Avoiding Instabilities- Influence of Minor Changes in Branched Architecture on the Extensional Behavior of Rubber Compounds

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Introduction

Sharkskin is a type of melt fracture commonly seen in linear polymers; e.g. LLDPE\(^1\)

Several processing and material parameters dictate the occurrence of sharkskin

Use of shear and extensional rheology methods in detecting melt fracture

MARS III - rotational rheometer
SER Device – extensional testing

\(^2\)Sentmanat et al., J. Rheol., 49, 585, 2005
Background and Theory

- Extrusion Instabilities
  - Melt Fracture
  - Sharkskin
  - Slip-stick
  - Gross melt fracture
- Origins
  - High levels of stress at the die wall and exit
  - Slip mechanism a slip-stick phenomenon
  - Extensional flow at die exit
  - High velocity gradients in melt

Extrudates of linear low-density polyethylene from controlled-rate experiments: (a) stable; (b) sharkskin; (c) slip-stick, showing alternating smooth and sharkskin regions; (d) wavy, initial portion of the upper branch of the flow curve; (e) Gross melt fracture.

Relevance of extensional flow
The rheological behavior of polymer melts in extensional flows differs dramatically from that in shear due to the nature of the stresses and molecular interactions involved, *i.e.*, morphology development is much more sensitive to extensional flows than to shear flows, which has dramatic implications:

**Polymer processing**
- Many polymer processing sequences are extension dominated, *e.g.*, blow molding, thermoforming, film blowing, fiber-spinning.
- Many others have a strong extensional component, *e.g.*, flow in mold cavities and extrusion heads.

**Structural studies**
- Behavior in extensional flows is much more sensitive to molecular structure, *i.e.*, molecular weight, molecular weight distribution and degree of branching, than in shear flows.
Uniaxial extension: i) Most common type of deformation in processing flows. ii) Easiest to replicate in laboratory conditions.

Uniaxial extension- controlled rate experiments
- Most common type of deformation: less difficult to perform because one imposes the kinetics of the deformations and not the dynamics.
- Direct relevance to most polymer processing sequences, which are normally kinetically controlled, i.e., the throughput is imposed and is normally constant.

Uniaxial extension- controlled stress (tensile creep)
- Typically approach steady state conditions more rapidly than constant rate ones; important for theoretical modeling.
- Flow instabilities related with extension-dominated phenomena (e.g. “sharkskin”, melt fracture) are essentially stress dependent ⇒ important for establishing proper operating windows during processing sequences
- Insight into rupture mechanisms and liquid-solid transition
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• Insight into rupture mechanisms and liquid-solid transition
By investigating the velocity field in the flow of LLDPE (unstable) and LDPE (stable), major differences can be detected.

**Fig. 3.** Velocity profiles for a LLDPE with and without a fluoropolymer additive [26]: circles: LLDPE with fluoropolymer at $T=220 \, ^\circ C$, $D = 146 \, \text{s}^{-1}$, squares: LLDPE without fluoropolymer at $T=220 \, ^\circ C$, $D = 128 \, \text{s}^{-1}$. The data has been acquired inside the die, $x = -20 \, \text{mm}$.

**Fig. 7.** Iso-contours of axial velocity gradients ($\partial V_x/\partial x$) for LLDPE: (a) right below the onset of sharkskin instability (experiment 6, Table 2) and (b) above the onset of sharkskin (experiment 7, Table 2). The full horizontal lines indicate the position of the die walls.

LLDPE and LDPE have significantly different extensional properties which lend to a ‘model’ study.

LLDPE and effect of processing velocity

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Rubber Compounds

‘A’ 85% Primary component
   15% Secondary ‘linear’ branched component

‘B’ 85% Primary component
   15% Secondary ‘brush’ branched component

<table>
<thead>
<tr>
<th>Reading/Characterization Method</th>
<th>% Diff. (A to B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extruder head pressure</td>
<td>9.7%</td>
</tr>
<tr>
<td>RPA Viscosity @ 100 C</td>
<td>6.0%</td>
</tr>
<tr>
<td>MDR Min Torque @150 C</td>
<td>7.2%</td>
</tr>
<tr>
<td>Mw</td>
<td>4.64%</td>
</tr>
<tr>
<td>Polydispersity</td>
<td>23.15%</td>
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</table>
Shear and Extensional Rheology Results
Oscillatory Shear

- Conditions: 110°C, 100 Pa shear stress
- Largest differences observed at higher frequencies
- Max % difference: 13% in $G''$

### Complex Viscosity

- $\eta^*$ - Compound 'A'
- $\eta^*$ - Compound 'B'

### Relaxation Spectrum

<table>
<thead>
<tr>
<th>Compound</th>
<th>$G'$ (Pa)</th>
<th>$\lambda$ (s)</th>
<th>$G''$ (Pa)</th>
<th>$\lambda$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>'A'</td>
<td>3.09E+05</td>
<td>6.69E-03</td>
<td>1.86E+05</td>
<td>4.19E-02</td>
</tr>
<tr>
<td>'B'</td>
<td>9.97E+04</td>
<td>1.84E-01</td>
<td>9.99E+04</td>
<td>1.53E-01</td>
</tr>
<tr>
<td></td>
<td>5.90E+04</td>
<td>8.92E-01</td>
<td>5.65E+04</td>
<td>8.29E-01</td>
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<tr>
<td></td>
<td>4.06E+04</td>
<td>5.25E+00</td>
<td>3.93E+04</td>
<td>4.99E+00</td>
</tr>
<tr>
<td></td>
<td>5.96E+04</td>
<td>2.21E+02</td>
<td>5.85E+04</td>
<td>2.31E+02</td>
</tr>
</tbody>
</table>

$\eta = (\lambda^*G)(1-e^{-t/\lambda})$
Extensional Rheology Results – Steady Strain

\[ 3\eta = 3\sum [(\lambda_i*G_i)(1-e^{-t/\lambda_i})] \]

- Conditions: 110 C, Strain rates of .01, .1, 1.0 s\(^{-1}\)
- Very similar, repeatable results in extensional behavior with steady strain

Compare with \(\eta/3\eta\) plot
Extensional Rheology Results – Steady Strain

η/3η vs. time

Time (s)

Normalized η/3η

η/3η vs. time

'\text{A}' 0.01 s\textsuperscript{-1}

'\text{A}' 0.1 s\textsuperscript{-1}

'\text{A}' 1.0 s\textsuperscript{-1}

'B' 0.01 s\textsuperscript{-1}

'B' 0.1 s\textsuperscript{-1}

'B' 1.0 s\textsuperscript{-1}
Extensional Rheology Results – Stress Relaxation

Conditions: 110C, sample rupture ~120% applied strain,
  • Stress relaxation after instantaneous applied strain
  • Largest difference between A and B in lower strain rate

Trend: decrease in strain results in a faster relaxation kinetics of the polymer chains and a larger total stress relaxation

Compare the slopes of 50% strain
Extensional Rheology Results – Stress Relaxation

**Tensile Stress Relaxation - Extension**

50% Strain - 110 C

\[ y = 147015x^{0.301} \quad R^2 = 0.997 \]

\[ y = 140523x^{0.324} \quad R^2 = 0.9992 \]

**Extensional Rheology Results – Stress Relaxation**

\[ E(t) = E_o * e^{-t/T} \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Charact. Relax. Time (s)</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.32</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>3.09</td>
<td>7.4%</td>
</tr>
</tbody>
</table>

**Compound Charact. Relax.**

- Compound ‘A’
- Compound ‘B’

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*Case Western Reserve University*  
*Center for Layered Polymeric Systems*  
NSF Science & Technology Center

think beyond the possible
Conclusion

<table>
<thead>
<tr>
<th>Rheological Characterization Method</th>
<th>% Diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Storage Modulus G’ (Pa)</td>
<td>7.5%</td>
</tr>
<tr>
<td>Average Loss Modulus G” (Pa)</td>
<td>11.4%</td>
</tr>
<tr>
<td>Complex Viscosity (Pa*s)</td>
<td>6.6%</td>
</tr>
<tr>
<td>Peak Strain Hardening - Extension</td>
<td>&lt; 4%</td>
</tr>
<tr>
<td>Characteristic Stress Relaxation Time (s)</td>
<td>7.4%</td>
</tr>
</tbody>
</table>

- Several studies were used in detecting minor differences in branch architecture
- G’, G” showed differences of 7.5% and 11.4%, respectively
- Negligible differences were found in extensional viscosity and strain hardening
- Stress relaxation in Extension provided a difference of 7.4%
Future Work

• Creep and creep recovery under shear and extension
• Repeat the above procedures at elevated temperatures
• CSER device (shown at right) with controlled stress and controlled rate modes
  • CSER capable of higher Henky strains up to 8.0 (SER up to ~3.4)
• Velocimetry experiments on the branched rubber compounds

Thanks!