Extensional Rheology: An Invaluable Tool for Material Characterization

Martin L. Sentmanat, Ph.D.
Xpansion Instruments, LLC
Rheology as an Analytical Tool

**rhe·ol·o·gy** /rēˈələjē/

*noun*:  
The branch of physics that deals with the deformation and flow of matter.

- The goal of any rheologist is to relate the rheological properties of a material measured in the laboratory to its molecular structure/architecture
  - Gain a fundamental insight into material deformation behavior
  - Develop constitutive models that embody these fundamental structure/property relationships
  - Predict how newly developed materials will behave to applied deformations during processing and end-product use
Rheological Characterization of Materials

- Most material deformations are generated with simple shear flows because they are the easiest to generate in the laboratory.
- As a consequence, shear rotational rheometers dominate the rheological characterization market.
- Although shear rheology has been very useful in establishing fundamental material structure-property relationships, shearing flows generated by rotational rheometers are typically limited to flows in the linear viscoelastic (LVE) regime [small strain, low-rate material deformations] and are unable to distinguish certain polymer macrostructural features.
- From an applications standpoint the types of flows witnessed in most polymer processing operations are both rapid and large - nonlinear viscoelastic (NVE) by nature.
Extensional Rheology

- Extensional flow refers to a type of flow deformation that involves the elongation, or stretching, of material and is the type of flow that dominates many polymer processing operations.

- Crystallization kinetics and final morphology are deeply affected by molecular orientation and stretch induced by flow during polymer processing.

- Extensional flow measurements are very useful in polymer characterization because they generate high molecular stretch and orientation flow fields that are very sensitive to the molecular structure (branching) of a polymeric system and are ideal for characterizing the flow induced crystallization (FIC) behavior of melts.
SER Technology

- The SER Universal Testing Platform is a miniature detachable fixture that can convert a conventional CSR or CRR rotational rheometer system into a single universal test station.

- SER Technology translates the precision rotational motion and torque sensing capabilities of a commercial rotational rheometer into precision linear motions and loads.

- By utilizing counter rotating windup drums, linear deformations can be precisely controlled in a fixed plane of orientation which can be viewed at all times during the material deformation process.

SER2 model line
How It Works

- The rotational motion of the rheometer spindle drives the counter rotation of the dual windup drums.
- Hence, a sample attached to the drum surfaces experiences a controlled linear deformation all within the confines of the oven enclosure.
True Strain Rate Validation

Frame Sequencing Videography

- Indicates Theoretical Width Dimension

Theoretical width dimension expression:

\[ W/W_0 = [\exp (-\varepsilon_H)]^{1/2} \]

- Note the excellent agreement between the actual and theoretical width dimension evolution

Detachable Drum Options
Fluid Immersion Capabilities

Because both of the detachable drums are cantilevered and suspended from the SER2 base chassis, the SER2 models that are configured for use on controlled stress/strain rotational rheometers are capable of fluid immersion testing… *Perfect for testing molten polymers susceptible to sag effects over long periods of time.*
Sample sizes less than 150mg can be used to characterize LVE & NVE properties at steady Hencky strain rates up to 30s$^{-1}$

Provides analytical insight with regard to
- molecular architecture, size, and structure
- processing behavior

Applications: polymer melts, uncured elastomers, TPE melts, highly viscous/semi-solid foodstuffs
FIC Studies in Uniaxial Extension

■ Part 1: Butyl
  - Tensile Stress Growth and Cessation of Uniaxial Extension Experiments
  - Bubble Instability in Unaxial Extension
  - Flow Birefringence

■ Part 2: Linear Polyethylene
  - Tensile Stress Growth and Cessation of Uniaxial Extension Experiments at Temperatures Near the Melt State
  - Flow Birefringence
Part 1: Butyl Elastomer

- Butyl elastomer (IIR) is the copolymer of isobutylene and a small amount of isoprene, typically in the order of 2%.

  Structure of Butyl Rubber

  \[
  \begin{align*}
  &\text{CH}_3 \\
  &\text{CH}_2-\text{C} \quad \text{CH}_3 \\
  &\text{CH}_3 \quad \text{C}\text{H}_3 \\
  &\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2
  \end{align*}
  \]

  (0.8 - 2.5 mole%)

- Due to its gas impermeability and resistance to heat and oxidation, butyl elastomers find application in tire innerliners, innertubes, curing bladders and envelopes, and other specialty applications where air retention and resistance to heat and oxidation are desired.

- Because of its gas impermeability, air voids are a common processing issue associated with butyl elastomers.
Part 1: Tensile Stress Growth – Butyl

**Diagram:**
- **Butyl 268**
- **η_E [Pa-s]**
- **t [s]**
- **Temperature Conditions:**
  - T = 23°C
  - T = 30°C
  - T = 50°C
- **Shear Rate Conditions:**
  - \( \dot{\varepsilon}_H = 30 \, \text{s}^{-1} \)

Graph showing the relationship between shear rate and time for different temperatures.
Part 1: Tensile Stress Growth

Note how the extensional behavior of Butyl at the higher temperature resembles the extensional behavior of a typical PIB, while at lower temperatures it resembles the behavior of a typical cis-PI.
Because the deformation remains in a fixed plane and in a well-defined stretch zone, rheo-optical measurements can easily be performed with the SER.
Part 1: Flow Birefringence - Butyl in Stress Growth

As the polarized ambient light passes through the sample, the refractive index of the stretching specimen changes as a function of molecular orientation and the onset of FIC.

Uniaxial Extension

Hencky strain rate = 1.0 s\(^{-1}\)
As the polarized white light source passes through the sample, the refractive index of the stretching specimen changes as a function of molecular orientation and the onset of FIC.
Part 1: Flow Birefringence - Cessation of Extension

Hencky strain rate = 1.0 s\(^{-1}\)
Flow Stopped @ \(t_0\)

Note that the degree of relative relaxation increases with increasing deformation history due to relaxation subsequent to FIC.
Part 1: Flow Birefringence - Cessation of Extension

*Hencky strain rate = 1.0 s\(^{-1}\)*

\(\varepsilon_H = 2.0\)
\(\varepsilon_H = 2.5\)
\(\varepsilon_H = 3.0\)

- Note the evolution of the color fringes during stress relaxation.
Part 1: Effect of Strain on Bubble Stability

- Samples were prepared with an air bubble void contained within the center of the sample.
Part 1: RheoOptics - Effect of Voids

Hencky strain rate = 1.0 s⁻¹

- Note how the larger deformation exceeds the critical strain for the onset of bubble instability which subsequently leads to cleaving of the sample
Part 2: Materials

- Because of the higher degree of crystallization that can be achieved in the solid state, linear polymers are particularly sensitive to extensional flows very near the melt temperature.

- Commercial Linear Polyethylenes:
  - Exact 3128: Film Grade m-LLDPE (ExxonMobil), MFI = 1.2
  - 58G: Blow Molding Grade HDPE (Nova Chemicals), MFI = 0.95
Part 2: FIC & Tensile Stress Behavior – m-LLDPE

Virgin Exact 3128
Onset: 87°C
Peak: 92°C

LLDPE Exact 3128

\( \dot{\varepsilon}_H = 1 \text{ s}^{-1} \)
Part 2: FIC & Tensile Stress Behavior – m-LLDPE

![Graph showing shear viscosity versus time for Exact 3128 at different temperatures and strain rates.](image)
Part 2: Strain Hardening Behavior – m-LLDPE

Graph showing the strain hardening behavior of m-LLDPE with an ultimate strain of 30 s⁻¹ and a temperature of 102°C.
Part 2: Strain Hardening Behavior – m-LLDPE

Graph showing the relationship between strain hardening behavior and temperature for Exact 3128 material. The graph indicates that the strain hardening behavior is tested at different strain rates ($\dot{\varepsilon}_H = 0.01 - 30 \, \text{s}^{-1}$) and a constant temperature of $T = 93^\circ \text{C}$. The y-axis represents the strain hardening ratio ($\sigma/\sigma_{LVE}$) on a logarithmic scale, and the x-axis represents the strain hardening parameter ($\varepsilon_H$) also on a logarithmic scale.
Part 2: Strain Hardening Behavior – m-LLDPE

Exact 3128

$\mathbf{\dot{\varepsilon}_H = 0.01 - 30 \text{ s}^{-1}}$

$T = 91^\circ\text{C}$
Part 2: Stress vs. Strain - 91°C @ 1 s⁻¹

T = 91°C

LLDPE Exact 3128

F/A₀ [Pa]

εₜ = 1 s⁻¹

t₀ = 1.0s

t₀ = 1.5s

t₀ = 2.0s

t₀ = 2.5s

t₀ = 3.0s

t₀ = 3.3s

Xpansion Instruments
Xpand Your Capabilities
Part 2: Cessation of Extension - 91°C @ 1s⁻¹

T = 91°C

\[ \varepsilon_H = 1 \text{ s}^{-1} \]

\[ t_0 = 3.3 \text{s}, \quad t_0 = 3.0 \text{s}, \quad t_0 = 2.5 \text{s}, \quad t_0 = 2.0 \text{s}, \quad t_0 = 1.5 \text{s}, \quad t_0 = 1.0 \text{s} \]

LLDPE Exact 3128

\[ 1.0 \times 10^{07}, \quad 1.0 \times 10^{06}, \quad 1.0 \times 10^{05}, \quad 1.0 \times 10^{04} \]

\[ 0.1, \quad 1, \quad 10, \quad 100, \quad 1000 \]
Part 2: Cessation of Extension - 91°C @ 1s⁻¹

\[ T = 91°C \]

\( \dot{\varepsilon}_H = 1 \text{ s}^{-1} \)

Cessation @ \( t_0 \)

\[ \sigma / \sigma_0 @ t_0 \]

\[ 1.0E+00 \]

\[ 1.0E-01 \]

\[ 0.01 \]

\[ 0.1 \]

\[ 1 \]

\[ 10 \]

\[ 100 \]

\[ 1000 \]

\( t_0 = 3.5 \text{ s} \)

\( t_0 = 3.0 \text{ s} \)

\( t_0 = 2.5 \text{ s} \)

\( t_0 = 2.0 \text{ s} \)

\( t_0 = 1.5 \text{ s} \)

\( t_0 = 1.0 \text{ s} \)
Because the deformation remains in a fixed plane and in a well-defined stretch zone, flow birefringence measurements can easily be performed with the SER.
Part 2: Tensile Stress Growth - HDPE

Virgin Nova 58G - HDPE
Onset: 125.2°C
Peak: 129.8°C

Nova 58G - HDPE

Heat Flow

T (°C)

100 110 120 130 140 150 160

η_E^+ [Pa-s]

1.0E+08
1.0E+07
1.0E+06
1.0E+05
1.0E+04

T = 150.0°C

\dot{e}_h = 10 \text{ s}^{-1}

t [s]

0.01 0.1 1 10 100 1000
**Part 2: Tensile Stress Growth - HDPE**

Virgin Nova 58G - HDPE

Onset: 125.2°C
Peak: 129.8°C

Nova 58G - HDPE

\[ T = 129.0°C \]
\[ T = 150.0°C \]

\[ \dot{\varepsilon}_H = 10 \text{ s}^{-1} \]
Part 2: Tensile Stress Growth - HDPE

Virgin Nova 58G - HDPE
Onset: 125.2°C
Peak: 129.8°C

Nova 58G - HDPE

\[ \eta_E = 10 \text{ s}^{-1} \]
Part 2: Tensile Stress Growth - HDPE

Virgin Nova 58G - HDPE
Onset: 125.2°C
Peak: 129.8°C

Nova 58G - HDPE

$t_e = 10 \text{ s}^{-1}$
Part 2: Tensile Stress Growth - HDPE

HDPE Melt / FIC Birefringence Comparison

- Clear
  - $T = 129.0^\circ C$
  - $\dot{\varepsilon} = 0.3 \, s^{-1}$
  - $\varepsilon = 0.3$

- Hazy
  - $T = 128.5^\circ C$
  - $\dot{\varepsilon} = 0.3 \, s^{-1}$
  - $\varepsilon = 0.3$

- Cloudy
  - $T = 128.0^\circ C$
  - $\dot{\varepsilon} = 0.3 \, s^{-1}$
  - $\varepsilon = 0.3$
Part 2: Tensile Stress - HDPE

Nova 58G - HDPE

\( \varepsilon_H = 0.03 \, \text{s}^{-1} \)

\( T = 128.0^\circ\text{C} \)
\( T = 128.5^\circ\text{C} \)
\( T = 129.0^\circ\text{C} \)
Melt fracture is a problem common in the polymer processing industry in which beyond a certain melt throughput extrudate distortion appears

*Sharkskin (SS)*: small periodic distortions appearing on the surface upon exiting the die
(unique to linear polymers - *LLDPE, HDPE*)

*Gross melt fracture (GMF)*: severe irregular distortions in extrudate appearance
(common with many polymers)
Case Study 3: Processing Aids

- Although processing aids such as fluoropolymer additives can eliminate sharkskin by coating the die walls and promoting slip, they have no effect on the occurrence of gross melt fracture.
Case Study 3: Boron Nitride (BN)

Recently certain Boron Nitride (BN) powder additives have been found to be effective in eliminating sharkskin and significantly delaying the onset of GMF, although the mechanism by which this occurs remains uncertain.

(h-BN: soft, graphite-like ceramic platelet particles)
Case Study 3: Objective

Elucidate the mechanism by which boron nitride powder additives affect the onset of gross melt fracture in commercial linear polyethylenes.

\[ \gamma_A = 617 \text{ s}^{-1} \]

泯-LLDPE (Pure)

泯-LLDPE + 0.1% BN
Case Study 3: Experimental

- BN Powders from Saint-Gobain Advanced Ceramics
  (5-20 µm particle size) compounded at 0.1wt. %
  - CarboTherm™ CTF5 (SE: 47.1 [11] mJ/m²)
  - CarboTherm™ CTUF (SE: 63.4 [27] mJ/m²)

- Polymers
  - ExxonMobil Exact 3128 (film grade m-LLDPE, MFI = 1.2)
  - ExxonMobil Exceed 143 (film grade m-LLDPE, MFI = 1)
  - BP Chemicals PF-Y821-BP (film grade ZN LLDPE, MFI = 0.8)
Case Study 3: Exact 3128 Processing Behavior

Despite displaying almost identical flow curves, the presence and type of BN appears to play a large role in melt fracture behavior.
Case Study 3: SAOS Exact 3128

LVE results from SAOS are incapable of revealing any unique information about the effect of BN on polymer behavior.
As the rate of extension increases, the sample rupture transitions from a ductile to a brittle-type mode of failure, coinciding with rubbery behavior at short times.

Only at high extensional flow rates are differences in the polymers clearly evident.
Case Study 3: Exact 3128 High-Rate Extensional Flow

- Note that the BN-filled polymers exhibit subdued stress growth and peak stresses at high extensional rates.
- These results suggest that the presence of BN serves as an energy dissipater/plasticizer that inhibits the elastic/rubber-like behavior of the m-LLDPE polymer at large deformations and rates.
Case Study 3: Exceed 143 High-Rate Extensional Flow

The presence of BN appears to have a similar energy dissipation effect on Exceed 143 (m-LLDPE)
The presence of BN also has a similar energy dissipation effect on PF-Y821-BP (ZN-type LLDPE)
Case Study 3: Mechanism of GMF Suppression by BN

- The large platelet structure of the BN particles allow for a significant number of polymer adsorption sites on the BN surface.
- At high rates and deformations in the die entry region, the energy normally borne by the polymer chain backbone is dissipated via the reconfiguration/release of polymer chains on the BN surface.
Case Study 3: Mechanism of SS Suppression by BN

- Upon exiting the die the polymer chains nearest the skin of the extrudate undergo very large and rapid stretching deformations.
- The presence of BN serves as a “plasticizer” for these polymer chains by dissipating the storage of elastic energy via the reconfiguration/release of polymer chains on the BN surface.
Case Study 4: Detecting Differences in Polymer Macrostructure - PE

Four Commercial Polyethylenes:

- LD200: Coating Grade LDPE (ExxonMobil), MI = 7.5
- LL3001.32: Film Grade LLDPE (ExxonMobil), MI = 1.0

**Part 1**

- EF606: Film Grade LDPE (Westlake Polymers), MI = 2.2
- Exact 3128: Film Grade m-LLDPE (ExxonMobil), MFI = 1.2

**Part 2**

Exercise:

Detect differences in polymer macrostructure between these four commercial polymers without having any specific macrostructural information about them a priori.
Despite some notable indications of MW very little can be clearly distinguished between polymer branching and MWD effects from the SAOS data alone.
Again, despite some notable indications of MW very little can be clearly distinguished between polymer branching and MWD effects from the stress relaxation data alone.
Case Study 4: Part 1 - LVE Extensional Relaxation Data

- Despite excellent agreement between the LVE extension and shear data, again very little can be clearly distinguished between polymer branching and MWD effects from the LVE data alone.
Note how the tensile stress growth data can clearly distinguish macrostructural features related to branching and MWD - the LDPE exhibits significant strain hardening, behavior consistent with highly branched polymers.
Again, despite some indications of MW & MWD very little with regard to macrostructural features such as polymer branching can be concluded from the LVE data alone.
Case Study 4: Part 2 - Tensile Stress Growth

Note how the tensile stress growth data can clearly differentiate subtle differences in branching as witnessed by the different strain hardening behaviors detected between the two grades of LDPE as well as differences in high-rate melt elasticity with the two LLDPEs.
Case Study 5: Elucidating Melt Flow Behavior of Linear & Branched PE

- It is a well known fact that linear polyethylenes exhibits far different processing/extrusion behavior than highly branched polyethylenes.

- Despite being investigated extensively for decades some of the fundamental mechanisms for these processing behaviors remain unclear.
Case Study 5: Typical LDPE Melt Processing Behavior

Features of Capillary Extrusion Behavior...

- **Flow curve**: monotonic increase in shear stress with shear - no discontinuity
- **Extrudate appearance**: beyond a critical point gross melt fracture (GMF) observed
Case Study 5: Typical LLDPE Melt Processing Behavior

LLDPE LL3001.32 @ 150°C

Features of Capillary Extrusion Behavior...

- **Flow curve**: at a certain point, notable discontinuity is observed in which the flow becomes unstable over a certain range of flow rates

- **Extrudate appearance**: extrudate gradually transitions from smooth, to sharkskin, to stick-slip, and eventually gross melt fracture
Although many efforts have been successful in manipulating processing behavior (viz a viz processing aids) many age-old questions remain unanswered:

- Why does stick-slip flow occur only with linear PE?
- Why does sharkskin not occur with branched PE?
Case Study 5: Experimental

- Four Commercial Polyethylenes:
  - LD200: Coating Grade LDPE (ExxonMobil), MI = 7.5
  - LL3001.32: Film Grade LLDPE (ExxonMobil), MI = 1.0
  - EF606: Film Grade LDPE (Westlake Polymers), MI = 2.2
  - Exact 3128: Film Grade m-LLDPE (ExxonMobil), MFI = 1.2

- Rheological Characterization
  - Characterize the processing behavior with capillary extrusion
  - Characterize the extensional flow behavior with the SER
  - Characterize the dynamic melt adhesion behavior with novel T-peel melt measurements with the SER
Case Study 5: Capillary Extrusion Results

All four polymers exhibit uniquely different extrusion behavior.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Sharkskin</th>
<th>Stick-slip</th>
<th>Gross MF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact 3128</td>
<td>20</td>
<td>120</td>
<td>420</td>
</tr>
<tr>
<td>LL3001.32</td>
<td>70</td>
<td>240</td>
<td>1400</td>
</tr>
<tr>
<td>LD200</td>
<td>-</td>
<td>-</td>
<td>270</td>
</tr>
<tr>
<td>EF606</td>
<td>-</td>
<td>-</td>
<td>50</td>
</tr>
</tbody>
</table>

Critical Shear Rates for onset of...
Case Study 5: Tensile Stress Growth Results

- Both LDPEs exhibit significant deviation from LVE behavior at large strains
- Despite having a much lower LVE melt viscosity the coating grade LDPE exhibits peak stresses almost equal to the film grade LDPE

- Both LLDPEs exhibit little deviation from LVE behavior at low rates
- Both polymers exhibit increasingly elastic/rubbery behavior at very high rates and strains, with the Exact 3128 melt displaying significantly higher stress growth
Case Study 5: Dynamic Melt Adhesion Experiments

- PE peel specimens were prepared by molding polymer samples between sheets of plane white paper
- Specimens were cut-to-width (0.25”) using a dual blade cutter
- The peel specimens were loaded onto the SER by securing the ends of the strips of paper to the windup drums, resulting in a T-peel configuration
- Peel rates: 0.01 to 200 cm/s @ 150°C
The peel strength curve of the film grade LDPE (EF606) has very distinct regions of peel behavior as indicated.

Despite adhesive failure, peel strength always increases with rate.
Case Study 5: Peel/Melt Adhesion Data

- The coating grade LDPE (LD200) also has a distinct “break” in the peel strength curve but exhibits superior peel strength to EF606
- LD200 does not exhibit adhesive failure
Case Study 5: Peel/Melt Adhesion Data

- The LLDPE (LL3001.32) exhibits an unstable region of peel behavior that appears qualitatively similar to stick/slip flow behavior.
- Upon adhesive failure, peel strength drops dramatically.
Case Study 5: Peel/Melt Adhesion Data

- Exact 3128 exhibits a larger region of peel instability that is very similar to its broad stick/slip flow region in extrusion.
- Upon adhesive failure, peel strength decreases even more dramatically.
At a peel rate of 0.333 cm/s, the peel strength trace for Exact 3128 is stable and the peel failure is purely cohesive.
Case Study 5: Exact 3128 Peel Traces

- At a peel rate of 0.7 cm/s, the peel strength trace for Exact 3128 becomes unstable accompanied by an instability in the mode of failure.
The peaks in the peel strength trace correspond to cohesive modes of failure and are abruptly followed by troughs corresponding to adhesive modes of failure.
Case Study 5: Exact 3128 Peel Traces

- At a peel rate of 1 cm/s, the peel strength trace and mode of failure remains unstable.
Case Study 5: Exact 3128 Peel Traces

- At a peel rate of 3.333 cm/s, the peel strength trace exhibits a brief peak followed by a significant drop in signal that remains steady - the mode of failure is purely adhesive.
Case Study 5: Exact 3128 Peel Traces

At a peel rate of 10 cm/s, the initial peel strength peak is greatly reduced and followed by a stable signal identical to the steady signal at 3.333 cm/s - the mode of failure is again purely adhesive.
These melt peel results with the SER appear quite promising as a fingerprint/laboratory predictor of melt processing behavior and may provide fundamental insight into the role of adhesion/slip in melt flow instabilities.
Case Study 5: Dynamic Work of Adhesion...

- By characterizing the dynamic peel behavior of polymer melts against a variety of thin film substrates (metal foils, teflon films, etc.), one may gain insight into dynamic work of adhesion at rates relevant to processing.
Case Study 5: High-Rate Tensile and Melt Fracture Behavior

High-rate tensile melt flow results appear to provide fundamental insight into the role of extensional flow behavior in processability and melt fracture phenomena.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Sharkskin</th>
<th>Stick-slip</th>
<th>Gross MF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact 3128</td>
<td>20</td>
<td>120</td>
<td>420</td>
</tr>
<tr>
<td>LL3001.32</td>
<td>70</td>
<td>240</td>
<td>1400</td>
</tr>
<tr>
<td>LD200</td>
<td>-</td>
<td>-</td>
<td>270</td>
</tr>
<tr>
<td>EF606</td>
<td>-</td>
<td>-</td>
<td>50</td>
</tr>
</tbody>
</table>
Case Study 5: Sharkskin Melt Fracture

- Exit phenomenon - stress governed flow

Localized region of high-rate stretch
Case Study 5: Sharkskin Melt Fracture

- Exit phenomenon - stress governed flow

Exact 3128 exhibits a much more rapid stress rise at high extensional deformations that can only be dissipated in the form of melt rupture propagated at the extrudate surface.

Critical Shear Rates for onset of...

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Sharkskin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact 3128</td>
<td>20</td>
</tr>
<tr>
<td>LL3001.32</td>
<td>70</td>
</tr>
</tbody>
</table>
Case Study 5: Sharkskin Melt Fracture

- Exit phenomenon - stress governed flow

The branched PE has an inherent stress retardation mechanism that enables stress to be rapidly dissipated upon exiting the die.

Critical Shear Rates for onset of Sharkskin Fracture:

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Sharkskin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact 3128</td>
<td>20</td>
</tr>
<tr>
<td>LL3001.32</td>
<td>70</td>
</tr>
<tr>
<td>LD200</td>
<td>-</td>
</tr>
<tr>
<td>EF606</td>
<td>-</td>
</tr>
</tbody>
</table>
Case Study 5: Gross Melt Fracture

- Entrance phenomenon - strain governed flow

GMF occurs beyond a critical stress condition achieved in the die entrance flow region

Critical Shear Rates for onset of...

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Sharkskin</th>
<th>Stick-slip</th>
<th>Gross MF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact 3128</td>
<td>20</td>
<td>120</td>
<td>420</td>
</tr>
<tr>
<td>LL3001.32</td>
<td>70</td>
<td>240</td>
<td>1400</td>
</tr>
<tr>
<td>LD200</td>
<td>-</td>
<td>-</td>
<td>270</td>
</tr>
<tr>
<td>EF606</td>
<td>-</td>
<td>-</td>
<td>50</td>
</tr>
</tbody>
</table>

Localized region of high stretch

Because the branched PE achieves higher stresses at elevated extensional strains, GMF is exhibited at an earlier onset in extrusion
Summary

- Because of the “strong” flow fields (providing high stretch and high orientation) generated, uniaxial extensional flows are very sensitive to flow induced crystallization effects in linear polymers and polymer macrostructure features in branched polymers.

- Extensional rheology is a powerful method of material characterization providing a fundamental understanding of polymer structure/property relationships and valuable insight into polymer processing behavior.