

Processing-Structure-Function Relationships in the Production of High-Performance Oriented Polyethylene

by Dayne A Plemmons

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Dayne A Plemmons DEVCOM Army Research Laboratory

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The ultra-high strength and modulus observed in oriented polymeric systems are the result of the high degree of molecular alignment of covalently bound repeating units. Orientation takes place under intense flow conditions when chains align with the direction of force. For flexible molecules such as polyethylene (PE), conditions for orientation are slightly more complicated given the chain-folded nature of the polymer crystals and the ability for chains to relax from a taut state. Nonetheless, under the appropriate processing conditions, highly oriented PE fibers exhibit among the highest specific tensile strength and modulus of any industrially relevant material. Structural factors dictating both the ability of the polymer chains to orient and the observed mechanical properties are numerous and multiscale. The molecular architecture of the chains, the morphology of the semi-crystalline lamellar clusters, and the fibrillar structure formed during solid-state deformation all play a significant role during processing and end-use. Here, processing-structure-property relationships across multiple stages of oriented PE production are reviewed and discussed. The production is divided into three distinct phases—polymer synthesis, consolidation, and orientation—each of which introduces new levels of structural hierarchy. At each level, structural features dictating functional behavior relevant to subsequent stages and end-use (i.e., rheology, solid-state deformation, and mechanical properties) are outlined and examined in relation to process parameters. As an illustrative processing relationship, resin characteristics and deformation behavior of a candidate HDPE resin are included and contextualized. It is expected that optimization of process conditions towards end-use properties will aid in development of novel structural and ballistic composites.			
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1. Introduction: Lightweight Armor Composite Program

1.1 Lightweight Armor State-of-the-Art and Motivation

The ballistic performance of fiber-based composites is directly related to energy dissipation properties of the constituent fibers. The product of the specific toughness (i.e., magnitude of energy dissipation before failure) and strain-wave velocity (i.e., rate of energy dissipation) of the fibers has been proposed as a scaling metric for ballistic performance.^{1,2} Given these criteria, polymeric fibers with ultrahigh stiffness and strength and low density are employed in lightweight armorbacker composites. Typically, unidirectional tapes composed of continuous aligned fibers in a binder matrix are stacked in a 0-90 configuration and consolidated to form a bidirectional composite. Commercial ultra-high molecular weight polyethylene (UHMWPE) fibers with tensile modulus and strength near 100 GPa and 3 GPa, respectively, represent the current state-of-the-art for the reinforcement phase. While properties of the individual fibers have been extensively studied in relation to processing conditions, the composite systems lack the same maturity. The consolidated composites are typically formed under resin-starved conditions $(\sim 15 \text{ vol}\% \text{ binder})$ in efforts to increase the composition of the reinforcement phase. These conditions result in binder voids and variations in fiber packing, which may initiate failure during ballistic loading.^{3,4} Similarly, delamination at the binder-fiber interface may result from insufficient adhesion. Limitations of the fibers themselves include extrinsic failure initiated by macroscale flaws; as such, the resulting tensile strengths can be significantly lower than theoretical predictions for a given modulus. Additionally, the solvent-based processing procedures used in the manufacturing of the fibers render them expensive compared to the raw material. These limitations suggest the current state-of-the-art has room for improvement from a cost-to-performance standpoint.

It is important to note that the current shortcomings of the armor composites are not imposed by any specific physical limits; rather, significant performance enhancement could be achieved through optimization of materials selection and processing conditions. Specifically, reducing the dimensions of fibers may further enhance the stiffness and strength of the fibers towards theoretical limits. Selecting a binder resin with improved mechanical properties and increased interfacial adhesion may eliminate early failure modes. The cost-to-performance ratio also stands to benefit by employing melt-based extrusion techniques that eliminate the need for costly solvent. Extrusion in oriented-film and -tape based format may reduce complexity and defects associated with consolidation. These factors motivate the present research program encompassing the manufacturing of polymer tapes for lightweight armor composites.

1.2 Program Objectives and Initial Results

The specific strategy for manufacturing high tensile modulus and strength tapes for lightweight armor applications focuses on a melt-based process called multi-layer forced assembly coextrusion (MLFACE). This process uses a sequence of dies that split and stack coextrusion melt flows to make highly layered structures. The primary advantage of this approach is the potential to make films or fibers with characteristic dimensions of tens to hundreds of nanometers. Additionally, the binder phase can be coprocessed with the reinforcement phase resulting in continuous interfaces even for small volume fractions ($< \sim 10 \text{ vol}\%$). Continuous coextrusion and in-line orientation represents an economically efficient strategy for tape-based precursors to armor composites.

Initial goals for the program involved selecting an appropriate polyethylene (PE) resin that is rheologically compatible with the extrusion equipment and has the potential for high modulus and strength (initial targets of 50 GPa and 1 GPa, respectively, for macroscale films) upon ultra-orientation. After identification of a candidate PE resin, target film/fiber dimensions of approximately 1 μ m were set for multi-layer coextrusion with an appropriate binder-phase. Scaling laws^{5–8} relating characteristic dimensions of fibers to modulus and strength suggest that the reduction in length-scale associated with MLFACE processing may yield tapes with stiffness and strength competitive with commercial UHMWPE fibers.

The experimental portion of this program initially surveyed a variety of candidate polyethylene resins for ultra-drawing experiments. A candidate resin was identified that exhibited sufficient drawability for melt-cast films. Under the appropriate melt-cast conditions, PE films (Marlex 6007 resin) were oriented to draw ratios approaching $40\times$ in a heated tensile chamber. These films showed high modulus (up to 50 GPa) comparable to literature values⁹ but had noticeably lower values of tensile strength. It was hypothesized that the lower tensile strength was the result of a lower fraction of high molecular weight chains and inability to form chain-extended structures, which can carry a greater load. Evidence for the structural hypothesis included small-angle X-ray scattering (SAXS) data that implied a purely lamellar structure. Melt-blends of the candidate resin with UHMWPE fractions between 2 and 20 wt% were compounded via twin-screw extrusion. With UHMWPE content up to 10 wt%, the films showed similar ultimate modulus as neat films (~50 GPa) but had increased tensile strength (>1 GPa). Structural

characterization of these films and translation to continuous extruded film processing is ongoing.

Preliminary experiments surrounding feedstock selection and orientation trials exhibited the complexity associated with ultra-orientation of polyethylene. The large number of process parameters with relatively narrow process windows render the task challenging. However, a wide body of literature exists surrounding the processing-structure-property relationships in the production of oriented PE films and fibers. The purpose of this report is to summarize this existing literature and contextualize our initial results in relation to established processes. Processing steps are divided into three stages: polymer synthesis, consolidation/preform production, and film/fiber orientation. For each stage the pertinent structural relations to functional behavior are discussed and associated with process parameters. It is expected that this knowledge will provide guidelines for the manufacturing of highperformance polymeric tapes.

2. Overview of Oriented Polyethylene Literature

Polyolefin materials are perhaps the most well-studied of any synthetic polymers. This is in part due to their superlative function as lightweight, chemically resistant, low-cost materials with service temperature spanning the full range of ambient conditions. Indeed, polyolefins today account for nearly half of all global plastics production.¹⁰ From a fundamental standpoint, PE is the prototypical chain-folding polymer and serves as a model system for semi-crystalline processing-structure-function relationships.¹¹ Stemming from catalytic advances leading to precise control over chain architecture,^{12–14} PE can exhibit material properties spanning orders of magnitude targeting diverse applications—from gel-like soft elastomers to ultra-rigid, high-strength reinforcements.^{15,16} Given the combinatorial outcomes possible with respect to processing conditions across synthesis, compounding, and consolidation, it is important to understand specific requirements for each unique application.

For ballistic protection applications, the ultra-high specific-strength of uniaxially oriented PE is exploited in high-performance composites.^{17,18} Commercially available ultra-high molecular-weight polyethylene (UHMWPE) fibers represent the state-of-the-art in ballistic-composite reinforcement and compete with carbon fibers and liquid-crystalline polymers (LCP) for the highest strength-to-weight ratio of any industrially relevant materials.^{19,20} Like LCP-based fibers and aramid fibers (e.g., Kevlar), the superlative stiffness of the material stems from chains packing into highly crystalline structures with the chain-axis oriented parallel to the fiber direction.^{21,22} For rod-like macromolecules this requirement is met across a range

of processing conditions involving shear and extensional flow. However, for flexible, chain-folding molecules like PE, the window in which chains orient efficiently can be narrow, often dependent on numerous resin characteristics and process variables. Despite these challenges, PE-based composites in theory have the potential for significant cost-advantages given the commodity-scale of the feedstock material. To date, the handful of oriented-PE producers often rely on semi-dilute, solvent-based fiber spinning,^{23–25} the economics of which cannot fully realize theoretical cost savings. However, across decades of industrial and academic research on the subject many potential pathways exist for increased cost-to-performance ratio.

The purpose of this technical report is to summarize the body of literature specific to processing-structure-function relationships in the production of high-strength oriented PE. The production process is divided into three stages, which take place in chronological order: polymer synthesis, consolidation, and orientation. Figure 1 illustrates schematically the process flow for the three phases and the pertinent materials design motif for each stage. Each phase has its own distinct process conditions, which dictate multiscale structural features: from chain architecture at the molecular level to macroscale specimen dimensions. These structural features govern functional behavior in the next stage of processing and ultimately the mechanical properties of the final material. In many cases, oriented PE production is not vertically integrated; as such, the role of the producer may be to select the appropriate feedstock from the output of a previous process stage. Because resin characteristics and processing history can have cascading effects on the resultant material properties, it is important to understand critical heuristics in each stage of processing from synthesis to end-use. An attempt is made to outline the pertinent resin specifications provided by the producers and what implications they have in terms of processing and final properties. Some characteristic data from example PE resins and solid-state orientation processes are included as a contextual example.



Fig. 1 Schematic process diagram in the production of oriented polyethylene

3. Polymer Synthesis/Resin Selection

3.1 Chain Architecture

While high-pressure, free-radical polymerization of branched PE dates to the 1930s, a seminal breakthrough yielding highly linear chains came in the 1950s through development of metal-organic catalysts by Karl Ziegler.^{26,27} The process allowed for ambient temperature and pressure processing conditions and resulted in high-density polyethylene (HDPE) with crystallinity near 75%. Additionally, with suppressed long-chain branching (LCB) as compared to the free-radical process, higher 1-alkene comonomers could be purposefully incorporated into the main chain. These so-called short-chain branches (SCB) in the linear chain significantly inhibit chain-folding and thus result in lower-crystallinity, linear lowdensity polyethylene (LLDPE). Concurrently, some of the first commercial HDPEs were being developed at Phillips Chemical Company using supported chromium oxide catalysts.²⁸ The Phillips catalyst was particularly useful for its ability to incorporate small amounts of LCB via macromer insertion.^{29,30} Indeed, the strategy of introducing structural moieties into the polymer chain architecture to target specific physical properties has played a significant role in the proliferation of polyolefins across diverse application spaces. However, because any type of irregular chain-branching can hinder the crystallization and chain-packing of PE, highly linear PE with minimal branching of any type has traditionally been used for applications where significant extended-chain orientation is required.

While a perfectly linear PE chain may result in the highest crystalline order and highest chain-orientation, there are practical rheological considerations that motivate incorporation of branching into the chain architecture. In particular, a small amount of LCB may be purposefully incorporated into PE resins to impart a shear-thinning melt-flow behavior, which reduces load during extrusion.³¹ Additionally, for the case of blown-film and blow-molding PE resins (or cases in which post-extrusion orientation steps occur) a small amount of LCB may be incorporated to otherwise linear chains to slightly increase melt elasticity for greater extensional-flow stability.^{32,33} Some of the earliest HDPEs from Phillips benefited from LCB resulting from the supported chromium oxide catalysts and still today account for a large portion of the commercial HDPE sector.²⁹ Single-site catalyst systems can also effectively incorporate a small amount of LCB (<0.44 branches per 10,000 carbons) in a well-distributed manner without affecting the molecular weight or molecular weight distribution;³⁴ consequently, the benefits of LCB can be realized without significantly impacting the crystallinity. PE resins with some degree of LCB are often categorized as blow-molding or blown-film resins and are sometimes classified by a melt-index ratio. The ratio of high-mass to low-mass melt flow index (e.g., I₁₀/I₂, I₂₁/I₅) is indicative of the amount of shear-thinning observed due to the moderate LCB effects and can be a good comparative metric during resin evaluation.

In addition to rheological implications, the molecular architecture of PE chains can have a substantial impact on the mechanical properties and morphological features of the resulting material. In particular, a controlled amount of SCB through comonomer insertion can drastically alter the crystallinity of the PE resin, from near-zero for very low-density PE (VLDPE) to 75+% for some HDPE resins. As mentioned previously, because branching reduces order required for highly regular chain-packing, substantially linear PE is typically used in the production of highly oriented material. Typically, linear PE shows higher modulus due to the percolating network of rigid crystals; however, these resins can suffer from long-term stress cracks under prolonged stress and chemical exposure. This phenomena-that is, brittle failure by environmental stress-cracking-stems from polymer chains pulling out from crystals under the plasticizing effects of a solvent or elevated temperature.^{35,36} Higher alkene comonomers are often incorporated into otherwise linear resins to decrease the rate of slow crack growth; increased branch content typically results in a greater number of tie-chains connecting crystalline lamella. Additionally, SCB decreases the likelihood and rate of chain disentanglement from lamella as the side groups render the chain less mobile in the crystalline region. The quantity and stability (i.e., resistance to pull-out) of the tie-chains in semicrystalline PE dictate both toughness and resistance to stress-cracking.^{37–39}

Although oriented PE often has different functional requirements, the microstructural features—namely, inter-crystalline tie-chains—enabling improved resistance to stress-cracking are also critical for achieving high tensile strength in the oriented material. An empirical quantity called the environmental stress-crack resistance (ESCR) is a good qualitative measure of morphological characteristics leading to inter-crystalline network formation and can be a useful resin specification when evaluating potential for high tensile strength. Increasing the concentration of crystalline tie-chains while maintaining crystallinity and chain-orientation, however, can be particularly challenging; the ESCR and density of commercial HDPE resins are often negatively correlated.

One particularly effective strategy for improving ESCR while maintaining crystallinity is to incorporate a high molecular weight (MW) fraction. While the MW aspect will be discussed further in Section 3.2, some comments on ESCR as it relates to SCB are appropriate here. On a statistical basis, SCBs in Ziegler-Natta and Phillips-catalyst polymerized chains are typically incorporated into the lower molecular weight fraction; this is due to the comonomer's tendency to terminate chain-propagation.⁴⁰ Consequently, even small fractions of comonomer have a large impact on crystallinity in most commercial HDPE resins. However, with advances in catalysis and reactor design, small amounts of short-chain branches can be incorporated specifically into high molecular weight fractions in a welldistributed manner. Thus, the linear portion in between branches may crystallize while the intermittent branches prevent chain pull-out. This so-called "inverse comonomer distribution" has only recently emerged with newer cascade reactor processes and site-specific catalysts.^{40–43} PE producers often tout newer resins exploiting this technology as having an excellent balance between rigidity and ESCR. While commercial applications have focused on down-gauging blowmolded containers and packages, the molecular architecture of these specialty resins could be particularly suitable for production of melt-processed ultra-drawn tapes.

While discussion has thus far focused on mechanical properties of HDPE resins as they relate to chain architecture, it should be noted that the orientation process has its own unique requirements. Orientation occurs most efficiently when unentangled chains loosely bound by a few stress transmitters can more freely align with the direction of flow. Thus, topological entanglements that prevent alignment should largely be avoided. In general, the balance between forming tie-chains to improve tensile strength and avoiding entanglements that prevent efficient orientation can be particularly delicate. This compromise is analogous (and indeed related) to the stiffness-toughness balance resin producers seek to achieve with new technology. As such, processes for the production of highly oriented drawn tapes may benefit substantially from next-generation HDPE resin development.

3.2 Molecular Weight/Molecular Weight Distribution

Apart from chain linearity, the molecular weight (MW) and molecular weight distribution (MWD) of a PE resin perhaps have the most substantial impact on both processibility and resulting structural features. For melt-processing in particular, the cubic dependence of viscosity on chain length dictates an upper end of suitable MW for given process equipment.^{44,45} From a structural standpoint, the MW and MWD drastically impact the crystallization kinetics and ultimately dictate the observed mechanical properties. Low-MW PE crystallizes much faster,⁴⁶ resulting in higher crystallinity, while high-MW PE has longer chains, which pervade more lamella thus increasing tie-chain concentration.^{39,47,48} As such, there has traditionally been a trade-off between rigid, low-MW PE and tough, high-MW PE. For melt-processed PE, very broad MWDs and targeted multimodal compositions are synthesized via multi-catalyst reactor systems, cascaded reactor systems, and melt-blending.^{41,49,50} By controlling MWD, resin producers can effectively target rheological and mechanical properties for given applications. For instance, many injection molding HDPEs have a melt flow index (MFI) near 8 dg/min (190 °C, 2.14 kg load) and have densities approaching 0.965 g/mL. The high crystallinity is achieved by centering a narrow MWD around a kinetically favorable MW for crystallization (M_w peak between 25 to 50 kg/mol).⁴⁶ Notably, traditional injection molding resins are not ideal for ultra-high tensile strength applications because of the substantially lower average M_w. Blow-molding and film-extrusion processes may require higher viscosity and higher melt elasticity from a rheological standpoint and higher toughness and resistance to cracking from a mechanical standpoint. In this case, a high-MW fraction, often with a particular chain architecture, is incorporated into the resin to impart the appropriate features.^{33,43} It should be noted that the process used in production of a targeted MWD is also important. Intimate mixing of chains of diverse MW may occur for some processes (e.g., multisite catalysis) while they may remain phase separated in others (e.g., melt compounding).⁴¹ The crystallization kinetics and resulting structural characteristics from these different processes continue to be an active field of research.

In the production of highly oriented PE, the appropriate MW and MWD is highly dependent on what type of process will be used in the initial consolidation of the polymer. In gel-spinning, for instance, the desirable MW can be much higher, as a

solvent is used to reduce viscosity and improve chain mobility. Typically, an M_w of approximately 1000–5000 kg/mol is used in gel-spinning with polymer concentrations in the semi-dilute regime between 1 and 10%.²² In solvent-based processes, the solvent quality^{51,52} and concentration⁵³⁻⁵⁵ also has a substantial impact in the initial morphology development. The concentration and solvent are chosen to prevent excess chain entanglements formed during the initial spinning process (i.e., form the minimal amount required for stress transmission during further drawing). In some ways, the lubricating effect of the solvent and its impact on crystallization kinetics is analogous to the role of low-MW fractions in meltprocessed PE. Melt-processed blends of UHMWPE and PE waxes (with Mw below 10 kg/mol) have been extruded and drawn in the solid-state.^{50,56} This could be viewed as an extreme of the bimodal MWD strategy for realizing appropriate melt viscosity for high-MW resins. It was found that, while similar tensile moduli could be achieved, blends with low MW fraction below a critical M_c of approximately 5 kg/mol all had roughly the same tensile strength; in other words, the low-MW fraction below M_c acts as a solvent-like processing aid that does not contribute to strength. The MW and MWD suitable for solid-state orientation of extruded HDPE follows similar guidelines. Increased entanglement concentrations in high-MW HPDE become intractable for solid-state orientation due to the immense stress build-up that occurs; conversely, low-MW PE cannot transmit stress efficiently and is unstable during drawing.^{57,58} In this view, broad MWD HDPE resins with a low-MW fraction that crystallizes efficiently and lubricates network-forming long chains help strike an appropriate balance.^{59,60} Density, MFI, and ESCR are helpful specifications in deciphering the MW and MWD where full characterization may not be possible. Linear PEs with density above approximately 0.963 g/mL and MFI below approximately 1dg/min (190 °C, 2.16 kg load) imply suitable crystallization kinetics (a proxy for chain mobility) with sufficiently high-MW for tie-chain formation.

3.3 Other Factors

From early works in the pursuit of high-strength, highly oriented PE, it was clear that balancing chain mobility required for ultra-drawing and network connectivity required for high tensile strength was a primary challenge.⁶¹ Conventional strategies improving processibility included dilution with a solvent or low-MW PE fraction to effectively increase chain mobility for a given M_w; however, an alternative approach focuses on exploiting polymerization and crystallization kinetics such that entanglement density remains low across all stages of the processing. The so-called "virgin PE" approach involves solution polymerization at temperatures well below the dissolution temperature such that chains are never

in a melt-like state.^{62,63} In the appropriate polymerization temperature regime, the resulting "virgin" state is composed of high crystallinity and large lamella with a small amount of entanglements for network connectivity.⁶⁴ This type of resin is specifically suited for processes that never fully melt or dissolve the PE (sintering,⁶⁵ high pressure consolidation,⁶⁶ etc.).⁶⁷ Building upon a similar idea, it can be seen that the drawability of melt-processed and solution-processed preforms increases with lamellar thickness. As entanglements are primarily in the amorphous portion of the semi-crystalline PE, it follows that the increased lamellar thickness results in reduced entanglement concentration; thus, melt-processed and solution-processed PE can be analogous to the "virgin PE" approach provided the conditions during crystallization are appropriate. It was recently shown that using poor solvents was a particularly useful strategy for increasing drawability of UHMWPE preforms cast from gels.⁵¹ The increased lamella size and drawability was attributed to the significantly lower values of under-cooling during crystallization observed for poor solvents; the increased chain mobility during precipitation from solution resulted in larger, more perfect lamella suitable for ultra-drawing. Similar strategies could exist for melt-processed PE. Altering the kinetics of heterogeneous nucleation via incorporation of a nucleating agent can result in increased lamellar thickness in appropriate HDPE resins.^{68,69} Additionally, differences in crystalline morphology—specifically, the departure from a spherulitic morphology—resulting from heterogeneous nucleation on pseudo-epitaxial interfaces may be useful for increasing drawability.⁷⁰ This could be a particularly important strategy in extrusion-based processes where rod-like nucleating agents⁷¹ align with the direction of flow during crystallization at the exit die.

3.4 Example Structure-Property Relationships in Commercial Resins

Figure 2 summarizes the relevant processing-structure-function relationships for PE synthesis/resin selection. During resin selection the process parameters and structural features may be unknown. Evaluation is more likely based on functional characteristics—that is, observables and specifications from the resin manufacturer (Fig. 2, right-hand column). Examples of suitable structural and functional resin characteristics became apparent during initial evaluation of feedstock material for production of oriented PE (specifically melt-processed HDPE). Given the primary goal of producing ultra-drawn tapes, a subset of HDPE resins with high density and medium melt-flow were selected to fulfill the requirements of chain mobility with simultaneous connectivity. Draw ratios approaching 40× and moduli exceeding 50 GPa were achieved during initial evaluation of candidate HDPE resins.⁷² Figure 3 illustrates the trade-off between crystallinity (calculated from quoted density) and

ESCR. The data⁷³ is a representative subset of commercial HDPE resins with flexural modulus greater than 1.35 GPa, density greater than 0.955 g/mL, and ESCR data available. Notably, HDPE resins with crystallinity approaching approximately 75% and ESCR near 10 to 20 h (Fig. 3, blue oval) are the product of linear PE processes that yield bimodal MWD. The MWD of two such candidate resins⁷⁴ are shown in Fig. 4. A commercial blow-molding resin with MFI of 0.7 dg/min (190C, 2.16 kg), density of 0.964 g/mL, and ESCR of 15 h (ASTM D1693, 100% Igepal) displays a low-MW peak around 25 kDa and a long-tail high-MW fraction with shoulder approximately near 100 kDa. A blown-film resin (Fig. 4, right) with similar characteristics is the product of a dual-catalyst in which a narrow peak around 30 kDa is achieved with a precise single-site catalyst and a broader higher-MW peak near 150 kDa is achieved with a Ziegler-Natta-type catalyst. Notably, these resins show similar nominal MW and MWD. However, alternative definitions of molecular weight can be defined to collapse features of the MWD into quantifiable metrics. In particular, M_z is defined as the ratio of the third and second moments of the MWD. This statistical indicator of MW is particularly suitable for quantifying the high-MW fraction of the broad MWD. It can be seen that M_z is higher for the blow-molding resin; that is, the long-chain tail of the distribution skews towards higher MW. It is expected that higher M_z contributes to higher tensile-strength of oriented material via increased tie-chain concentration.



Fig. 2 Processing-structure-function relationships in polyethylene synthesis/resin selection



Fig. 3 Trade-off between rigidity and stress-crack resistance for high-density polyethylenes



Fig. 4 Molecular weight distributions and features of pertinent HDPE resins⁷⁴

The two resins also differ in crystallization temperature, T_c . For various quench conditions, T_c is the result of crystallization thermodynamics in which the freeenergy penalty of surface generation must be overcome by formation of nuclei of critical size. Heterogeneous nucleation occurs when crystals form at lowerundercooling through growth on existing surfaces (catalyst particles, dust, nucleating agents, etc.). In this regard a higher T_c under similar cooling conditions likely implies that a greater concentration existing nuclei are present. It is unclear if the higher T_c of the blow-molding resin stems from a purposefully added nucleating agent or is the result of the other factors such as residual catalyst or high-MW fraction. Nonetheless, the substantially altered crystallization kinetics result in greater lamellar thickness for a given cooling rate. Similar T_c can be achieved for the blown-film resin via the incorporation of a commercial nucleating agent.

The blow-molding and blown-film resins are notably different from common injection-molding HDPEs with marginally higher densities (~0.965 g/mL). Shown in the table in Fig. 4, the injection-molding resin lacks a high-MW fraction and thus has a lower M_w and higher MFI. These resins are not particularly suitable for orientation as they do not form a sufficient amount of tie-chains for stress distribution during ultra-drawing. Interestingly, as seen in the capillary rheology data in Fig. 5, the blow-molding resin and injection-molding resin have similar viscosities at shear rates near 1000 Hz despite having significant variation at low shear. This is likely the result of a minor amount of LCB⁷⁵ in the blow-molding resin, which contributes to the shear-thinning behavior.



Fig. 5 Capillary rheology data for blow-molding and injection-molding grade PE resins

Although they have not been tested initially, another subset of resins with potential for high-strength and high-orientation are outlined in the orange oval of Fig. 3. These resins are engineered for increased ESCR while maintaining excellent rigidity through multimodal MWD processes that may incorporate a fraction of SCB. In particular, resins with an inverse comonomer distribution may exhibit particularly high ESCR as compared to common HDPEs of similar density. For drawn film processes in which the transverse strength may be of importance (in contrast with uniaxial fiber applications), the addition of a small amount of comonomer may substantially impact the adhesion between the highly crystalline microfibrillar components.⁷⁶ Additionally, the potential for greater clarity and transparency exists as the stable amorphous fraction may fill regions that would otherwise form voids or low-density cavities.⁷⁷ Depending on the exact requirements for the oriented PE production, these types of resins may be well worth considering.

4. PE Consolidation and Precursors to Oriented Material

Like most polymers, the properties of linear PE are sensitive to temperature and processing history. At higher temperatures when chains have sufficient flexibility, the formation of topological entanglements give rise to observed viscoelastic properties both in the melt and after cooling.⁷⁸ Additionally, the shear and extensional flow conditions experienced by the polymer in the melt state may have long-lasting consequences on performance.⁷⁹ In particular, due to the semicrystalline nature of PE, the cooling rates from melt processes and precipitation rates from solution processes have a drastic impact on morphology via the crystallization kinetics.¹¹ These differences in crystalline morphology and amorphous features give rise to a large variability in ultra-drawing characteristics for PEs as a function of process parameters. An attempt is made here to summarize the pertinent structural features as they relate to orientability.

4.1 Semi-Crystalline Morphological Features Governing Drawability

At the molecular level, chains pack into ordered structures described by the crystalline unit cell and symmetry parameters. The most common crystal structure for PE has an orthorhombic unit cell with chains oriented along the c-axis. Two confirmations of zig-zag planes lie perpendicular to one another and are offset approximately 45° from the b-axis.¹¹ Given the differences in interactions along the orthogonal planes in the crystal (i.e., hydrogen bonding vs. covalent bonding), polyethylene single crystals show extreme anisotropy in mechanical properties. The room-temperature moduli along the a- and b- axes are estimated around 3.2 GPa

and 3.9 GPa, respectively, while the modulus along the c-axis individual unit cell is estimated to fall between 240 to 360 GPa.⁸⁰ The extreme stiffness along the chain direction gives rise to the superlative mechanical properties for highly oriented PE. Single-crystals of PE, however, rarely form with large dimensions along the c-axis; the chain-folding nature of polymer gives rise to thin, layered structures called lamella.^{81,82} The thickness of lamella in PE is on the order of 10 nm, while the lateral dimensions are much larger and can exceed 10 μ m. Typically, PE cooled from the melt or precipitated from solution forms stacks of crystalline lamella with amorphous material sandwiched in between; the extent and orientation of the lamella as well as the nature of the interface between the crystalline and the amorphous region largely governs the mechanical properties of material.⁸³

Hoffman and Lauritzen first described the kinetics of crystallization and radial growth of PE lamella from the melt.⁸⁴ A spherulitic superstructure—that is, a structure in which the thin lamella are oriented radially outward from a central nucleus-is often observed for melt-crystallized PE. Notably, depending on the nucleation kinetics, the extent of individual spherulites can vary from a few microns (high concentration of nucleation sites) to a few millimeters (low concentration of nucleation sites).¹¹ It is often observed that very large spherulites, though more crystalline, show poor mechanical properties due to segregation and voiding effects at the boundaries.⁸⁵ However, polyethylene spherulites are typically fairly small, and as such the mechanical properties may be dictated by the finer features of the morphology. While complex sheafed, dendritic-like, and spiral features can result from lamellar branching during growth,⁸⁶ the mechanisms of deformation may be simplified by classifying polar and equatorial regions with respect to the direction of force (shown in Fig. 6a).^{87,88} Lamella off-normal from tensile force, for instance, may tilt or twist, while the orthogonal orientations may undergo crystal slip.⁸⁹ For different cases, the yield characteristics are often described in relation to properties of individual lamella and the interlamellar amorphous features (i.e., at a lower level of structural hierarchy).87



Fig. 6 Structural features of semi-crystalline polyethylene as they relate to deformation. Modified from Butler et al. (1997) and Séguéla (2007).^{87,96}

For ultra-drawing or other high orientation processes, mechanisms of irreversible and high-strain plastic deformation are of primary importance. In this regime, observed behavior is the result of competition between cavitation and fibrillation processes occurring in the amorphous region and crystal-slip and fragmentation processes occurring in the crystalline region.^{89,90} In describing these processes, it is necessary to understand the structural features that give rise to such behavior. Considering one period of a lamellar cluster unit, a variety of structural features can be defined and are illustrated in Fig. 6b. The length of one period, the long period, L_p, is often experimentally determined through SAXS. The lamellar thickness, L_c, can then be evaluated as the product of L_p and the crystallinity, X_c. Alternatively, the melting peak in DSC is also sensitive to the surface area of the lamella and can be used to estimate crystal thickness.^{84,91} Topological features at the surface of the lamella include stems, chains which fold directly back into the crystalline portion; tie-chains, chains which traverse the amorphous region into neighboring lamella; loops, chains which fold back into the crystal at a non-adjacent entry-point after traversing the amorphous region; and cilia, chains which have their chain-ends on the crystal surface or just into the amorphous region.¹¹ The interlamellar amorphous region may consist of free-chains and chains entangled with the tie-chains, loops, and cilia that emanate from adjacent lamella.

For highly regular crystals, plastic deformation via crystallographic slip and subsequent chain unfolding permits more strain than any other deformation mechanism.⁸⁹ Crystal slip and lamellar fragmentation is greatly aided by chain mobility within the crystalline lamella. In linear PE, two overlapping mechanical relaxations associated with block slip motion and chain sliding diffusion within the crystalline region—the alpha-I and alpha-II relaxations, respectively—are observed above approximately 60 °C.⁹² This additional mobility of the crystalline chains and inter-phase material greatly alters mechanisms of deformation at temperatures exceeding the transition region and plays a significant role in the ultra-drawability of PE.⁹³ Notably, cavitation and stress-whitening is no longer observed during plastic deformation at temperatures exceeding the alpha-transition, indicating that yield is more easily achieved via crystal plasticity rather than void formation in the amorphous region.⁹⁰

Deformation via crystal-slip and lamellar fragmentation processes occur at lower flow stress relative to the yield stress; this plastic instability causes necking to occur during drawing.⁹⁴ Stress-transmission after necking is dictated by topological features at the surface and interlamellar region. Analogies between cross-links in rubber and the stress-transmitting entanglements are often used to describe the strain-hardening that follows large chain-extension.⁹⁵ It is hypothesized that the balance between the strain-hardening resulting from chain-extension and plastic strain-softening resulting from crystal-slip impose a natural draw ratio;⁹⁶ beyond the natural draw ratio, further extension primarily takes place by pulling in more material from the un-necked portion. These mechanisms are shown schematically in Fig. 6c. Although the structural mechanism for natural draw ratio is quite complicated, some commonalities among theories exist. Greater crystal thickness increases the natural draw ratio as a single slip or fragmentation event results in a longer portion of chain to unravel.⁹⁷ On the other hand, tie-molecule density decreases the natural draw ratio as cleavage and unfolding events are suppressed.⁹⁶ It is important to note that the natural draw ratio is not equivalent to the maximum achievable draw ratio; certain mechanistic features (void coalescence,³⁶ melting⁹⁸ and recrystallization⁹⁹ processes, etc.) occurring after neck propagation can have a substantial impact in later stages. Strobl et al.¹⁰⁰ have suggested further that the limits of drawability are fully determined from entanglement density in the amorphous region and other characteristics are fleeting features of the drawing process. Despite the complexity, it is clear that reduced entanglement density and more ordered crystals result in increased drawability. Additionally, tie-molecules connecting the initial crystalline network are required for plastic stability (i.e., preventing runaway strain-softening).^{101,102}

4.2 Kinetic and Thermodynamic Factors Impacting Intermediate Structure Formation

The kinetics and thermodynamics of crystallization have a significant impact on the formation of the topological features of the lamellar clusters. It has been shown from neutron scattering that the radius of gyration R_g is significantly reduced upon crystallization from solution.¹⁰³ Crystals solidified from the melt, however, do not see a commensurate reduction (under the fast-quenching condition).^{104,105} The implication that the crystalline portion may largely take on the same chain confirmation as the melt-state has significant consequences for structural features. Most notably, trapped entanglements in the melt-state likely persist in the solidified material and may be present in the amorphous material or as non-regular chain folds at the lamella surface.¹⁰⁶ Additionally, the tie-chain concentration in such case can be rationalized from the ratio of R_g in the melt to L_c of the crystal.³⁷ On the other hand, the observation that R_g significantly decreases during solution crystallization implies that the molecular mobility of the chains has a significant role in the progression towards a thermodynamic equilibrium. Given the larger free energy of the fold surface as compared to the lateral crystal surface, thicker crystals with adjacent chain-folding or chain-ends at the surface are thermodynamically favored.^{82,91} As such, the greater chain mobility during crystallization at a higher temperature (or alternatively in more dilute solutions) enables faster progression toward thermodynamic equilibrium and larger, more perfect crystals.¹⁰⁷ Ward et al. described this phenomena in relation to the solid-state drawing behavior of HDPEs as a function of MW;⁵⁷ the critical parameter connecting the behavior across thermal treatments and MWDs was the viscosity during crystallization. Lower molecular weight and higher crystallization temperature favors more uniform lamella, while higher molecular weight and lower crystallization temperature results in complex twisting and branching during radial growth. These structural features directly impact the drawability of the cast or extruded PE preforms.

Given the nature of continuous extrusion processes, it is also important to consider the formation of structural features as they relate to flow. Departure from spherulitic-type morphology has been observed under melt-spinning,61,108,109 blown-film,¹¹⁰ and gel-spinning^{54,111,112} conditions, and the resulting structures have been attributed to differences in the types of nuclei and kinetics of lamellar growth. In particular, so-called "shish-kebab" type features are often observed under intense flow conditions.^{61,109} Under these conditions, some higher MW chains are stretched and act as fibril-like nuclei for the crystallization of coiled chains.¹¹³ Interestingly, the stretched chains need not be crystalline to promote nucleation but require some threshold amount of orientational order.¹¹⁴ Chain stretching is highly dependent on the polymer relaxation dynamics as a function of temperature and molecular weight; prevalence of chain extension can be predicted from the product of the chain relaxation time and the strain-rate imposed by flowa dimensionless quantity called the Weissenberg number (Wi). For Wi greater than approximately 0.5, chain-stretching can have a significant impact on both the resulting structures and the kinetics of crystallization. The orientational order of the chains helps overcome entropic barriers to crystallization and thus significantly impacts the crystallization rate.¹¹⁵ Systematic variation of strain-rate in a gelspinning apparatus showed that crystallization rate was a monotonically increasing function of Wi, while local maxima exist for the lamella orientation parameter (as determined from SAXS) and the crystallinity.¹¹¹ Melt-processed precursors to drawn films, however, have shown a negative effect of extensional flow. Ultimate tensile strength and moduli decreased for increasing draw-down during PE castfilm extrusion as the maximum obtainable draw ratio was significantly lower.¹¹⁶ It is likely that the conditions for chain orientation are more favorable during the solid-state drawing process in relation to melt-drawing (as relaxation effects are greatly reduced at lower temperature). Therefore, absent significant flow-induced crystallization, it may be undesirable to significantly pre-orient chains in the meltstate given the reduced extensibility. The reduction in maximum draw ratio associated with pre-orientation may be related to the thermal transport associated with the take-up speed. Large draw-down with correspondingly large take-up rates greatly affects the quench conditions during cooling from the melt. On the basis of greater cooling rates (leading to lower T_c), preforms cast with a high degree of preorientation may show lower crystallinity, thinner lamella, and greater entanglement density as compared to films with minimal pre-orientation.

4.3 Processing-Structure-Property Relationships in PE Consolidation

Summarized in Fig. 7, the processing-structure-function relationships for the PE consolidation step of oriented PE production are immensely important but sometimes overlooked; industrial processes which have in-line drawing processes downstream from the extrusion or spinning equipment may not always fully characterize the intermediate material. However, the implications of processing in this consolidation stage are equally as substantial as the resin selection and orientation process; ultimately, the intermediate structure dictates structures observed post-orientation. While phenomenological explanations for structural features were described previously, it is important to understand how they are related to specific process parameters.



Fig. 7 Processing-structure-function relationships in the initial polyethylene consolidation/ preform processing

The extrusion temperature is significant on multiple accounts. Chain confirmations in the melt-state are largely governed by the melt temperature and shear-rate; most notably, entanglements monotonically decrease with increasing temperature while R_g monotonically increases.⁴⁴ Upon quenching, these conditions can become locked-in as chains are no longer sufficiently mobile to significantly alter their confirmations. One may envision a scenario for melt processing in which the

extrusion occurs at a sufficiently high temperature (~250 °C⁹) to reduce chain entanglement, and the melt is subsequently quenched to just above the crystallization temperature such that the melt structure is largely "frozen in" before formation of lamellar crystals. From a practical standpoint, the melt temperature is also important as a parameter in the thermal transport kinetics at the die-exit. Additional enthalpy at higher temperatures may slow the cooling process and thus impact the crystallization kinetics.¹¹⁷ The quench conditions are also of primary importance in the formation of the crystalline morphology from the melt and solution state. In melt-based extrusion processes, the extrudate is typically quenched with "chill" rollers at the exit die. The cooling-rate and thermal gradient experienced by the polymer is directly affected by the roller temperature and geometry, respectively. In efforts to increase crystallinity and lamellar thickness of the extruded material, the roller can be operated at elevated temperature to increase crystallization temperature via decreased cooling rate. To limit the deleterious effects of thermal gradients, the extrudate can pass through calendar-type "nip" rollers or a quenching "air-knife" to impart symmetric heat-transfer characteristics (as opposed to one-side quenching on a roller).⁴⁵ Similarly for fiber spinning operations, the extrudate may pass through a quench bath at a given temperature and set distance from the die-exit before being wound by a take-up winder. The dissolution temperature dictated by the choice of solvent may be a primary factor in addition to the temperature and location of the extraction bath with respect to the die-exit.⁵¹

Careful consideration must also be given to extensional flow characteristics imparted by process equipment and parameters near the die-exit. The take-up rate at the exit with respect to the extrusion flow-rate governs the draw-down or preorientation of the polymer chains. This extension during crystallization from the melt can have a significant impact on observed morphology; it may improve the kinetics and seed a row-nucleated lamellar structure in some cases (e.g., gelspinning¹¹¹ and melt-spinning^{61,114}) but may not be desired in all circumstances (e.g., cast film melt extrusion¹¹⁶). Similarly, the exit-die geometry with respect to the flow channel can also result in chain-stretching flows.⁴⁵ In many cases the flow within the die interior is characterized by uniaxial or biaxial compression. In melt extrusion processes, chain extension may result in significant elastic stress at the die-exit and lead to instability-based film defects and non-uniformities.¹¹⁸ Although often empirically determined, stable process conditions eliminating such elastic defects are a staunch requirement for melt-extruded preforms with sufficient drawability. It should be noted that in certain cases the die geometry is specifically chosen to impart an initial degree of chain orientation; this is particularly true for gel-spinning¹¹⁹ and melt-spinning¹⁰⁹ processes in which row-nucleated and shishkebab morphology structures form in the precursors to solid-state drawing. Preorientation in contraction dies can provide a more consistent initial draw than tension-based methods and results in reduced fiber dimensions, which may be desirable in many cases.¹¹⁹

4.4 Example Structure-Property Relation in PE Consolidation

In the evaluation of a suitable feedstock, drawing characteristics of a blow-molding PE resin were observed as a function of different thermal treatments. Films approximately 750 μ m thick were melt-pressed from 2 mm thick consolidated preforms at 190 °C for 10 min at 2.5 bar. The films were crystallized under a variety of non-isothermal cooling conditions as summarized in Table 1. Shown in Fig. 8, the melting temperature—indicative of lamellar thickness—linearly decreases with the log of cooling rate. Crystallinity varied in a similar manner from approximately 58% for the fastest quench to approximately 75% for slow-cooling. The drawing behavior of each film was evaluated by performing constant cross-head speed extension in an oven at 100 °C. A waisted specimen 20 mm wide with 10 mm gauge length was extended at 50 mm/min (500%/min, nominally).

Cooling method	Description	Under pressure?	Estimated cooling rate
Slow-cool	Cool under pressure from 190 °C to 80 °C at	Yes	1 °C/min
Method #1	1 °C/min		
Slow-cool	Cool under pressure from 190 °C to 140 °C at	Yes	1 °C/min
Method #2	20 °C/min then 140 °C to 100 °C at 1 °C/min		
Natural	Let film cool between 5 kg steel plates left at 25 °C	No	10 °C/min
convection			
Cooling water	Cool under pressure from 190 °C to 40 °C at 30	Yes	30 °C/min
	°C/min		
Water bath	Quench in water bath at 20 °C	No	300 °C/min
Dry-ice bath	Quench in acetone/dry-ice bath at -25 °C	No	500 °C/min

 Table 1
 Thermal treatments for illustrative drawing experiments



Fig. 8 Melting temperature (T_m) for various illustrative processing conditions

The nominal engineering stress-strain curves are shown in Fig. 9. Note that the length of the region that initially experiences plastic deformation is used as the gauge length in generating strain measurements; this has the effect of skewing the elastic portion of the curve. A double-yielding¹²⁰ type phenomena is observed for the fast-quenched specimens while a single sharper yield is observed for the slower cooling. This may indicate a transition between a disordered spherulitic superstructure with lamella twists and branches to more uniform distribution of lamella. From the drawing curves, the yield stress, Y, and strain-hardening modulus, G, are extracted, and their ratio, Y/G, is used as an indicator of the natural draw ratio.⁹⁵ Figure 10a shows that Y/G increases nearly linearly with increasing observed melting point; this follows predictions that the natural draw ratio scales with lamellar thickness.⁹⁷ Importantly, the natural draw does not necessarily equate to the ultimate drawability. The maximum drawability for these samples was quantified by the ratio of the cross-sectional area near failure to the pre-drawn cross-section in the middle of the gauge region. Figure 10b shows that, while maximum draw ratio follows a general trend with natural draw, there are outliers from the trend. Most notably, the sample cooled under pressure at approximately 30 °C/min shows higher maximum draw ratio than the trend. While there is insufficient data to confidently assert the mechanism, it could be hypothesized that the pressure during crystallization plays a significant role. It is known that void coalescence and the related crazing phenomena plays a role in the failure during creep-type deformation^{36,37}; it is possible that the increased pressure during crystallization reduces formation of microvoids in the amorphous region that contribute to failure at high strain.



Fig. 9 Nominal engineering stress-strain curves during hot-drawing of polyethylene preforms at 100 $^{\circ}\mathrm{C}$



Fig. 10 Ratio of yield stress to strain-hardening modulus as a measure of natural draw ratio and ultimate drawability

5. PE Orientation Process

Given the extreme tensile modulus along the c-axis of a polyethylene single-crystal, achieving similar properties at the bulk scale largely can be reduced to two factors: 1) Obtaining the highest possible crystallinity; 2) Orienting the chain-axes of the crystals along the tensile direction. As outlined previously, the intermediate morphology has a significant role in enabling suitable deformation-induced structural transitions; the most notable distinction is between spherulitic-type and row-nucleated-type (often shish-kebab) morphologies. The structural progression generally can be described as a lamellar-to-fibrillar transition and subsequent fibrillar structural refinement at extreme draw ratios. Evidence for the observed structural transformations is abundant with numerous SAXS and WAXS studies on

the high-temperature deformation of HDPE^{121–126} and UHMWPE.^{127–132} The mechanical properties—specifically, the tensile modulus—of the ultra-oriented PEs may be described in analogy to short-fiber composites; herein, large chain-extended crystals formed during orientation act as inter-crystalline bridges across the amorphous regions of lamella clusters.^{133,134} Consequently, the volume fraction and continuity of the chain-axis-oriented crystalline-phase largely governs the observed modulus at ambient conditions.

5.1 Structural Transitions During Orientation

After an initial elastic deformation of the amorphous component, orientation processes take place through a complex plastic deformation process. Stresses during tensile drawing are often inhomogeneously distributed throughout highly anisotropic semi-crystalline regions. Under many drawing conditions this results in cavitation occurring in the amorphous region and a process called "micro-necking", which results in transformation of chain-folded crystals into a network of microfibrils.⁹⁴ This process is particularly apparent in the orientation of meltprocessed HDPE at room temperature where cavitation abruptly results in a significant opacity under large strain. The destruction of the amorphous component during cavitation and creation of voids is generally not desirable for ultraorientation given its implication on stress concentration. Cavitation can largely be avoided by deforming PE at elevated temperature or employing largely compressive stress. At temperatures above PE's alpha-I relaxation,⁹² the mobility of the crystalline component allows plastic deformation to occur through crystallographic slip processes.⁸⁹ Under compressive stress, the increased pressure provides additional constraints preventing void formation.⁹⁰ In general, slip processes occur along preferred planes that contain the molecular chain such that large strain can be accommodated by the unbroken PE chain.

For spherulitic and complex semi-crystalline morphologies, lamellar normals are statistically distributed in various orientations with respect to the crystal nucleus and orientation direction. As such, numerous slip processes may be active depending on the direction of stress with respect to the crystal axes. Classification of the equatorial, polar or meridional, and inclined regions of the spherulite is helpful in describing plastic deformation modes active in different regions.⁸⁸ Note that this terminology varies slightly depending on the direction of force with respect to the spherulite orientation. Typically, the equator of the spherulite is the area parallel to the sheaf-like central nucleus. Generally speaking, the orientation of the nucleus may be randomly distributed; for the following discussion, the equator is assumed to be perpendicular to the tensile direction. In this equatorial region definition, the tensile direction is nearly parallel with the lamella normals and the

crystalline chain-axis direction (which may not always be perfectly collinear⁶¹). Crystal plasticity in this region typically stems from the (100)[001] slip-system via a screw dislocation motion with low free-energy barrier.⁸⁹ Fine-slip processes occur through small displacement of chains in many adjacent parallel columns (Fig. 11a, top) and result in an alignment of the chains toward the tensile direction while effectively tilting the lamellar orientation. The tilted lamella can appear in a "herringbone" or "parquet-floor" type arrangement,¹³⁵ which may augment mechanical properties via an inter-locking mechanism.⁶¹ Coarse-slip processes, on the other hand, occur when a single plane experiences large slip and results in mosaic block fragmentation (Fig. 11a, bottom).^{87,88,136} It is expected that these mechanisms typically occur simultaneously during the transition from lamellar to fibrillar type crystals.



Fig. 11 Schematic illustration of crystallographic slip processes occurring during the lamellar-to-fibrillar transition. Modified from Adams et al. (1986).¹⁴³

In the polar region, where the direction of stress is near perpendicular to the lamella normals, deformation is thought to proceed via transverse-slip and inhomogeneous micro-necking processes.^{89,136,137} In addition to transverse slip, deformation occurs through crystal twinning, shearing processes, and a martensitic phase transition. These mechanisms accommodate lower strain as compared with slip processes along the chain-axis. Accordingly, the polar region exhibits far greater resistance to deformation and can see local stress concentration lead to cavitation. Some intermediate between polar and equatorial behavior is observed in the inclined region—the region with lamellar orientation between the two extremes. Notably,

the large variation in resistance to plastic strain for lamella in different environments underpins the importance of crystalline superstructure in the orientation process. For maximum drawability, a substantial fraction of uniform lamella oriented with their normal parallel to the tensile direction is advantageous. This type of morphology is most commonly induced by linear, fibril-type nucleation points; observed morphologies include vertically oriented sheaf-like and dendritic superstructures^{138–140} or row-nucleated type structures.^{141,142}

Evidence across TEM studies^{143,144} and X-ray methods^{124,125,145} show that extreme strains result in a lamellar-to-fibrillar transition mediated by chain-extension in the interlamellar region and plastic deformation of the crystalline region. Illustrated in Fig. 11b, a lamellar cluster becomes a microfibril via a combination of blockfragmentation (coarse slip), crystal tilt (fine-slip), chain-unfolding, and amorphous chain-extension.^{97,143,144} The fibrillar structure itself consists of fragments of the remaining lamella connected by chain-extended crystals and amorphous material with varying degrees of orientation along the tensile direction. This is in agreement with SAXS and WAXS observations of an initial reduction in long period and crystallinity immediately following yield.^{121,122,124} The degree of orientation is often quantified by the Herman's orientation function, f, of the orthorhombic peaks in WAXS measurements.^{11,146} This measurement quantifies the orientation of the crystal axes, and it is often seen that high levels of orientation occur fairly quickly after yield during drawing at elevated temperatures.^{124,147} A similar method can be applied to the amorphous halo in WAXS to determine orientation of the noncrystalline component. Amorphous orientation¹⁴⁸ shows significant temperature dependence given the ability of the chains to relax at higher temperatures.^{59,124} Orientation in SAXS measurements quantifies the alignment of hierarchical features such as lamella and shish. This is useful in quantifying the morphologies of both the as-extruded and oriented material. Spherulitic morphologies have lamella that are oriented isotropically (f = 0) while row-nucleated structures (f < 0)and lamellar stacked (f > 0) structures have some degree of orientation with respect to the machine direction. Upon ultra-orientation, the lamellar-to-fibrillar transition in SAXS measurement is accompanied by intense equatorial streaks corresponding to long shish-like chain-extended structures. The length of shish crystals can be determined from a Ruland analysis,¹¹¹ in which the width of the streaks are quantified as a function of scattering vector. Further deformation at extreme strains (i.e., those relevant in ultra-drawing) is often accommodated by refinement of this fibrillar crystalline structure. At increasing draw ratio, shish crystals increase in size and volume fraction by lamellar thickening processes and recrystallization of fragmented crystalline components.^{59,122,124,149} Notably, the gradual increase in crystallinity and crystal thickness with increasing extension sustains the monotonic

relation between modulus and draw ratio, which holds for PEs of varying MW and processing conditions.¹⁵⁰

Starting morphologies, which are significantly impacted by flow-induced crystallization from the melt or gel-state, may show a somewhat different structural progression. Most notably, gel-spun UHMWPE precursor fibers with rownucleated shish-kebab structure undergo a transition from a fibrillar-type structure to a more single-crystal like structure with very-high crystallinity and large crystals.^{127,131,132,151} These types of structures initially have some portion of large extended chain crystals resulting from chain-stretching during spinning.^{111,151} In some ways, these types of fibers may be viewed as having started further along in the structural progression; that is, shish-kebab type fibers are already pseudofibrillar structures, therefore the drawing process entails fibrillar refinement rather than a lamellar-to-fibrillar transition. Observations from orientation processes under different drawing conditions lead to a general picture of the structural development of the modulus. The structural model can viewed as a three-phase system: an interlamellar amorphous phase, a chain-folded crystalline phase, and an extended-chain phase with large crystallites or rigid oriented amorphous material.¹⁵² During later stages of drawing, the volume fraction of the extendedchain phase grows at the expense of the serially connected interlamellar amorphous phase and lamellar crystalline phase.^{127,152} The combined reduction of interlamellar amorphous material and increase in large crystal fraction results in substantial increase in both modulus¹²⁷ and thermal conductivity.¹⁵² Structural evidence for the phenomena is slightly nuanced but similar features were observed independently with WAXS and NMR¹²⁷ and polarized Raman spectroscopy.¹⁵²

5.2 Tensile Properties of Oriented PE in Relation to Structure

Notably, the phenomenological model describing the refinement of fibrillar structures at high draw ratio has commonality with the quantitative mechanical model originally used to describe the elastic modulus of highly oriented HDPE.^{133,134,153} Illustrated schematically in Fig. 12, the fibrillar morphology consists of a continuous crystalline phase and a two-phase matrix consisting of lamellar cluster units. This elastic model simplifies many of the structural nuances into volume fractions and moduli of three constituent phases. In this view, the origins of the extreme stiffness at high draw ratio may be similar across a range of morphology variations. In the generalized case, a fraction of crystalline extended-chains cross interlamellar boundaries and are thus load-bearing. This crystalline fraction (or possibly oriented, taut amorphous chains) acts as a rigid percolating network within a matrix of periodic lamella and interlamellar amorphous material. Analogous to Cox's model of discontinuous fiber reinforcement,¹⁵⁴ an efficiency

factor may be used to describe the fraction of the reinforcement phase that is effective at transmitting stress. The probability that the large crystallites in oriented PE—akin to the reinforcing filler material in fiber-matrix composites—act as intercrystalline bridges is directly related to both the crystallite size and the long period of the "matrix" material.¹⁵³ It has been shown that the oriented PE modulus scales directly with this so-called "crystal continuity."^{153,155}



Fig. 12 Structural and quantitative elastic model describing high modulus of oriented PE. Modified from Zhu et al. (2017).¹⁵²

The monotonic relation between draw-ratio and elastic modulus mediated by the crystalline structure progression is relatively well-established.^{22,147,150} Structural origins of the tensile strength of oriented PE fibers and films, however, can be more complicated. Debate remains whether the tensile strength of oriented PE is largely dictated by intrinsic factors (i.e., atomic and microstructural features) or extrinsic factors (i.e., defects and macroscale flaws).²² It is generally agreed that the absolute upper limit of theoretical tensile strength is around 25 to 30 GPa, as dictated by the carbon-carbon bond energy.^{156–158} The effects of finite chain-length, however, impose an upper end of tensile strength at lower values between 8 to 15 GPa for relevant molecular weights.^{159,160} In the limit of low MW or a low degree of chain overlap, chain-slippage effects are thought to dominate over chain rupture given the relatively weak intermolecular forces (i.e., van der Waals forces) between the

neighboring chains. Experimentally, the power-law relations observed between molecular weight and equivalent-modulus tensile-strength^{161–163}—that is, tensile strength observed at similar draw-ratio-largely fall in line with theoretical scaling predictions.^{159,164} However, PE fibers have rarely approached the upper-end of the theoretical limit. Studies aimed at determining the nature of early failure using statistical models in combination with fracture mechanics have yielded varying conclusions. Some empirical correlations between fiber diameter and tensile strength^{8,165–168} point to extrinsic failure mechanisms while others¹⁶⁹ suggest molecular factors prevail. Difficulties stem from the varying nature of fracture across different testing conditions and processing conditions.¹⁵⁰ The hierarchical structure development in particular can play an important role in the failure mechanisms.¹⁷⁰ Voids and cavities formed during fibrillation at high draw-ratio (during specific processing conditions) may reduce lateral adhesion while creating tri-axial stress.^{161,165} This can have dire consequences given the low shear and compressive strengths of the oriented fibers.¹⁷¹ Structural evidence for microscopic defects^{77,127} at high draw ratio has also been used to explain a decreasing or constant break-load for increasing tensile modulus. Given the evidence, it is fair to assume that in many cases an accumulation of defects can play a significant role in fracture though mechanistic theory and scaling relations may be far from universal.

5.3 Processing-Structure-Property Relationships in Industrial Processes

The processing-structure-property relationships in the orientation phase of highperformance PE production are summarized in Fig. 13. A large body of systematic studies across academic and patent literature relate process conditions to observed structures and mechanical properties.^{172,173} As discussed previously, the temperature-dependence of chain mobility and relaxation plays a significant role in obtaining maximum orientation. Temperatures above the alpha-I relaxation are required for sufficient plasticity,⁹³ and optimum temperatures between the alpha-I relaxation and melting temperature are a function of M_w.^{58,59} Optimal strain-rates are intimately related to temperature via time-temperature superposition, though it must be noted that strain-rate may be difficult to control during heterogeneous plastic deformation.¹⁷⁴ Nonetheless, rates sufficiently high to avoid significant relaxation and low enough to prevent heat accumulation under nearly adiabatic conditions⁹⁸ may be determined empirically.



Fig. 13 Processing-structure-function relationships in the polyethylene drawing/ orientation

The deformation mode also plays a significant role in the structural development. Important distinctions between tensile extension (e.g., drawing and stretching processes) and compression (solid-state extrusion, rolling, etc.) include the propensity for void formation.^{90,175} Void formation occurs more readily in tensile extension and may be detrimental during early stages of deformation. However, the fibrillation process may rely on void formation in later stages to accommodate larger strain. There are limits to each deformation mode and common industrial processes may incorporate different modes in various stages of processing. Additionally, the stress conditions during both tensile loading and compression loading may be either uniaxial or biaxial. Interestingly, it is thought that similar structural processes (i.e., lamellar-to-fibrillar transition) occur regardless of the geometry of the stress state, ^{176,177} though the ultimate mechanical properties may vary. Biaxial processes in particular show greater transverse strength at the expense of longitudinal strength.^{178–180}

Summarized in Table 2, processes for the production of ultra-high stiffness and strength PE have been well-outlined in academic literature. Distinction must be made between melt-based processes, which use lower M_w HDPE resins, and solvent-based processes, which can accommodate the extreme M_w of UHMWPE. It can be seen that the moduli and strengths (as measured by a dead-load creep test such as ASTM D882¹⁸¹) of optimized laboratory-scale HDPE-based processes fall between 60 to 75 GPa and 1 to 2 GPa, respectively. Limitations on ultimate draw ratio (typically between 30 and 50) and chain overlap in the crystalline region

prevent further improvement of mechanical properties. Gel-spinning processes pioneered at DSM¹⁸² come closer to production of oriented PE near theoretical limits. Moduli exceeding 150 GPa and strengths exceeding 4 GPa have been produced at commercial scale.¹⁸³ While the gel-spun fibers represented the state-of-the-art for many years in terms of tensile performance, alternative approaches using "nascently disentangled" UHMWPE reactor powder have comparable performance in a tape-based format.^{67,184} This strategy places an increased emphasis on synthesis parameters which yield highly crystalline structures with low entanglement density. Sintering the powder and stretching the consolidated tape under appropriate conditions below the melting temperature can accommodate total draw ratios of approximately 200.

A variety of additional fundamental studies, outlined in Table 2, have made significant contributions in the understanding of processes, structure, and mechanical properties of oriented PE materials. In general, various application spaces may benefit from improved ancillary properties at the sacrifice of ultimate tensile modulus and strength. Most notably, the cost of UHMWPE-based products may be prohibitive in some cases. Additionally, features such as transverse strength, optical transparency, and consolidation potential (e.g., film vs. fiber) may have significant impact on process design. Cost-reduction and optimization of these properties motivate on-going research and development efforts.^{22,64,76,185}

Process	Material	Contribution	Tensile modulus /	Citation / Note
			strength	
Solid-state	HDPE	MW-, T-dependence	60 GPa modulus at $40 \times$	57,58
drawing films			draw	
Solid-state	HDPE	T-dependence, MWD-	75 GPa modulus,	9,186
drawing fibers		dependence, take-up	1.7 GPa strength	
		rate		
Solid-state	HDPE	Optical transparency	30 GPa modulus, 800	77,116
drawing films			MPa strength, 90%	
			visible light	
			transmission	<i>ci</i> 400
Melt-drawing /	HDPE	Structure-property	Up to 90 GPa modulus	61,109
capillary		relation		
crystallization				147 107 100
Solid-state	HDPE	Pressure-, rate-, MW-	65 GPa modulus, 600	14/,18/,188
extrusion		dependence	MPa strength	190.190
Hot compaction	HDPE fibers	Process parameters,	35 GPa long.	160,169
		kinetics, T-, P-	Modulus, 4 GPa trans.	
I Inclus statis	LIDDE	dependence	modulus	145 190
Hydro-static	HDPE	Process parameters,	60 GPa modulus	110,190
drowing		M w-dependence,		
Uniavial /	норе	Process parameters	25 GPa long	178,179
biavial rolling	IIDI L	transverse properties	modulus 300 Mpa	
roll_drawing		transverse properties	long strength: 3.3 GPa	
ion drawing			trans	
			modulus	
Solid-state	UHMWPE /	Concentration-	45 GPa modulus.	50,56
drawing films	PE wax	dependence.	1.5 GPa strength	
0	blends	mechanical property	6	
		relations		
Gel-spinning	UHMWPE	Process parameters,	~150 GPa modulus,	DSM commercial
		concentration-	~6 GPa strength	process
		dependence, draw		trademarked under
		temperature		Dyneema ^{53,112,163,191}
Solid-state	UHMWPE	Process parameters,	~200 GPa modulus,	192,193
extrusion +		extrusion draw-ratio	~4 GPa strength	
tensile drawing		dependence		
Sintering +	Nascent	Polymerization	~160 GPa modulus,	Basis for Dupont's
solid-state	UHMWPE	kinetics, sintering	3.75 GPa strength	Tensylon, Teijin's
drawing reactor		process, drawing		Endumax ^{62,67}
powder		behavior	0 00 CD 1 1	51 52
Gel-spinning	UHMWPE	New solvents for	~200 GPa modulus,	51,52
		greater draw-ratio	~4 GPa strength	

 Table 2
 Processes for production of oriented high-performance PE material

6. Conclusion

Over years of development, high-performance oriented PE remains superlative in specific tensile strength and modulus; as such, the material is ubiquitous across enduse applications where high energy dissipation at low deformation is required. Most notably, multiply ballistic composites formed from consolidation of PE fibers and tapes into a binder matrix offer significant light-weighting and ultra-fast distribution of impact energy.¹⁹⁴ The latter is enabled by the high sonic velocity (directly related to tensile modulus). Despite representing the current state-of-theart, potential improvements in the cost-to-performance of composites could be realized via increased volume of reinforcement phase, increased lateral strength of the reinforcement, and decreased cost of the feedstock material. Additionally, production of high-performance PE in varying formats (e.g., tapes, films, and fibers) and with varying ancillary properties (optical properties, compressive strength, etc.) could lead to significant design flexibility in the manufacturing of structural and ballistic composites. These factors motivate the continued applied and fundamental studies on the PE orientation process.

This report attempts to summarize and organize the wide body of literature related to the production of ultra-high modulus PE. Processing-structure-property relationships across three stages of oriented PE production-synthesis, consolidation, and orientation-have been outlined. Due to the numerous process parameters and functional characteristics associated with the various production stages, it is important to understand the individual relationships at each phase of processing to identify specific contributions to observed end-use behavior. Indeed, many phenomena at various stages may be interrelated through the chain-mobility and kinetic phenomena dictated by synthetic properties of the polymer-like architecture and MWD. The regular packing afforded by highly linear chains and chain-mobility afforded by broad MWD (or use of solvent) is a general theme across all relevant processes. However, numerous intermediate structures resulting from various processing history can lead to disparate properties for a given resin. Most notably, chain entanglements and complex lamellar superstructures formed during melt processing and subsequent cooling impose limitations on extensibility during orientation processes. On the other hand, certain intermediate structures with highly regular fold-surfaces perpendicular to the direction of force are specifically suited for ultra-deformation via activation of plastic processes accommodating large strain. At extreme draw ratios, a high volume-fraction of large, extendedchain crystallites form bridges across remaining lamellar clusters. Ultimately, these percolated structures form the basis for the observations of ultra-high modulus and strength. While short of theoretical limits, PE with high M_w and high degree of chain overlap can reach tensile strengths exceeding 4 GPa. It is expected that these extreme properties will motivate continued efforts in development of precursor materials and novel composite structures.

7. References

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List of Symbols, Abbreviations, and Acronyms

ARL	Army Research Laboratory
DEVCOM	US Army Combat Capabilities Development Command
PE	polyethylene
HDPE	high-density polyethylene
LCB	long-chain branching
LCP	liquid-crystalline polymers
LLDPE	lower-crystallinity, linear low-density polyethylene
MLFACE	multi-layer forced assembly coextrusion
MW	molecular weight
MWD	molecular weight distribution
SAXS	small-angle X-ray scattering
SCB	short-chain branches
UHMWPE	ultra-high molecular weight polyethylene
VLDPE	very low-density PE

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