion of the molecular weight distribution on the rate of fiber formation is of greatest interest. For these particular polymers, the high end of the molecular weight distribution typically includes those molecules with a molecular weight greater than 500,000 g/mole.
To incorporate the necessary parameters, the zero shear viscosity, which is the extrapolation of the viscosity curve of the polymer to the zero shear rate (Equation 28) and is an indicator to the molecular weight of the polymer, was obtained from rheology. Higher zero shear viscosities indicate a more developed network and a greater resistance to small perturbations and generally a higher average molecular weight for the polymer. Also of interest is the breadth of the high molecular weight portion of the distribution, indicated by the $E_T$ value (Equation 29). The greater the $E_T$ value, the broader the molecular weight distribution is at the high end of the total molecular weight distribution curve. The final term, $M_{z+1}$, is of interest since it provides an average molecular weight of the higher portion of the molecular weight distribution.

After much analysis, an excellent correlation was observed between the constant $C$, which indicates the volume fraction of fibers in the undrawn film, and the ratio of the zero shear viscosity to the $z+1$ average molecular weight. This ratio is representative of the unperturbed response of the polymer, normalized about the higher molecular weight component of the molecular weight distribution. Figure 40 shows this relationship:
A similar relationship was seen when comparing the values of B, the rate constant for fiber formation, with the ratio of the zero shear viscosity to $E_T*10^5$, as shown in Figure 41. This ratio may be indicative of a type of relaxation time for the higher molecular weight components of the molecular weight distribution.

**Figure 40.** Plot of the values of constant C from Equation (46) for each polymer studied vs. $\eta_0/M_{z+1}$

**Figure 41.** Plot of the constant B of Equation (46) vs. $\eta_0/E_T$
Substituting these empirical relationships into Equation (46), we obtain the following relationship between $V_F$ and the polymer characteristics, namely $\eta_0$, $E_T$, and $M_{z+1}$.

\[
V_F = \left[ -m_C \left( \frac{\eta_0}{M_{z+1}} \right) + b_C \right] \ast \exp \left[ \left( m_B \ast \left( \frac{\eta_0}{E_T \ast 10^5} \right) + b_B \right) \ast (DR - 1) \right]
\]  (48)

Where:

- $m_C = \text{slope of regression in Figure 40}$
- $b_C = \text{intercept of regression in Figure 40}$
- $m_B = \text{slope of regression in Figure 41}$
- $b_B = \text{intercept of regression in Figure 41}$

The relationship of the rate of formation of the fibers to the general characteristics of the polymer is one that deserves greater analysis and will be the focus of future work.

This discussion has presented a model and empirical functions for studying and predicting the effects of uniaxial drawing on both machine and transverse direction moduli of HMW-HDPE films. The model predicts the linear relationship between the characteristic draw ratio and the natural logarithm of the volume fraction of fibers present in the composite. In the case of the machine direction modulus, the property increases exponentially with respect to the characteristic draw ratio until all lamellae are converted into fiber structures. This
translates to a linear relationship between the machine direction modulus and the volume fraction of fibers present in the structure. Figure 42 depicts this correlation.

![Figure 42. Plot of Machine Direction Modulus vs. V_F.](chart)

The relationship between the machine direction modulus and the volume fraction of fibers holds true to the theory proposed in fiber composite theory and shown in Equation (32).

In the case of the transverse direction modulus, the property increases logarithmically with respect to draw ratio until all lamellae are converted into fiber structures. This approximates to a linear relationship between the transverse direction modulus and the inverse of the volume fraction of fibers. Figure 43 shows this correlation:
The relationship between the transverse direction modulus and the volume fraction of fibers holds true to the theory proposed in fiber composite theory and shown in Equation (37). In addition, correlations have been presented that show the relationship between the volume fraction of fibers in the undrawn film and the rate constants for fiber formation with the characteristics of the high molecular weight portion of the polymer.

2.4.2. TENSILE PROPERTIES: MACHINE DIRECTION BREAK STRESS AND STRAIN

The machine direction tensile properties are of great importance when selecting polymer films for packaging applications. When choosing a film, the load that will compromise the integrity of the package must be considered to prevent unnecessary breakage during use. The elongation at which this failure occurs is
also of importance in determining the necessary film strength for the package filling processes. For the case of water softener rock salt bags, films with high break strengths must be utilized to hold the contents of the bag during filling, storage, and transportation. In other cases, such as refuse can liners (garbage bags), films with high yield and break strengths and low elongations are necessary due to the handling associated with filling a bag, removing it from a primary can, and transporting and depositing it into a curbside container.

Derivation of Machine Direction Break Stress as a function of $V_F$

From infinitely long fiber composite theory\textsuperscript{12}, we know the following relationship is used to calculate the machine direction break stress of a composite system:

$$\sigma_{C,MD} = \sum_{i=1}^{n} \sigma_i V_i \quad (49)$$

Where:  
\begin{align*}
\sigma_{C,MD} &= \text{composite machine direction break stress} \\
\sigma_i &= \text{break stress of the } i^{th} \text{ component} \\
V_i &= \text{volume fraction of the } i^{th} \text{ component}
\end{align*}

Based on the assumption that the amorphous region does not contribute significantly to the overall strength of the composite, relative to the crystalline region, Equation (49) simplifies to:

$$\sigma_{C,MD} = \sigma_F V_F + \sigma_{NF} V_{NF} \quad (50)$$
Substituting Equation (31) into Equation (50), the composite break strength is obtained in terms of the volume fractions of fibers present in the composite.

$$\sigma_{\text{C,MD}} = V_F \sigma_F + \sigma_{NF} (V_C - V_F)$$  (51)

To understand how the experimental data correlates with the fiber composite theory, the relationship between the machine direction break stress and the characteristic draw ratio is examined. An exponential relationship between the break strength of the film and the characteristic draw ratio is observed and shown in Figure 44.

![Figure 44. Plot of Machine Direction Break Stress vs. Characteristic Draw Ratio.](image)

Considering the linear relationship between the characteristic draw ratio and the natural log of the volume fraction of fibers previously discussed in the modulus section, a linear relationship is obtained between the machine direction break...
stress and the volume fraction of fibers present in the composite. This relationship is shown in Figure 45.

![Figure 45](image)

**Figure 45.** Plot of Machine Direction Break Stress vs. \( V_F \).

It should be noted that the last two data points for the HD 1 series and the last data point for the HD 2 series are omitted. The values reported for these points are falsely low due to the limitations of the testing equipment. Gibson, et al.\(^{11}\) reported similar issues in their work, and addressed the situation by using a three point bend technique. This was a possibility for their study, since their specimens were thicker dumb bell and extruded rods. With the samples of this study, some at thicknesses as low as 12 \( \mu \text{m} \), such a technique does not seem practical. Future work should be conducted on a tensile testing device with either high pressure jaws or a high strength clamping chuck. Regardless, the inclusion of this erroneous data could lead to an incorrect interpretation of the relationship
between the machine direction break stress and the volume fraction of fibers. The
remainder of the data has an excellent linear relationship between the machine
direction break stress and the volume fraction of fibers and supports the omission
of these inaccurate data points. As with the film moduli, a close relationship is
seen between the percent crystallinity and the break stress of the films. The films
produced with the polymer of highest percent crystallinity polymer had the
highest break stress.

When considering the machine direction break strain of a composite film:

\[ \varepsilon_{C,MD} = \varepsilon_F = \varepsilon_{NF}^* \quad (52) \]

Where:

- \( \varepsilon_{C,MD} \) = composite machine direction break strain
- \( \varepsilon_F \) = break strain of the fiber
- \( \varepsilon_{NF}^* \) = break strain of the non-fiber crystallites at the break
  stress of the fiber

In the case of Equation (52), the composite will only elongate to the extent that
the fiber is willing to extend. Beyond this point, the fiber breaks and the
composite fails due to the significantly lower break strength of the more flexible
lamellae and amorphous regions. Figure 46 demonstrates this behavior.
Figure 46. Machine Direction Stress-Strain Curves for a Fiber, Non-Fiber Crystalline, and Amorphous Composite.

With the case of the oriented films in this study, we see a deviation from this concept at low fiber volume fractions. Figure 47 shows this relationship in the plot of the machine direction break strain vs. volume fraction of fibers.

Figure 47. Plot of Machine Direction Break Strain vs. $V_F$. 

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For Equation (52) to be true, the assumption must be made that perfect bonding exists between the components of the composite, in this case the fiber, non-fiber crystalline, and amorphous regions. This means that no slippage can occur at the interface between the phases. The deviation from Equation (52) at fiber volume fractions less than 0.25 is likely the result of interfacial slippage between the few fibers that are present, the non-fiber crystalline, and the amorphous regions. In addition, the flexibility of the amorphous region dominates at the lower draw ratios, allowing for more energy to be absorbed by this phase. This would not be the case with highly drawn systems where the deformation of the amorphous region is significantly hindered. Beyond the 0.25 fiber volume fraction, an ample amount of fibers have been generated where they dominate the tensile properties and control the extensibility of the film. This concentration is known as the critical volume fraction of fibers. Also worth noting is that beyond the 0.25 fiber volume fraction, all of the films converge upon a uniform, very low machine direction break strain value. This supports Equation (52) by showing that all the films have similar machine direction break elongations when the fibers generated by the drawing process dominate the tensile properties of the composite.

2.4.3. OPTICAL PROPERTIES: HAZE AND GLOSS

The optical properties of the films, namely haze and gloss, are critical for high clarity applications. Typically, films produced with HDPE do not have acceptable optical properties to compete with other polymers, such as LDPE,
LLDPE, PET, and PP. Unfortunately, those films with acceptable optical properties typically do not have the stiffness necessary to solely produce an acceptable package, so costly laminations and coextrusions are necessary to obtain the final balance of properties. A film with a balance of stiffness and optical properties would be desirable to reduce the overall cost of the structure by minimizing both materials and processing costs. Such a film can be produced by machine direction orienting HMW-HDPE films.

Figure 48 shows the improvement in haze with respect to fiber volume fraction.

![Figure 48. Plot of Haze vs. $V_F$.](image)

It is evident that for each polymer, the haze values decay with the volume fraction of fibers and approaches a minimum value. This minimum value is directly correlated with the density of the films. As the film density decreases, the value of the minimum haze also decreases.
To better observe the power decay of the haze at intermediate volume fractions of fibers, we normalize the haze value about the minimum value attainable for that given polymer.

\[
Haze_o = \frac{Haze}{Haze_{\text{min}}} \quad (53)
\]

Where: \( Haze_o \) = Normalized Haze (%)  
\( Haze \) = Haze value at a given \( V_F \) (%)  
\( Haze_{\text{min}} \) = Minimum Haze Value for a given Polymer (%)  

Upon normalization, we observe a power relationship between the haze and the volume fraction of fibers, represented in Figure 49. By normalization, we drive the relative percent change in haze of all five films to a common minimum, fully exposing the power decay associated with drawing the film. From this plot, a definite correlation can be seen between the rate of decay and the density of the polymer. As the film density decreases, the decay rate increases, exposing the effects of the resin characteristics on how the volume fraction of fibers present in the composite changes the haze values of the film.
This observation results in the following empirical relationship:

\[ Haze_o = Q V_f^{-R} \]  \hspace{1cm} (54)

Where:
- \( Haze_o \) = Normalized Haze (%)
- \( V_f \) = Volume Fraction of Fibers
- \( Q, R \) = Constants specific to the polymer

A power law relationship is observed between the reciprocal of the gloss values of the films and the volume fraction of fibers, shown in Figure 50.
As with haze, the gloss was normalized by the following empirical equation:

\[
Gloss_o = \frac{Gloss}{Gloss_{max}} \tag{55}
\]

Where: \(Gloss_o\) = Normalized Gloss (%)

Gloss = Gloss value at a given \(V_F\) (%)

\(Gloss_{max}\) = Maximum Gloss Value for a given polymer (%)

A similar power relationship is evident for the gloss data upon normalization, shown in Figure 51.
As with the case of haze, the gloss improves at a much higher rate with the lower density products.

The haze and gloss values can be related to each other to better understand the improvements in optics as a result of film orientation. A power law relationship is seen when plotting the normalized haze values versus the reciprocal of the normalized gloss values. This relationship is depicted in Figure 52.

**Figure 51.** Plot of $1/\text{Normalized Gloss}$ vs. $V_F$. 
Figure 52. Plot of Normalized Haze vs. the Reciprocal of the Normalized Gloss.

The relationship seen between both haze and gloss to density is consistent, with the improvements in optical properties increasing at a much more significant rate with decreasing film density.

The relationship shown in Figure 52 is represented by the following equation:

\[
\text{Haze}_o = S \ast \left( \frac{1}{\text{Gloss}_o} \right)^T
\]  \hspace{1cm} (56)

Where:  
\( \text{Haze}_o = \text{Normalized Haze (％)} \)
\( \text{Gloss}_o = \text{Normalized Gloss (Units)} \)
\( S, T = \text{Constants specific to the polymer} \)

Substituting Equation (54) into Equation (56), the normalized gloss values can be related to the volume fraction of fibers present in the oriented film.
The improvements in the optical properties are the direct result of the changes in the crystalline morphology of the polymer and smoothing of the film surface caused by the orientation process. In general, lower density polymers are less crystalline, resulting in a smoother film surface and less light diffracted and better optical properties. The optical properties are improved as a result of two aspects associated with the MDO process. First, the reheating process smoothes the surface of the film as it passes over the smooth finished rollers. Second, the transformation of the crystalline phase into fibers reduces the amount of irregularities caused by the lamellae protruding from the surface of the film as discussed by Bafna, et al. Contributions to the lack of optical clarity from both the surface and bulk portions of the film are discussed by Ashizawa, Spruiell, and White. They concluded that the majority of light scattered by HDPE films was the result of crystalline induced surface roughness and the optical properties can be improved by reducing this surface effect.

From this discussion, it is evident that the optical properties of HMW-HDPE films can be significantly enhanced through the orientation of lower density films and are directly related to the volume fraction of fibers present in the polymer film.
3. CONCLUSIONS

The work presented explains how the morphology of the crystalline region of high molecular weight high density polyethylene (HMW-HDPE) films changes when the film is subjected to uniaxial drawing. Various analytical techniques, such as WAXS, SAXS, birefringence, and optical microscopy, were used to provide an explanation that describes how the lamellae stacks of the polymer are transformed into fibers with large aspect ratios, which are oriented along the drawing direction. Composite theory for infinitely long fibers has been utilized for explaining how the machine direction and transverse direction moduli and the machine direction break stress and strain relate to the volume fraction of fibers present in the film. The infinitely long fiber model was used because the linear structure and high molecular weights of the polymers studied closely mimic a fiber with an extremely large aspect ratio. To construct the model, the film is considered a two-phase composite consisting of non-fiber crystallites and fibers. Due to its minor contribution to the mentioned properties, the amorphous region has been omitted to simplify the model. The volume fraction of fibers was bound to constrain the maximum attainable volume fraction of fibers to the crystalline volume fraction in the film. This normalization is supported by both density gradient column and DSC data showing that the overall percent crystallinity does not change with changing draw ratio. Based on this fact, the amorphous region is not crystallized by the strain of the orientation process. By orienting the films at a temperature near their melting point, the amorphous phase is free to conform around the changing crystalline region, significantly reducing the possibility of strain induced crystallization.
From the moduli data, the volume fractions of fibers present at various draw ratios were calculated. This volume fraction of fibers is exponentially related to the characteristic draw ratio and reaches its limiting value at the volume fraction of crystallinity of the film. Linear relationships are observed between the machine direction modulus relative to the fiber volume fraction and the transverse direction modulus relative to the reciprocal of the fiber volume fraction. Both trends correlate with the theory for infinitely long fiber composites.

The machine direction break stress is linearly related to the volume fraction of fibers and the machine direction break strains converge to a common, low value, regardless of the polymer, when the volume fraction of fibers is greater than 0.25. The break strain of the composites with fiber volume fractions greater than 0.25 is independent of the characteristic draw ratio. Both the break stress and break strains at fiber volume fractions greater than 0.25 correlate with fiber composite theory. For composites with less than the 0.25 fiber volume fraction, the break strain decreases with the power of the volume fraction of fibers. This deviation from the composite theory is likely the result of the domination of the tensile properties of the more plentiful non-fiber crystalline and amorphous regions. As more fibers are generated, a critical volume fraction of fibers is reached, and they begin to dominate the tensile properties of the overall composite. At this point, the break strain of the system more closely resembles an infinitely long fiber composite.
The optical properties of the films, haze and gloss, were also studied. A power relationship between the normalized haze and the volume fraction of fibers was observed. This improvement in haze is the result of smoothing the surface of the film by transforming the lamellae into narrow fibers. During this process the two dimensional lamellae are transformed into one dimensional rod-like fibers, which produces a smoother film surface and allows more unperturbed light to pass through the film. A power relationship was also observed between the reciprocal of the normalized gloss and the volume fraction of fibers. The improvement in gloss is the direct result of the reduction in surface roughness by transforming lamellae into fibers and smoothing of the film surface from the orientation process.
4. FUTURE WORK

The goal of this program is to identify the mechanism that occurs during the uniaxial drawing of high molecular weight high density polyethylene (HMW-HDPE) films and build correlations with specific physical properties, such as moduli, break stress and strain, and optics. With this model, a portion of the understanding of how fundamental polymer research (catalyst, polymerization process, etc.) can be correlated to the final physical properties desired by the marketplace. Further work should be conducted that links the proposed mechanism to both polymer characteristics and final film properties. The following diagram shows how polymer research can be converted to commercial products through a series of characterization steps.

Figure 53. Process flow for product development from a market need.
To complete this connection, detailed analysis of the molecular weights, molecular weight distributions, viscosities, and crystallization behaviors of the polymers must be conducted. The films should also be characterized with various techniques, such as WAXS, SAXS, birefringence, IR dichroism, and microscopy to determine the overall orientation of the crystalline, and if possible, the amorphous regions. Thermal techniques, such as DSC and DMA, should also be used in an attempt to characterize the crystallite size and distribution in the oriented films. In addition, further work should be conducted to expand the proposed relationship between the rate constants for the formation of fibers with the disclosed characteristics of the polymer. This final concept will be the underlying driver for all future work in oriented HMW-HDPE films. With such knowledge, endless opportunities are available to design polymers that provide a balance of new and innovative properties through uniaxial orientation.

Some specific topics of interest for future work include:

- Characterize the HD 2 through HD 5 film sets with the previously mentioned analytical techniques for further relating the enhancements in physical properties to polymer characteristics.
- Characterize the orientation of the amorphous region and incorporating its contribution to the physical properties into the model.
- Build upon the disclosed model that correlates the change in the volume fraction of fibers with the characteristics of the polymer, namely those associated with the high molecular weight fraction of the molecular weight distribution.
• Investigate the effects that any variation in a finite aspect ratio of the fiber structure has on the changes in the physical properties of the oriented film.

• Correlate the changes in the surface and bulk morphology caused by orientation to improvements in the optical properties of the films.

• Incorporate the effects of changes in MDO line operating conditions, such as preheating, annealing, line speed, and draw gap, into the prediction of physical properties.

• Correlate polymer characteristics with the effects that uniaxial drawing has on the physical properties of the tilted and partially unraveled lamellae region.

• Study the effects of the MDO process on monolayer, coextruded, and blended films consisting of at least a portion of HMW-HDPE.
REFERENCES


APPENDIX

6.1. DSC CURVES OF THE POLYMERS STUDIED

a.) HD 1

![DSC Curve](image1)

Sample: A03-03831 R. BREESE
Size: 2.4100 mg
Method: 10C/min to 160C
Comment: 1497-1
DSC File: D:\Data\DSC2\A0303831.01
Operator: CHRIS BARLEY
Run Date: 9-Apr-03 13:15
Instrument: 2910 DSC V4.4E

b.) HD 2

![DSC Curve](image2)

Sample: A03-03888 R. BREESE
Size: 2.3200 mg
Method: 10C/min to 160C
Comment: 1501-1
DSC File: D:\Data\DSC2\A0303888.01
Operator: CHRIS BARKLEY
Run Date: 9-Apr-03 21:18
Instrument: 2910 DSC V4.4E
c.) HD 3

Sample: A03-03901 R. BREESE
Size: 2.4000 mg
Method: 10C/min to 160C
Comment: 1491-1

DSC
File: D:\Data\DSC\A0303901.01
Operator: CHRIS BARKLEY
Run Date: 10-Apr-03 01:15
Instrument: 2910 DSC V4.4E

Second Heat

Heat Flow (W/g)
0 20 40 60 80 100 120 140 160
Temperature (°C)

129.82°C

Sample: A03-03915 R. BREESE
Size: 2.3700 mg
Method: 3 10C/min to 280C
Comment: 1509-1

DSC
File: D:\Data\DSC\A0303915.01
Operator: CHRIS BARKLEY
Run Date: 10-Apr-03 14:19
Instrument: 2910 DSC V4.4E

First Heat

Heat Flow (W/g)
50 100 150
Temperature (°C)

125.88°C

d.) HD 4
e.) HD 5

Sample: A03-03921  R. BREESE  
Size: 2.4200 mg  
Method: 10C/min to 160°C  
Comment: 1505-1

DSC File: D:\Data\DSC2\A0303921.01  
Operator: CHRIS BARKLEY  
Run Date: 10-Apr-03 09:23  
Instrument: 2910 DSC V4.4E

Heat Flow (W/g)  
Temperature (°C)
### 6.2. FILM MICROGRAPHS AT APPROXIMATE CHARACTERISTIC DRAW RATIOS

<table>
<thead>
<tr>
<th>Draw Ratio</th>
<th>HD 1</th>
<th>HD 2</th>
<th>HD 3</th>
<th>HD 4</th>
<th>HD 5</th>
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<tr>
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<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>8:1</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
</tbody>
</table>
### 6.3. FOURIER TRANSFORMS AND CALCULATED ORIENTATION FUNCTIONS FOR THE MICROGRAPHS OF THE HD 1 FILM SET

<table>
<thead>
<tr>
<th>Calculated Draw Ratio</th>
<th>50X Image</th>
<th>Fourier Transform</th>
<th>( f_m )</th>
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<tr>
<td>1.0:1</td>
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<td>![Image](218x534 to 284x584)</td>
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<td>2.0:1</td>
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<td>![Image](218x413 to 283x463)</td>
<td>0.363</td>
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<tr>
<td>2.1:1</td>
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<td>![Image](218x293 to 283x343)</td>
<td>0.377</td>
</tr>
<tr>
<td>6.0:1</td>
<td>![Image](218x233 to 283x283)</td>
<td>![Image](218x173 to 283x223)</td>
<td>0.404</td>
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<tr>
<td>8.0:1</td>
<td>![Image](218x114 to 283x163)</td>
<td><img src="218x59" alt="Image" /></td>
<td>0.439</td>
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<td>8.7:1</td>
<td><img src="218x59" alt="Image" /></td>
<td><img src="218x59" alt="Image" /></td>
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<td><img src="218x59" alt="Image" /></td>
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<td><img src="218x59" alt="Image" /></td>
<td><img src="218x59" alt="Image" /></td>
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### 6.4. WAXS POLE FIGURES AND ORIENTATION FUNCTIONS FOR THE HD 1 FILM SET

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<th>(200) Pole</th>
<th>$f_{c,MD}$</th>
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### 6.5. SAXS SCATTERING PATTERNS AND ORIENTATION FUNCTIONS FOR THE HD 1 FILM SET

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<tr>
<td>2.1:1</td>
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<td>6.0:1</td>
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<tr>
<td>8.0:1</td>
<td><img src="image" alt="SAXS Scattering Pattern" /></td>
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<td>0.512</td>
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6.6. ASTM TESTING PROCEDURES

6.6.1. Density: D 1505

6.6.2. DSC: E 793

6.6.3. DORS: D 4440

6.6.4. Moduli: E 111

6.6.5. Yield and Break Strengths: D 882

6.6.6. Haze: D 1003

6.6.7. Gloss: D 2457