SER Universal Testing Platform: The Ultimate in Physical Material Characterization Technology

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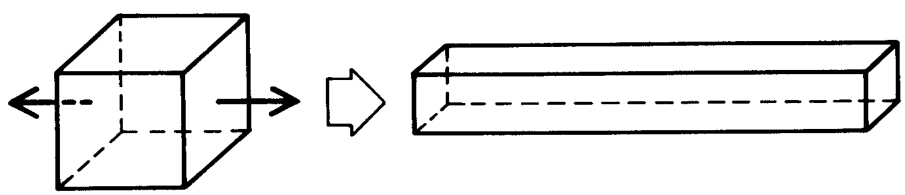
Introduction

- Extensional flow refers to a type of flow deformation that involves the elongation, or stretching, of material
- Extensional flow measurements are very useful in polymer characterization because they generate highly directional flow fields that are very sensitive to the molecular structure of a polymeric system



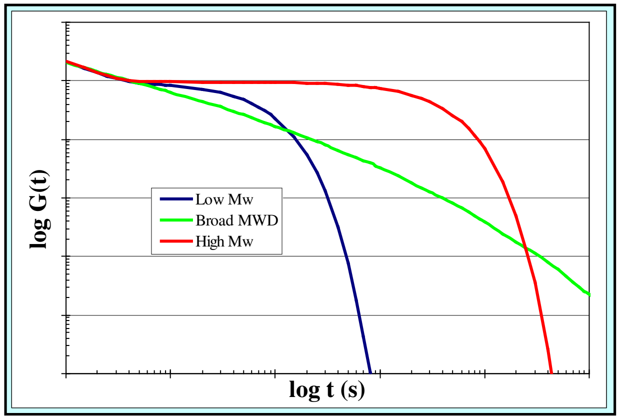
A cubic element shown in simple extension

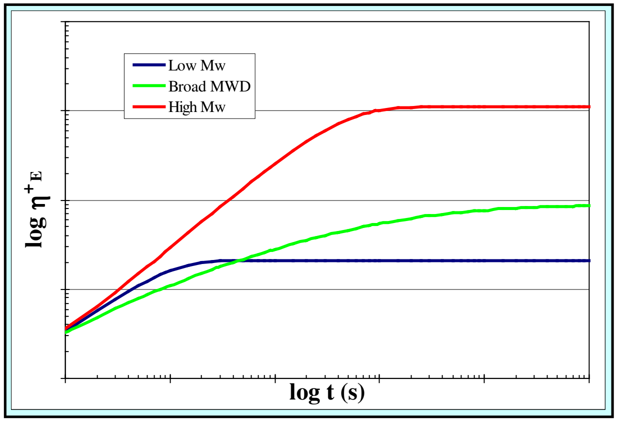
- Historically, however, extensional measurements have been very difficult to perform

LVE Behavior in Extension

- For LVE Behavior: $\eta_E^+(t) = 3\int G(t)dt = \sigma_E / \dot{\varepsilon}_H$

- Effects of MW and MWD (linear polymers):



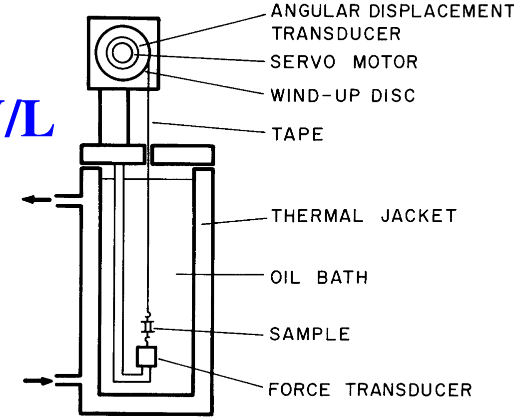


The same LVE properties that are typically measured in simple shear can be determined from the LVE portion of the tensile growth curve

Prior Art

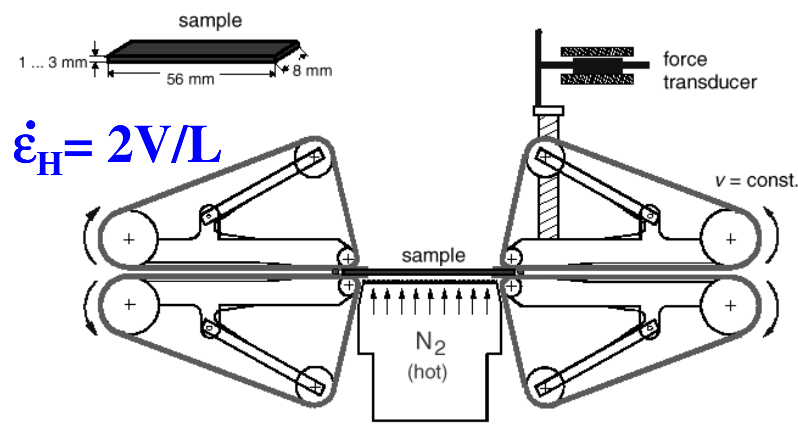
- Münstedt Rheometer
  - End Separation Method
    - *Non-uniform deformation at ends*
    - *Limited deformations and rates*

$\dot{\varepsilon}_H = V/L$



- Meissner Rheometer
  - Fixed Gage Length Method
    - Uniform deformation along stretch zone
    - *Must correct for true extensional rates due to slip between clamps*

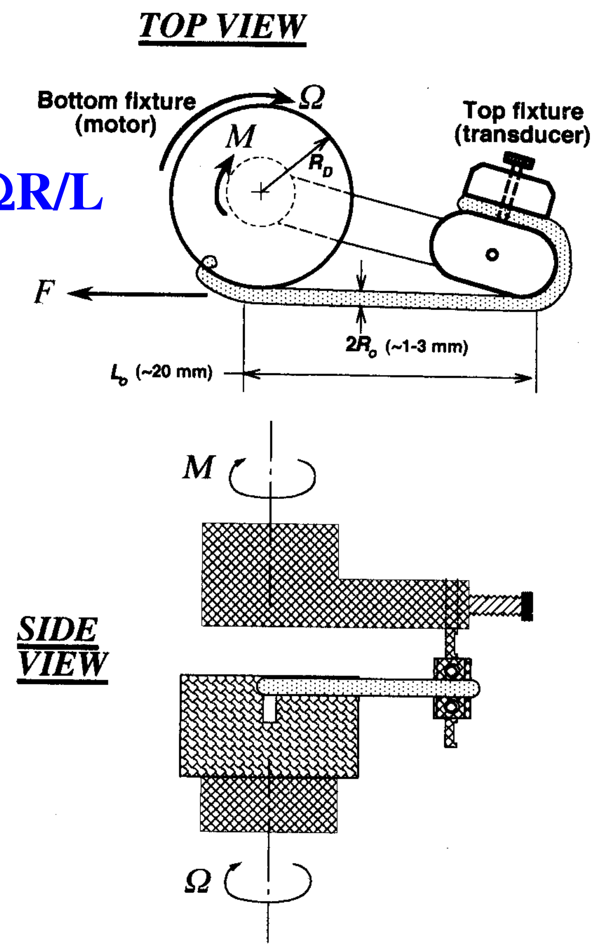
$\dot{\varepsilon}_H = 2V/L$



Both types of rheometers have been commercialized (RER & RME)

Prior Art (cont.)

$\dot{\varepsilon}_H = \Omega R/L$

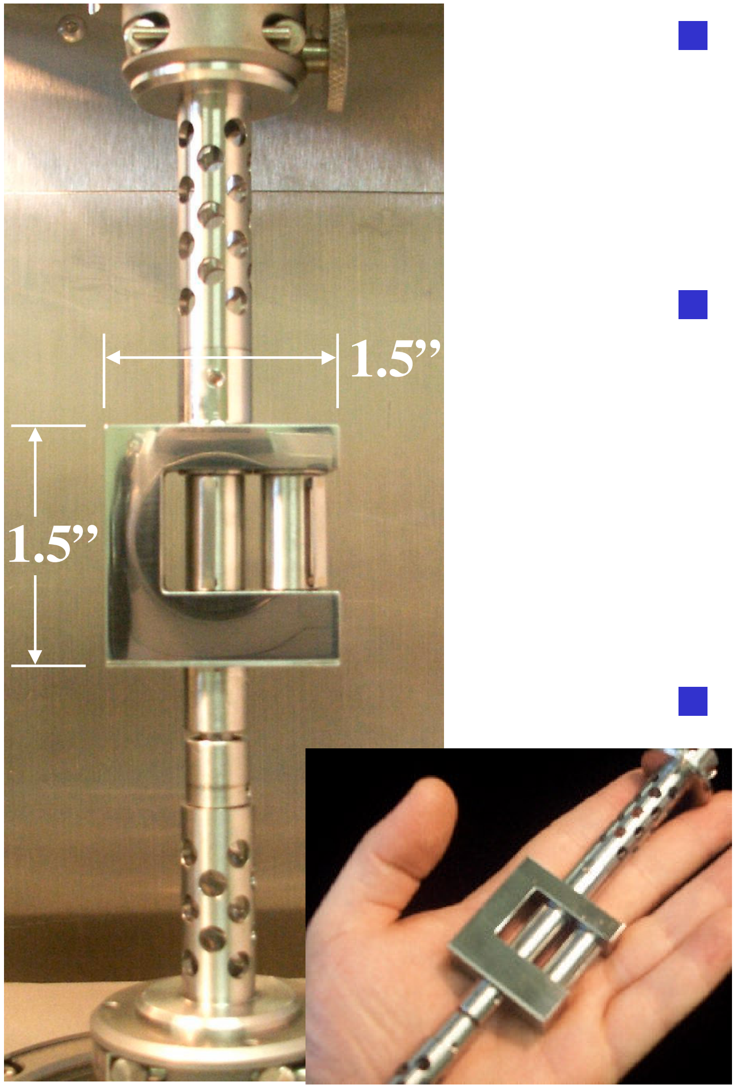


- Wind-Up Drum Rheometer
  - Can be used as a fixture on a rotational rheometer
  - Fixed Gage Length Method
    - *Non-uniform deformation near fixed end can lead to false rupture condition*

Taken from Padmanabhan et al., J. Rheol. **40**, 473-481 (1996)

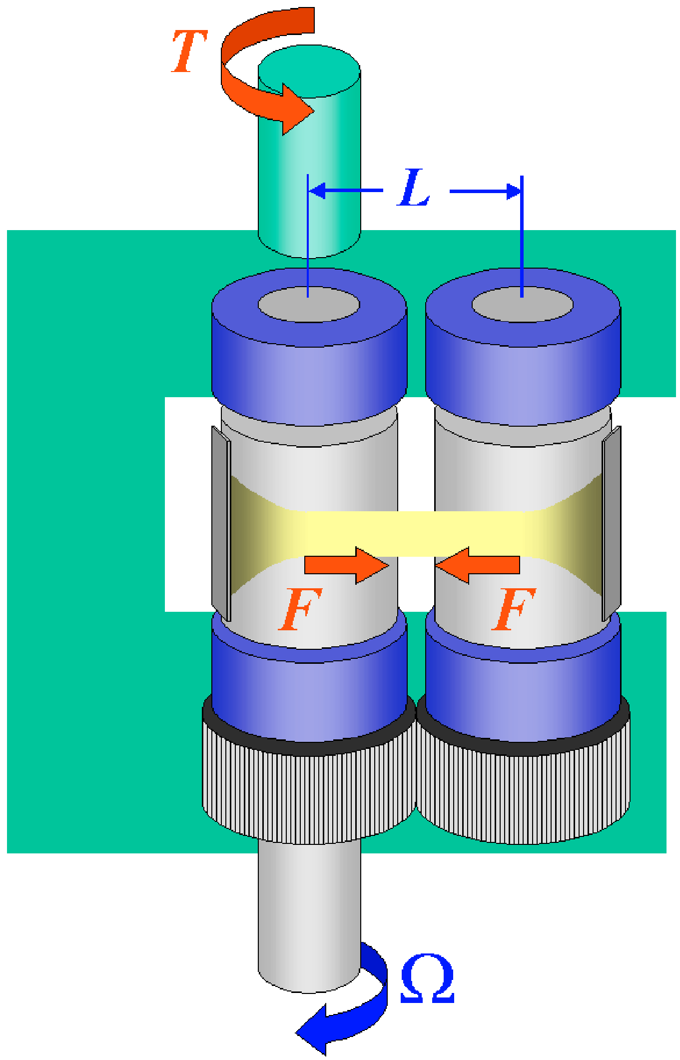
Shortcomings in prior art unacceptable - New Technology Needed

SER Universal Testing Platform



- The material characterization technology first pioneered at Goodyear has been exclusively licensed to **Xpansion Instruments, LLC (www.xinst.com)**.
- The **SER** is a fixture that has been specifically designed so that it can be easily accommodated onto a number of commercially available R&D grade rotational rheometer host systems and can be housed within the host system’s environmental chamber for controlled temperature experiments.
- XI’s initial product offering, the **SER-HV-A01**, has been targeted for use on ARES, RDA3, & RDA2 host systems - additional models to accommodate other host systems will be launched.
  - Requires only 5-200mg of material
  - Can be used up to temperatures of 250°C
  - Easily detachable for fixture changeover

SER Principle of Operation



- Ends of sample affixed to windup drums, such that for a constant drum rotation:

$$\dot{\varepsilon}_H = 2\Omega R / L$$

- As the sample stretches it offers a resistant force, *F*, on the wind-up drums which consequently imparts a torque that is translated through the housing where the drums are mounted
- The resulting torque, *T*, on the torque transducer attached to the housing is then simply:

$$T = 2\,(F + F_{friction})\,R$$

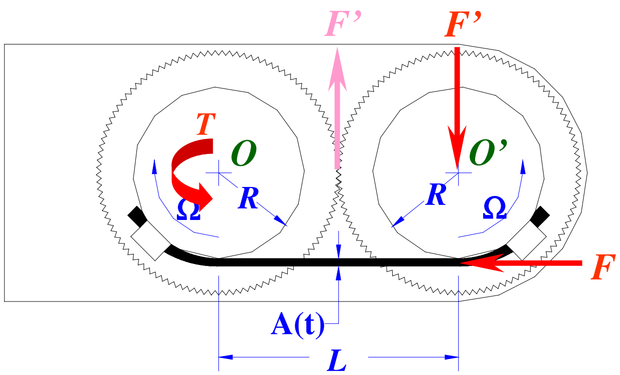
where $F_{friction}$ is the friction contribution from the bearings and gears (typically < 2%)

- The instantaneous cross-sectional area of the sample is simply:

$$A(t) = A_0 \exp\,[-\varepsilon_H]$$

where A_0 is the initial cross-sectional area

Derivation of Stretching Force



- As the sample begins to stretch it offers a resistant force, F, on the slave wind-up drum
- This force F and any frictional contribution from the bearings, $F_{friction}$, consequently impart a force, F', at the point of intermeshing gear contact, such that:

$$F' = (F + F_{friction})\, R \,/\, (L/2)$$

- This intermeshing force is then translated as a radial force on the slave shaft bearings centered about axis, O', mounted in the housing
- A sum of moments about axis O reveals that the resultant torque, T, measured by the torque transducer attached to the housing is then simply:

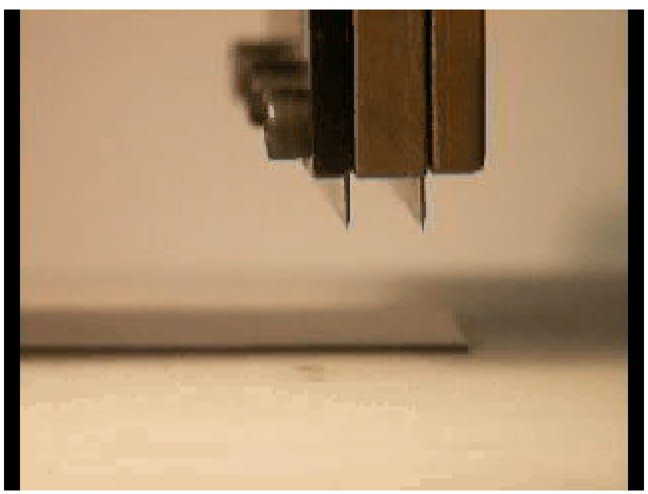
$$T = F'\, L = 2\,(F + F_{friction})\, R$$

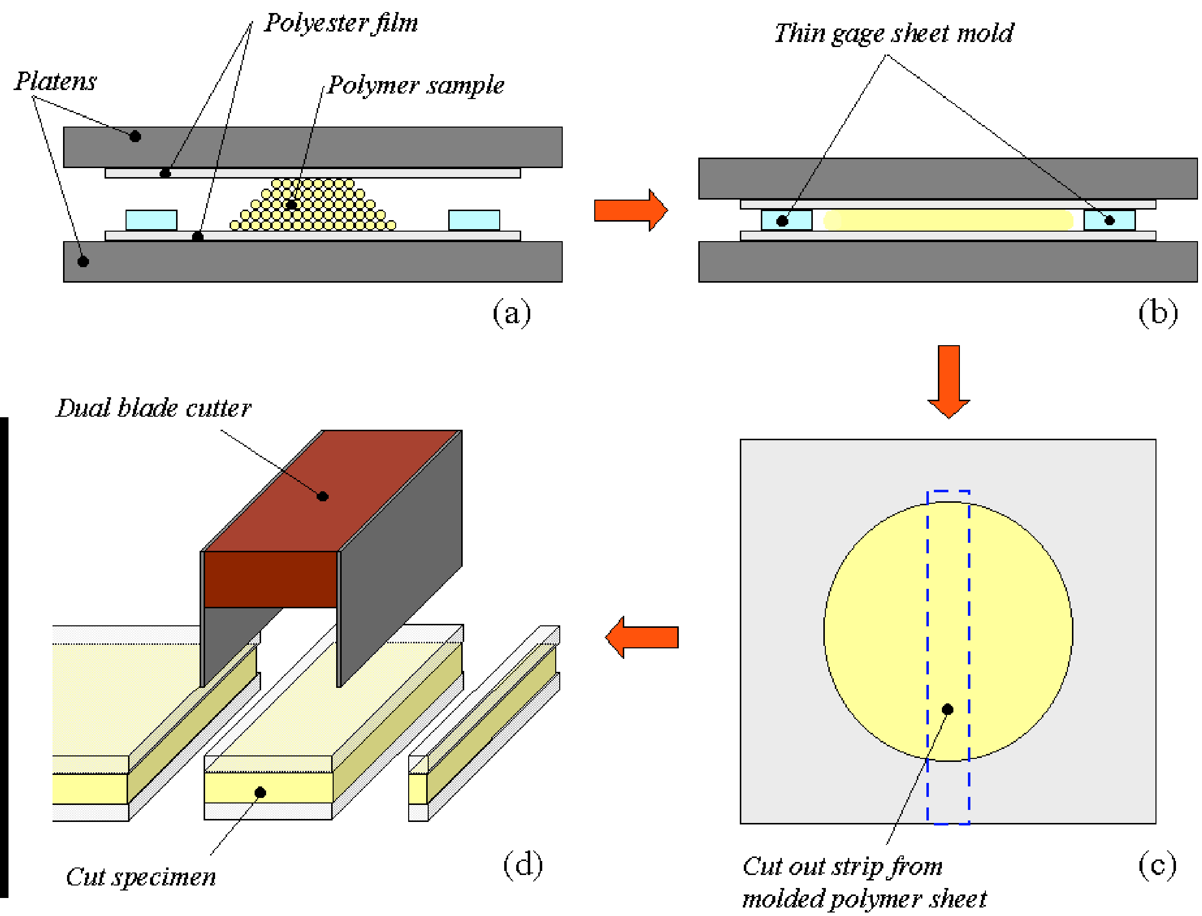
where $F_{friction}$ is the friction contribution from the bearings (typically < 2%)

- Thus by offsetting the slave drum from the primary axis of rotation and using a 1:1 gear ratio, a mechanical gain of 2 is achieved.

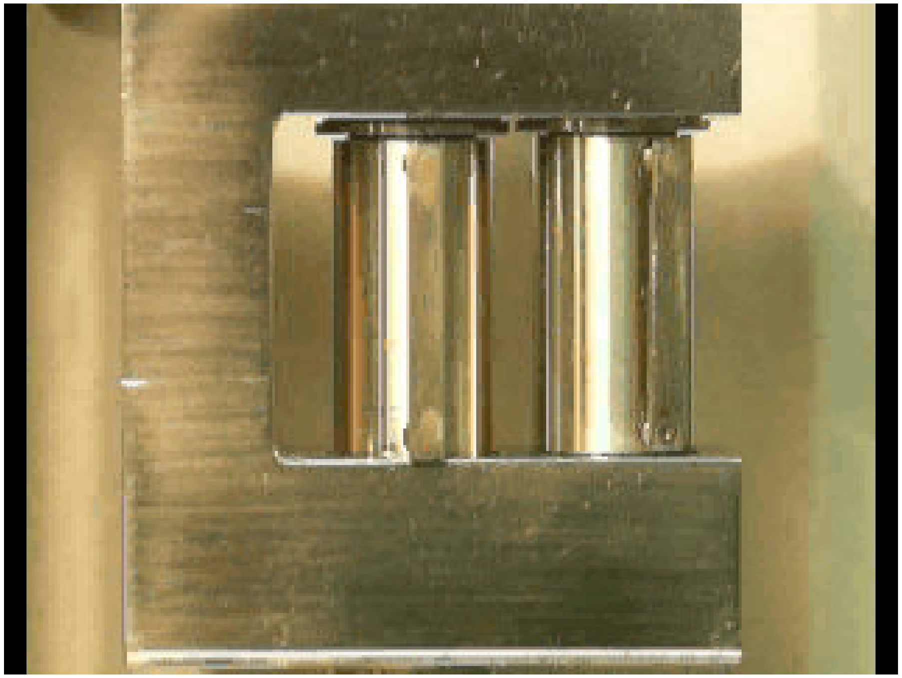
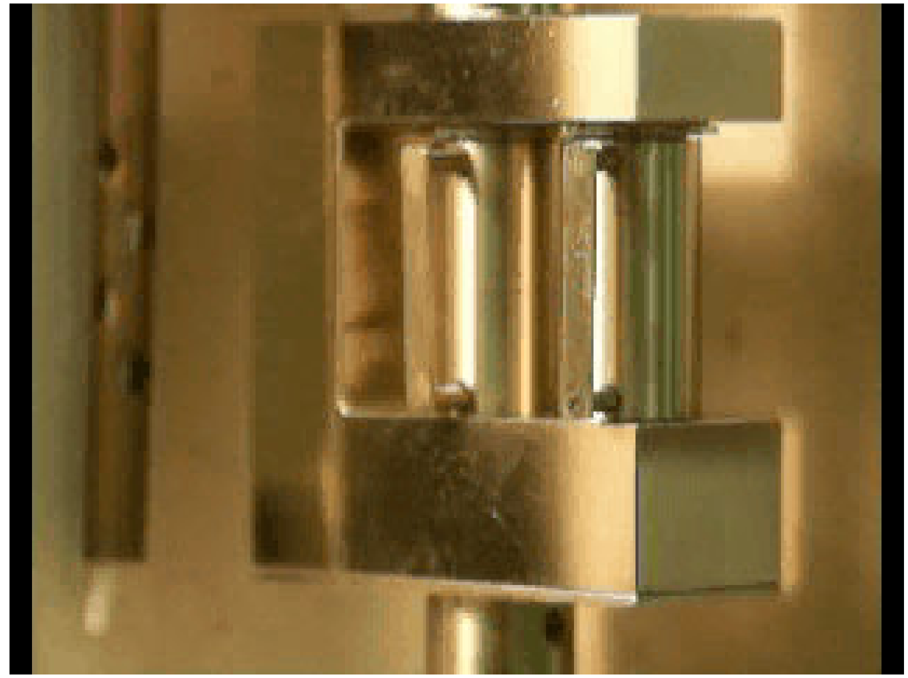
Extensional Specimen Preparation

Fixed gage thickness compression molded sheets and strips cut-to-width with a dual blade cutter





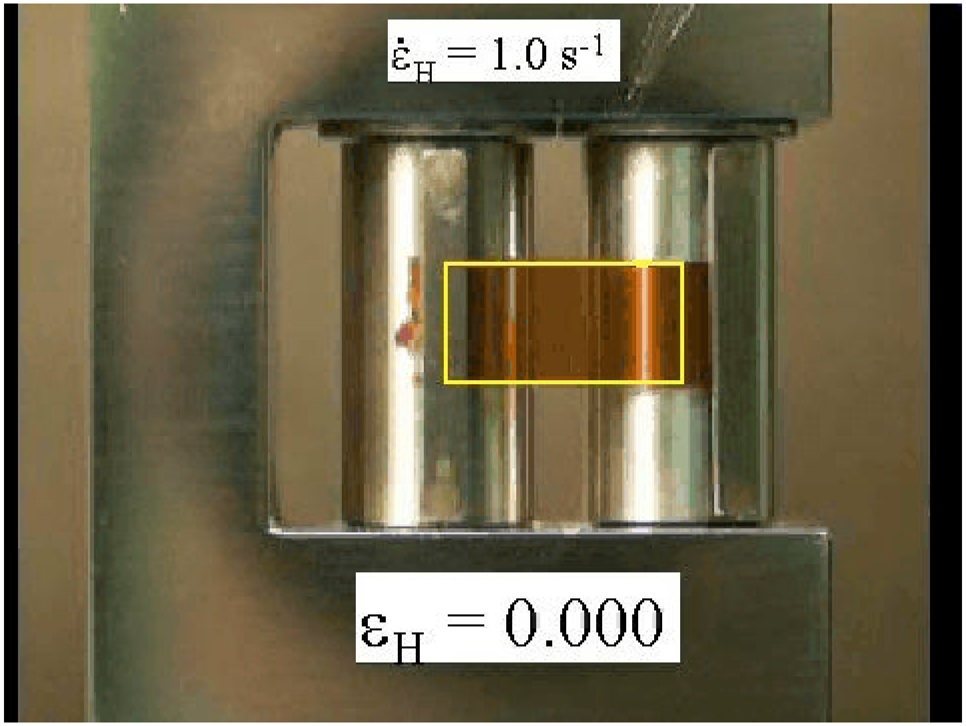
Specimen Loading Procedure

- ***Simple securing means effective for both polymer melts and uncured elastomers***
- ***Specimen loading takes less than 20 seconds***

True Strain Rate Validation

Frame Sequencing Videography



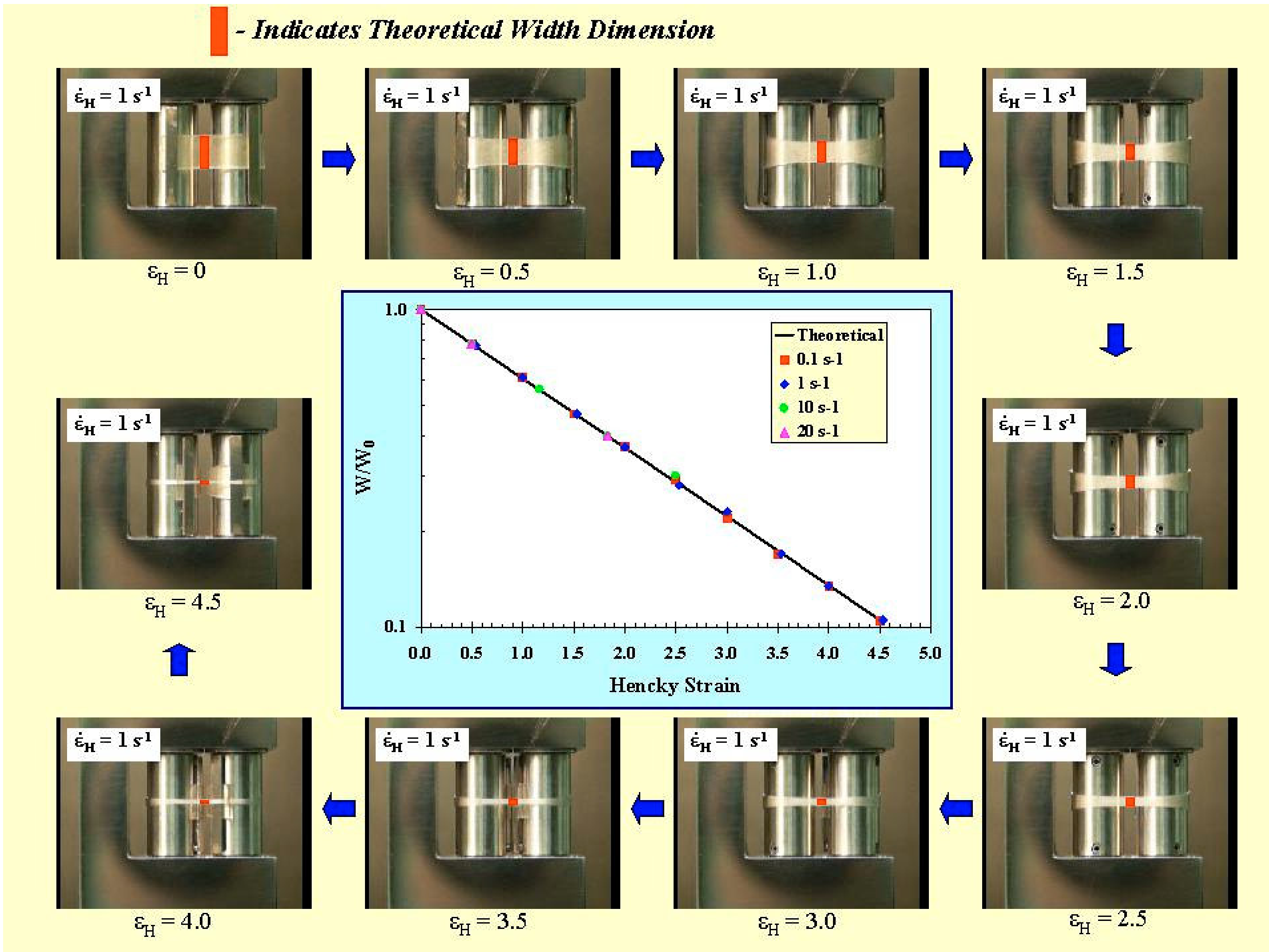
- Indicates Theoretical Width Dimension

Theoretical width dimension expression:

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

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

True Strain Rate Validation



Validation Experiments - Part I

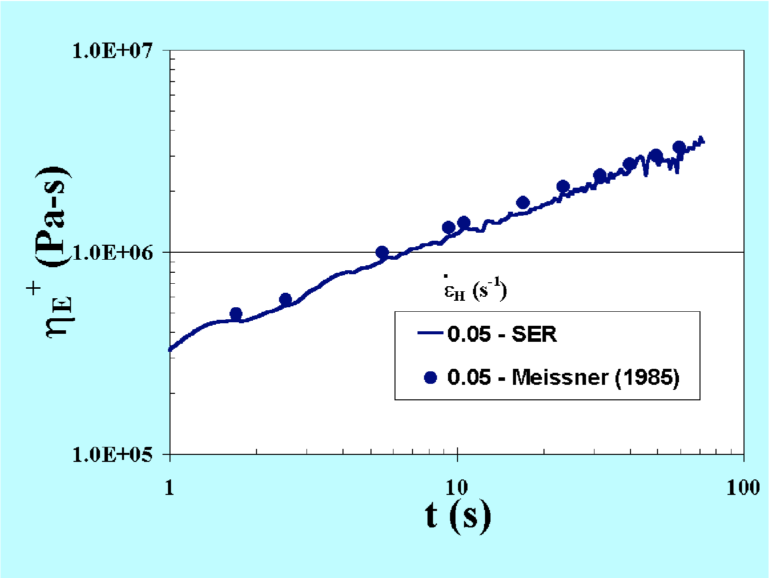
- Material - Elastomer
  - PIB (BASF Oppanol® B15)
    - M_w ~ 88,000
    - $M_w / M_n = 2$
    - Same polymer as that used by

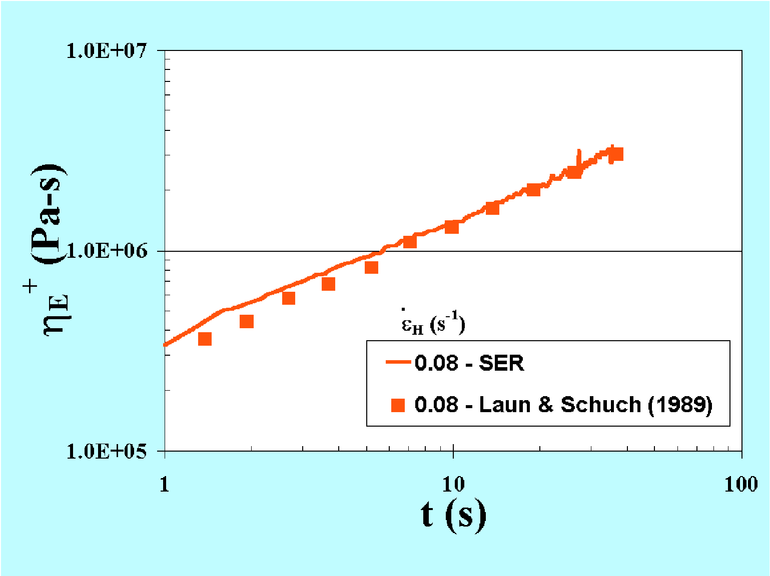
      Meissner, J., Chem. Eng. Commun. **33**, 159-180 (1985)

      Laun, H. M. & H. Schuch, J. Rheol. **33**, 119-175 (1989)

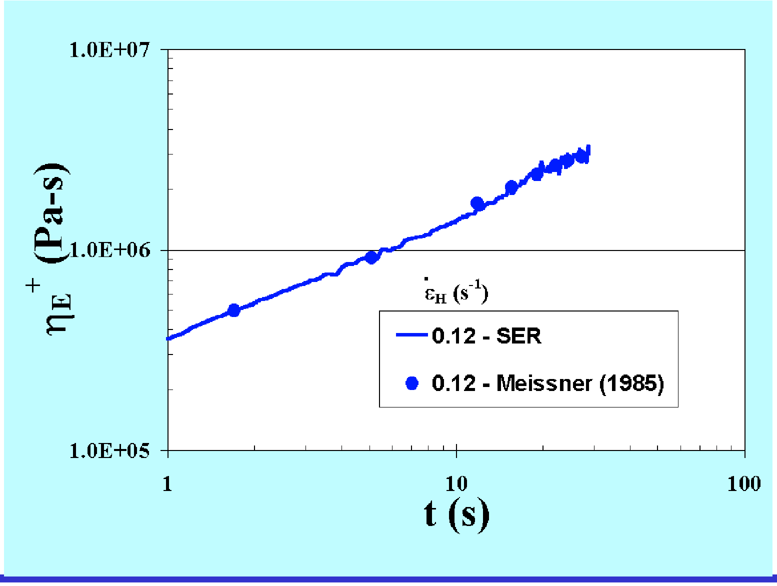
- Types of Extensional Rheometers used:
  - Meissner - rotating gear clamp (fixed gage length method)
  - Laun & Schuch - Münstedt rheometer (end separation method)

Comparison of PIB Stress Growth Curves

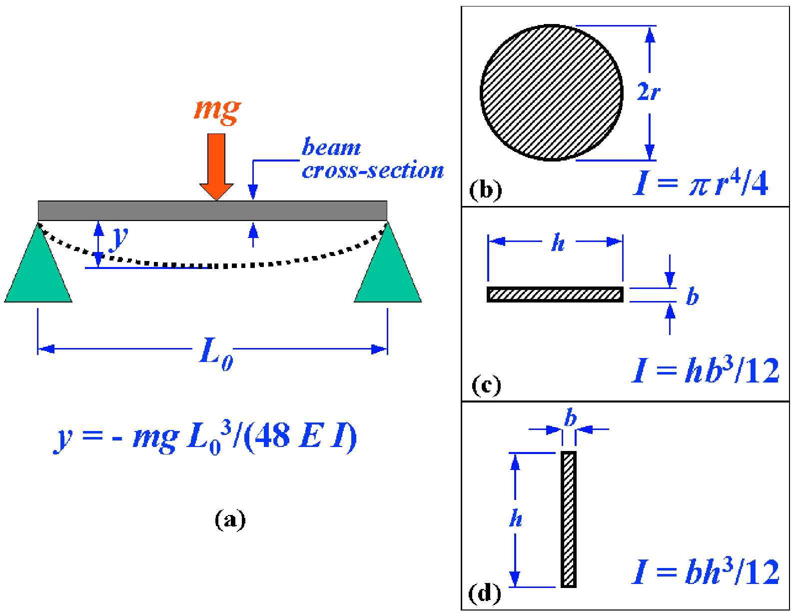




The results with the SER show excellent agreement with results from the other independent studies utilizing different extensional rheometer technologies



Comments on Melt Sag Effects



- With proper design of the sample and testing geometry the effects of sag are greatly reduced.
- The effects of sag can be modeled with a simple beam flexure analysis, where it can be shown that for the sample cross-sections depicted the rates of can be expressed as:

  Case (b): $\rho g\, L_0^4/(36\, \eta_0\, r^2)$ - Orig. Meissner

  Case (c): $\rho g\, L_0^4/(12\, \eta_0\, b^2)$ - RME Case

  Case (d): $\rho g\, L_0^4/(12\, \eta_0\, h^2)$ - SER Case

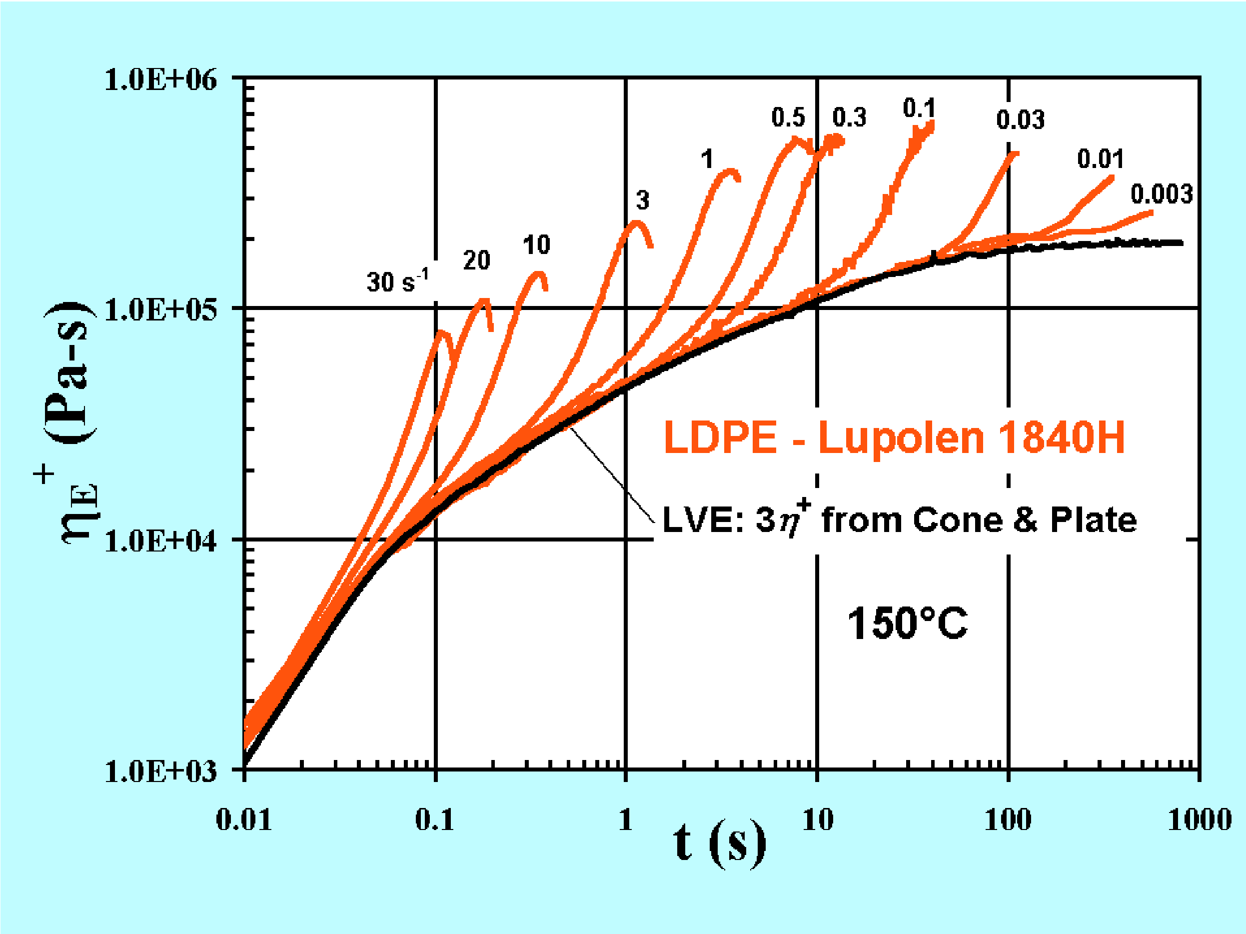
- If L_0 is the same for all three cases and if we let $h = 10b = 20r$, then Case (c) would sag at a rate 100 times faster than Case (d); Case (b) 133 times faster.
- Extending this analysis to a typical RME geometry (L_0 = 50mm, h = 7mm, b = 1.5mm) versus a typical SER geometry (L_0 = 12.7mm, h = 12.7mm, b = 1mm), w/o the buoyant gas cushion the RME specimen sags at a rate **17,000 times faster** than the SER specimen!

Validation Experiments - Part II

- Material - Polymer Melt
  - LDPE (BASF Lupolen® 1840H)
    - M_n = 17,000
    - M_w = 243,000
    - M_w / M_n = 14.3
    - CH_3/1000C = 23
    - Same polymer as that used by

      Münstedt, H et al., Rheol. Acta **37**, 21-29 (1998)
    - Very similar to the IUPAC A
- Type of Extensional Rheometer used:
  - Münstedt et al. - Münstedt rheometer (end separation method)

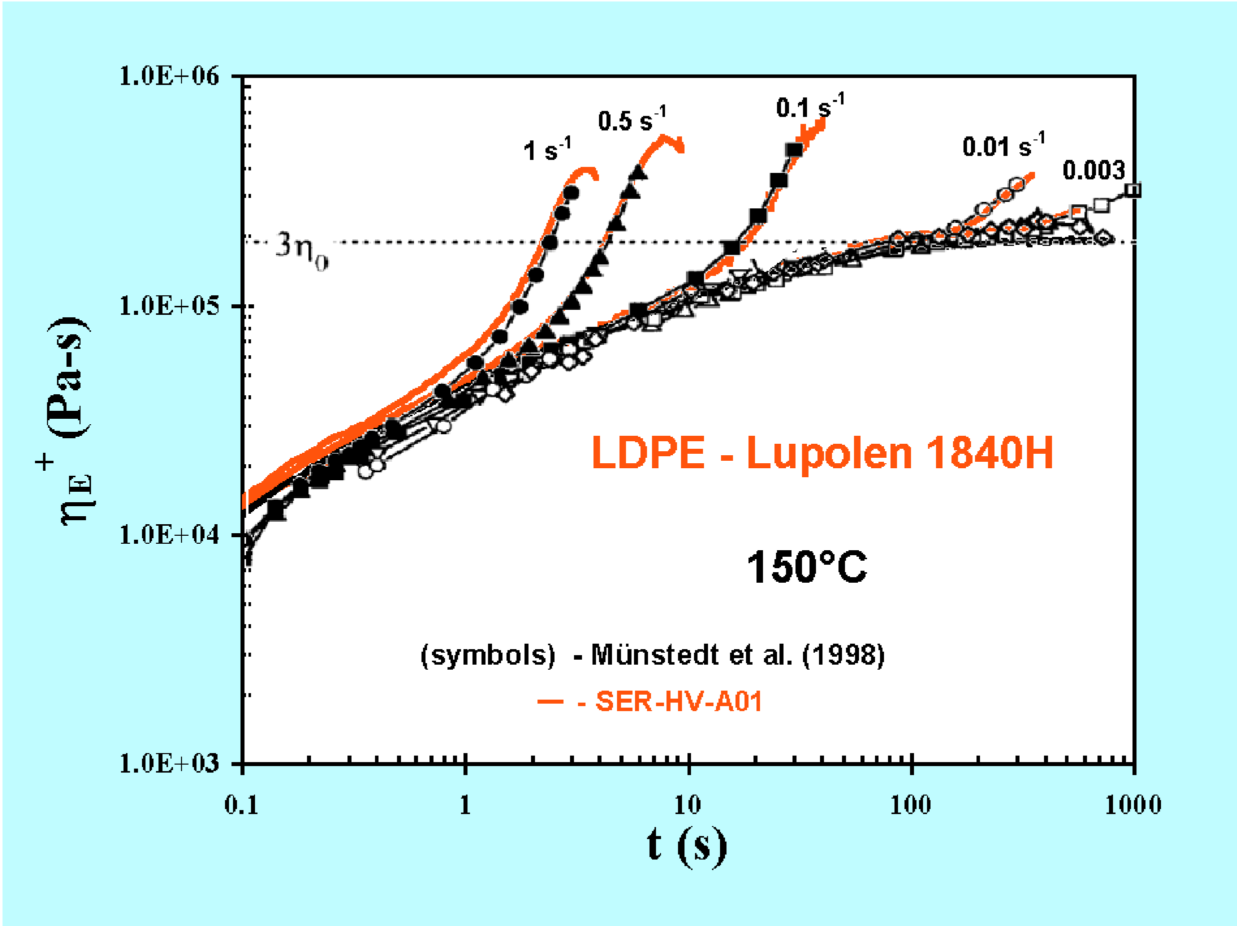
Stress Growth Curves with the SER



All of this extensional melt data took less than 1.5g of material and just over one hour to generate with the SER

Note the excellent agreement between the low strain data and the LVE 3η^+ stress growth curve taken from cone & plate start-up of steady simple shear experiments

Comparison of LDPE Stress Growth Curves



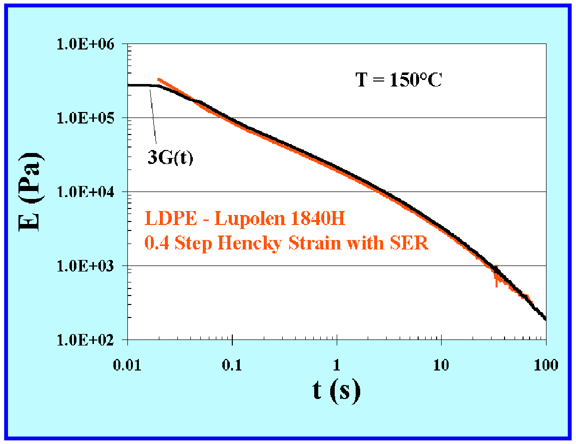
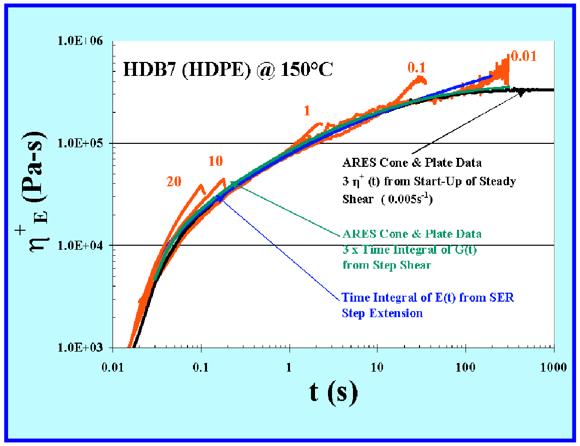
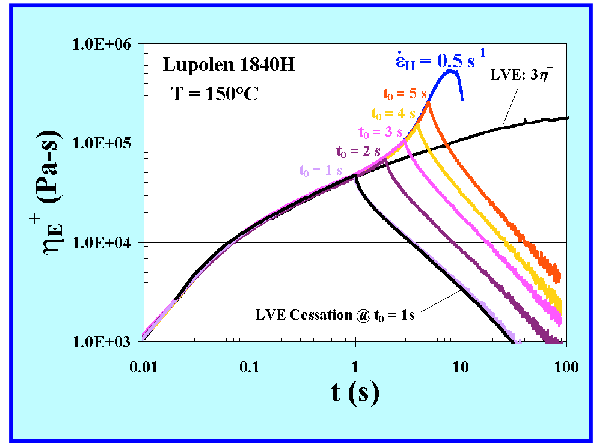
The results with the SER (red curves) show excellent agreement with literature results from Münstedt et al. (black symbols & lines)

Characterization Capabilities

This single SER Universal Testing Platform is capable of condensing a vast amount of material information typically obtained from several different test methods and instruments.

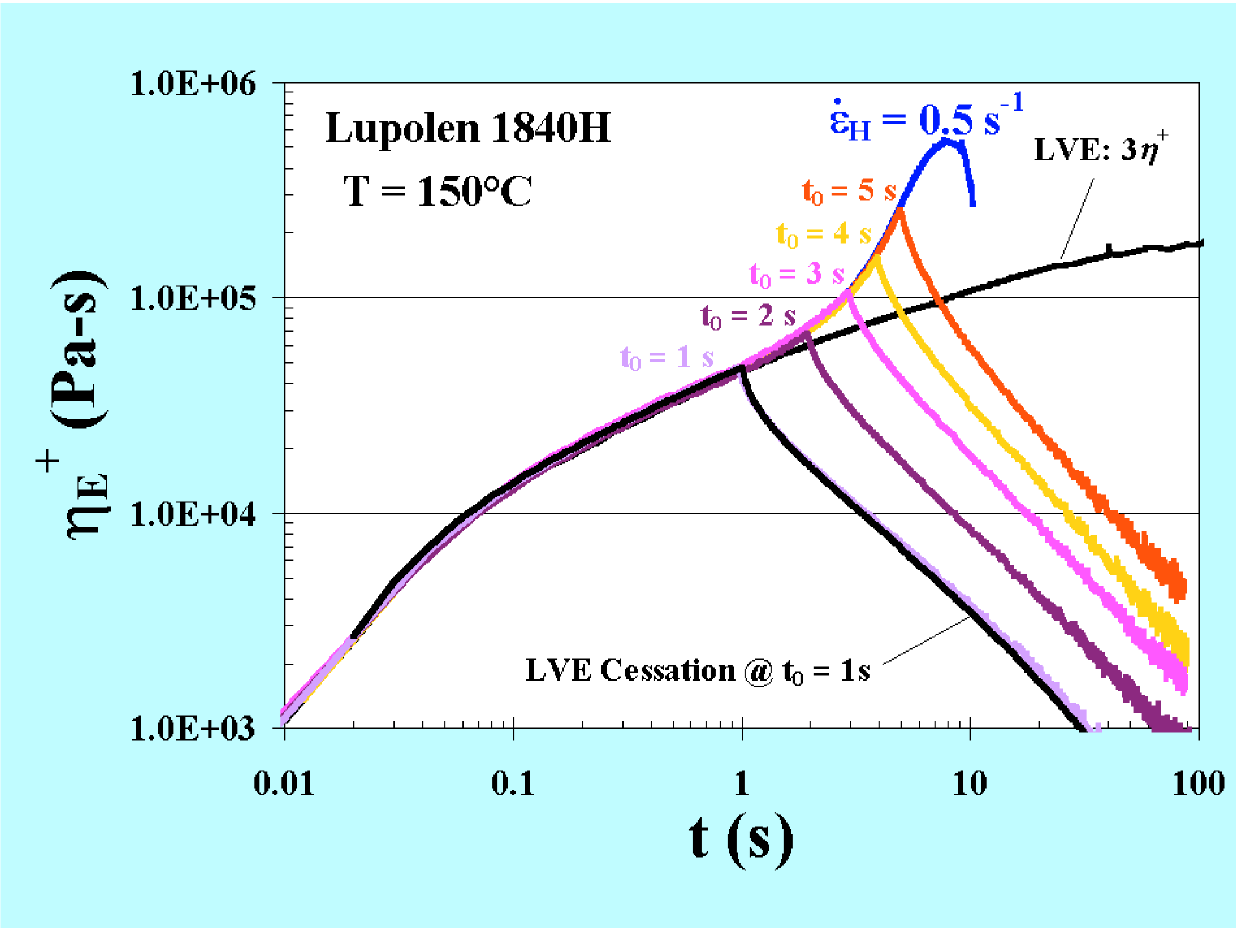
- Extensional Rheology
- Solids Tensile Testing
- Tear Testing
- Peel/Adhesion Testing
- Dynamic Friction Testing
- Cut Growth/Fracture Testing

Extensional Rheology

LVE	***LVE & NVE***	
		
Step Extension	Start-up of Steady Extension	Cessation of Extension

- Sample sizes less than 150mg can be used to characterize LVE & NVE properties at steady Hencky strain rates up to 20s^{-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

Cessation of Extension: LDPE

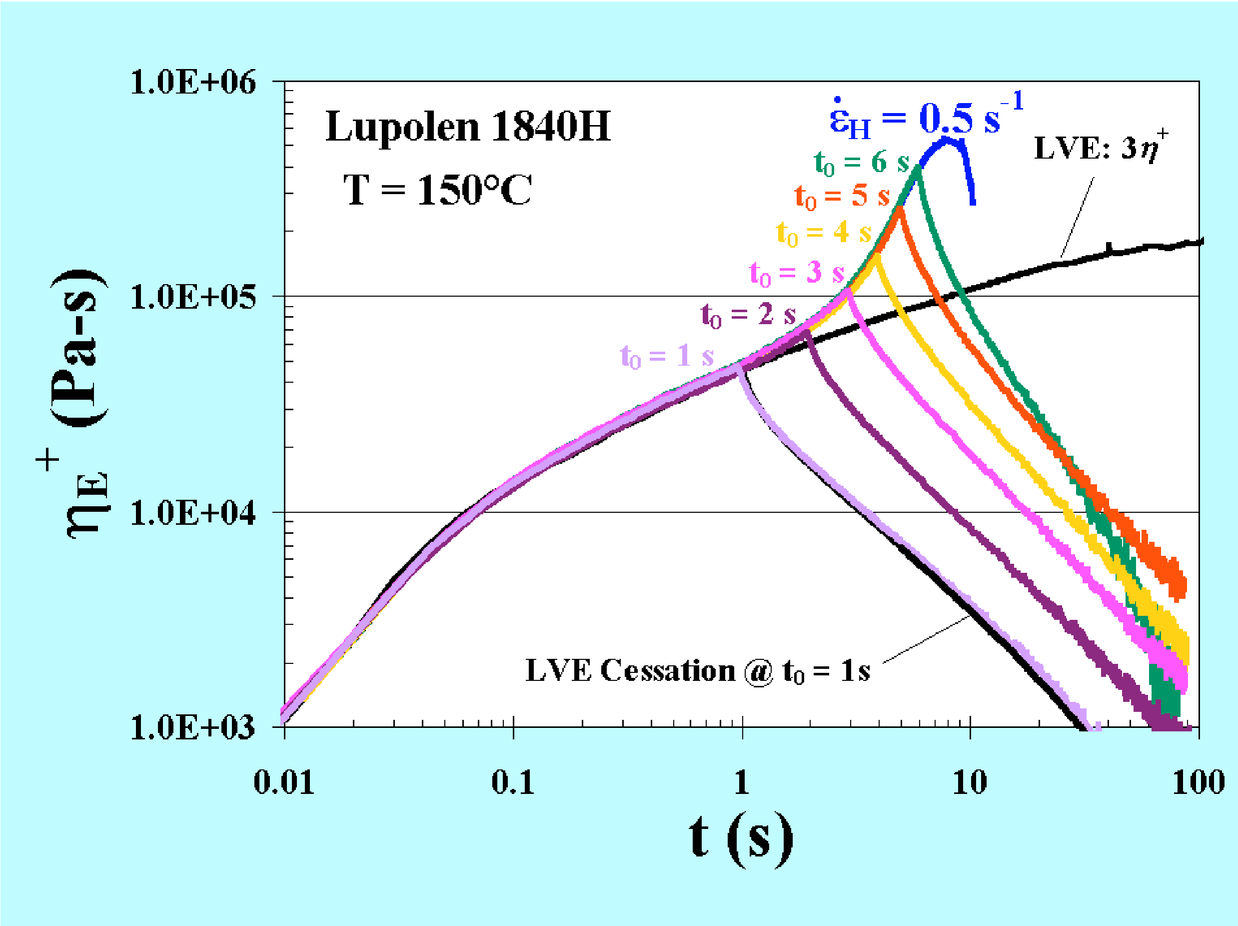


Note the superposition of stress growth data prior to cessation - 8 independent sets of experimental data!

Relaxation behavior is consistent for Hencky strains up to 2.5 (t_0 = 5s)

- Because of the uniformity of deformation in the stretch zone, cessation experiments can easily be performed with the SER

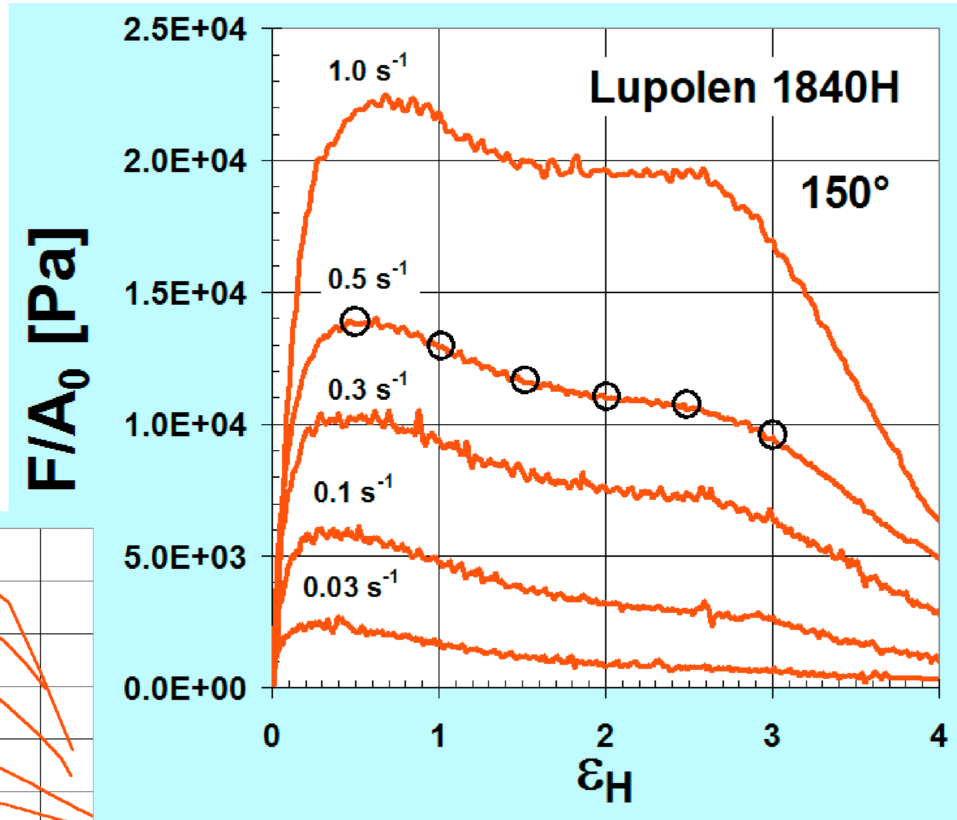
Cessation of Extension: LDPE

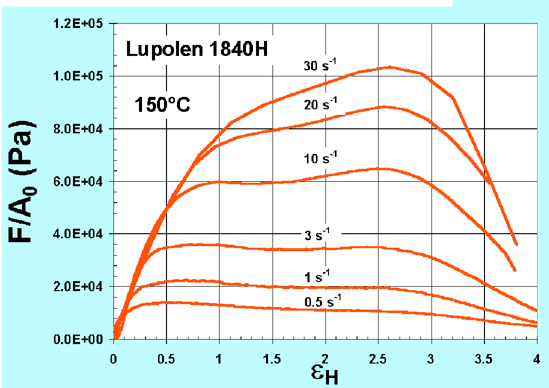


Note that above an applied Hencky strain of 2.5 (t_0 > 5s), the stress relaxation is greatly accelerated due to a subtle necking phenomenon that occurs in the sample

- This additional high strain relaxation data suggests that the extensional flow deformation becomes unstable

Tensile Melt Stress Behavior: LDPE

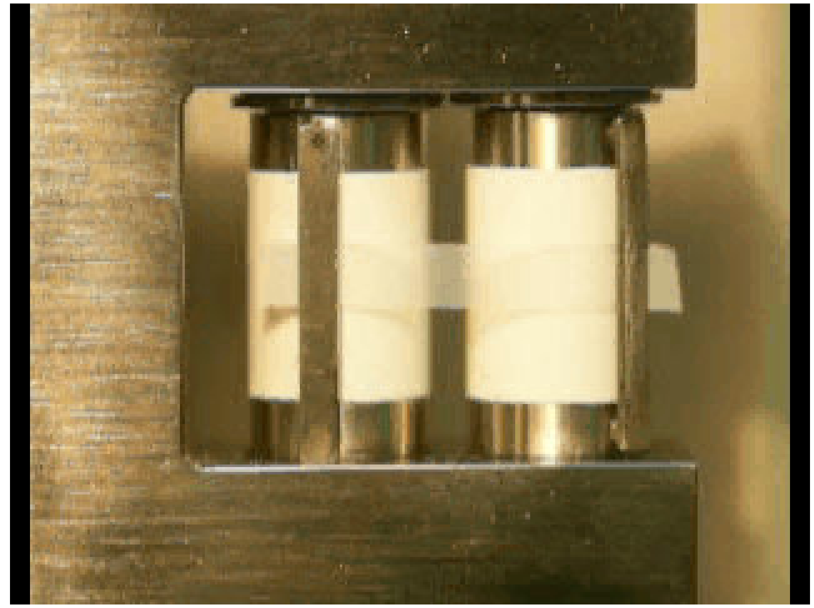




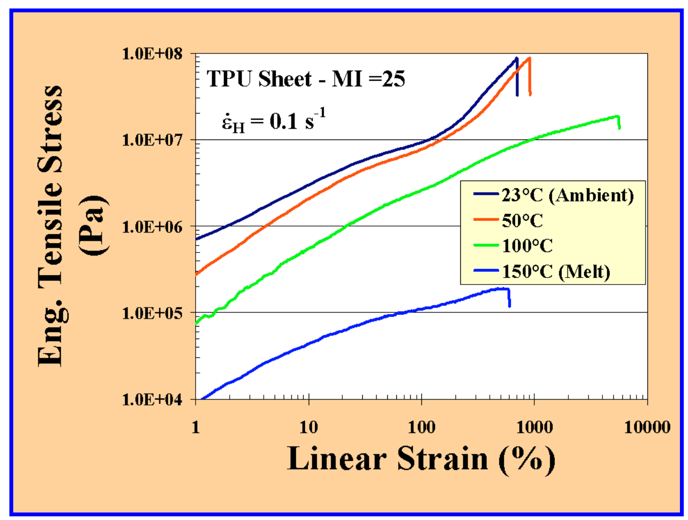
Above an applied Hencky strain of 2.5, the nominal tensile stress passes through a relative maximum before decaying - dramatically with increasing rate

- Hence, beyond a critical strain the material is unstable to viscoelastic necking and rupture, in general agreement with the Considère criterion.

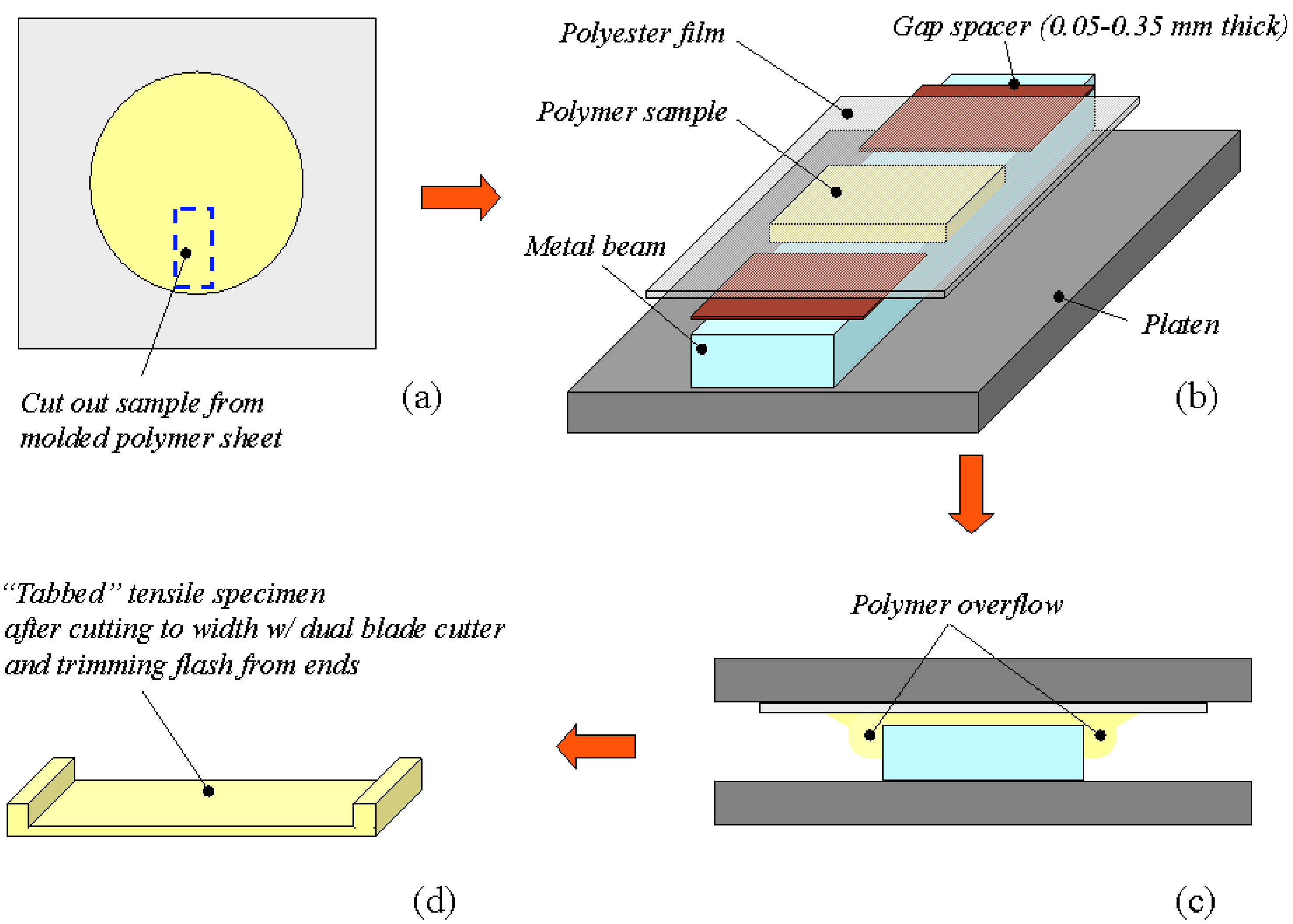
Solids Tensile Testing



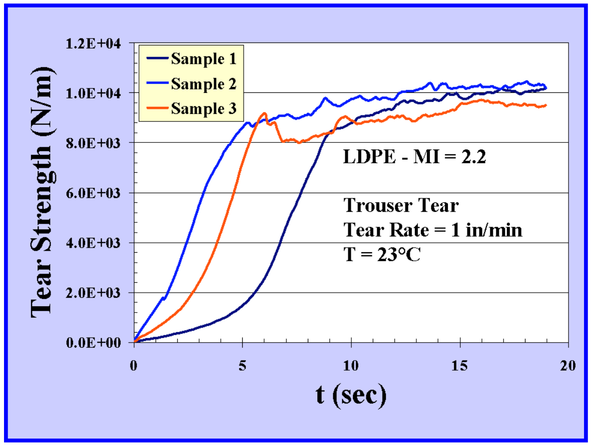
- Sample sizes from 5-50mg can be used to characterize tensile properties over a broad range of temperatures at steady Hencky strain rates up to $20s^{-1}$
- *Applications*: solid and crystalline polymers, cured rubber, solid TPE

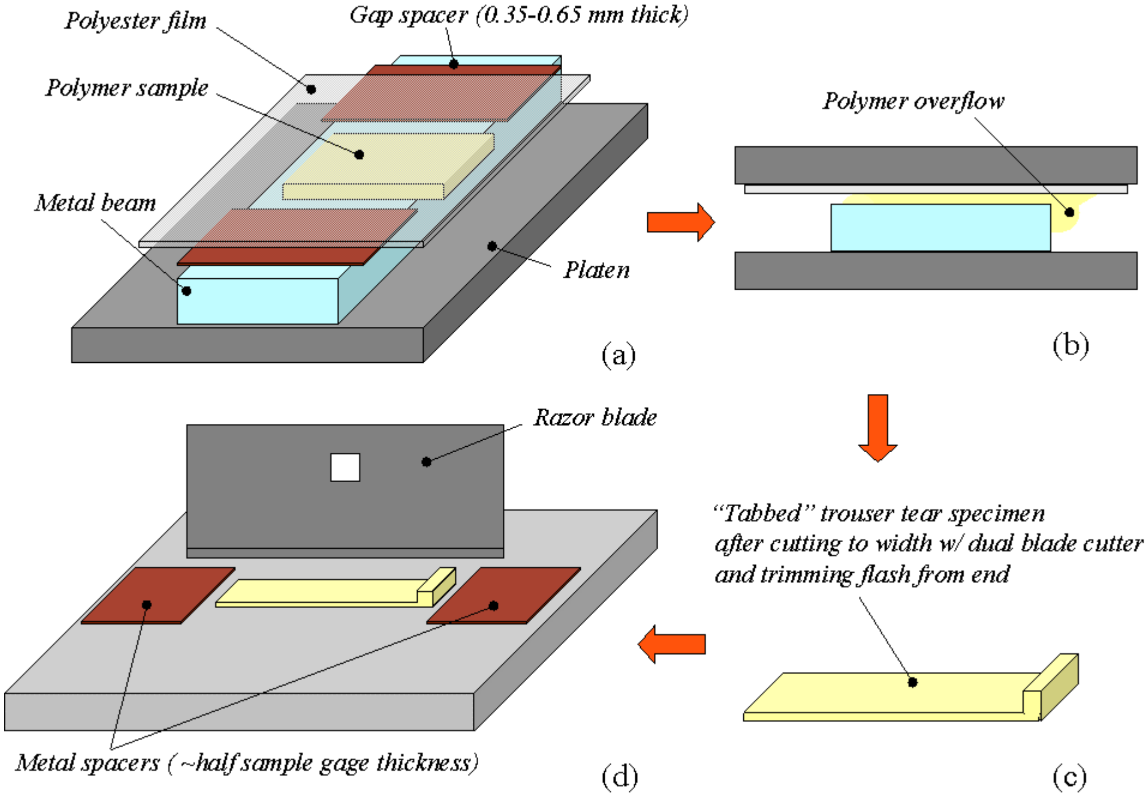


Tensile Specimen Preparation



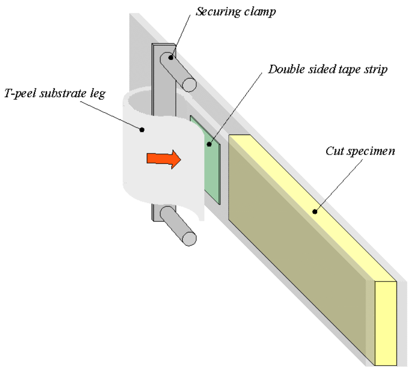
Tear (Pure Shear) Testing

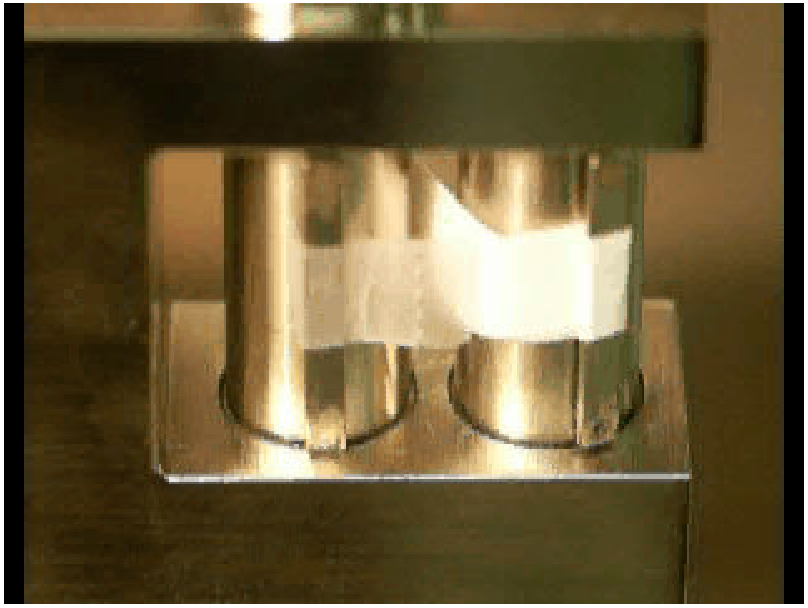


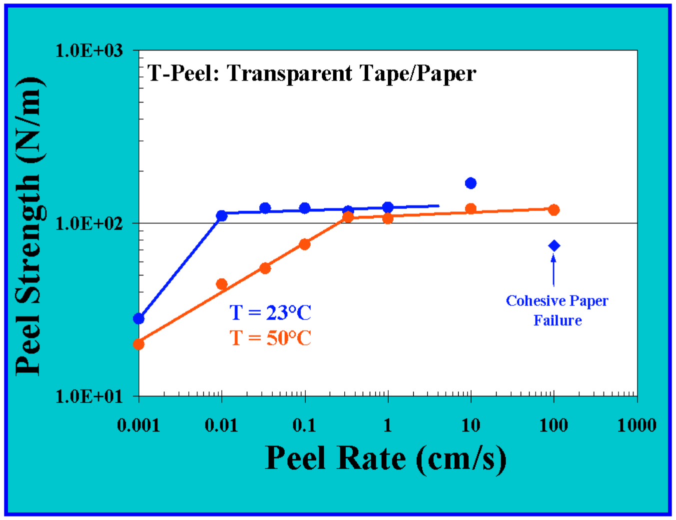


- Sample sizes from 25-50mg can be used to characterize tear properties over a broad range of temperatures at tear rates up to 200cm/s
- *Applications*: solid and crystalline polymers, cured rubber, solid TPE

Peel/Adhesion Testing

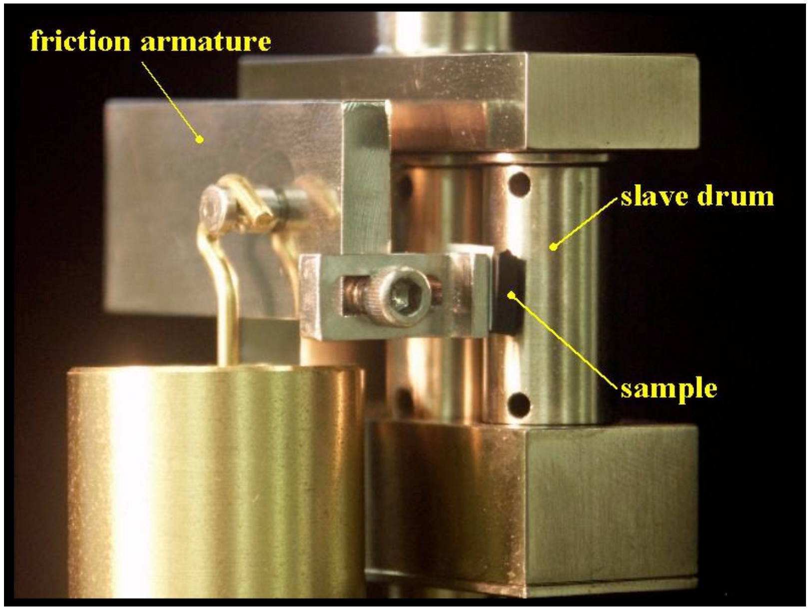


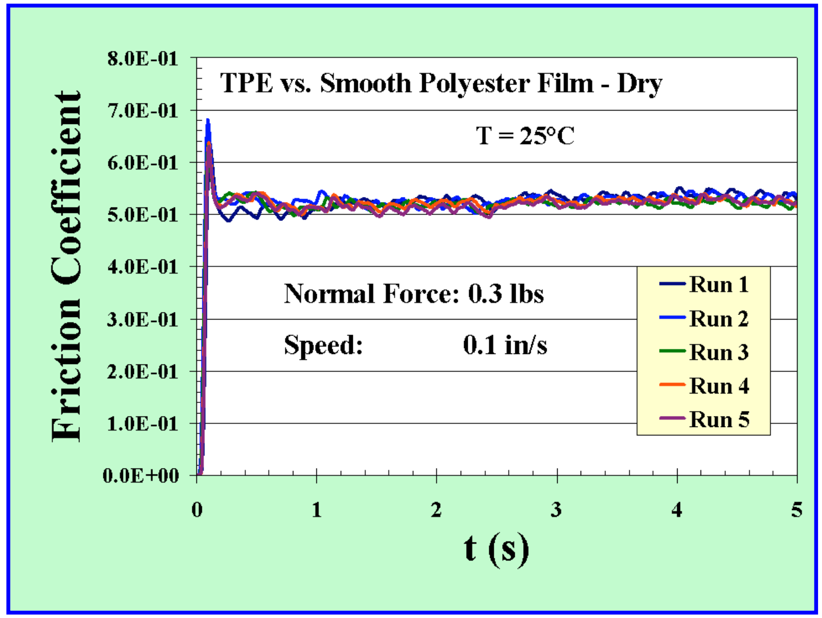




- Sample sizes from <1-50mg can be used to characterize adhesion properties against a variety of thin film substrates over a broad range of temperatures and peel rates up to 200cm/s
- *Applications*: adhesives, gels, pastes, polymer melts, cured rubber (bond strength), coatings

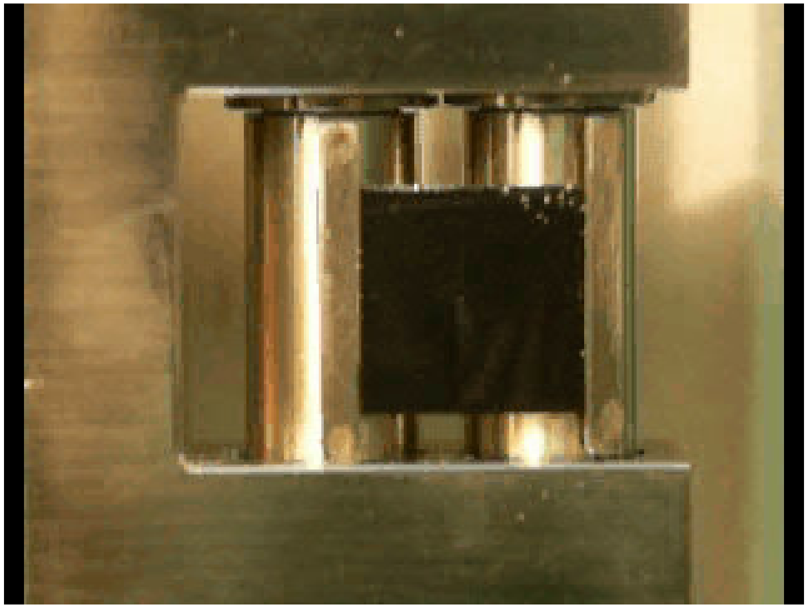
Dynamic Friction Testing

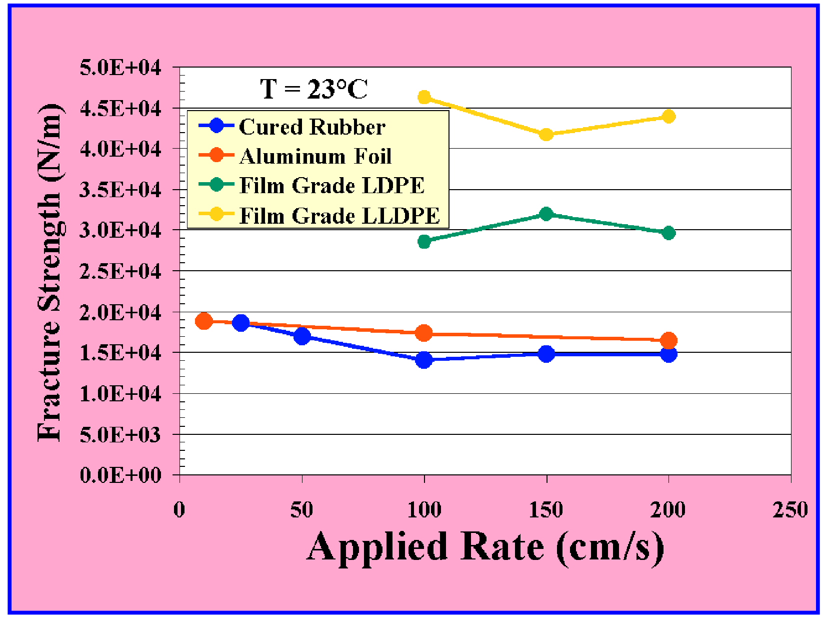




- Sample sizes from 5-25mg can be used to characterize dynamic friction/slip properties against a variety of substrates over a broad range of temperatures and surface sliding rates up to 200cm/s
- *Applications*: solid and crystalline polymers, cured rubber, solid TPE, coatings, films, dry and wet lubricants

High-Speed Cut Growth/Fracture



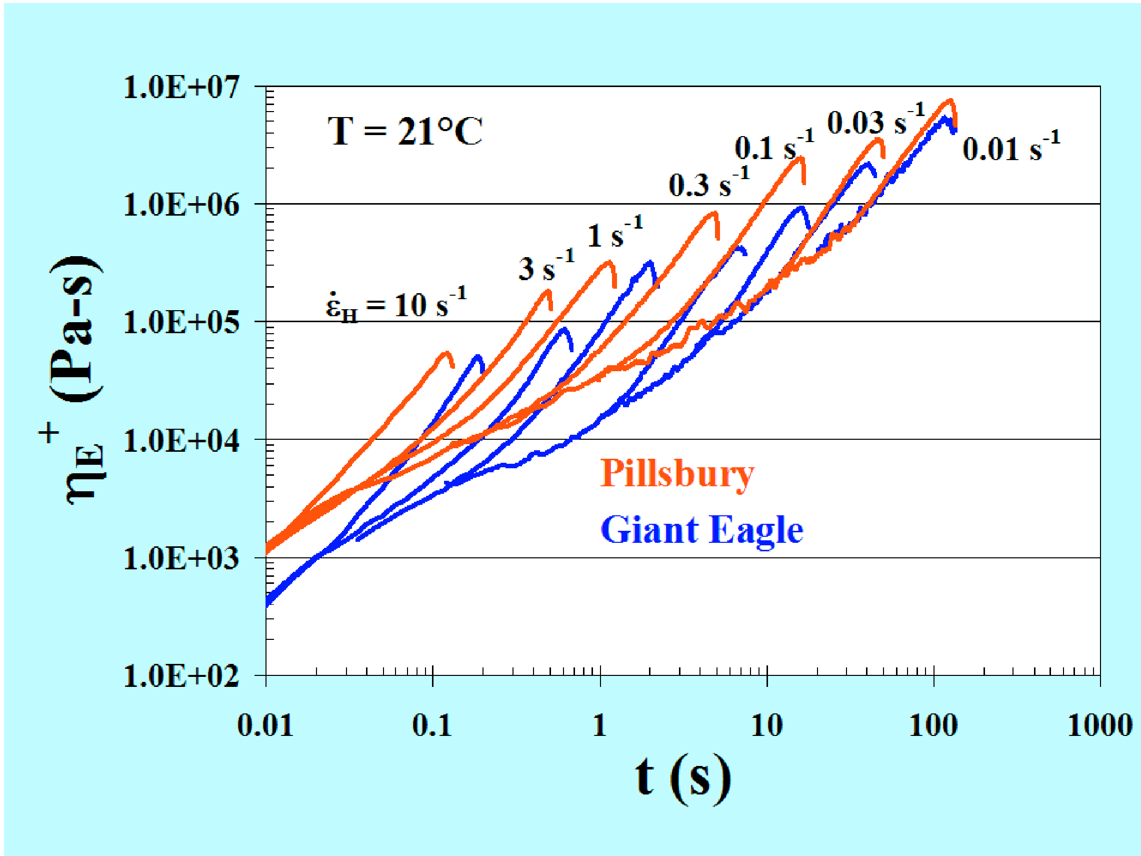


- Sample sizes from 25-150mg can be used to characterize high-speed material fracture properties over a broad range of temperatures and rates up to 200cm/s, rates relevant to impact fracture strength
- *Applications*: solid and crystalline polymers, cured rubber, solid TPE, thin gage elastic solids (metal foils, paper, etc.), coatings

Case Study 1: Extensional Flow Behavior of Dough

- The art of bread making was developed by primitive cultures thousands of years ago, yet even today bread dough is an extremely difficult material to characterize rheologically
- Conventional rheological methods and tools are often incapable of assessing the basic fundamental deformation behavior of dough and are far less capable of detecting subtle material variations
  - Slip is always present in simple shear
- Consider the following two commercial pizza doughs of similar composition and texture:
  - Pillsbury Classic Pizza Crust - exhibits recoil during sheeting
  - Giant Eagle Pizza Crust - tackier/tendency to stick to roll during sheeting

Case Study 1: Extensional Rheology Data



- Extensional rheology results with the SER clearly reveal significant material differences in the two products that elucidate observed processing behavior

Case Study 2: 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

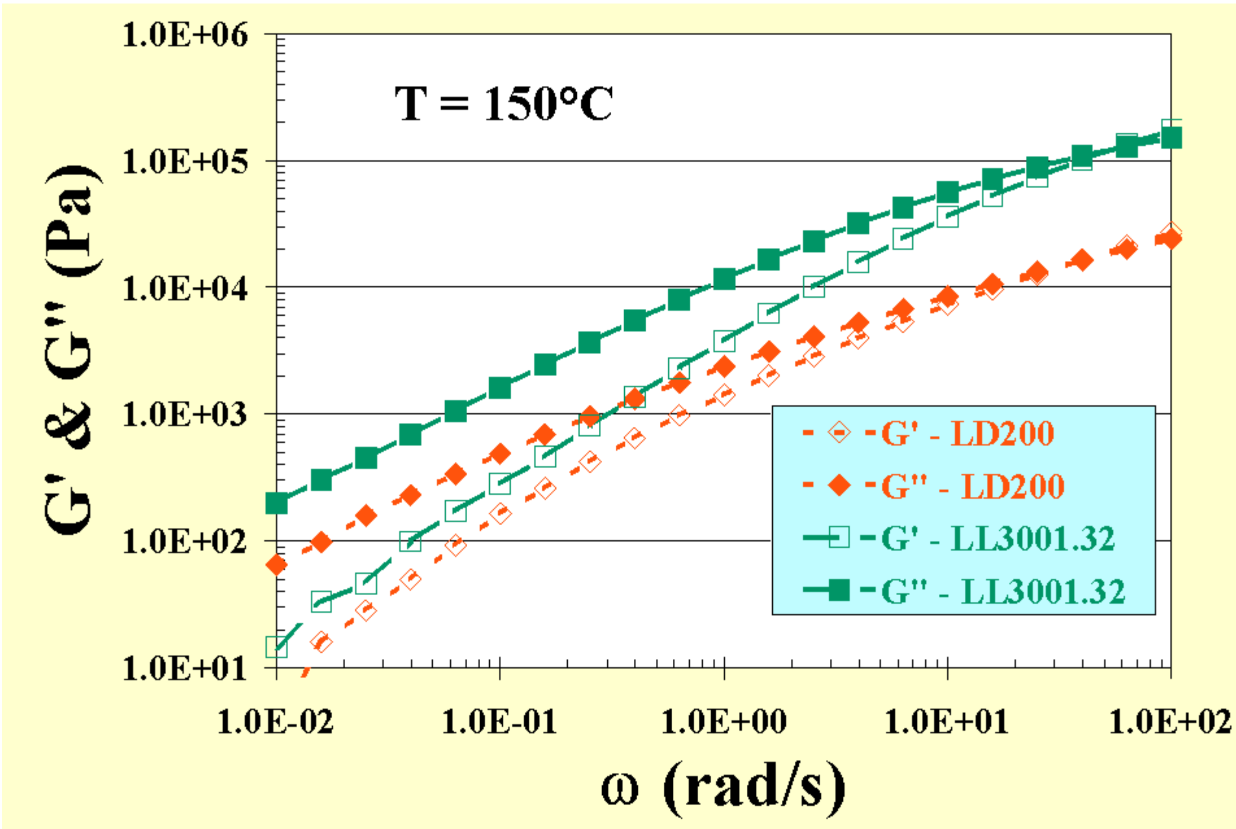
  - EF606: Film Grade LDPE (Westlake Polymers), MI = 2.2
  - Exact 3128: Film Grade m-LLDPE (ExxonMobil), MFI = 1.2

  Part 2

- ***Exercise:***

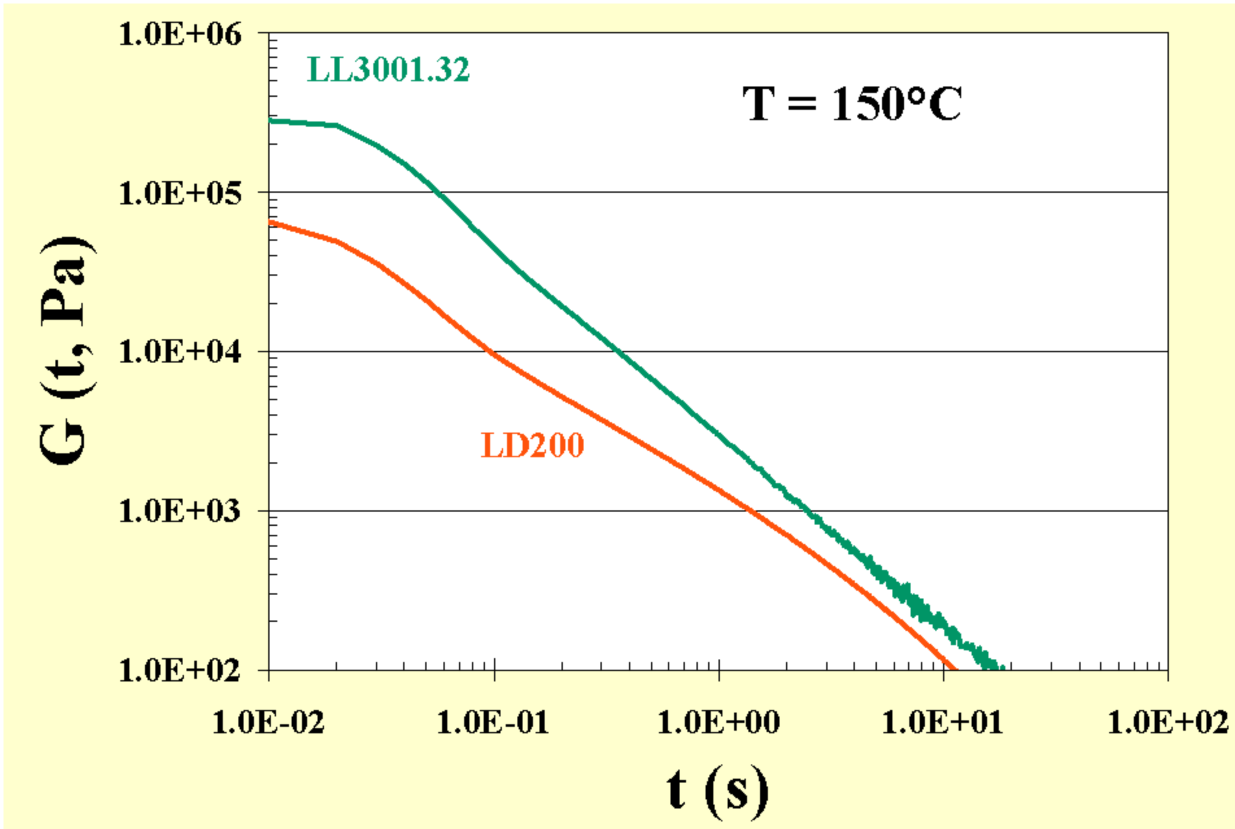
Detect differences in polymer macrostructure between these four commercial polymers without having any specific macrostructural information about them a priori.

Case Study 2: Part 1 - SAOS Data



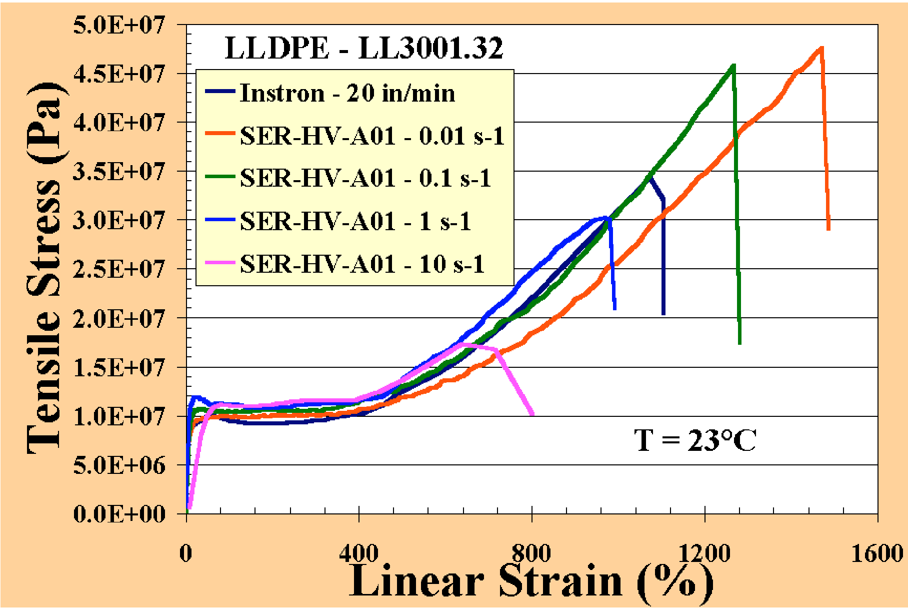
- Despite some notable indications of MW very little can be clearly distinguished between polymer branching and MWD effects from the SAOS data alone.

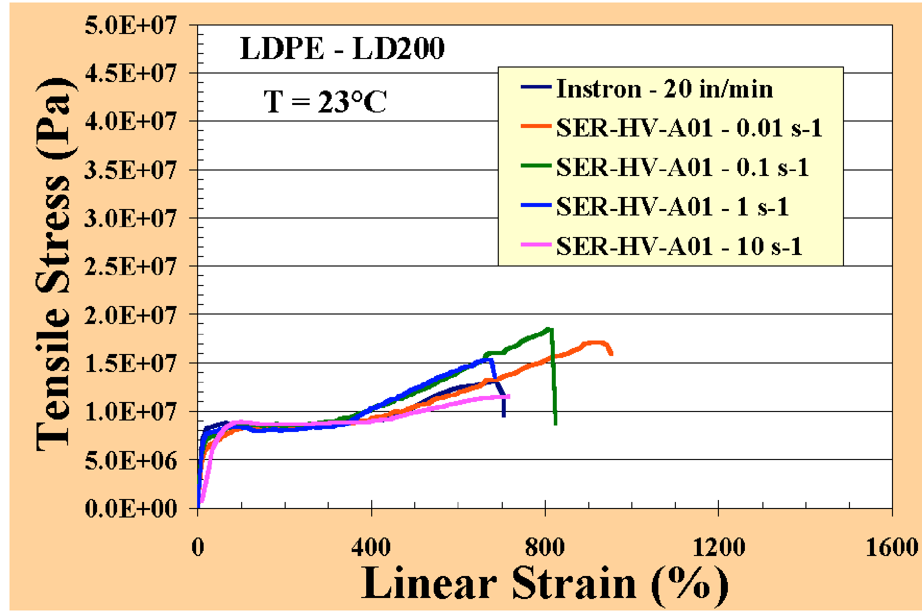
Case Study 2: Part 1 - LVE Shear Relaxation Data



- 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.

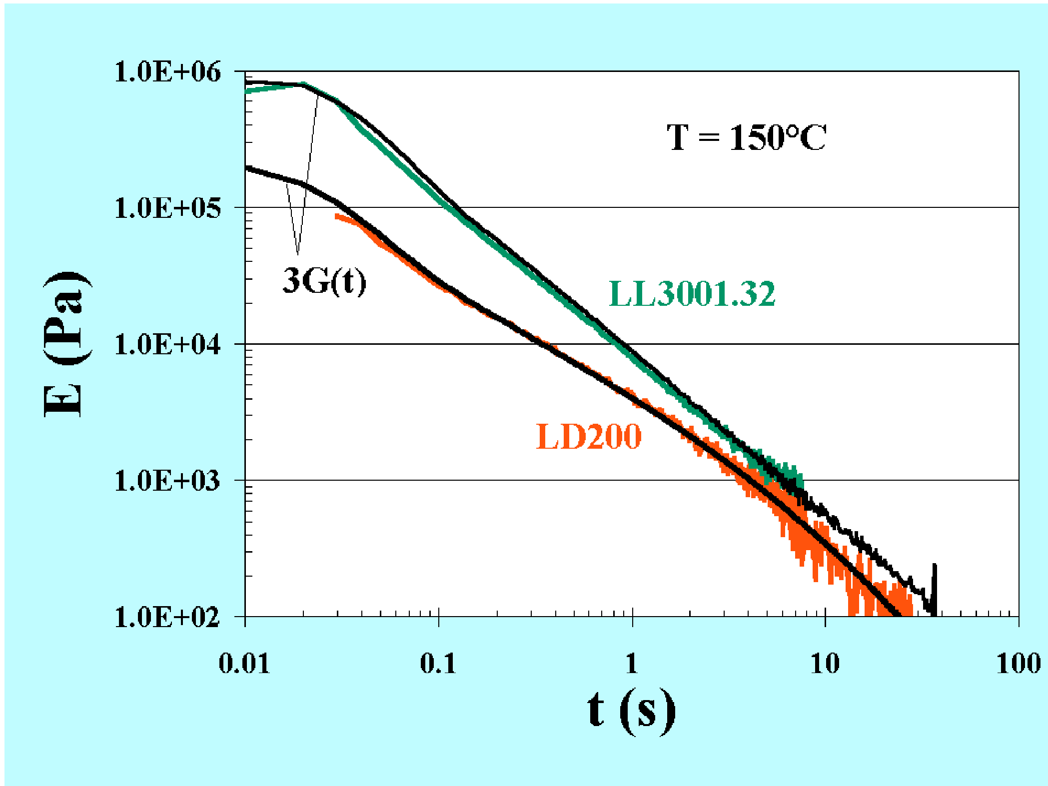
Case Study 2: Part 1 - Tensile Behavior





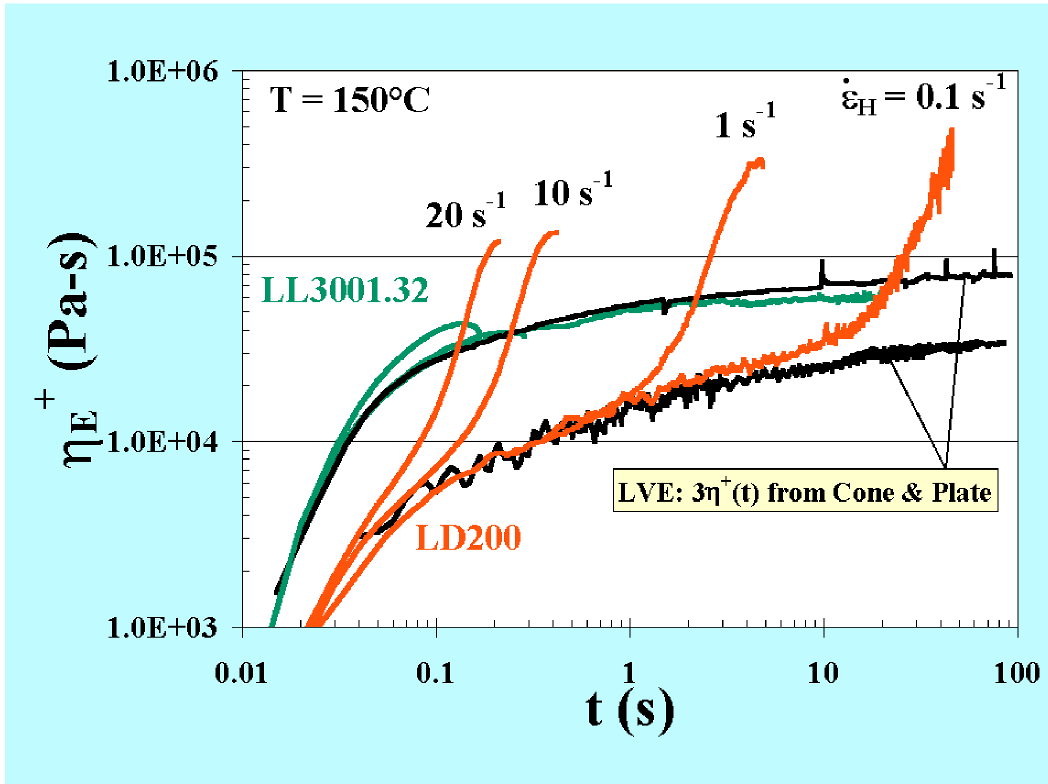
- A much higher degree of strain crystallization is exhibited with the LLDPE - behavior consistent with linear polymer structure, although hardly conclusive

Case Study 2: Part 1 - LVE Extensional Relaxation Data



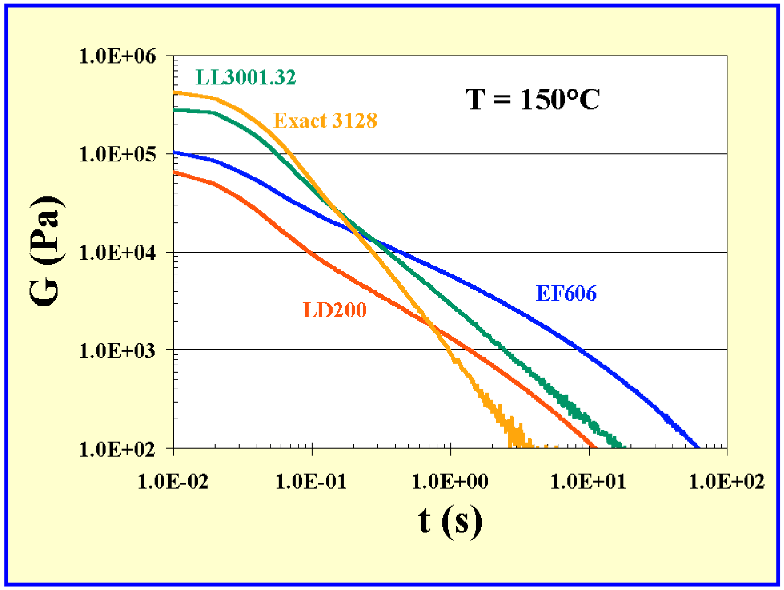
- Despite excellent agreement between the LVE extension and shear data, again very little can be clearly distinguished between polymer branching and MWD effects from the LVE data alone.

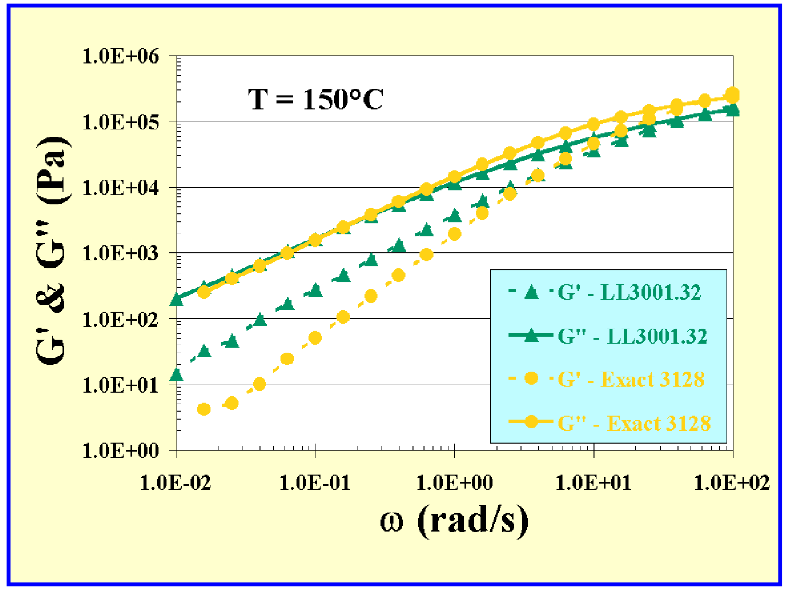
Case Study 2: Part 1 - Tensile Stress Growth



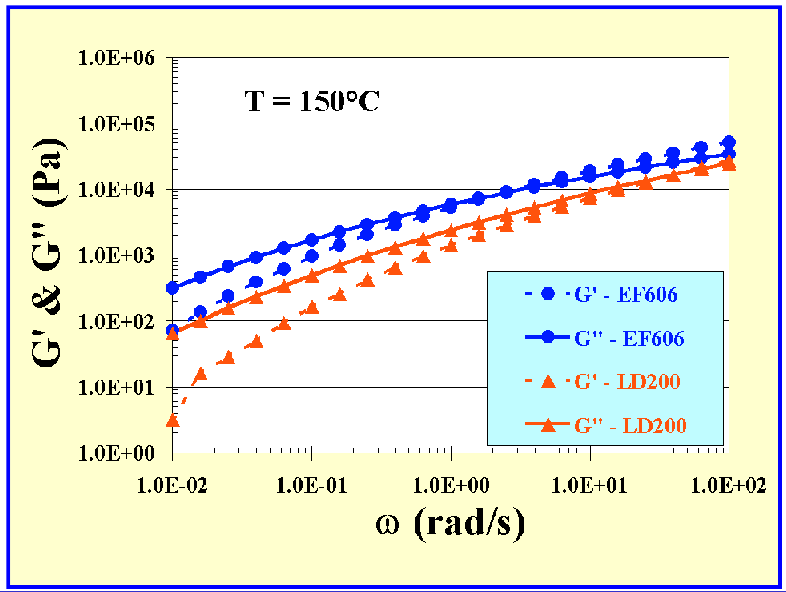
- Note how the tensile stress growth data can clearly distinguish macrostructural features related to branching and MWD - the LDPE exhibits significant strain hardening, behavior consistent with highly branched polymers

Case Study 2: Part 2 - LVE Data



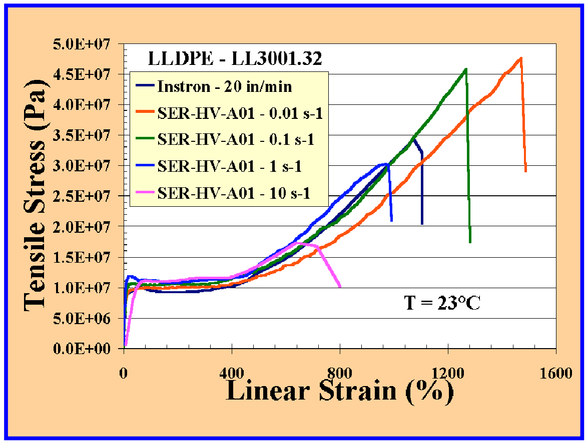


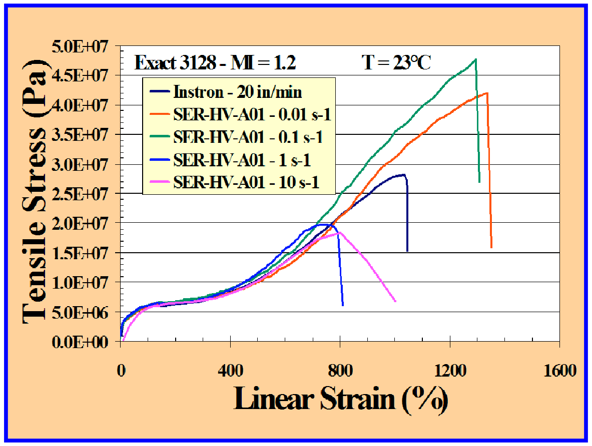
- Again, despite some indications of MW & MWD very little with regard to macrostructural features such as polymer branching can be concluded from the LVE data alone.

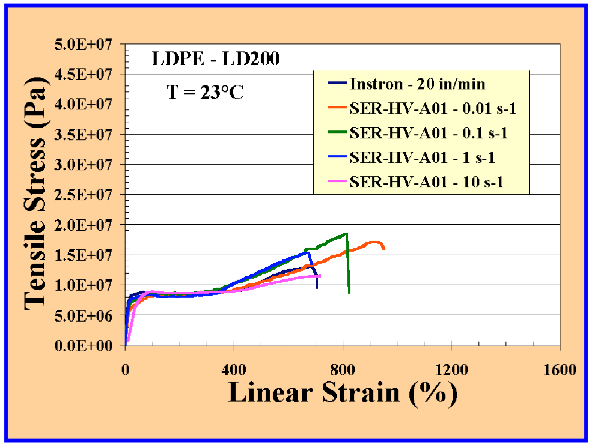


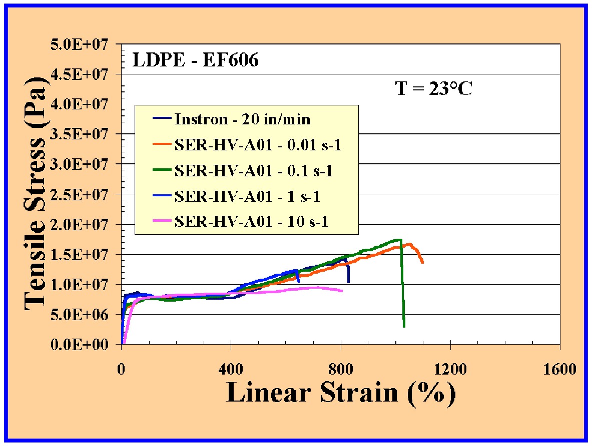
Case Study 2: Part 2 - Tensile Behavior

- A much higher degree of strain crystallization is exhibited with the LLDPEs - behavior consistent with linear polymer structure
- Very few conclusions can be drawn from the tensile behavior of the two LDPEs.



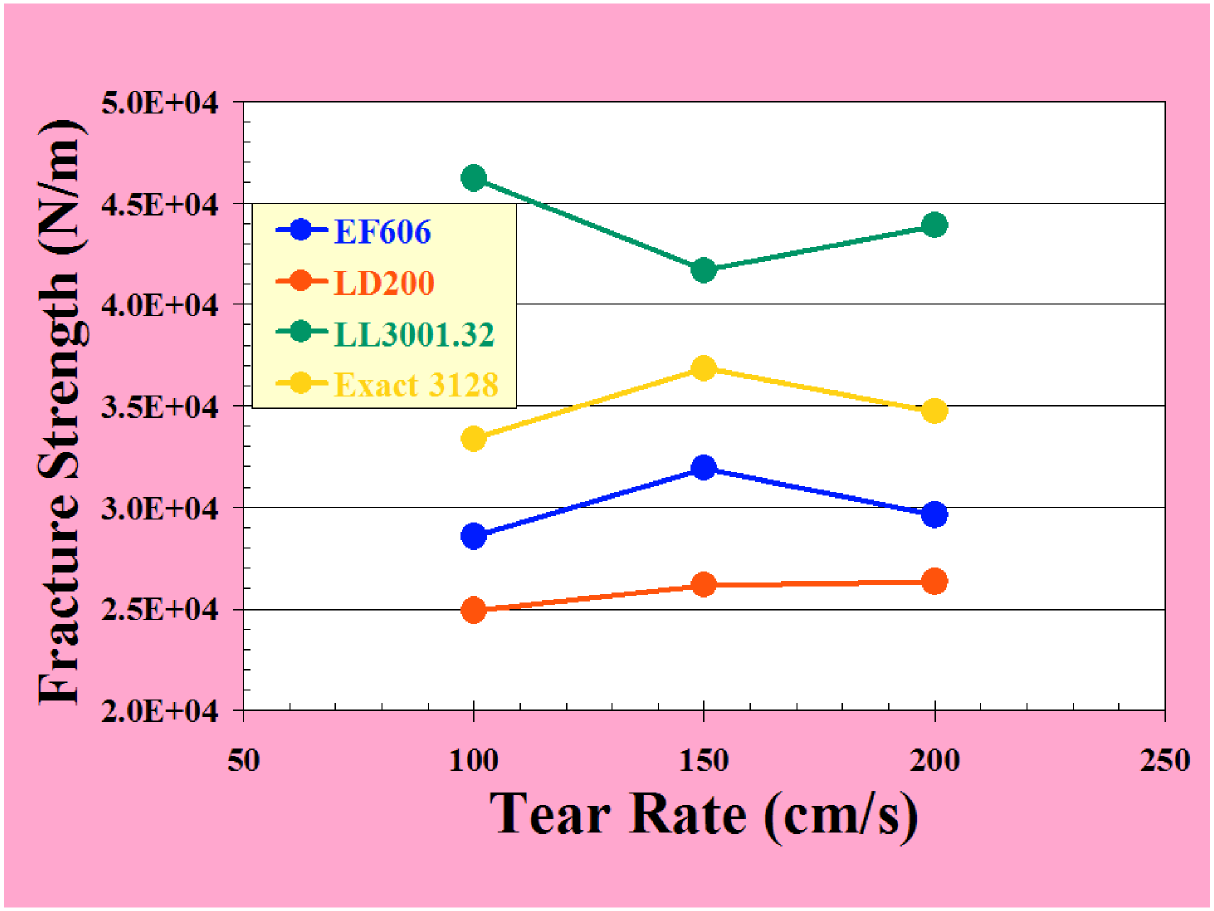




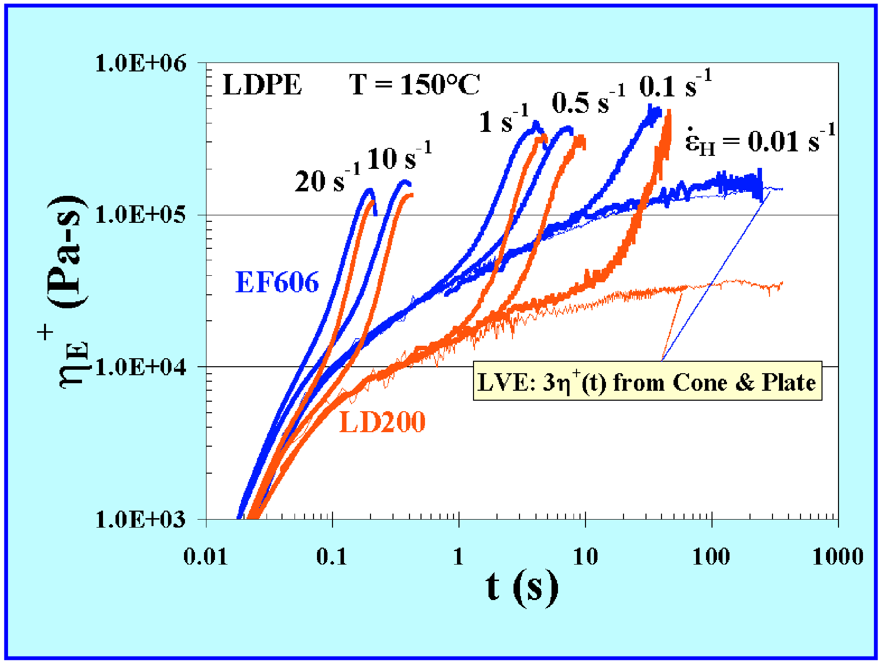


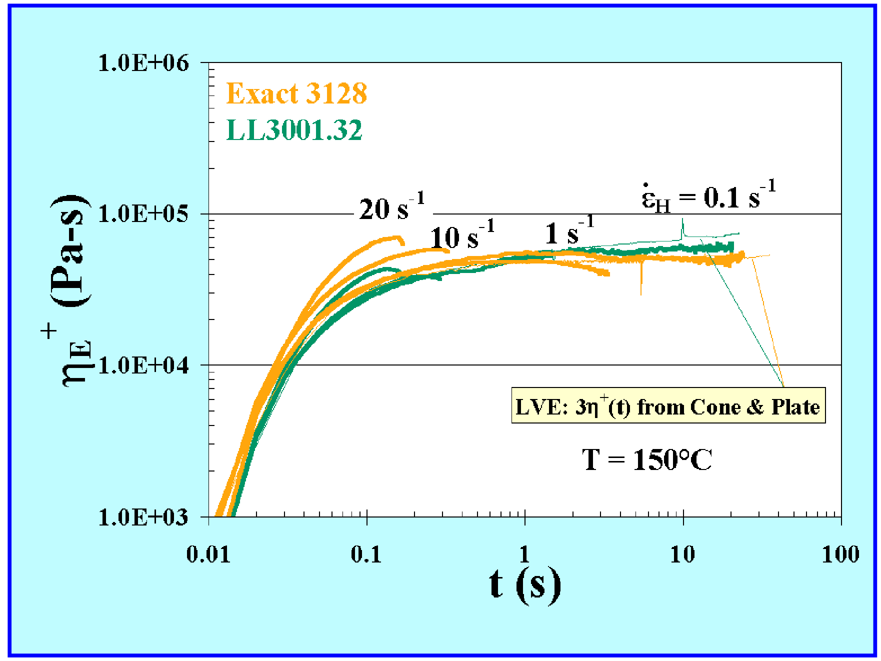
Case Study 2: Part 2 - Fracture Behavior

- Although there is a general trend and the fracture strength behaviors are consistent with the reported tear strengths of the polymers there is no definitive evidence with regard to polymer macrostructure



Case Study 2: Part 2 - Tensile Stress Growth

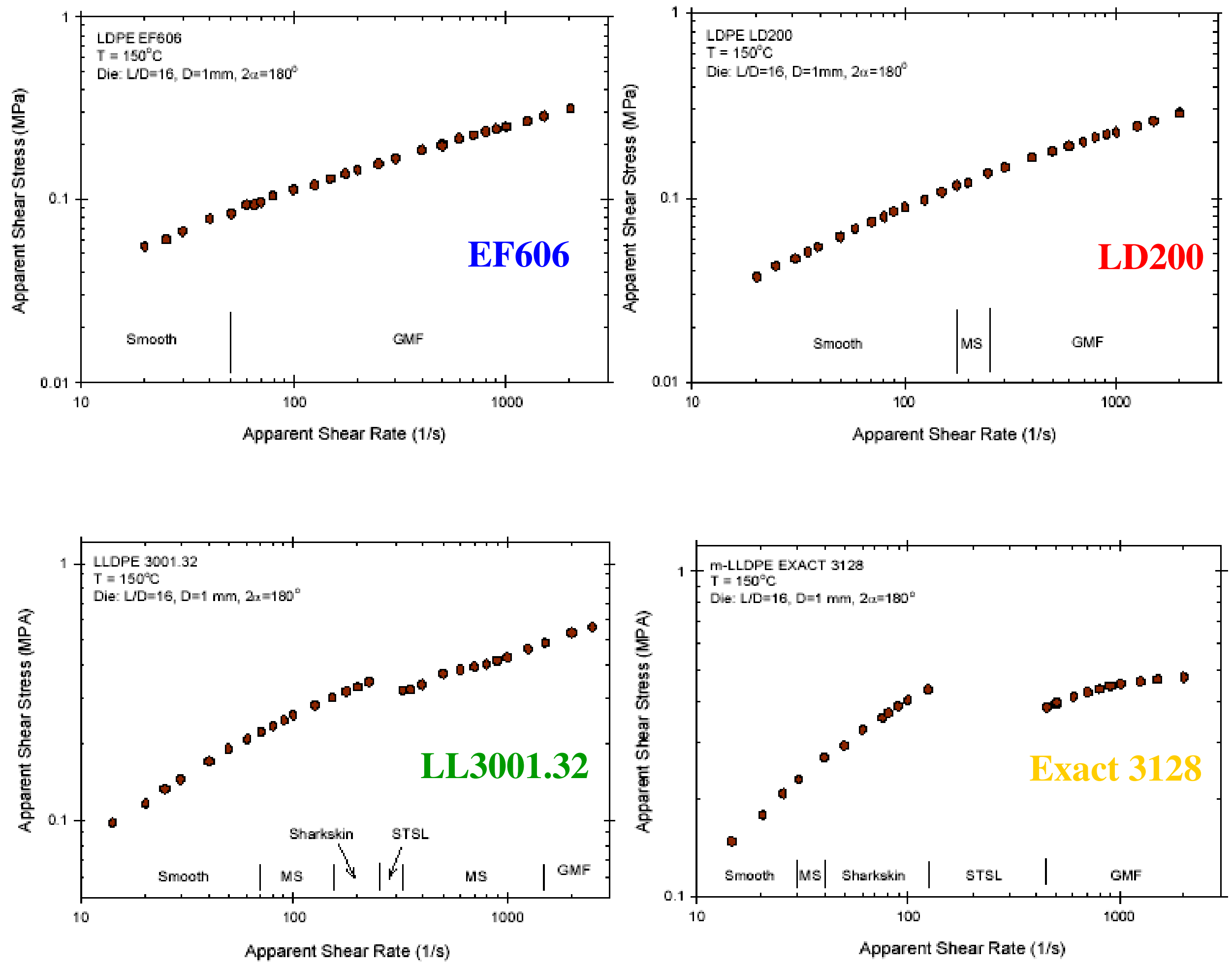




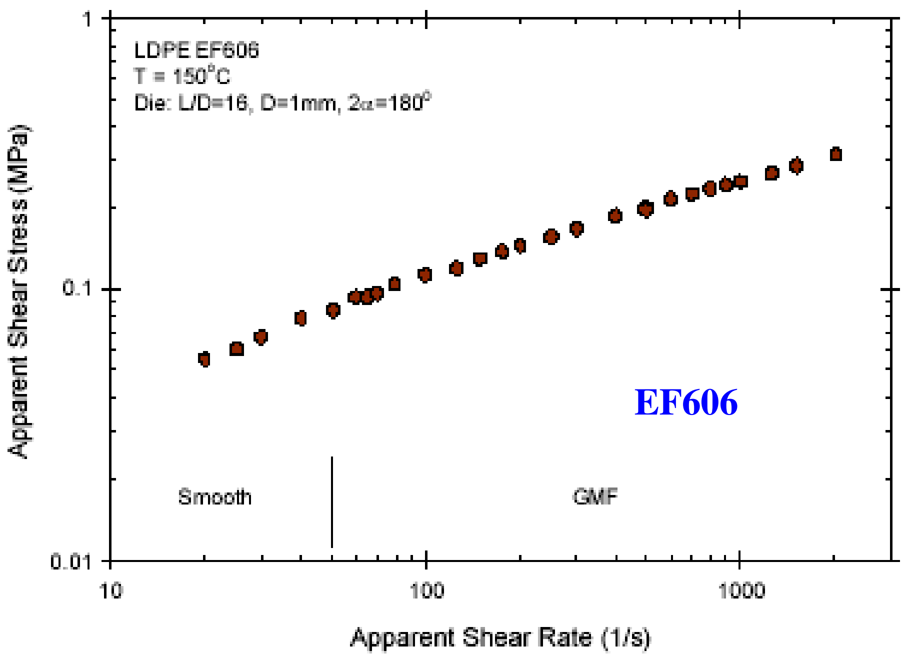
- Note how the tensile stress growth data can clearly differentiate subtle differences in branching as witnessed by the different strain hardening behaviors detected between the two grades of LDPE as well as differences in high-rate melt elasticity with the two LLDPEs

Case Study 3: Insight Into Processing Behavior

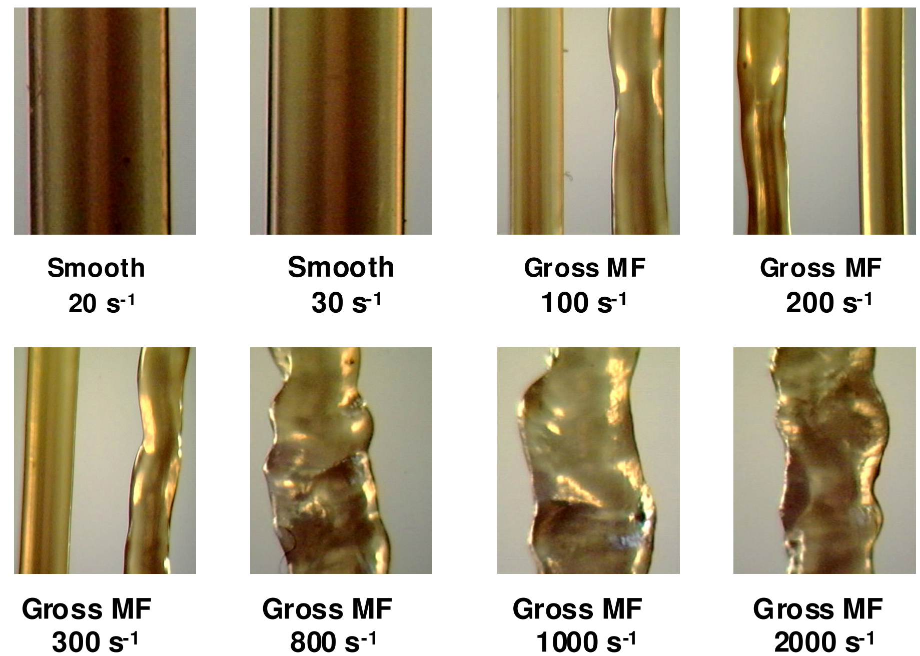
- LLDPE exhibits far different extrusion behavior than LDPE although the mechanisms for this behavior have remained a mystery (flow curve data courtesy of E. Muliawan and Prof. S.G. Hatzikiriakos, UBC)



Case Study 3: LDPE EF606 Melt Processing Behavior



LDPE EF606 @ 150°C

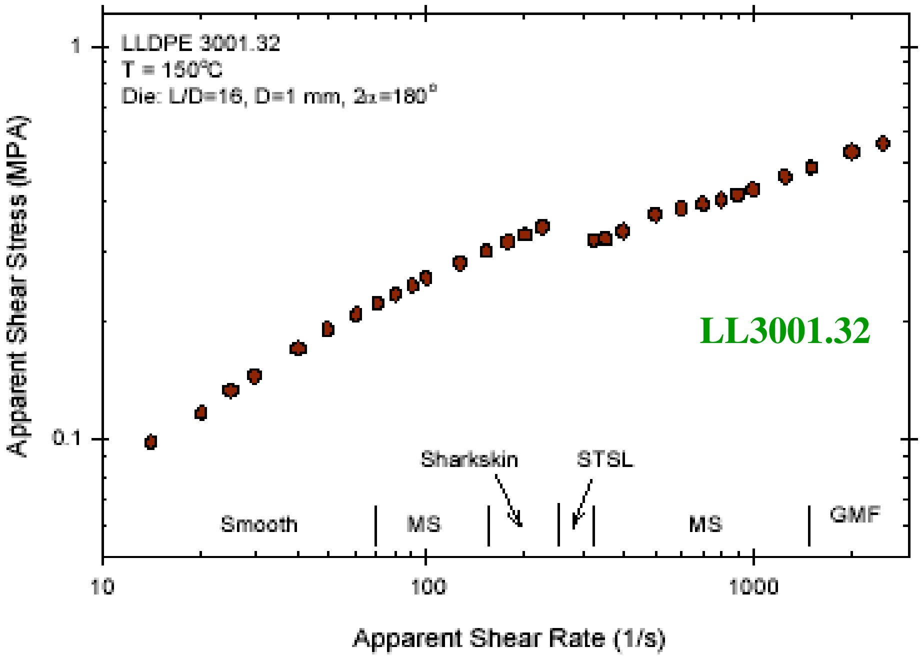


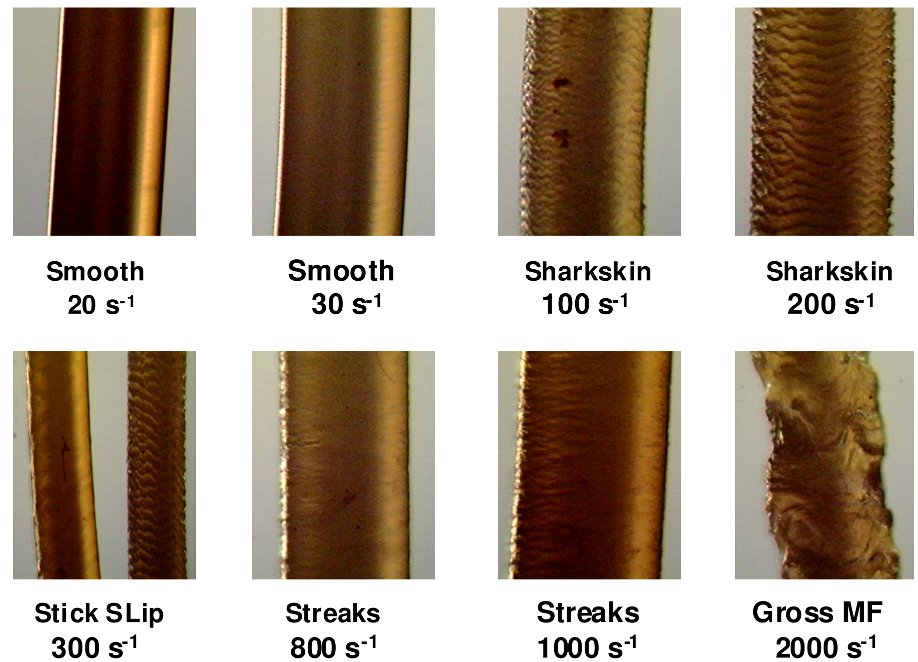
Data and images courtesy of E. Muliawan and Prof. S.G. Hatzikiriakos, UBC

Note the continuity of the apparent flow curve and the early onset of gross melt fracture

Case Study 3: LLDPE LL3001.32 Melt Processing Behavior

LLDPE LL3001.32 @ 150°C



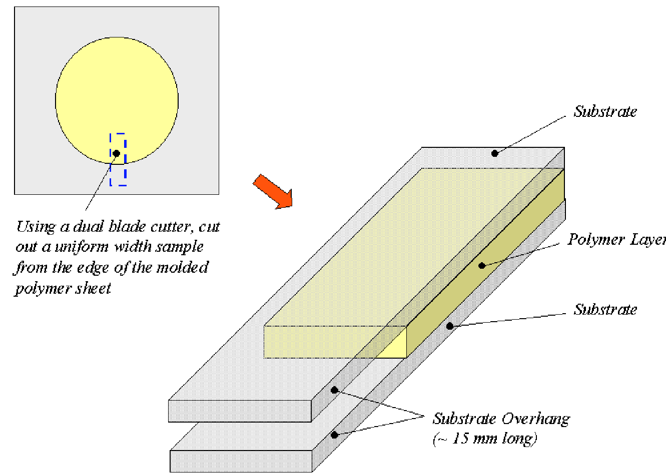


Data and images courtesy of E. Muliawan and Prof. S.G. Hatzikiriakos, UBC

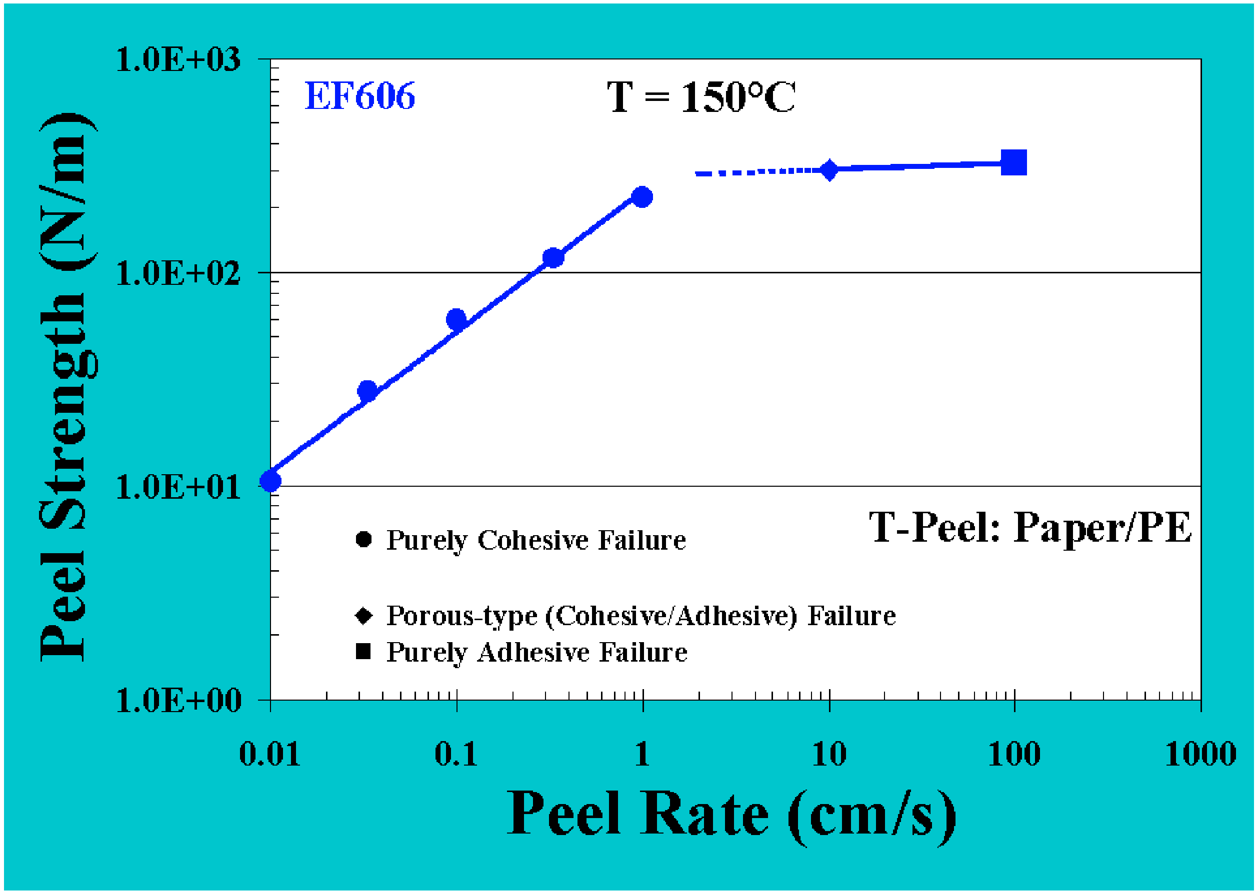
Note the discontinuity in the apparent flow curve and the corresponding zones of extrusion behavior - sharkskin, stick slip, gross melt fracture

Case Study 3: T-Peel/Adhesion Behavior

- 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

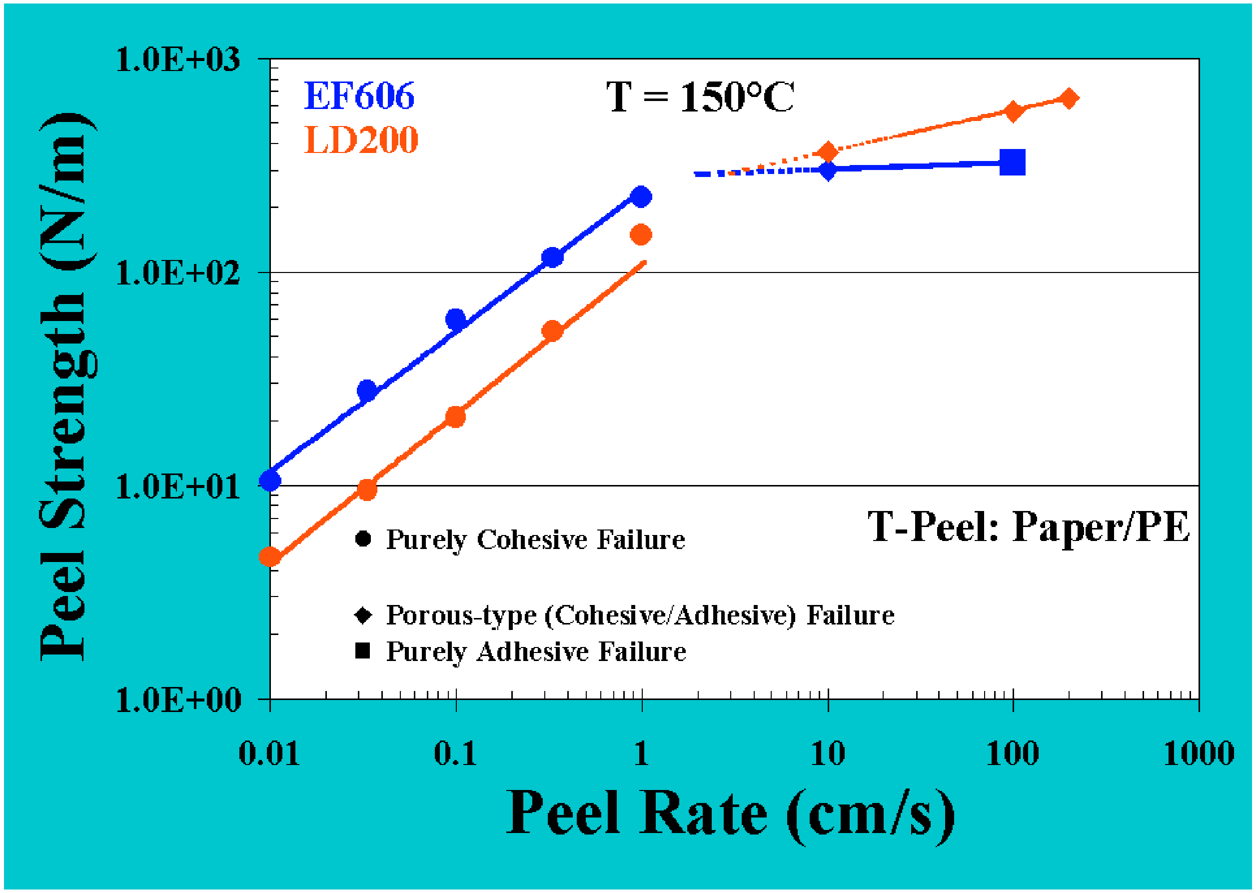


Case Study 3: Peel/Adhesion Data



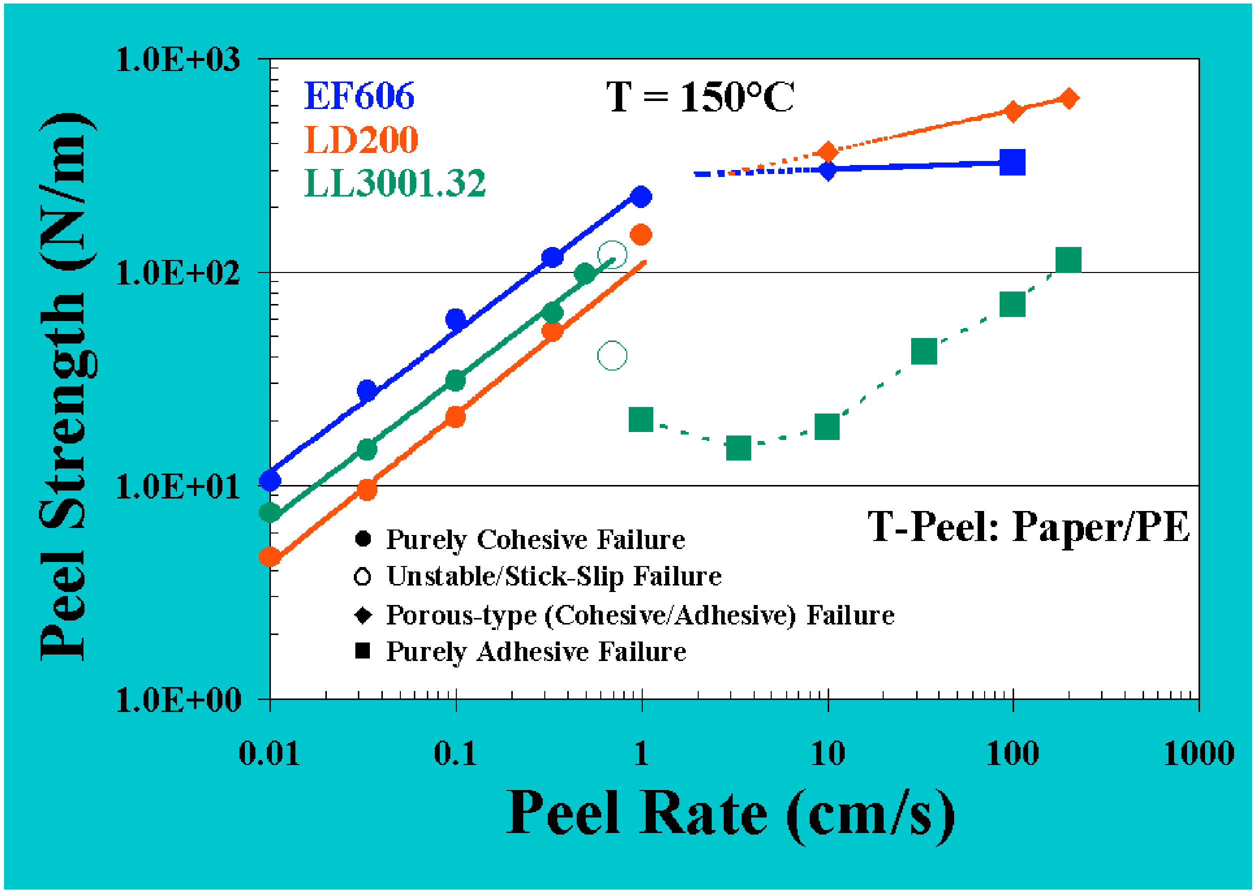
- The peel strength curve of the film grade LDPE (EF606) has very distinct regions of peel behavior as indicated

Case Study 3: Peel/Adhesion Data



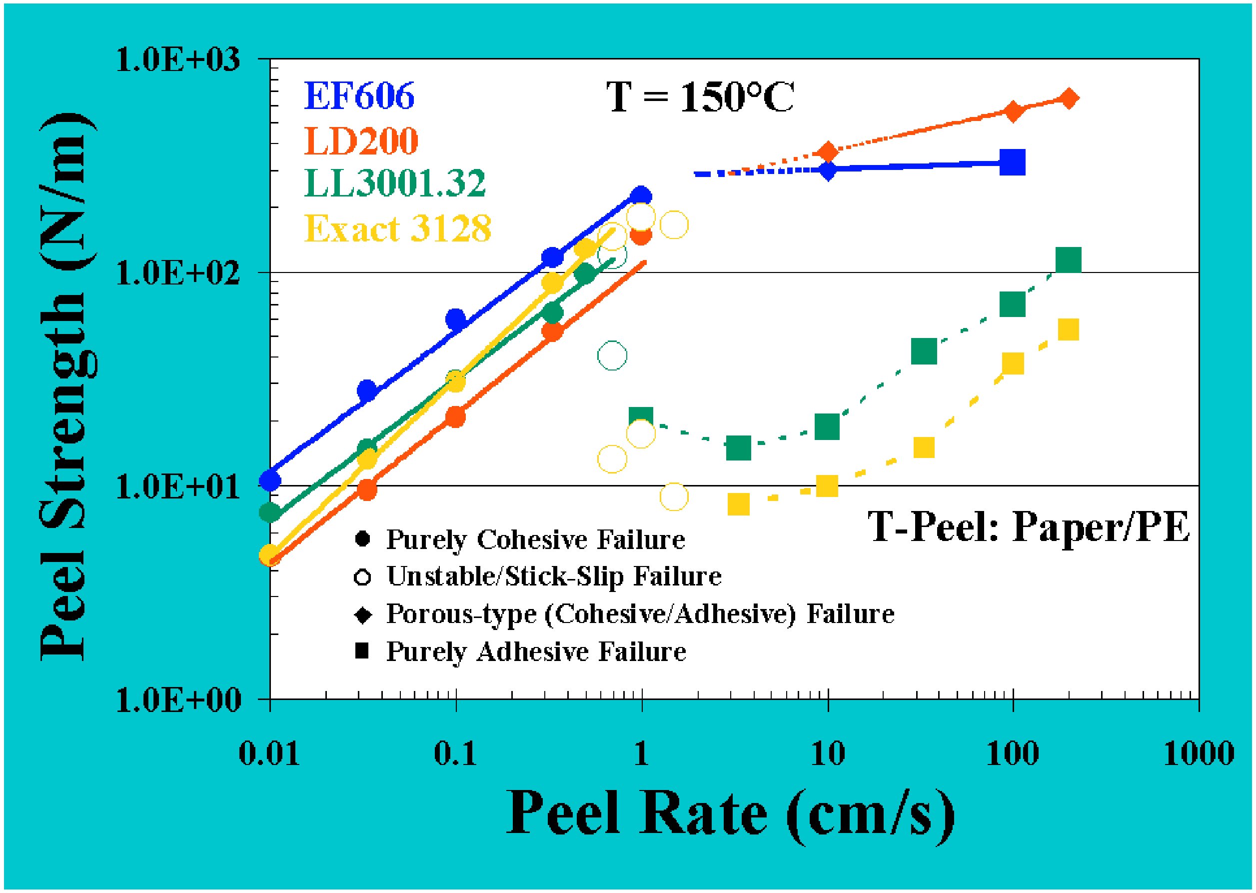
- The coating grade LDPE (LD200) also has a distinct “break” in the peel strength curve but exhibits superior peel strength to EF606

Case Study 3: Peel/Adhesion Data



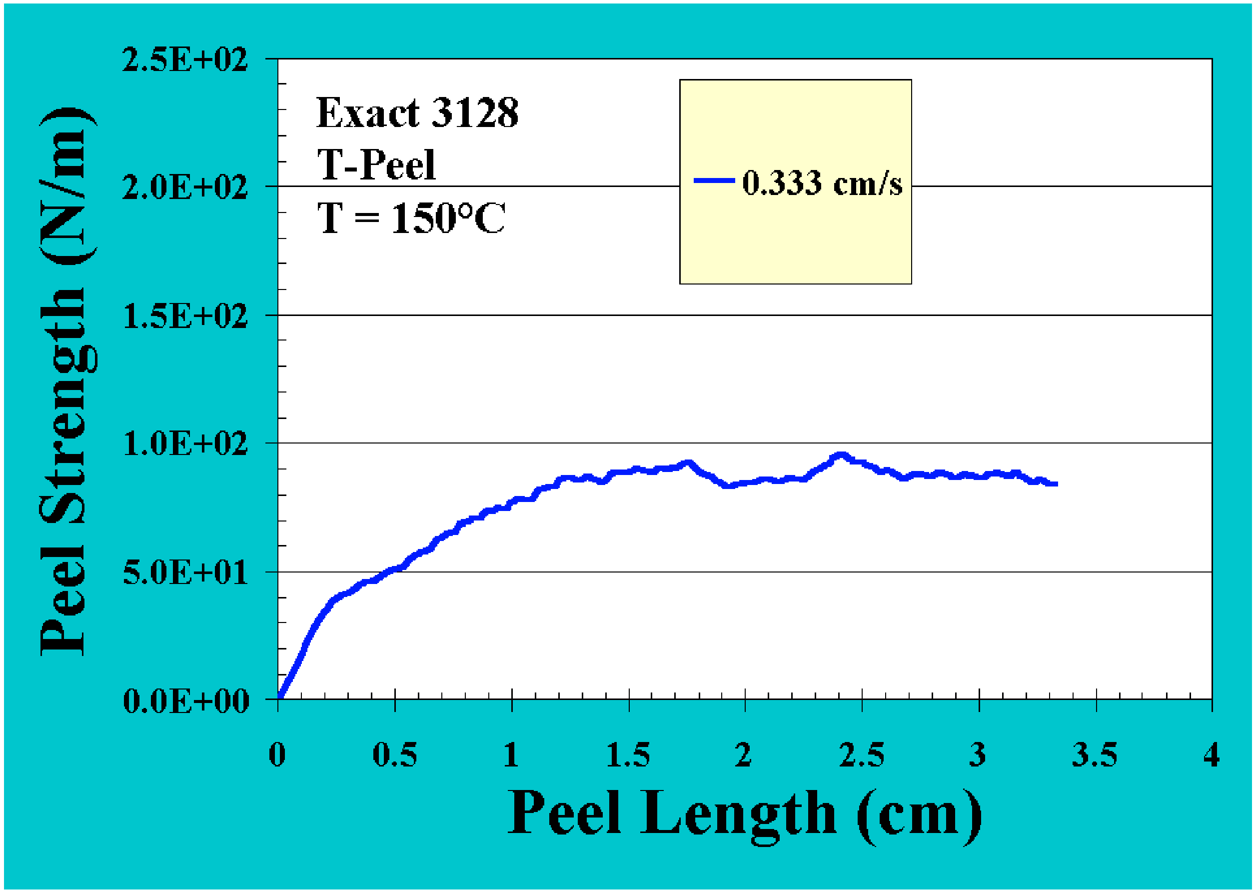
- The LLDPE (LL3001.32) exhibits an unstable region of peel behavior that appears qualitatively similar to stick/slip flow behavior

Case Study 3: Peel/Adhesion Data



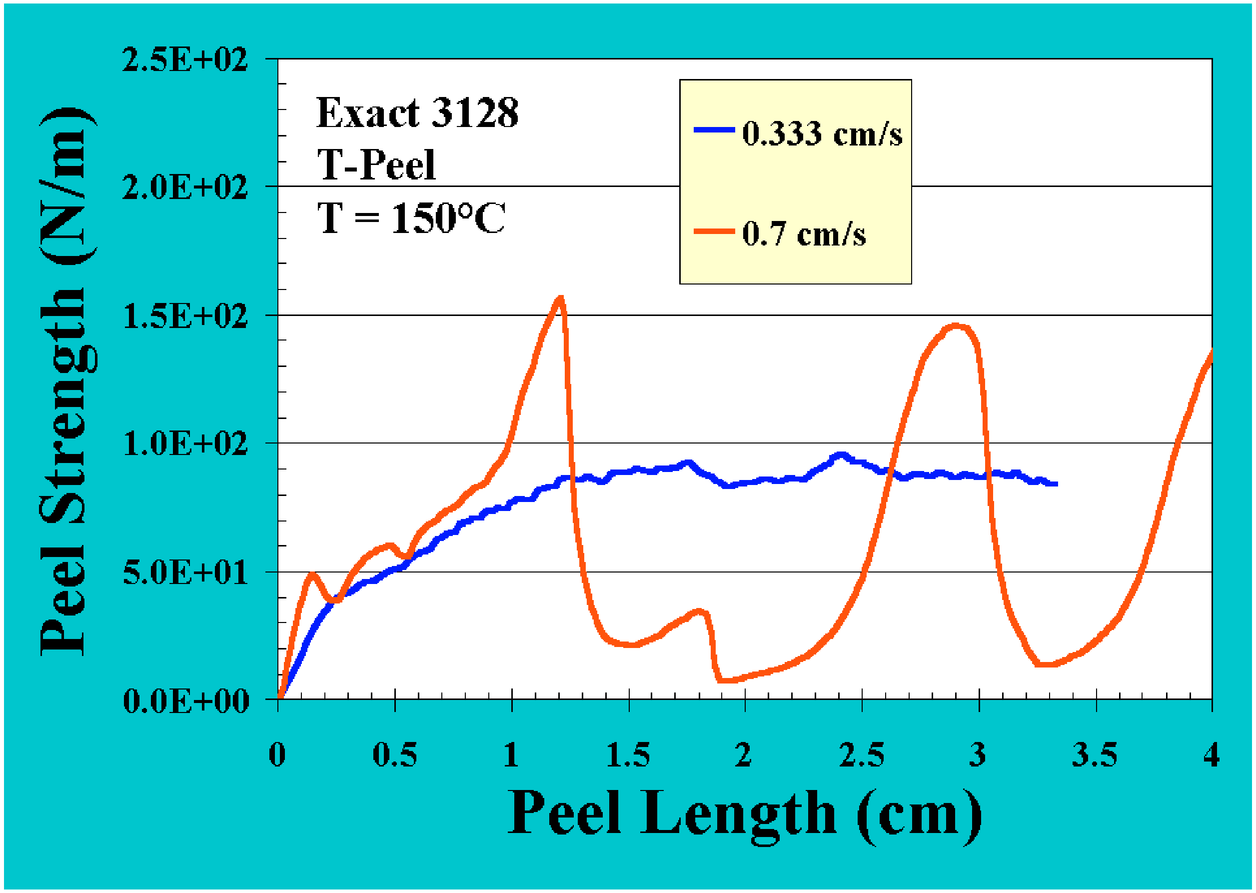
- Exact 3128 exhibits a larger region of peel instability that is very similar to its stick/slip flow behavior in extrusion

Case Study 3: Exact 3128 Peel Traces



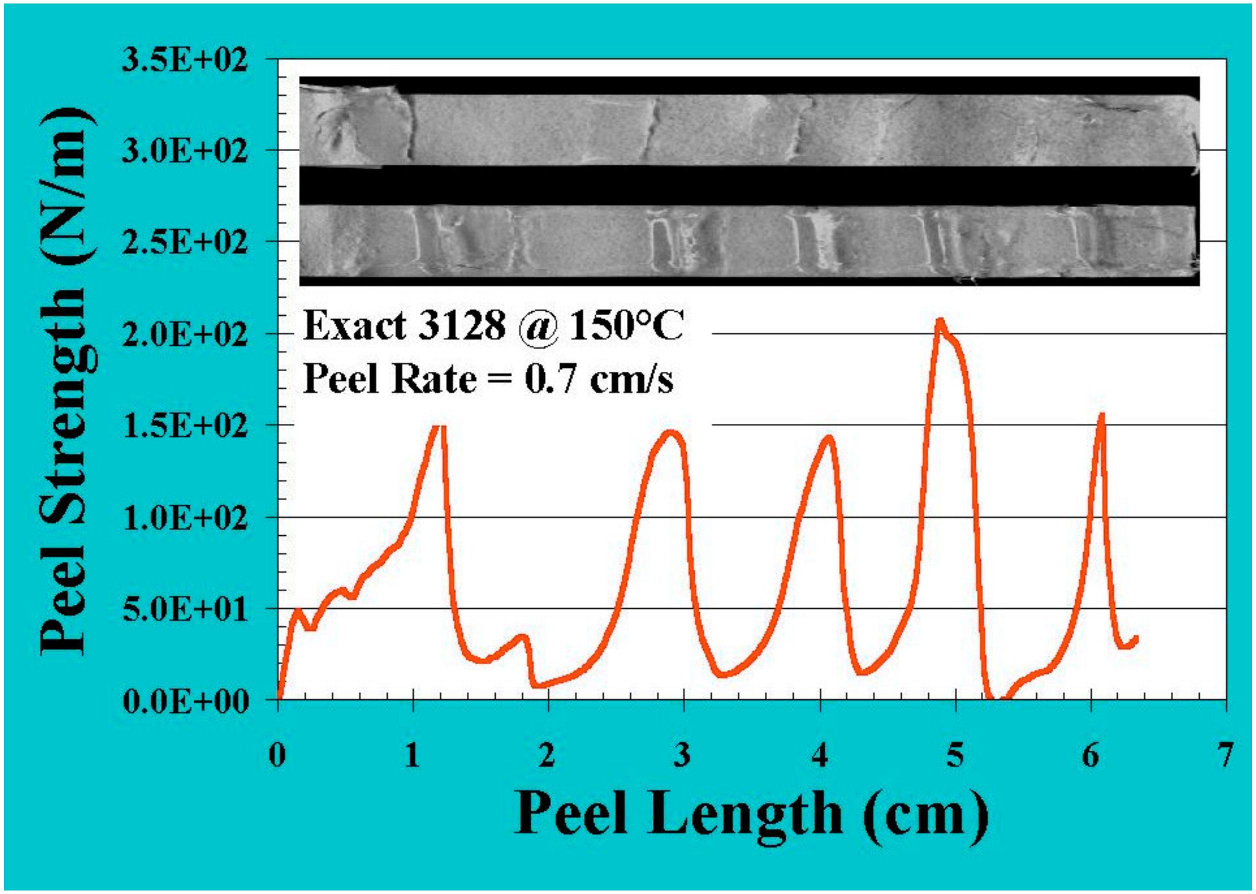
- At a peel rate of 0.333 cm/s, the peel strength trace for Exact 3128 is stable and the peel failure is purely cohesive.

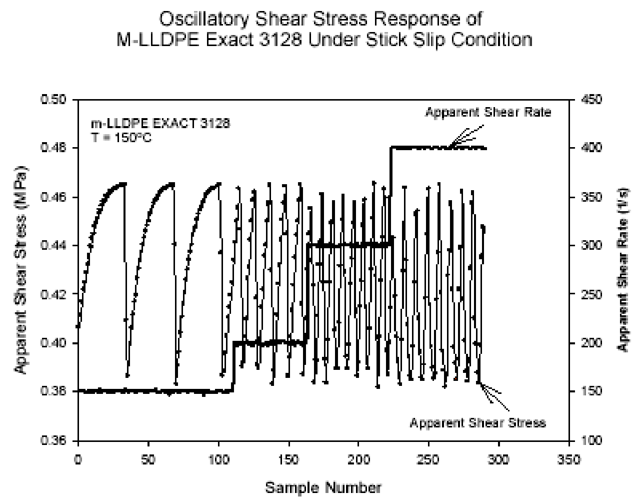
Case Study 3: Exact 3128 Peel Traces



- At a peel rate of 0.7 cm/s, the peel strength trace for Exact 3128 becomes unstable as well as the mode of failure.

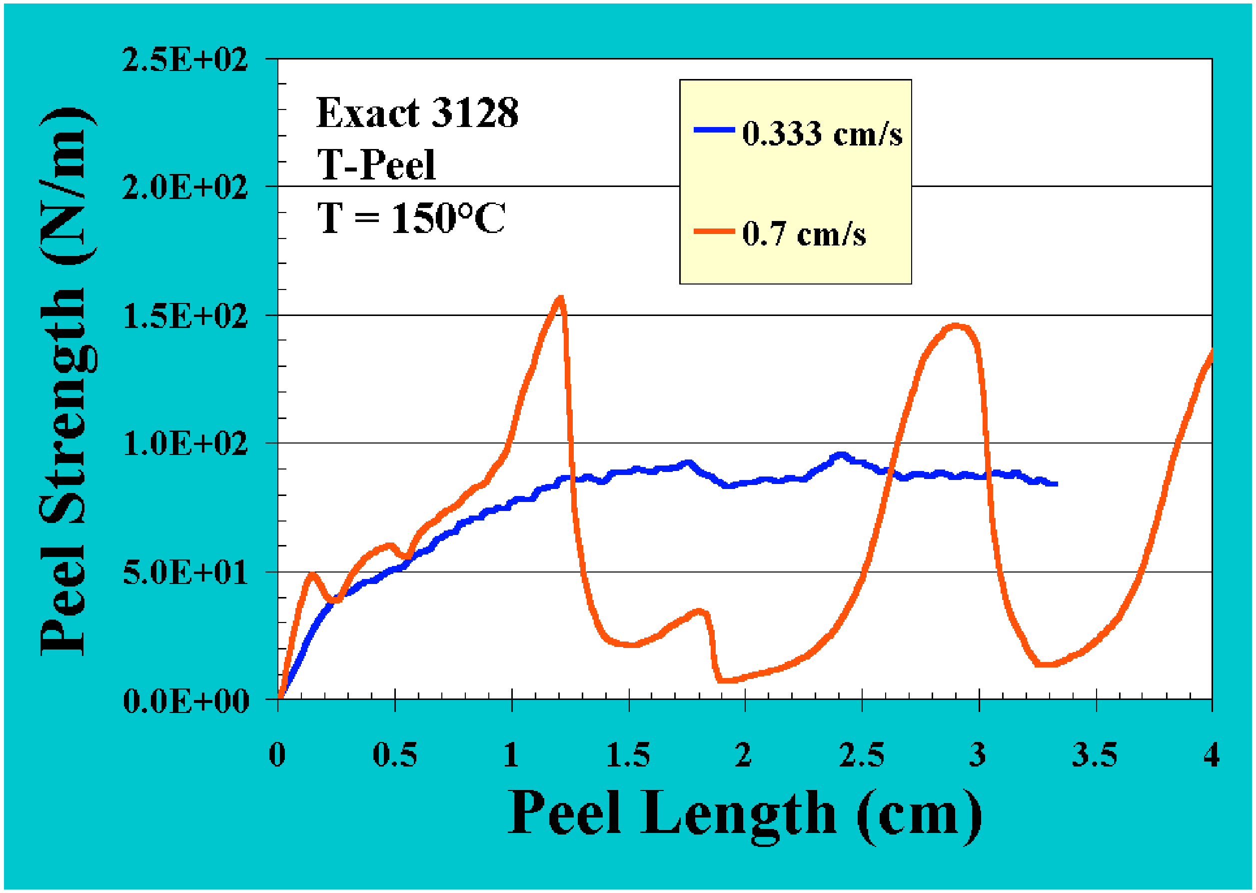
Case Study 3: Exact 3128 Peel Traces





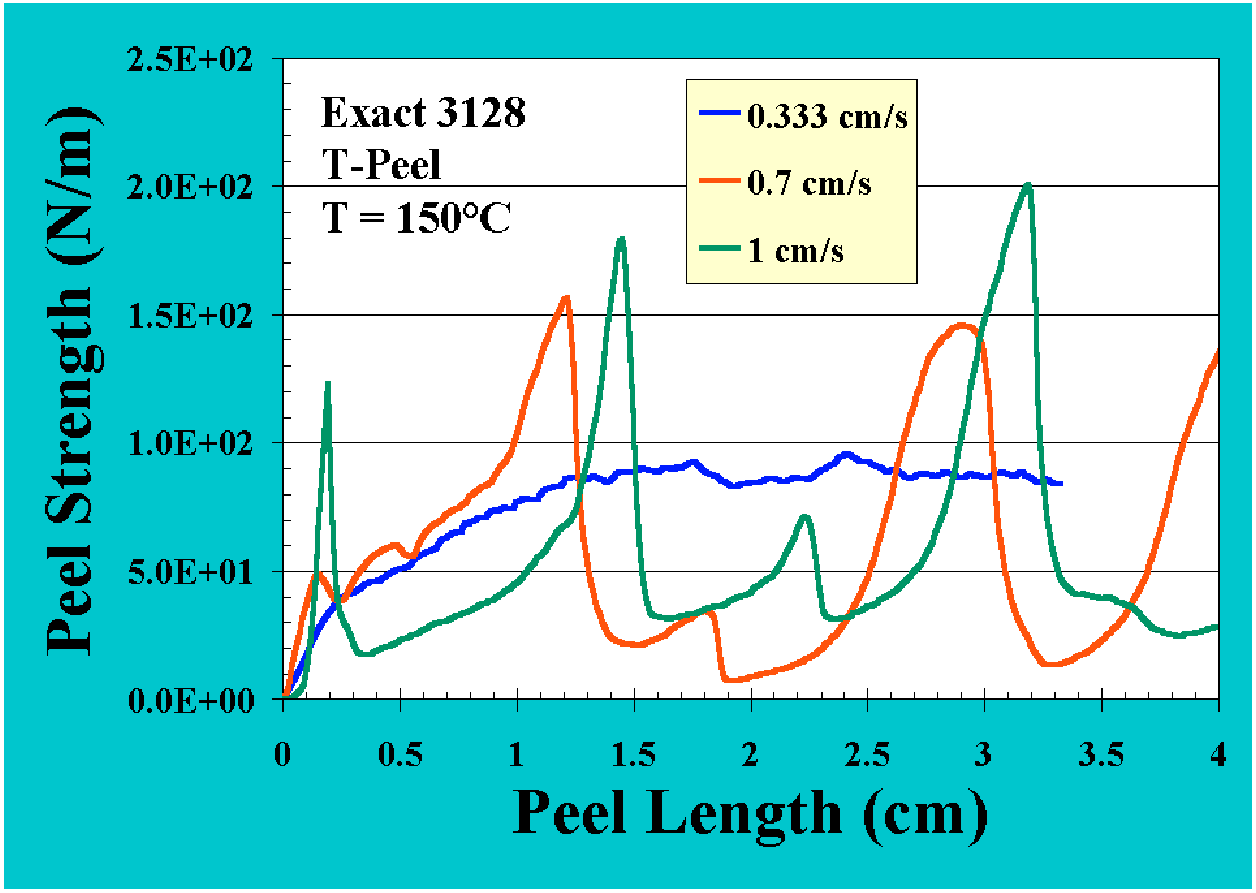
- The peaks in the peel strength trace correspond to cohesive modes of failure and are abruptly followed by troughs corresponding to adhesive modes of failure.

Case Study 3: Exact 3128 Peel Traces



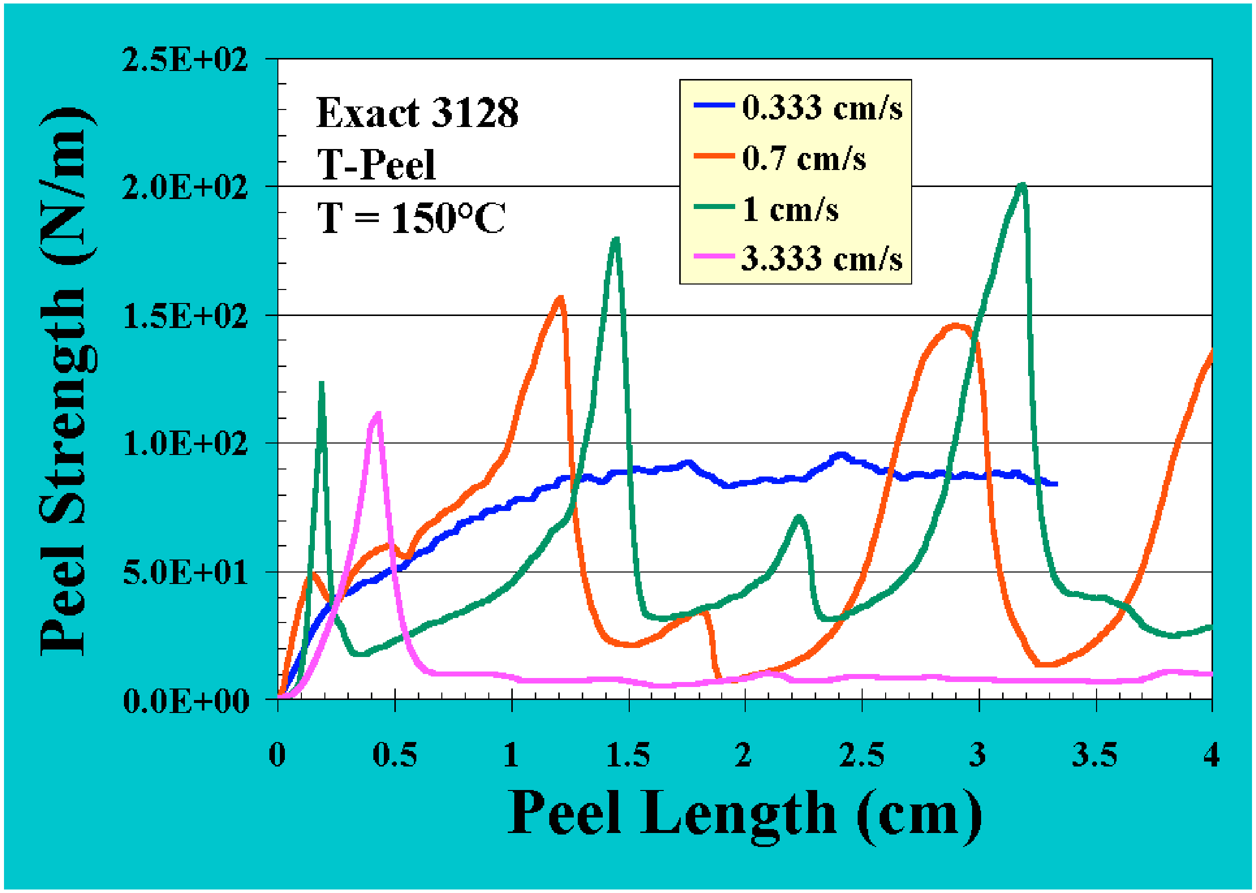
- At a peel rate of 0.7 cm/s, the peel strength trace for Exact 3128 becomes unstable as well as the mode of failure.

Case Study 3: Exact 3128 Peel Traces



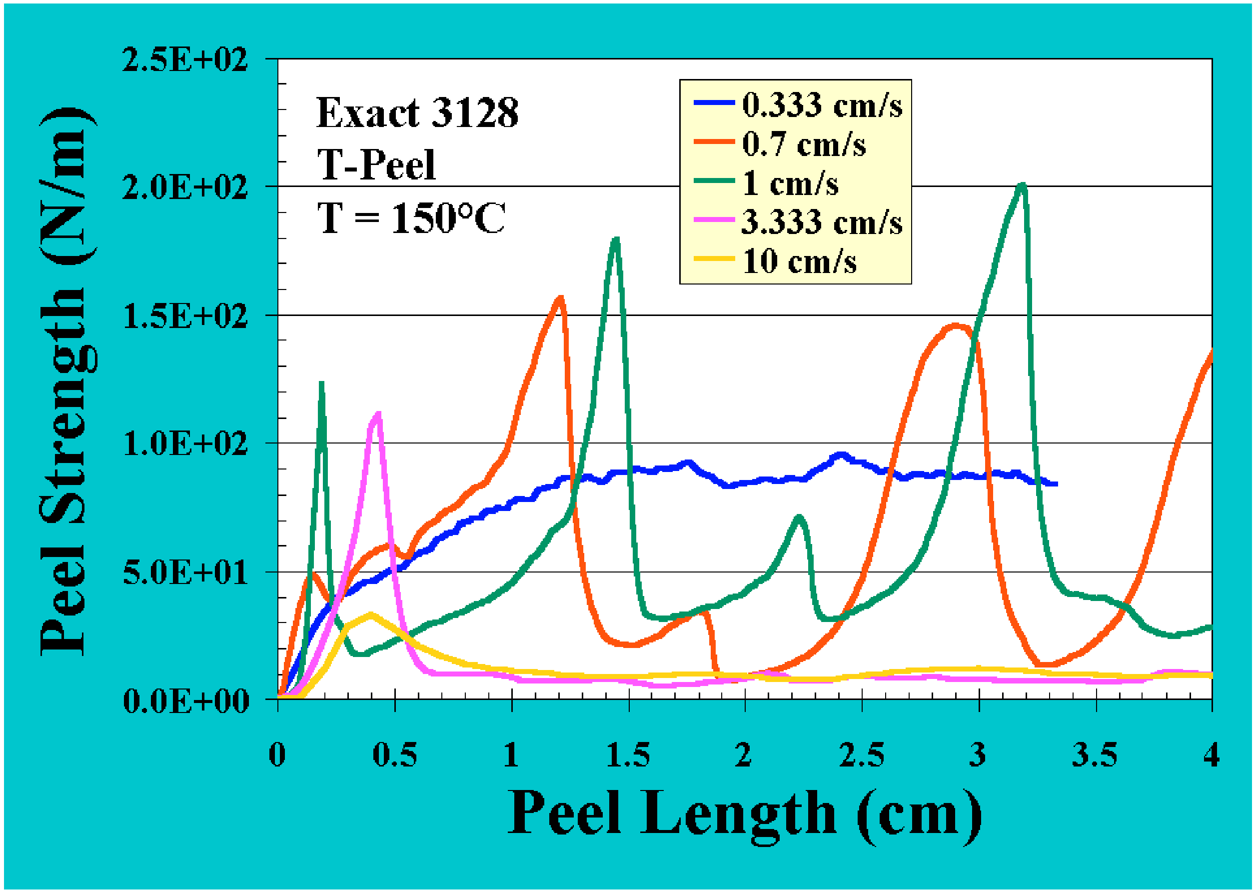
- At a peel rate of 1 cm/s, the peel strength trace and mode of failure remains unstable.

Case Study 3: Exact 3128 Peel Traces



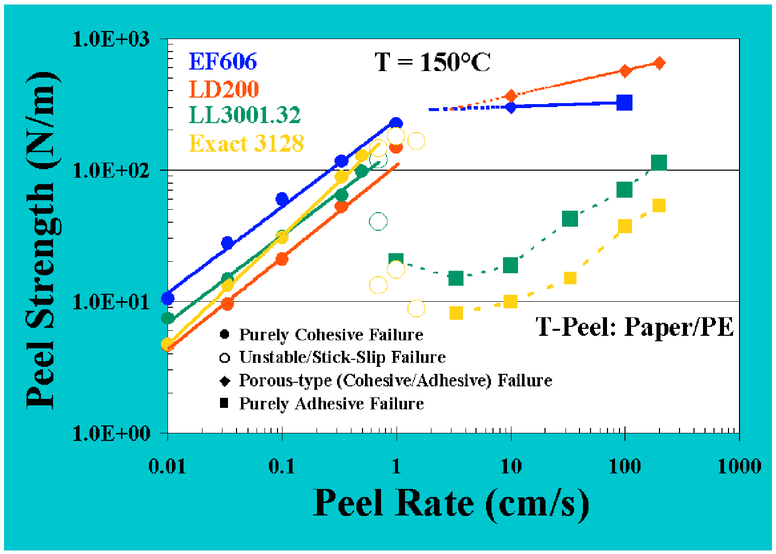
- At a peel rate of 3.333 cm/s, the peel strength trace exhibits a brief peak followed by a significant drop in signal that remains steady - the mode of failure is purely adhesive.

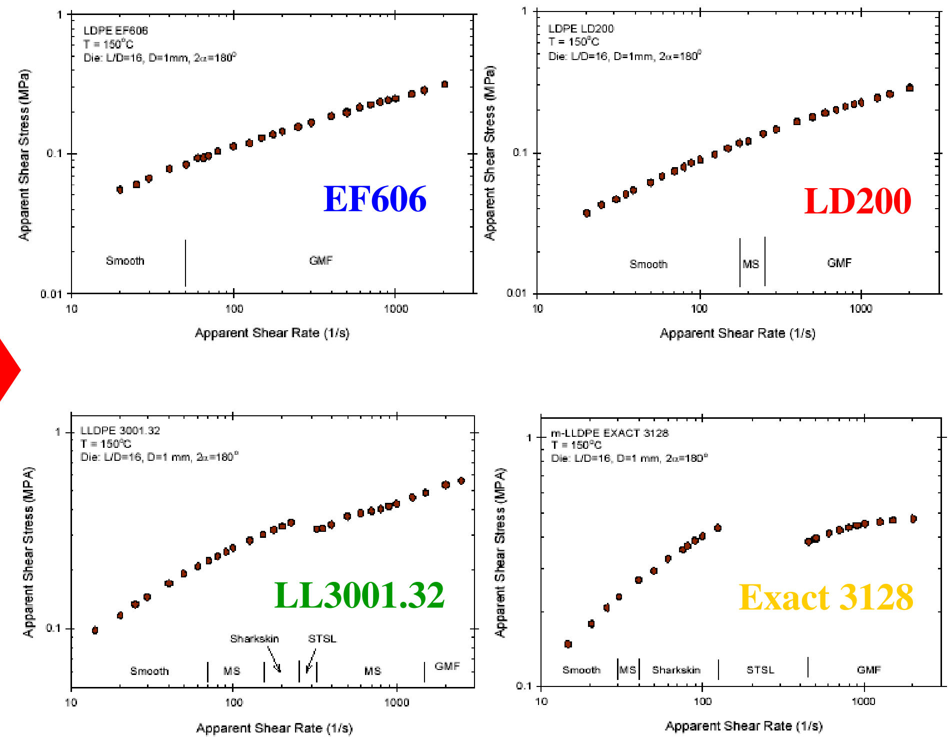
Case Study 3: Exact 3128 Peel Traces



- 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.

Case Study 3: Insight into Processing Behavior





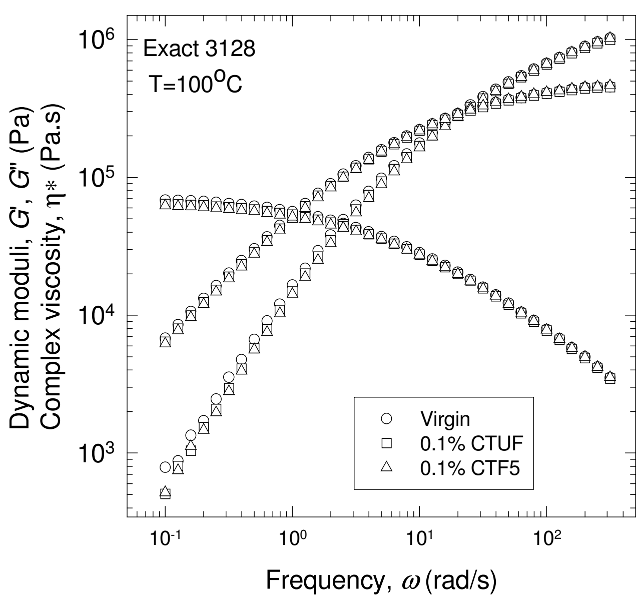
- These melt peel results with the SER appear quite promising as a laboratory predictor of processing behavior and may provide fundamental insight into the role of adhesion/slip in melt flow instabilities.

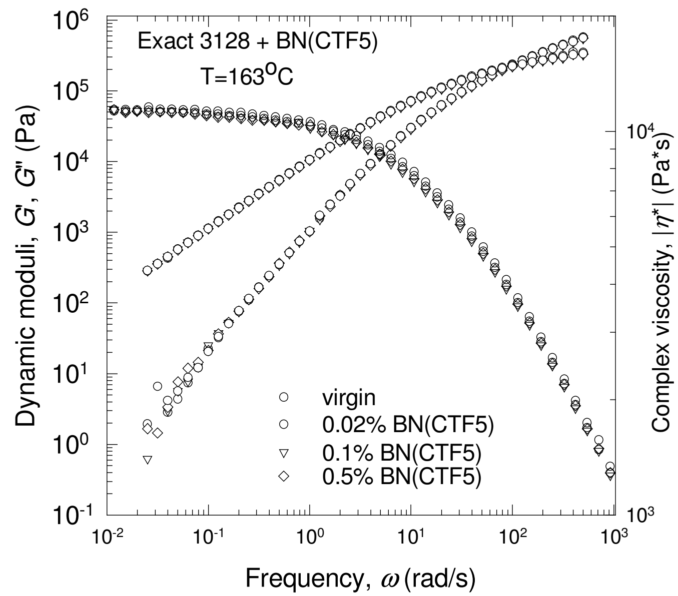
Dynamic Work of Adhesion...

- 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 4: Fundamental Mechanisms of Melt Fracture Behavior

- The addition of 0.1% of an adsorptive Boron Nitride filler in Exact 3128 can delay the onset of gross melt fracture.

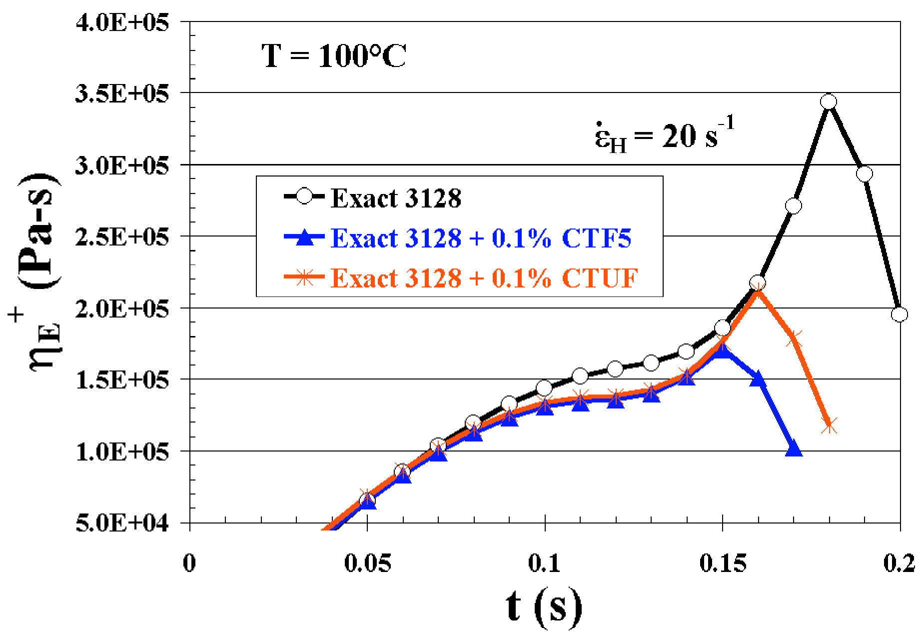


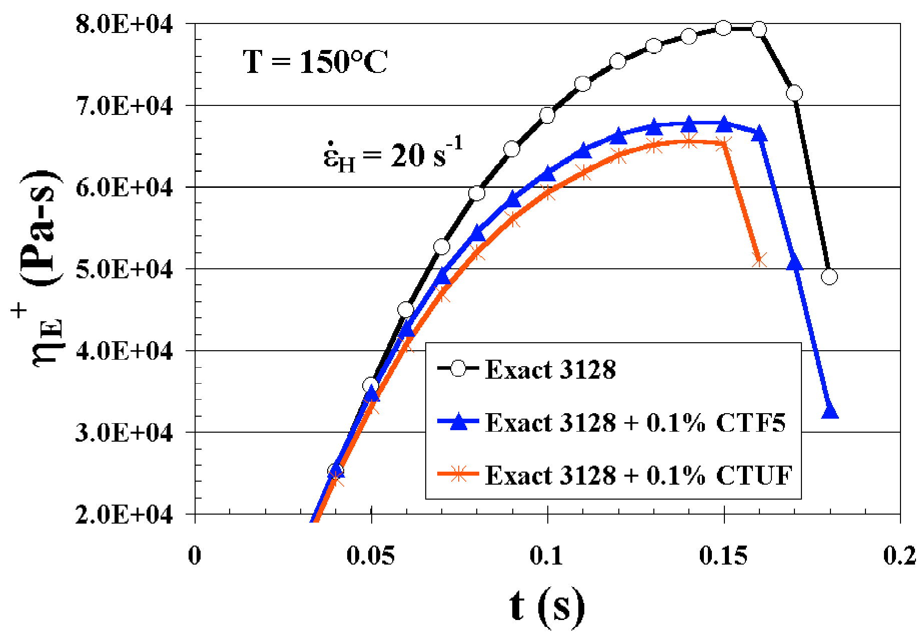


Data courtesy of Prof. S.G. Hatzikiriakos, UBC

- LVE data from SAOS and other conventional rheological characterizations are incapable of detecting any difference in rheological behavior.

Case Study 4: High-Rate Tensile Stress Growth





- Only at high rates of flow in extension can the subtle energy dissipation mechanisms governing melt fracture behavior be clearly distinguished.

Summary

- Demonstrated certain distinguishing features of a breakthrough in the field of material characterization technology - **SER Universal Testing Platform**
  - *Multiple modes of physical testing with one unit*
  - *True control of extensional deformation and rate*
  - *Miniature design allows for accommodation within a host system's environmental chamber for temperature testing*
  - *Small sample sizes ensure the characterization of materials available only in limited quantities*
  - *Easy operation, sample loading, and cleaning*
  - *Quick test time & high reproducibility*
  - **Reduces testing equipment costs, labor & material use**

Summary (cont.)

- Distinguished macrostructural features within a representative family of polyethylenes
  - Extensional Melt Rheology
    - Clear differentiation demonstrated between linear and branched PE
    - Subtle differences in polymer branching
    - Subtle differences in high-rate melt elasticity
  - Solids Tensile Testing
  - Melt Processing Behavior
    - Clear differences in peel/adhesion behavior may for the first time provide valuable insight into observed processing behavior
    - High-rate extensional flow behavior of BN-filled LLDPE displayed for the first time the role of energy dissipation on melt fracture