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

Patrick J. Harris, Eric Sullivan, Joao M. Maia

Case Western Reserve University
Cleveland, OH

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Presentation Outline

Section 1 – Introduction

Section 2 – Background and Theory
- Sharkskin and Melt Fracture
- Extensional Flow
- Material and Processing Effects
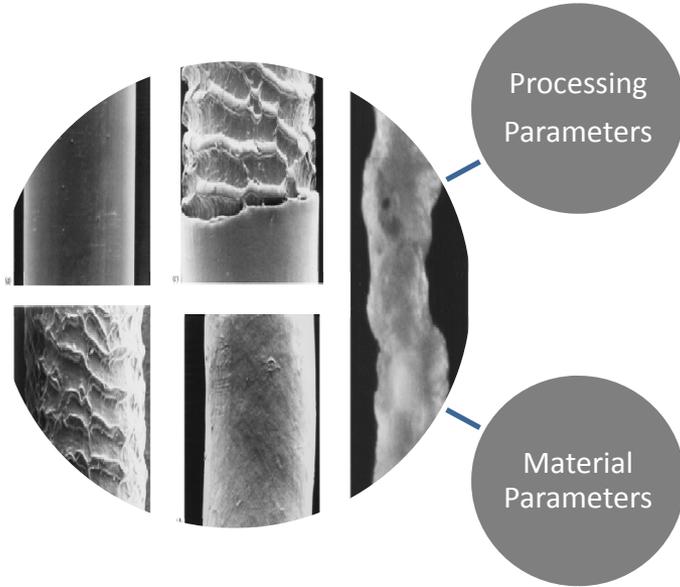
Section 3 – Project Description
- Research Problem
- Compounds Rheologically Investigated

Section 4 – Rheology
- Oscillatory Shear
- Extensional Rheology
- Stress Relaxation in Extension

Section 5 – Conclusions and Future Work

Introduction

Processing Parameters
- Extrusion temperature
- Screw speed
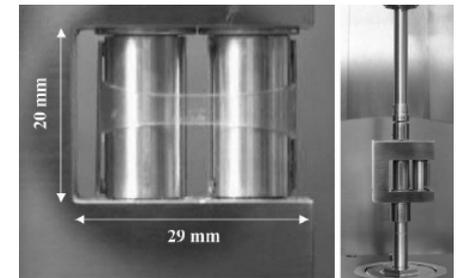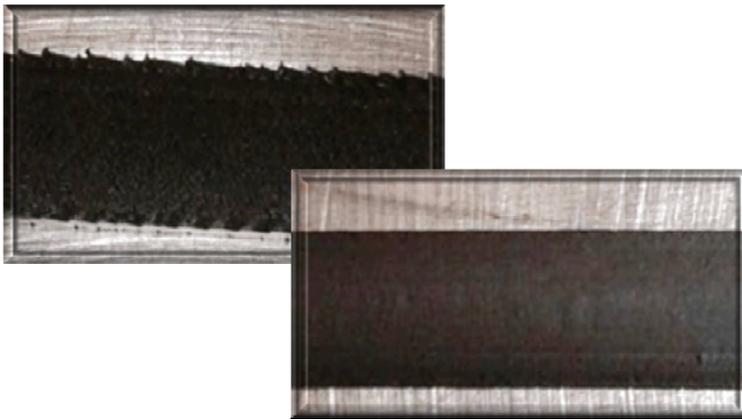- Wall slip/stick

Material Parameters
- Viscosity/Elasticity
  - Mw
  - Architecture
    - Linear/Branched polymer

Sharkskin is a type of melt fracture commonly seen in linear polymers; e.g. LLDPE[1]

Several processing and material parameters dictate the occurence of sharkskin

Use of shear and extensional rheology methods in detecting melt fracture

MARS III - rotational rheometer
SER Device – extensional testing

20 mm

29 mm

[1]Burghelea et al. J. Non. Newt. Fluid. Mech. 165, 1093-1104, 2010
[2]Sentmanat et al., *J. Rheol.*, 49, 585, 2005

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- **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

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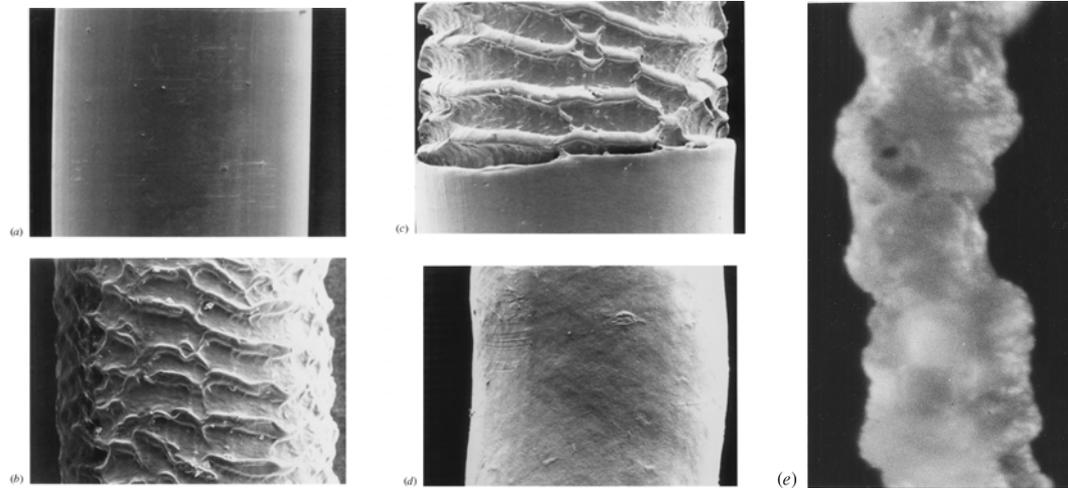
Extrudates of linear low-density polyethylene from controlled-rate experiments: (*a*) stable; (*b*) sharkskin; (*c*) slip-stick, showing alternating smooth and sharkskin regions; (*d*)wavy, initial portion of the upper branch of the flow curve; (*e*) Gross melt fracture.

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.

<u>Uniaxial extension:</u> i) Most common type of deformation in processing flows. ii) Easiest to replicate in laboratory conditions.

<u>Uniaxial extension- controlled rate experiments</u>

- 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.

<u>Uniaxial extension- controlled stress (tensile creep)</u>

- 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 $\Rightarrow$ important for establishing proper operating windows during processing sequences

- Insight into rupture mechanisms and liquid-solid transition

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Controlled stress (tensile creep)

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Background and Theory
Burghelea - Role of Velocity Gradient

By investigating the velocity field in the flow of LLDPE (unstable) and LDPE (stable), major differences can be detected.
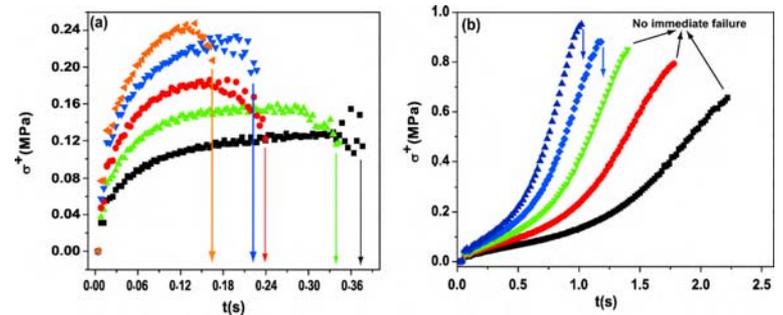
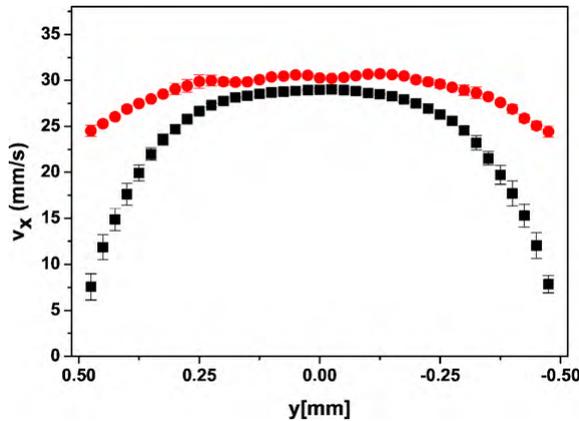LLDPE and LDPE have significantly different extensional properties which lend to a 'model' study

Fig. 3. Velocity profiles for a LLDPE with and without a fluoropolymer additive [26]: circles: LLDPE with fluoropolymer at T=220 ∘C, D = 146 s−1, squares: LLDPE without fluoropolymer at T=220 ∘C, D = 128 s−1. The data has been acquired inside the die,x = −20mm.

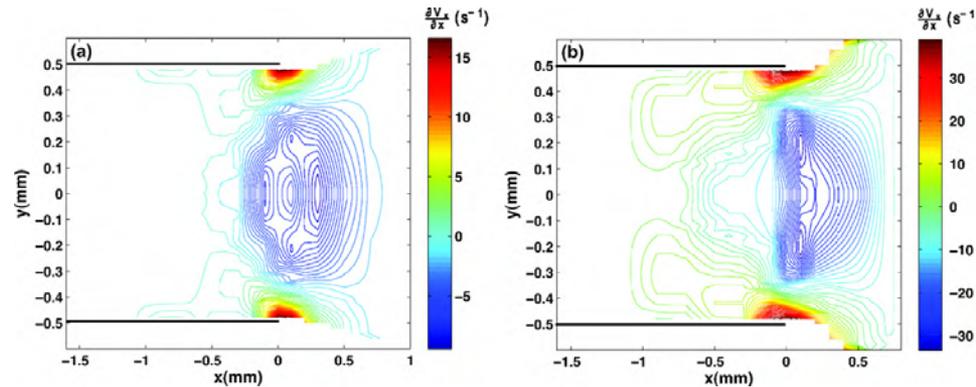**Fig. 7.** Iso-contours of axial velocity gradients (∂Vx/∂x) for LLDPE: (a) right below the onset of sharkskin instability (experiment 6, Table 2) and (b) above the onset of sharkskin (experiment 7, Table 2). The full horizontal lines indicate the position of the die walls.

LLDPE and effect of processing velocity

[1]**Burghelea et al. J. Non. Newt. Fluid. Mech. 165, 1093-1104, 2010**

Rubber Compounds

'A' 85% Primary component
15% Secondary 'linear' branched component

'B' 85% Primary component
15% Secondary 'brush' branched component

Reading/Characterization Method	% Diff. (A to B)
Extruder head pressure	9.7% ↓
RPA Viscosity @ 100 C	6.0% ↓
MDR Min Torque @150 C	7.2% ↓
Mw	4.64% ↓
Polydispersity	23.15% ↑

Shear and Extensional Rheology Results

Oscillatory Shear

Complex Viscosity

Chart: Complex Viscosity — η^* (Pa.s) vs Freq (rad/s), showing n* - Compound 'A' and n* - Compound 'B'. Annotation: 6.6% average difference η^*

G',G"

Chart: G', G" (Pa) vs Freq (rad/s), showing G' - Compound 'A', G" - Compound 'A', G' Compound 'B', G" - Compound 'B'. Annotations: 7.5% average difference G'; 11.4% average difference G"

- Conditions: 110 C, 100 Pa shear stress
- Largest differences observed at higher frequencies
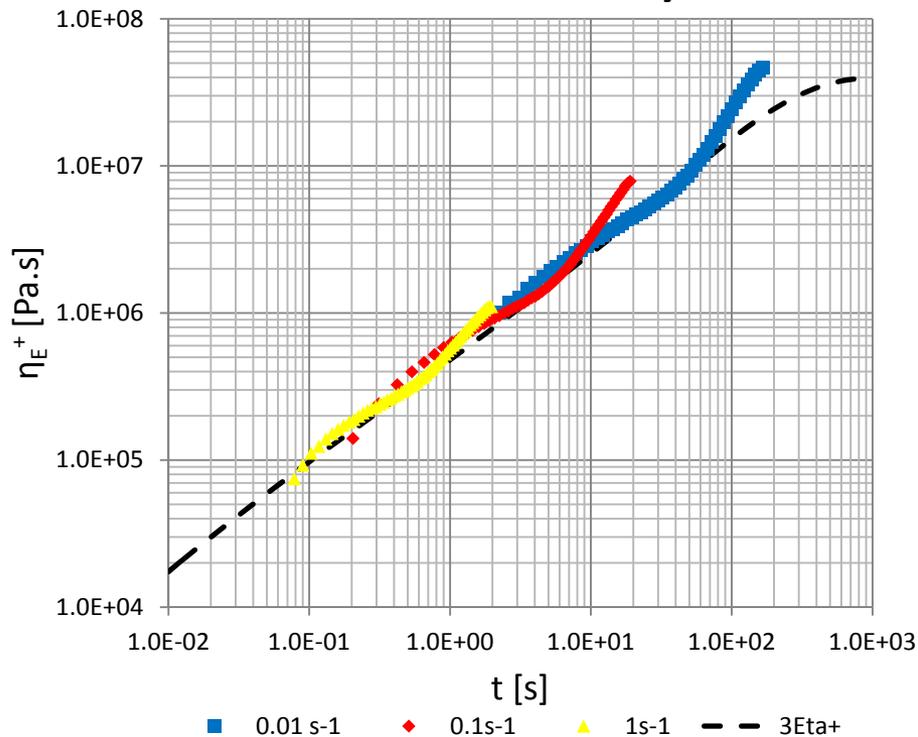- Max % difference: **13% in G"**
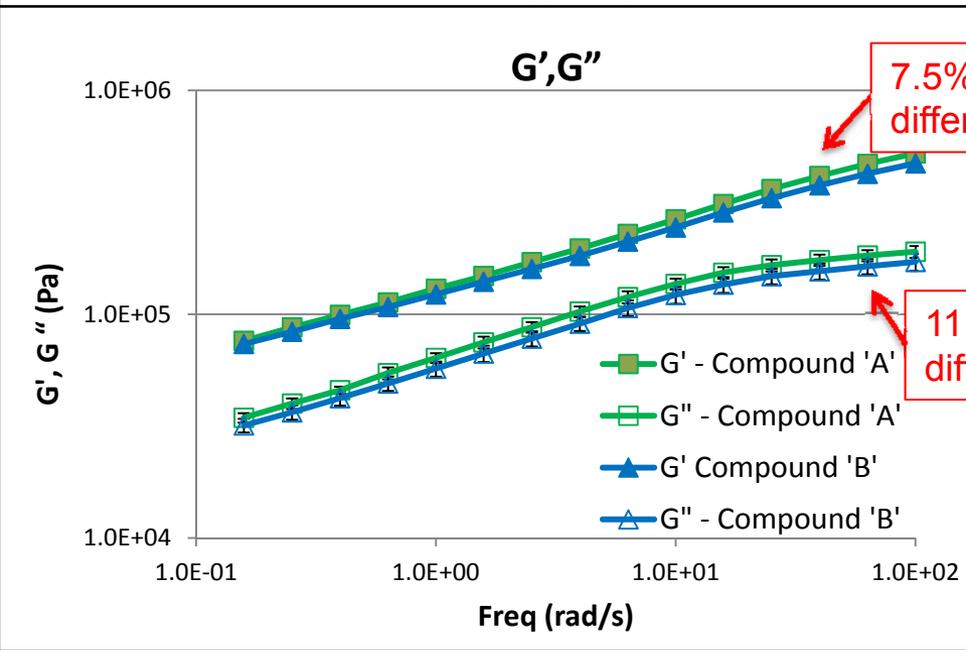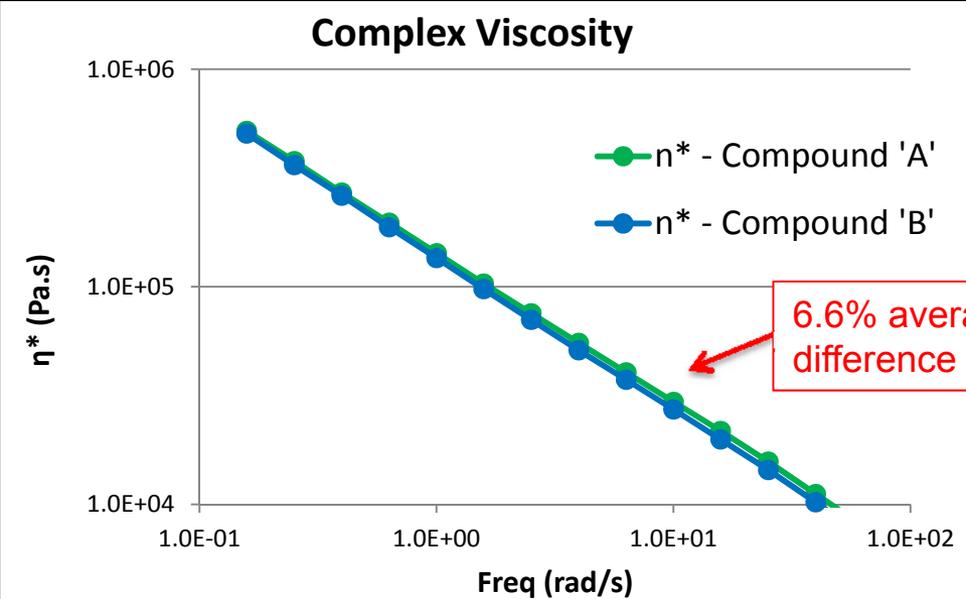
Relaxation Spectrum

A		B	
G (Pa)	λ (s)	G (Pa)	λ (s)
3.09E+05	6.69E-03	2.82E+05	5.91E-03
1.86E+05	4.19E-02	1.61E+05	3.65E-02
9.97E+04	1.84E-01	9.99E+04	1.53E-01
5.90E+04	8.92E-01	5.65E+04	8.29E-01
4.06E+04	5.25E+00	3.93E+04	4.99E+00
5.96E+04	2.21E+02	5.85E+04	2.31E+02

$$\eta = (\lambda * G)(1 - e^{(-t/\lambda)})$$

Extensional Rheology Results – Steady Strain

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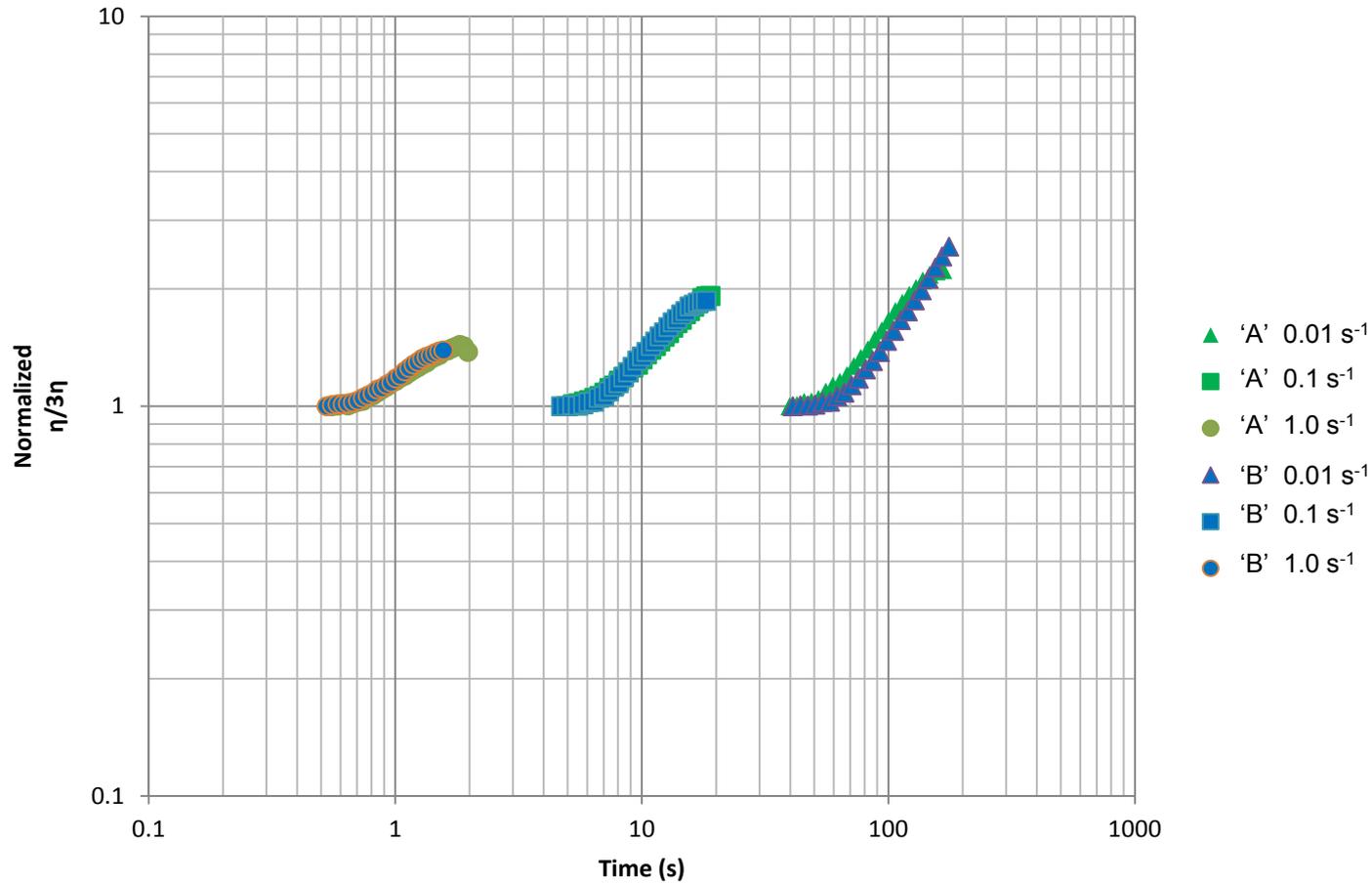

- Conditions: 110 C, Strain rates of .01, .1, 1.0 s^{-1}
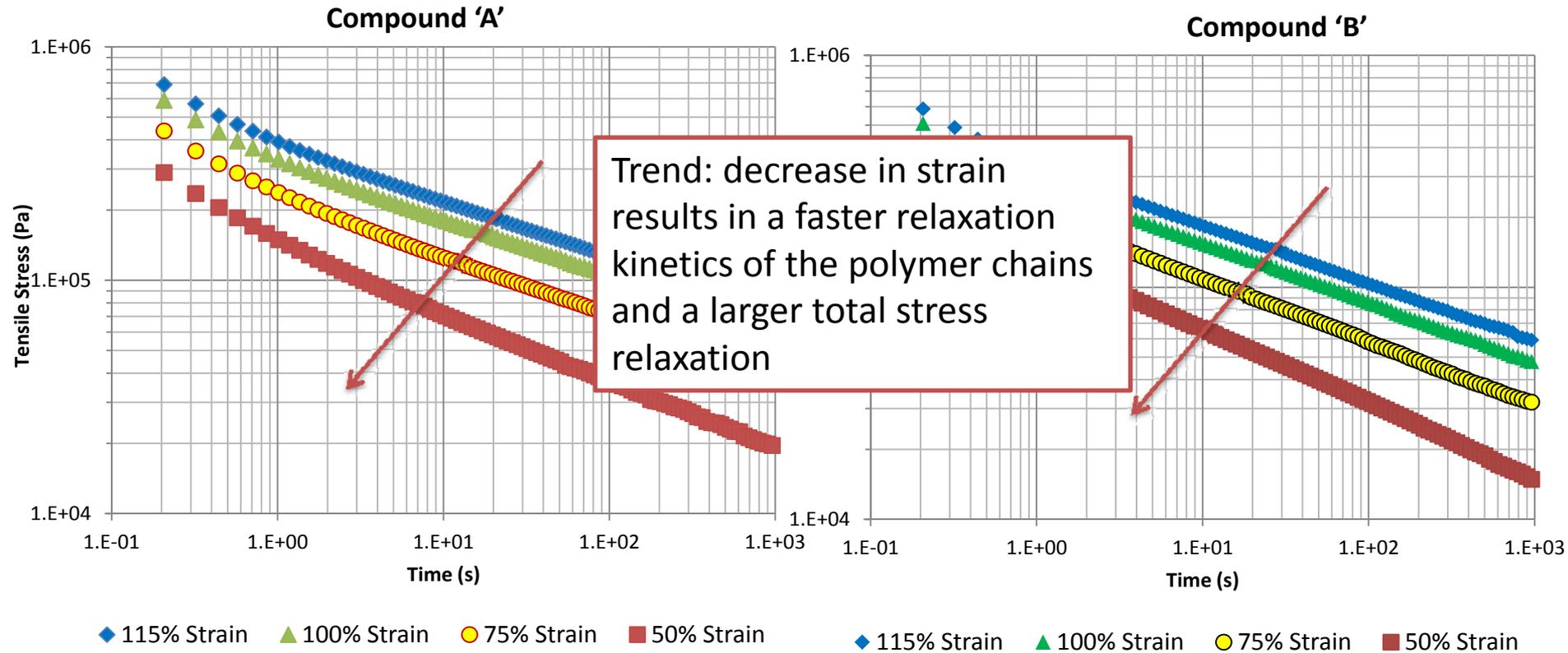- Very similar, repeatable results in extensional behavior with steady strain

Compare with η/3η plot

Extensional Rheology Results – Steady Strain

η/3η vs. time

Extensional Rheology Results – Stress Relaxation

Compound 'A'

Compound 'B'

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

◆ 115% Strain   ▲ 100% Strain   ○ 75% Strain   ■ 50% Strain

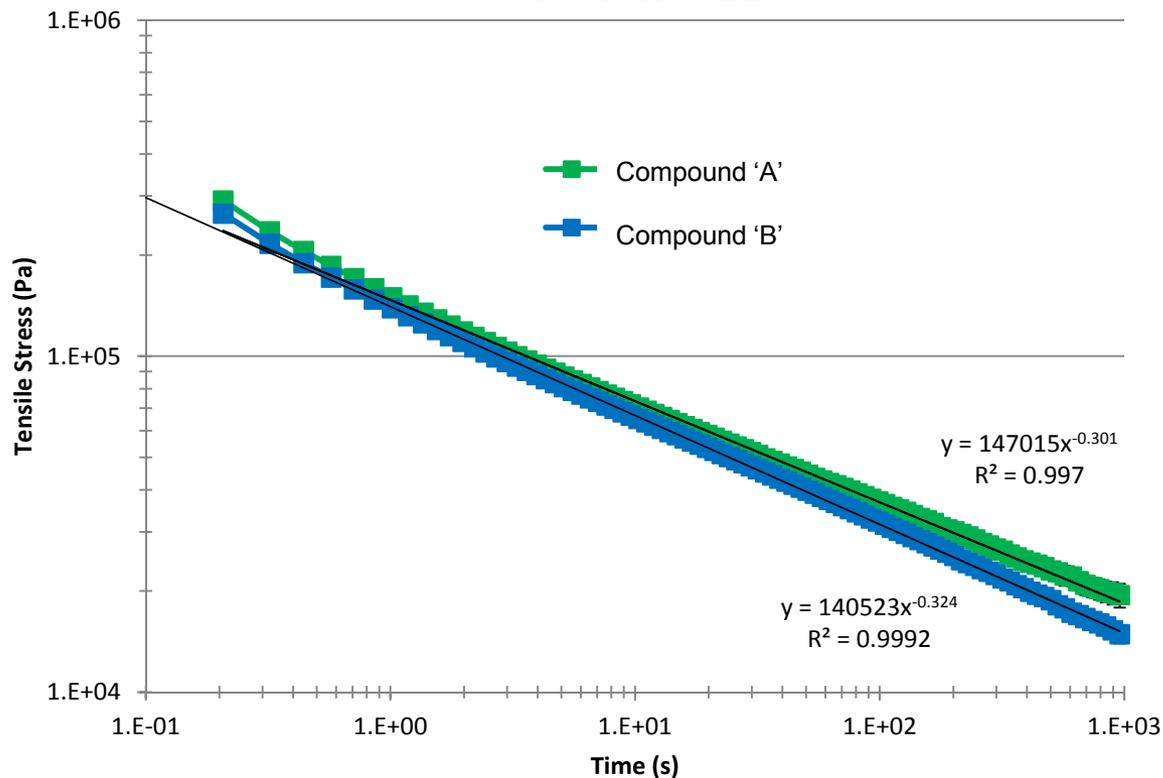◆ 115% Strain   ▲ 100% Strain   ○ 75% Strain   ■ 50% Strain

Conditions: 110C, sample rupture ~120% applied strain,
- Stress relaxation after instantaneous applied strain
- Largest difference between A and B in lower strain rate
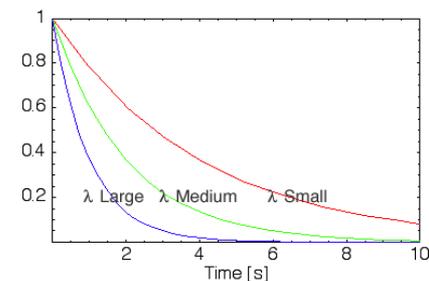
Compare the slopes of 50% strain

Extensional Rheology Results – Stress Relaxation

**Tensile Stress Relaxation -Extension
50% Strain - 110 C**

- ■ Compound 'A'
- ■ Compound 'B'

$y = 147015x^{-0.301}$
$R^2 = 0.997$

$y = 140523x^{-0.324}$
$R^2 = 0.9992$

Tensile Stress (Pa)

Time (s)

Compound	Charact. Relax. Time (s)	% Difference
A	3.32	**7.4%**
B	3.09	

$$E(t) = E_o * e^{(-t/T)}$$

λ Large   λ Medium   λ Small

Time [s]

Conclusion

Rheological Characterization Method	% Diff.
Average Storage Modulus G' (Pa)	7.5%
Average Loss Modulus G" (Pa)	11.4%
Complex Viscosity (Pa*s)	6.6%
Peak Strain Hardening - Extension	< 4%
Characteristic Stress Relaxation Time (s)	7.4%

- Several studies were used in detecting minor differences in branch architecture
- G', G" show`ed 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!