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A review of modeling approaches for oriented semi-crystalline polymers

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Abstract

Modeling changes in the physical properties of oriented semi-crystalline polymer films is beneficial for understanding the fundamentals associated with structure property relationships and could be used for developing new polymer films with significantly enhanced physical properties. Relating the molecular changes observed in oriented polymer films to inherent polymer characteristics provides valuable insight for the development of new polymers which exhibit enhanced physical properties upon orientation. Modeling efforts will be reviewed that have attempted to use fiber composite theory to explain the transitions seen during the orientation process.
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1. Introduction

Semi-crystalline polymer films can be oriented to improve physical properties, namely the moduli 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 structural transitions that occur during the drawing process, as shown in Fig. 1 [**1].

Included in Fig. 1 are atomic force and optical micrographs (50× magnification) taken under cross-polar lenses at various draw ratios captured throughout the orientation process. The undrawn sample (0%) has randomly oriented stacks of crystallites. Upon drawing, the stacks begin to arrange in the drawing direction and beyond the yield point, the stacks begin to transform into fiber-like entities. These fibrous structures are composed of piled lamellae with long range order and/or tightly packed extended chains which are highly oriented in the drawing direction. The sample quickly fails at an extremely high tensile stress (∼10× of the undrawn film's break strength) after the crystalline region has been completely transformed into fibers [**1].

As the fibrous structures are formed by the orientation process, significant changes in the patterns of both wide and small angle X-ray scattering (WAXS and SAXS) experiments are evident, as shown in Fig. 2 [**1].

As the draw increases, the scattering patterns from SAXS converge about the meridian of the image, indicating the preferential alignment of the normal of the lamellar basal plane in the machine direction. The scattering patterns for the various poles from WAXS converge upon a focal point at a fixed angle specific to the geometry of that pole relative to the machine direction of the film. In the case of the (110) pole figure, two symmetrical lobes converge along the equator with an increase in drawing, indicating a high level of c-axis orientation in the machine direction. For the (200) pole figure, a bright lobe is located in the center of the pole figure, indicating a high level of a-axis orientation in the normal direction of the film. By combining the (110) and (200) pole figures, as shown in Fig. 2, it is obvious that the unit cells have their c-axis highly oriented in the machine direction, their a-axis highly oriented in the normal direction, and their b-axis highly oriented in the transverse direction of the film at high levels of orientation.

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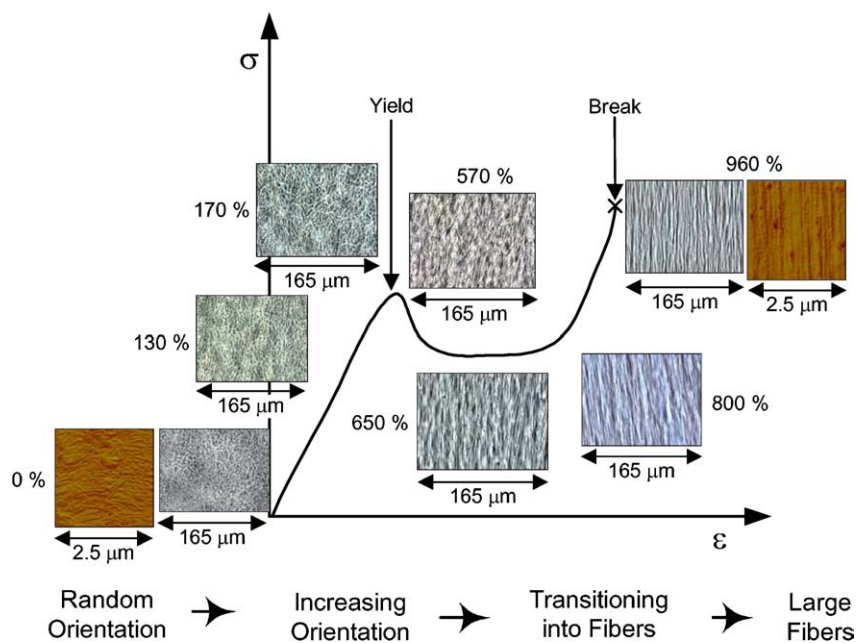
Fig. 1. Stress–strain curve with micrographs that display the crystalline microstructure of drawn high molecular weight high density polyethylene films (2.5 µm scale images are AFM, 165 µm scale images are optical micrographs).
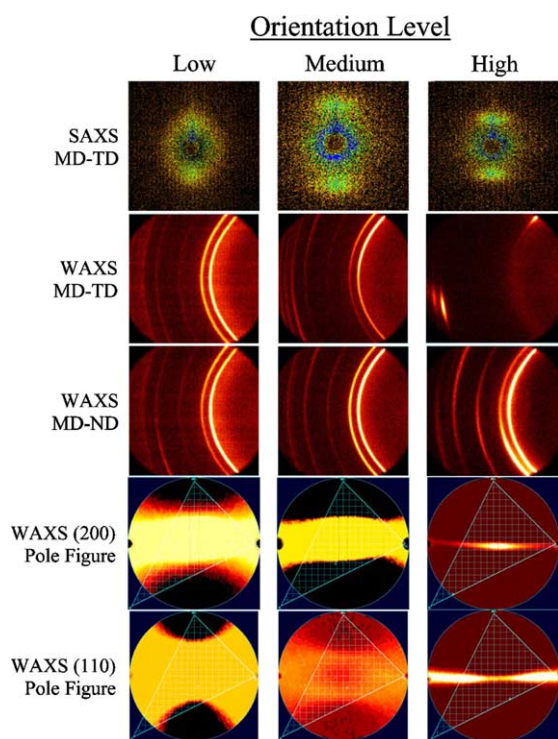

Fig. 2. Small and wide angle X-ray scattering images and (200) and (110) pole figures from the wide angle X-ray scattering patterns for a set of oriented polyethylene films at various elongations.

2. Models and discussion

Several approaches have been used since the early work of Takayanagi [*2] to explain the enhancements in the physical properties, namely the moduli, of semi-crystalline polymers when they are uniaxially oriented. Each method has involved the use of various characterization techniques, such as SAXS, WAXS, birefringence, microscopy, and IR dichroism. Previous research has provided the tools for creating structural models of semi-crystalline polymers during draw. Of specific interest is the combination of multiple techniques to better understand semi-crystalline systems [**3,4,**6,7,8]. With these newly developed tools, the relationships between polymer properties and processing conditions could be modeled to understand the enhancement in physical properties. Some key works focused on relating density and annealing conditions [**9], molecular weight and molecular weight distribution [*10], and operating temperature, strain rate, and frequency [11] to changes in properties, such as modulus.

The first step in generating a model is to define the various phases present in the polymer. From the micrographs in Fig. 1, it is obvious that some type of fibrillar structure forms. This has been noted in the literature [**1,**9,**12,*13,*14,**15]. A model for oriented films should include at a minimum, fibers in a matrix. A more complicated composite model would incorporate a matrix that is semi-crystalline with both amorphous and non-fibrous crystalline components. A general structural model should be based on experimental observations of the film. The evidence of highly anisotropic crystalline regions of large aspect ratios (length/width ratios) aligned in the drawing direction from various microscopy techniques [**1,**9,**12,*13,*14,**15], 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

Table 1
A tabulation of the attributes of the various models for oriented semi-crystalline polymer films

Model	Transitional model	Explaining structure and property relationship
Infinitely long fiber [*19]	No	No
Short fiber [**20]	No	No
Peterlin [**17]	Complex fiber structures of various length scales	Elaborate hierarchical structure
Barham–Arridge [**18]	Increasing A (aspect ratio)	Nebulous structure
Gibson–Davies–Ward [**16]	Increasing V_f (volume fraction of fibers)	Incompressible structure
Breese–Beaucage [**1]	Transforming morphology of matrix	Observed morphological structure modulus and break strength/strain

MD refers to machine direction (orientation direction) and TD refers to transverse direction (perpendicular to orientation and thickness directions).

upon orientation, i.e. fiber formation. The various transitional models [**1,**16,**17,**18] differ on numerous accounts, including the geometry and structure of the fiber, the mechanism by which the fiber is formed, and details of the matrix's contribution to the overall composite's physical properties. 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.

The models in Table 1 range from simple empirical models loosely related to the composite morphology, to extravagant micro- and macrostructural 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. While none of the proposed theories satisfy this request, Breese and Beaucage utilized key attributes from each model to design a practical model that predicts oriented film properties based on the molecular weight, molecular weight distribution, and zero shear viscosity [**1]. Fig. 3 shows the schematic drawings of the molecular structure of each model. A commonality in all of the methods is the presence of fiber-like structures reinforcing a less rigid matrix.

Fig. 3(a) represents the infinitely long fiber composite [*19], which consists of infinitely long, rigid fibers extending uniaxially through a softer matrix. The short fiber composite [**20] shown in 3(b) is similar to the infinitely long fiber composite, except that the reinforcing fibers have a finite aspect ratio (length/diameter ratio). The Peterlin [**17] model depicted in 3(c) consists of spherulitic lamellae prior to orientation, with the formation of parallel mosaic fibrils (microfibrous) that intertwine to form macroscale packs. Imperfections, such as vacancies from chain ends, chain ends in the amorphous region, boundary layer between mosaic crystalline blocks, and inter- and intra-microfibril tie molecules are shown. The Barham and Arridge [**18] model represented in 3(d) 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. The Gibson,

Davies, and Ward [**16] model presented in 3(e) 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 figure. For the case of (c) (Peterlin i.), the spherulitic growth direction is indicated as vertical in the drawing.

2.1. Infinitely long fiber composite model

The infinitely long fiber composite (ILFC) [*19] is the simplest model and 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 Fig. 2(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 Eqs. (1)–(3). The composite's elongation at break is equivalent to that of the strongest, most rigid component, the fiber, as indicated in Eq. (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.

$$E_{C,MD} = \sum_{i=1}^{n} E_i V_i \qquad (1)$$

$$E_{C,TD} = \frac{1}{\sum_{i=1}^{n} \frac{V_i}{E_i}} \qquad (2)$$

$$\sigma_{C,MD} = \sum_{i=1}^{n} \sigma_i V_i \qquad (3)$$

$$\varepsilon_{C,MD} = \varepsilon_F \qquad (4)$$

$E_{C,MD}$ 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 ith component, V_i is the volume fraction of the ith
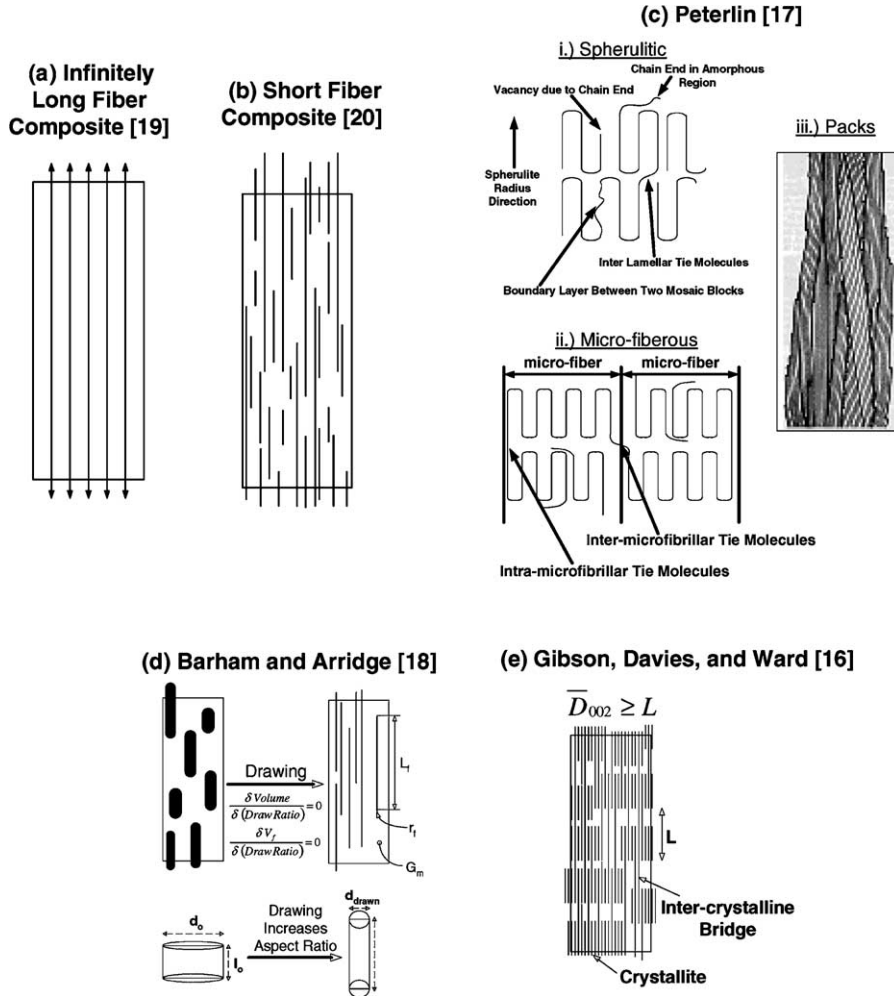
Fig. 3. Schematic drawings of the molecular structure evident in each model.

component, $\sigma_{C,MD}$ is the machine (fiber) direction break strength of the composite, σ_i is the machine (fiber) direction break strength of the ith component, $\varepsilon_{C,MD}$ is the machine (fiber) direction break elongation of the composite, and ε_F is the machine (fiber) direction break elongation of the fiber component.

Due to its simplicity, the infinitely long fiber theory is often used to approximate the properties of composites. Its shortcoming is that is does not consider the actual structure of the fiber or surrounding matrix and any transformation of those phases that are 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 [**1,**16,**18,**20,**21,*22]. The ILFC model is best suited for systems where the fiber has

a relatively large aspect ratio (length/diameter ratio $>10^3$) [**21], such as epoxy reinforced with long glass fibers.

2.2. Short fiber composite model

The short fiber composite (SFC) model proposed by Halpin and Tsai [**20] 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 Fig. 3(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.

$$\frac{E_L}{E_m} = \frac{1 + \left(2\frac{l}{d}\right)\eta_L V_f}{1 - \eta_L V_f} \tag{5}$$

$$\eta_L = \frac{\left(\dfrac{E_f}{E_m}\right) - 1}{\left(\dfrac{E_f}{E_m}\right) + 2\left(\dfrac{l}{d}\right)} \tag{6}$$

$$\frac{E_{\mathrm{T}}}{E_{\mathrm{m}}} = \frac{1 + 2\eta_{\mathrm{T}} V_{\mathrm{f}}}{1 - \eta_{\mathrm{T}} V_{\mathrm{f}}} \tag{7}$$

$$\eta_{\mathrm{T}} = \frac{\left(\dfrac{E_{\mathrm{f}}}{E_{\mathrm{m}}}\right) - 1}{\left(\dfrac{E_{\mathrm{f}}}{E_{\mathrm{m}}}\right) + 2} \tag{8}$$

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 [**20] 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 [**21,23]. This theory could be more effectively used in lower molecular weight, lower density polymers where the amorphous phase is known to be continuous [**16]. 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 [*19] or rubber strips within a lower modulus matrix [**21].

A critical shortcoming of applying both the infinitely long and short fiber (Halpin–Tsai) 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 [**16,**17,**18] 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.

2.3. Peterlin model

Peterlin [**17] 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 claimed 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. Fig. 2(c) shows a schematic on the molecular scale of the crystalline and amorphous regions in a (i) spherulitic and (ii) microfibrous material. As shown in Fig. 2(c) (iii), Peterlin claims that these lamellar microfibrils are grouped together 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 states that 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 taunt 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, making the enhancements in strength and stiffness the result of the auto-adhesion from between the long, narrow microfibrils within the macrofiber packs.

Peterlin's model is the most complex of all of those mentioned, with multiple variables that make it difficult for predicting properties. This is evident with the theory's omission 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 cannot be measured by current analytical techniques. Peterlin used IR dichroism, a commonly used technique for studying the amorphous phase, to characterize the orientation of this phase and implied this was indicative of the orientation of the tie molecules. By 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 concept of a reinforced amorphous phase could be applicable to a lower density semi-crystalline polymer or a rubber, but would not likely apply to a higher density semi-crystalline polymer. Past work has been documented that shows significant improvements in the moduli and tensile properties in higher density polymers when they are oriented [**1,**9,24,25]. The tie molecules may play a role in the overall properties of the composite for these higher

density semi-crystalline polymers at low strains, but their contribution is drastically suppressed by the transformation of the crystalline region into oriented lamellae stacks and eventual extended chains at moderate and high strain values [*14].

Micrographs of oriented films reveal narrow, crystalline rod-like structures having significantly large aspect ratios [**1,**9,**12,*13,*14]. The presence of such a crystalline region indicates 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 of higher density semi-crystalline polymers 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. Past research in higher density semi-crystalline polymers [*10,11,26,*27,*28,*29] has shown significant changes in orientation measurements from various techniques that correlate to enhancements in physical properties. While he did not emphasize the importance of the crystalline phase, Peterlin's work was one of the forerunners to show that the crystallographic techniques show alignment, and eventual tilt to 34.4° of the lamellae normal relative to the machine direction [**1,*29,30–33] (SAXS: $f_c \sim 0.521$), resulting from the near perfect alignment of the unit cell's c-axis parallel to the orientation direction (WAXS: $f_c \sim 0.960$) [**1]. 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. Again, this phenomenon is most likely to be seen in lower density semi-crystalline polymers and rubbers, but not higher density semi-crystalline polymers. Early work by Read and Stein [*34] showed significant changes in the orientation of both the amorphous and crystalline phases in low density polyethylene, ethylene–acrylonitrile and ethylene–methacrylic acid copolymers upon drawing. Koenig et al. [**12] contradicted Peterlin's generalized 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 for linear high density polyethylene. This decrease in orientation is likely the result of the greater mobility of the chains in the less viscous amorphous phase at higher temperatures. Koenig et al. [**12] did comment that the amount of orientation in the crystalline region, regardless of temperature, was significantly higher than that of the amorphous phase for linear higher density polyethylenes.

Peterlin claims that annealing drives the oriented polymer's properties back to those of the unoriented sample by relaxing the taunt, 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 lower density semi-crystalline polymers 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. This type of mechanism is also expected for a rubbery polymer, but would not be applicable to higher density semi-crystalline polymers where the drawing process causes a transformation in the abundant crystalline phase. The research by Koenig et al. [**12] with linear high density polyethylene 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 in higher density semi-crystalline polymers, one should consider the difference in melting temperatures (T_m) between the fibers (higher T_m) and less ordered crystalline lamella stacks (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 [**9]. 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 well ordered fiber, annealing would only affect the fibrillar crystalline regions at temperatures closer to the melting point of an infinitely large crystal (T_∞). 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 since 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 [**9,*14]. This means that typical annealing conditions are not conducive to full molecular relaxation of the fibrillar crystalline region to their pre-oriented state.

Bassett and Carder [**9] observed a brief decrease in modulus at a specified annealing temperature between the lamellae and extended chain melting temperatures for high molecular weight high density polyethylene. This was due to a temporary melting of the crystalline region resulting from the conversion of folded chain 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 a 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 higher density polyethylenes have been produced that retain their enhanced physical properties after annealing at 5 °C below the DSC peak melting temperature of the polymer [**1,24,25].

While there are significant uncertainties in applying Peterlin's general theory to oriented linear polymers, there are several concepts that can be of use for modeling drawn higher density 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 crystalline phase of 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 macroscale fibers. Peterlin was also one of the first to describe 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 seen in oriented linear high molecular weight polyethylene samples by Breese and Beaucage [**1] and described by others [*29,30–33]. This pattern is associated with the tilt of lamella crystals as discussed below (Fig. 4).

2.4. Barham and Arridge model

Barham and Arridge [**18] 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 Fig. 3(d). The following set of equations is used to calculate the machine (fiber) direction modulus of the composite.

$$E_{\text{Composite}} = \Phi E_{\text{fiber}} V_{\text{fiber}} + E_{\text{matrix}} V_{\text{matrix}} \tag{9}$$

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

$$\varepsilon_{f,\text{XRD}} = \left(1 - \frac{1}{\cosh(\Phi)} \right) \varepsilon_{\text{composite,tensile}} \tag{11}$$

$E_{\text{Composite}}$ is the composite modulus in the machine (fiber) direction, Φ is the shear lag factor calculated from the X-ray and tensile elongations, E_{fiber} is the modulus of the fiber, E_{matrix} is the modulus of the matrix, V_{fiber} is the volume fraction of fibers, V_{matrix} is the volume fraction of the matrix, $\varepsilon_{f,\text{XRD}}$ 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, 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 [35]. Cox's theory accounts 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 (Φ), 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 (Φ) is related to the shear modulus of the matrix material (G_{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) (Eq. (10)). If there is perfect adhesion
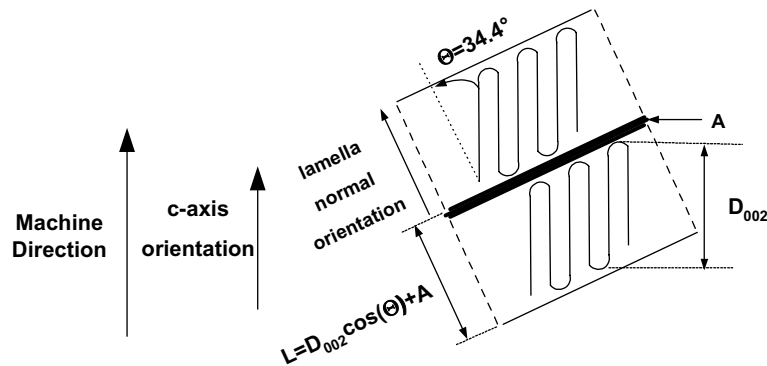

Fig. 4. Schematic drawings of the tilted *c*-axis of the unit cell within the lamella. At high draw ratios, the *c*-axis of the unit cell is aligned with the machine direction, while the lamellae normal is 34.4° relative to the machine direction. The tilting of the *c*-axis results in the perception of a larger value of D_{002}, explaining how L could be observed to be less than D_{002}.

between the matrix and the fiber, stress is efficiently transferred from the matrix to the fiber and Φ 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 ($\varepsilon_{composite,\ tensile}$), the shear lag factor (Φ) can be determined (Eq. (11)) [**18]. 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 ($E_{Composite}$) (Eq. (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 shear modulus of the matrix are well known (Eq. (10)).

Barham and Arridge [**18] showed that the relationship between the increase in the composite modulus and the extent of which the sample 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. [**12] and Peterlin [**17]. 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 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 [36], 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, and contributes little to the physical properties of the composite, and does not change significantly with draw ratio. This concept contradicts that of Peterlin [**17], who states that the tightening of the tie molecules within the amorphous component is the reason for the improvement in physical properties. Barham–Arridge do agree with part of Peterlin's model by suggesting that upon heating, the medium between the fibrils relaxes (and possibly melts), with its shear modulus dropping an order of magnitude, but disagree with Peterlin's model by stating that upon cooling, the medium begins to recrystallize and the shear modulus approaches its original value.

One of the key omissions in the Barham–Arridge model is that it does not account for transformations that are occurring in the matrix as a result of the deformation of the non-fiber crystalline region. 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.

2.5. Gibson, Davies, and Ward model

Gibson, Davies, and Ward [**16] 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 Fig. 3(e). The following set of equations is used to calculate the machine (fiber) direction modulus of the composite.

$$p = \frac{\overline{D}_{002} - L}{\overline{D}_{002} + L} \tag{12}$$

$$E = V_f E_f \Phi' + V_m E_m \tag{13}$$

$$\frac{E}{E_f} = V_f \Phi' = \chi p(2 - p)\Phi' \tag{14}$$

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 scatter-

ing, p is the probability that a certain number of crystal blocks are linked together, E is the composite modulus in the machine (fiber) direction, Φ' 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 χ is the volume fraction of crystallinity.

While Gibson, Davies, and Ward [**16] 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 interfibrillar tie molecules. According to Gibson, Davies, and Ward's depiction of their composite system (Fig. 3(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 (Eq. (12)). For a polymer of given crystallinity (χ), 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 ($\sim$250–300 GPa) [37], 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 (Φ'), as indicated in Eq. (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 a relatively large amount of crystalline blocks linked by inter-crystalline bridges. While both this model and the one proposed by Barham and Arridge [**18] 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, Davies, and Ward state the improvements are the direct result of 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 cannot 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 ($L = D_{002} + A$) (Fig. 4). 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 Fig. 3 [**1,*29,30–33]. This tilting could explain why the authors saw D_{002} values (from WAXS) greater than L (from SAXS).

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 [**1,24,25]. An average shear lag factor that is not only dependent on the volume fraction of crystallinity (χ) 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 the 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 $E_{matrix} \lll E_{fiber}$. This simplification may be acceptable when the properties of the matrix and the fiber are known, however, the simplification may not be reasonable in semi-crystalline polymers 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, if like Gibson, Davies, and Ward, the modulus of the fiber is estimated to be equivalent to that of a perfectly elongated chain (perfect crystal ~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 (Φ') 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. [24], who saw significant enhancements in the moduli and tensile properties of medium molecular weight high density polyethylene (MMW-HDPE) films. Duckwall et al. [25] 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.

3. Conclusions

In conclusion, several approaches have been discussed that attempt to relate the changes in the rigid crystalline phase to enhanced physical properties during the orientation process of semi-crystalline polymer films. While no one model presents a complete understanding of the process, key characteristics of each can be combined to build a more detailed description of the drawn system. In addition, a model that relates transformations and changes in physical properties to inherent polymer characteristics is needed for the development of new polymers.

Future work should combine the strengths of each of the proposed models to address their shortcomings and generate a comprehensive model that predicts how the modulus of a semi-crystalline polymer changes upon stretching. Such a model should incorporate the dynamics of the changing crystalline region as a function of strain. A link to morphologies of strained solids, such as oriented piled lamellae [*13] and/or extended crystalline chains [*14], should be made. Eventually, the enhanced property should be related to easily measured polymer characteristics, such as rheological properties, molecular weight, and molecular weight distribution [**1,*10,*38]. Doing so would enable the development of polymer films that would have unique physical properties when oriented. Analytical techniques, such as microscopy, X-ray scattering, birefringence, IR dichroism, and Fourier-transform optical microscopy [**1] can be utilized to characterize the orientation of the polymer at vari-ous draw ratios, and add significant insight to any transformations that are occurring in the crystalline region. With a better understanding of how polymer characteristics affect the transformation of the crystalline region, a practical model can be developed that describes the enhancements in physical properties of the oriented film.

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The papers of particular interest have been highlighted as:

* of special interest;
** of very special interest.

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