Melt Fracture of Polyethylene and the Role of Extensional Flow Behavior

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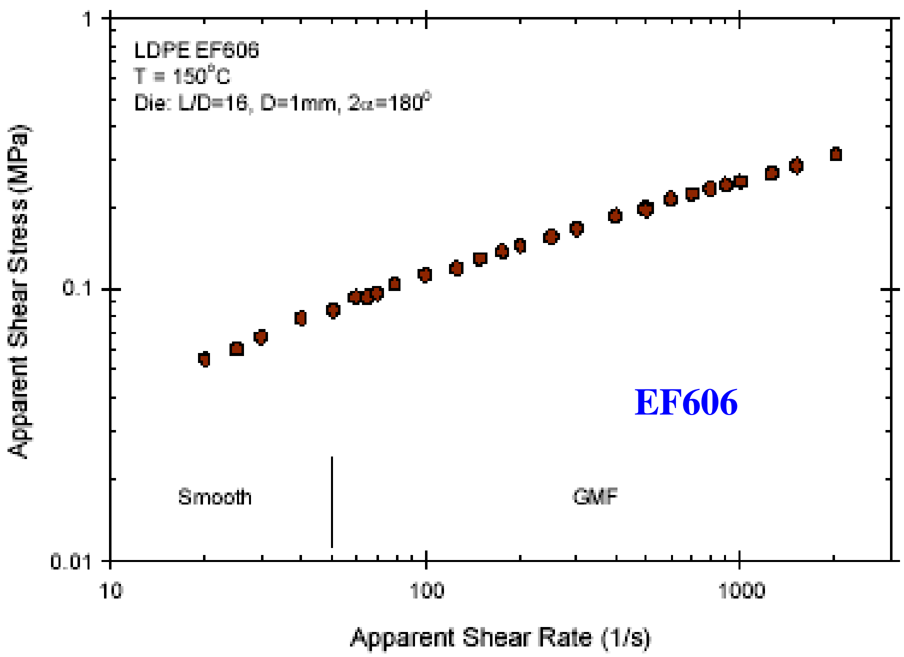
Introduction

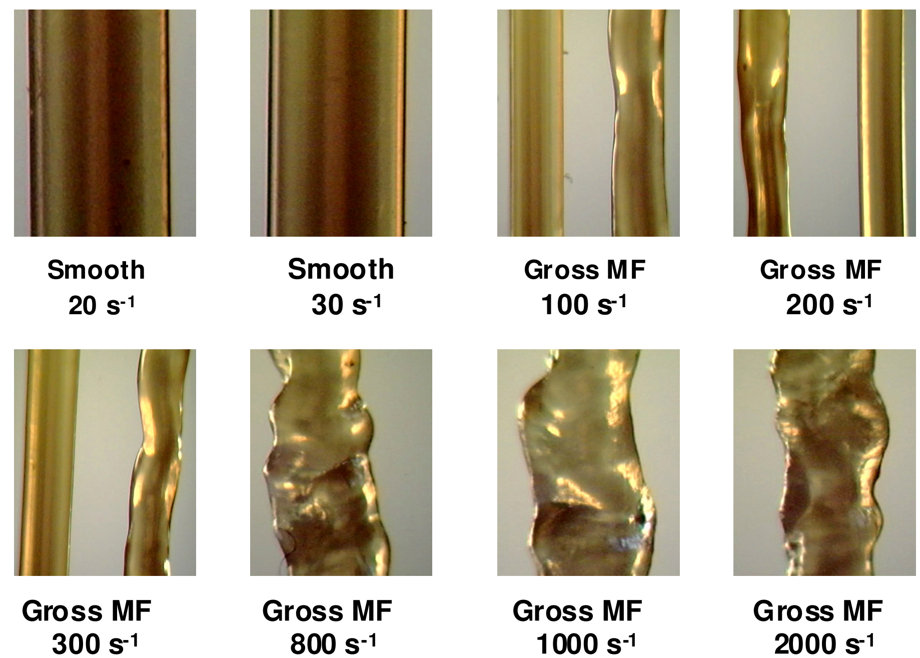
- It is a well known fact that linear polyethylenes exhibit far different processing/extrusion behavior than highly branched polyethylenes

- Despite being investigated extensively for decades some of the fundamental mechanisms governing these processing behaviors still remain unclear

Typical LDPE Melt Processing Behavior



LDPE EF606 @ 150°C

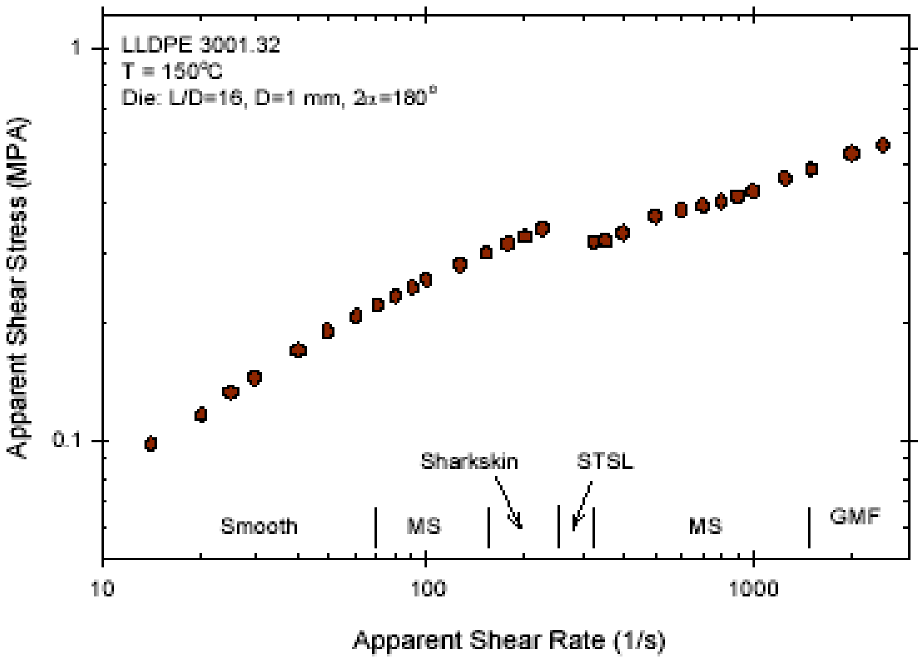


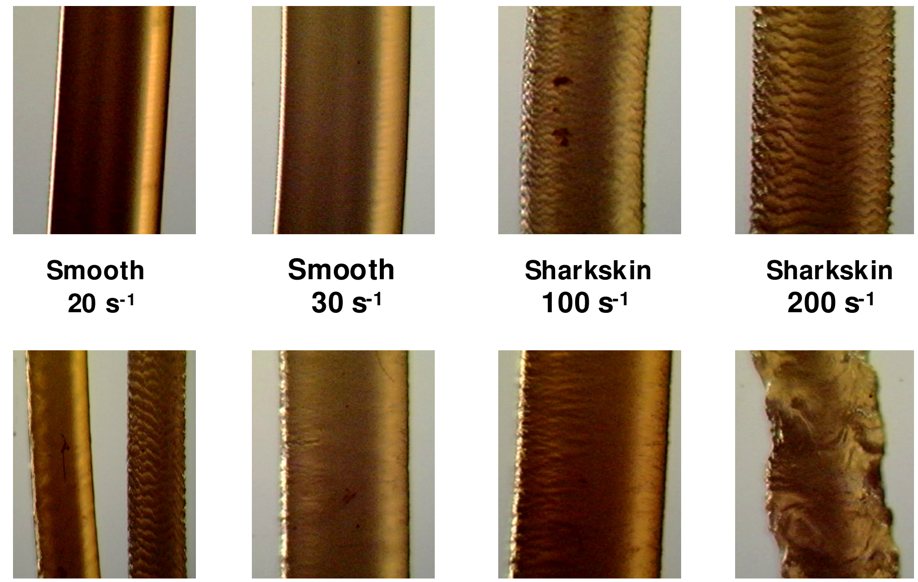
Features of Capillary Extrusion Behavior...

- *Flow curve*: monotonic increase in shear stress with shear - no discontinuity
- *Extrudate appearance*: beyond a critical point gross melt fracture (GMF) observed

Typical LLDPE Melt Processing Behavior

LLDPE LL3001.32 @ 150ºC





Smooth 20 s^{-1} | Smooth 30 s^{-1} | Sharkskin 100 s^{-1} | Sharkskin 200 s^{-1}

Stick SLip 300 s^{-1} | Streaks 800 s^{-1} | Streaks 1000 s^{-1} | Gross MF 2000 s^{-1}

Features of Capillary Extrusion Behavior...

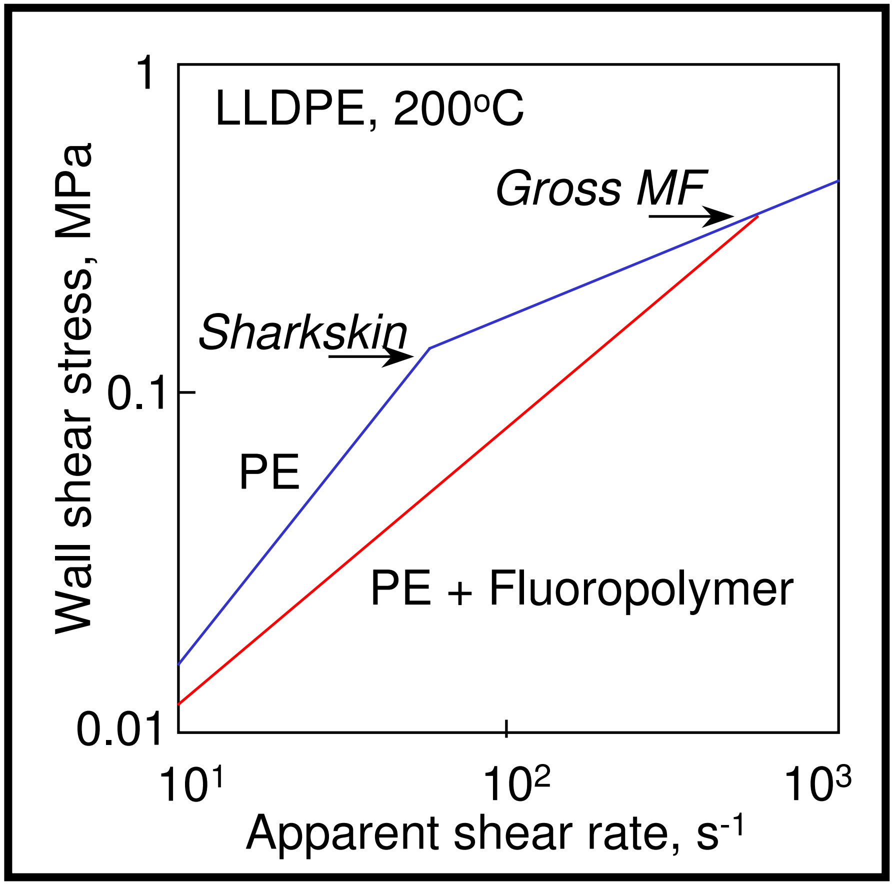
- *Flow curve*: at a certain point, notable discontinuity is observed in which the flow becomes unstable over a certain range of flow rates
- *Extrudate appearance*: extrudate gradually transitions from smooth, to sharkskin, to stick-slip, and eventually gross melt fracture

Affecting Processing Behavior

Although many efforts have been successful in manipulating some processing behavior (*viz a viz* processing aids) many age-old questions remain unanswered:

- Why does sharkskin occur only with linear PE and not branched PE?
- Is it possible to affect the onset of GMF and by what mechanism?
- Why does stick-slip flow occur only with linear PE?

Part I: Sharkskin Melt Fracture



- ***Why does sharkskin occur at all?***
- ***Why does it only occur with linear PE?***

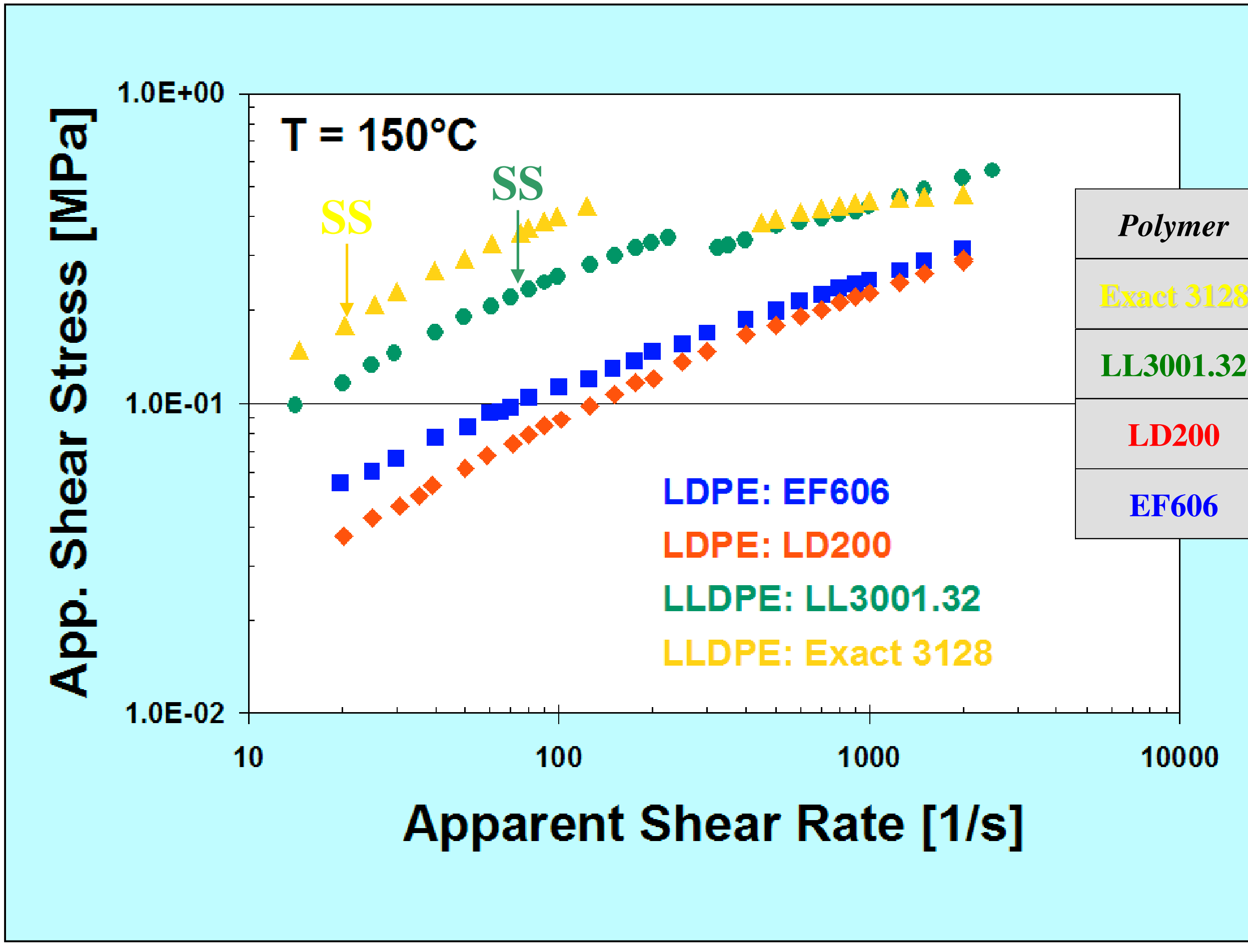
- Processing aids such as fluoropolymer additives can eliminate sharkskin by coating the die walls and promoting slip

Part Ia: 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

Capillary Extrusion Results

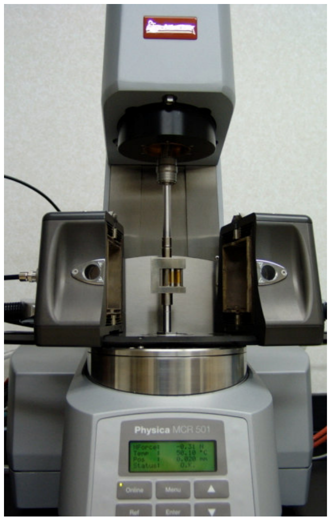


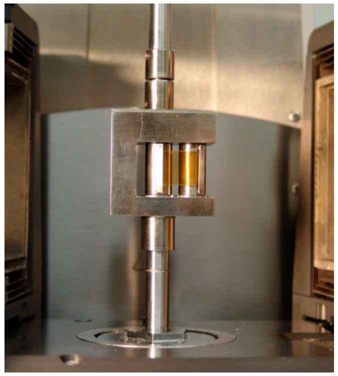
Critical Shear Rates for onset of...

Polymer	*Sharkskin*	*Stick-slip*	*Gross MF*
Exact 3128	20	120	420
LL3001.32	70	240	1400
LD200	-	-	270
EF606	-	-	50

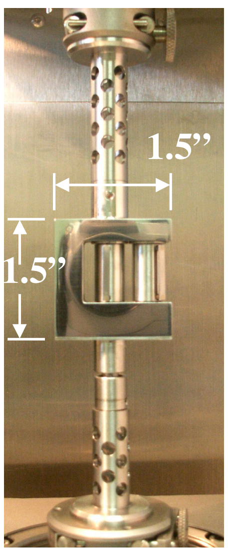
- Only the two LLDPE exhibit sharkskin, with Exact 3128 having an earlier onset with regard to extrusion rate

SER Universal Testing Platform

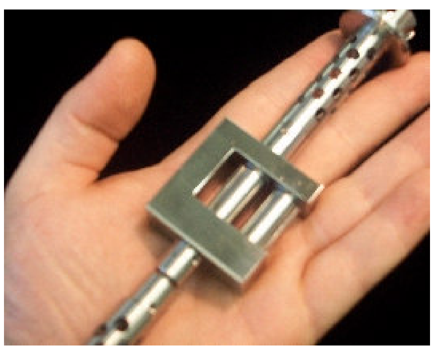




SER-HV-P01 shown here mounted on an Anton Paar MCR501

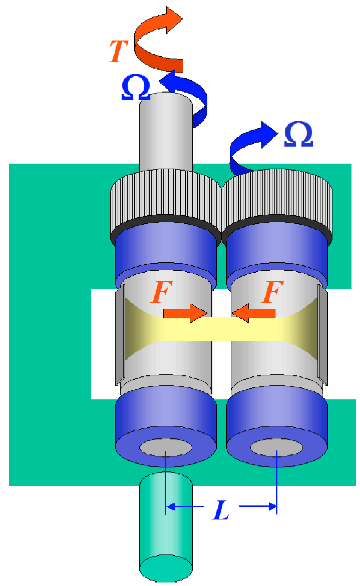


SER-HV-A01 shown here and mounted on an ARES

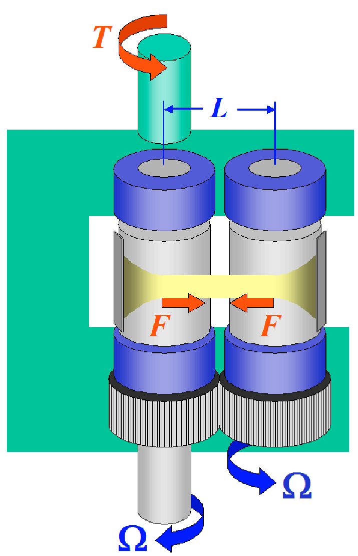


- The material characterization technology first pioneered at Goodyear has been exclusively licensed to **Xpansion Instruments, LLC (www.xinst.com)**.
- The **SER** is a fixture that has been specifically designed so that it can be easily accommodated onto a number of commercially available R&D grade rotational rheometer host systems and can be housed within the host system’s environmental chamber for controlled temperature experiments.
- The model **SER-HV-P01** has been targeted for use on Anton Paar’s MCR line of rheometers, while the model **SER-HV-A01**, has been targeted for use on ARES, RDA3, & RDA2 host systems.
  - Requires only 5-200mg of material
  - Can be used up to temperatures of 250°C
  - Easily detachable for fixture changeover

SER General Principle of Operation



SER-HV-P01 Configuration



SER-HV-A01, SER-HV-B01, & SER-HV-R01 Configurations

- 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 translates into a torque about the primary axis of rotation as the sample continues to stretch
- The resulting torque, T, measured by the torque transducer is then simply:

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

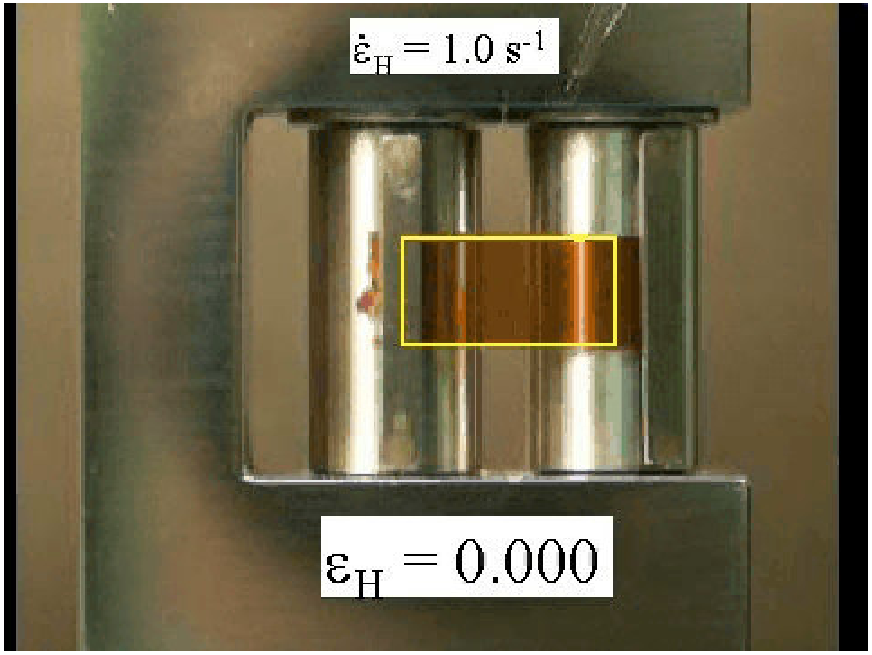
where $F_{friction}$ is the friction contribution from the bearings and gears (typically < 2%)

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

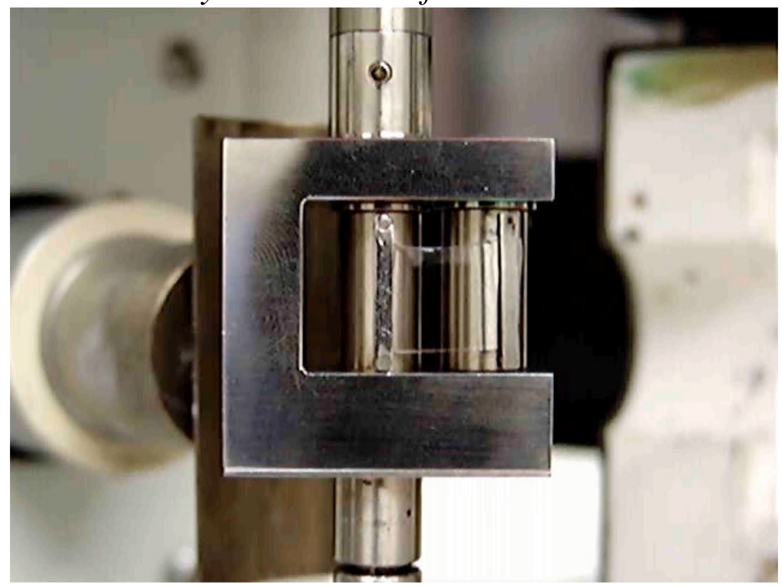
$$A(t) = A_0 \exp\,[-\varepsilon_H]$$

where A_0 is the initial cross-sectional area

Extensional Rheology with the SER



Polyethylene melt at 150°C and a Hencky Strain Rate of 1.0 s^{-1}

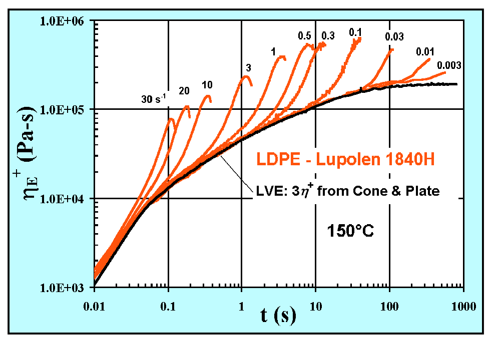


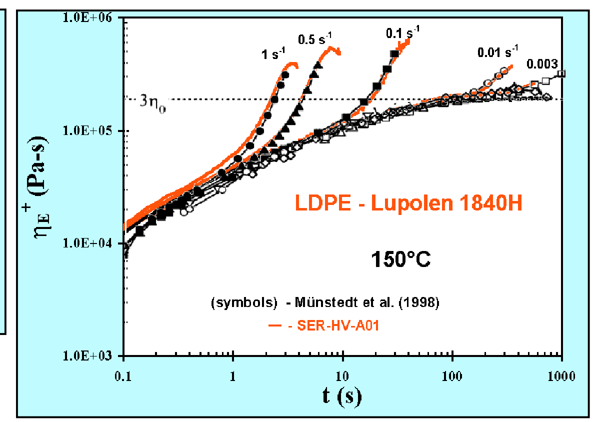
- Indicates Theoretical Width Dimension

Theoretical width dimension expression:

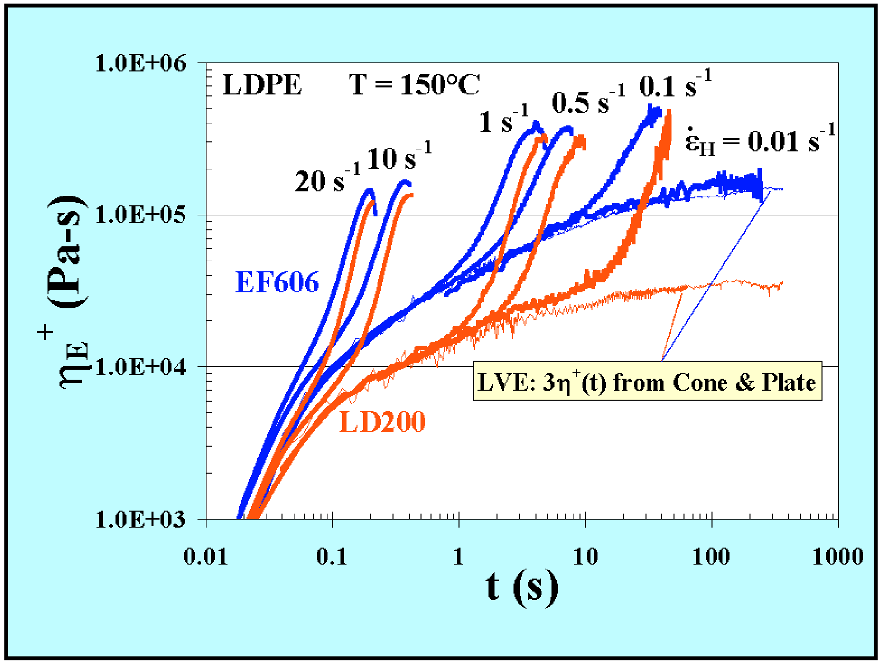
$$W/W_0 = [\exp(-\varepsilon_H)]^{1/2}$$

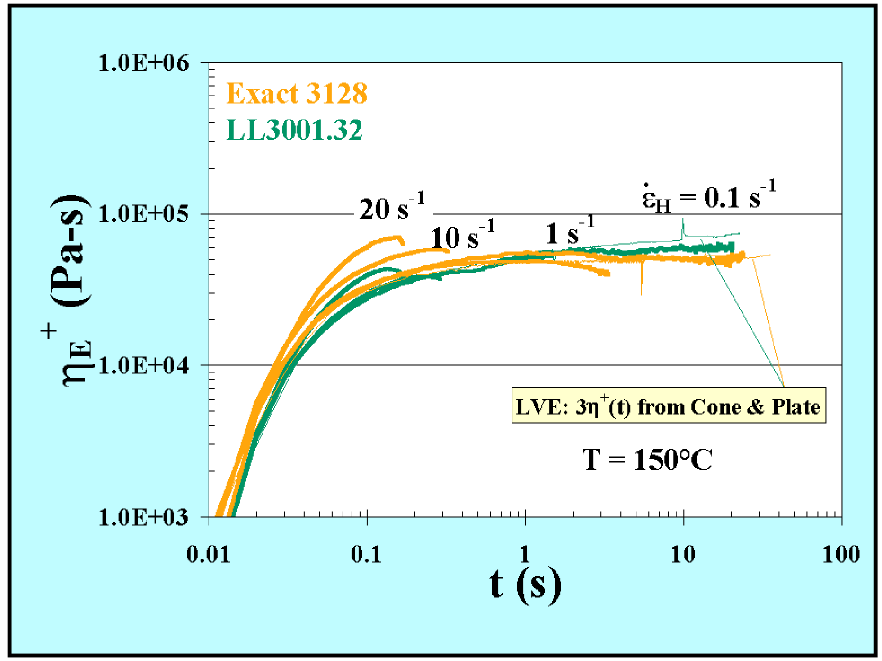
- Note the excellent agreement between the actual and theoretical width dimension evolution





Tensile Stress Growth Curves

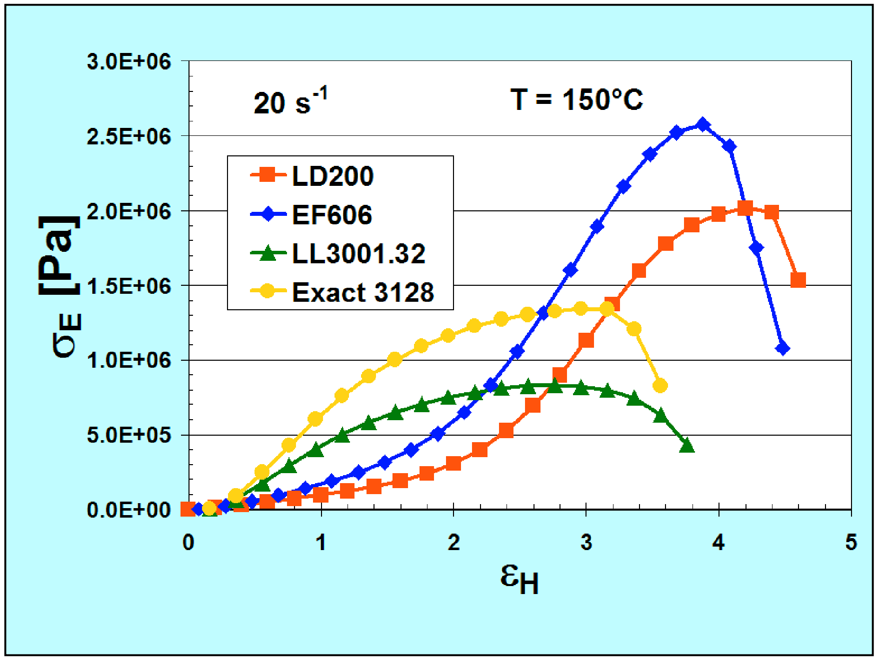




- Both LDPEs exhibit significant deviation from LVE behavior at large strains
- Despite having a much lower LVE melt viscosity the coating grade LDPE exhibits peak stresses almost equal to the film grade LDPE

- 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

High-Rate Tensile and Melt Fracture Behavior



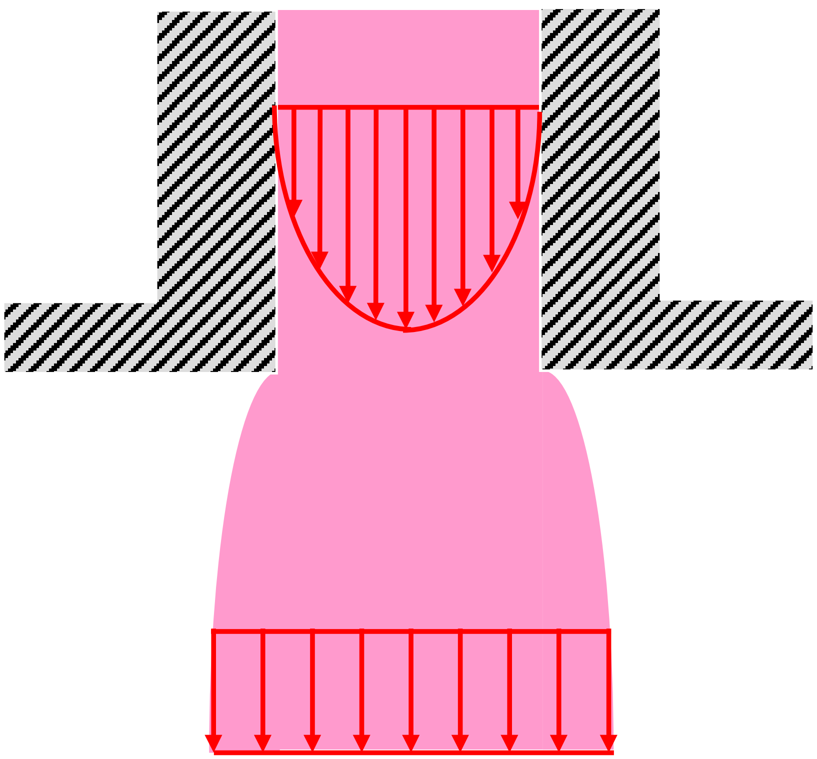
Critical Shear Rates for onset of...

Polymer	*Sharkskin*
Exact 3128	20
LL3001.32	70
LD200	-
EF606	-

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

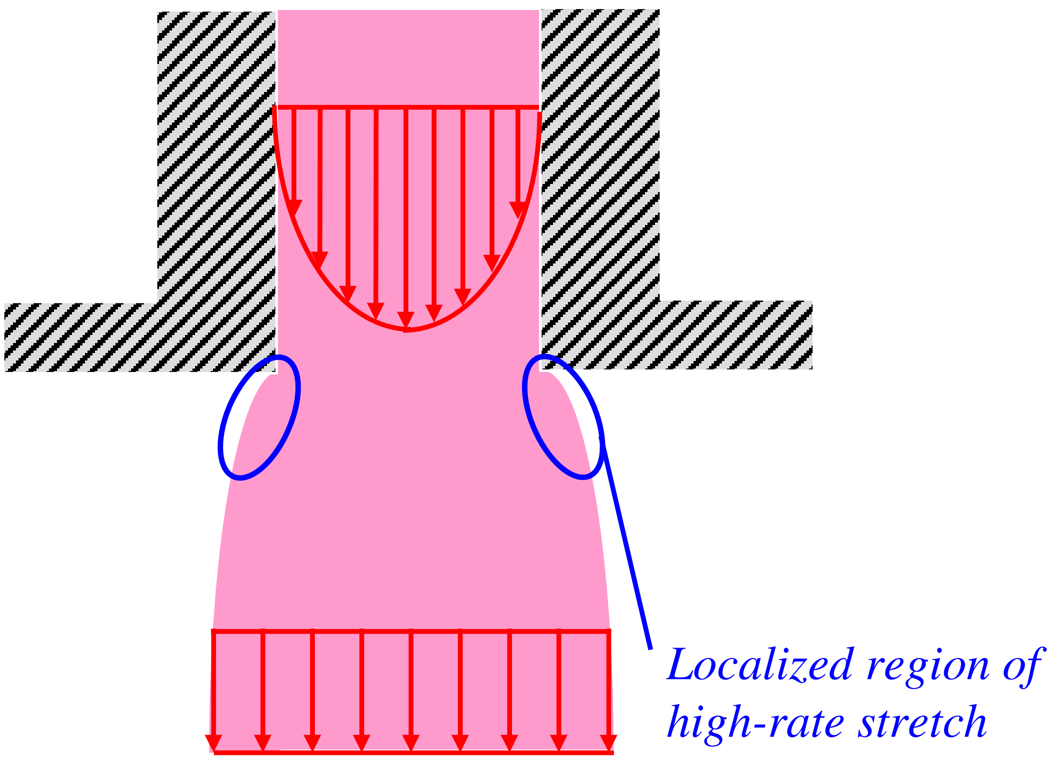
Sharkskin Melt Fracture

- Exit phenomenon - stress governed flow



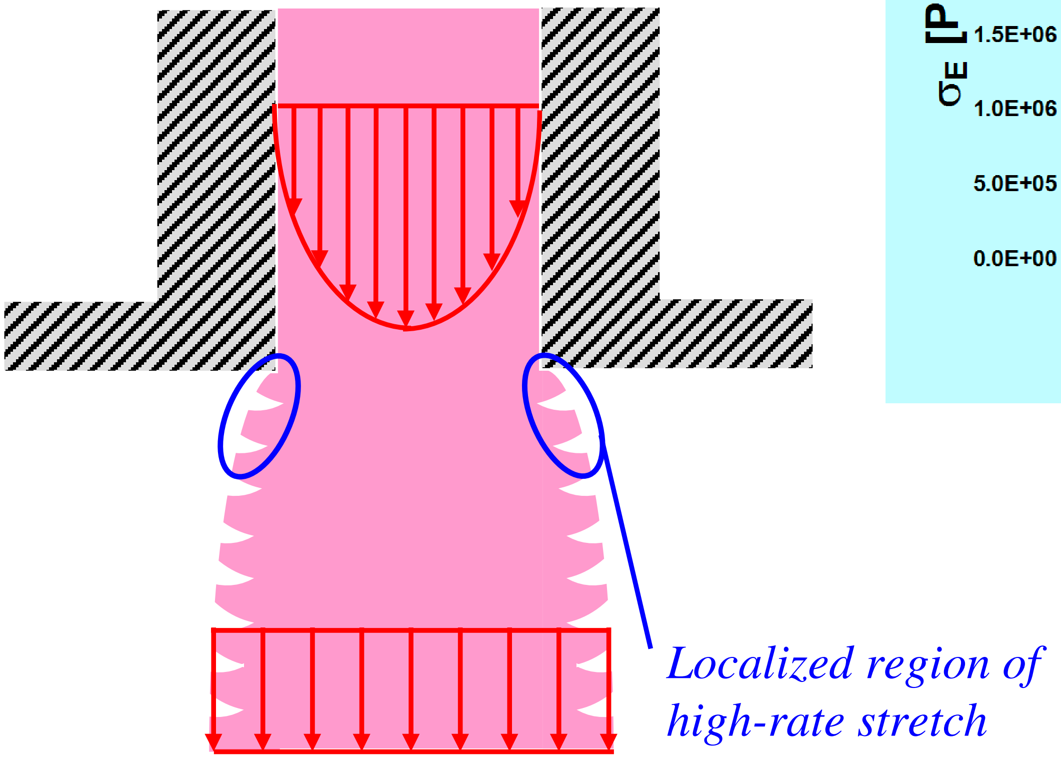
Sharkskin Melt Fracture

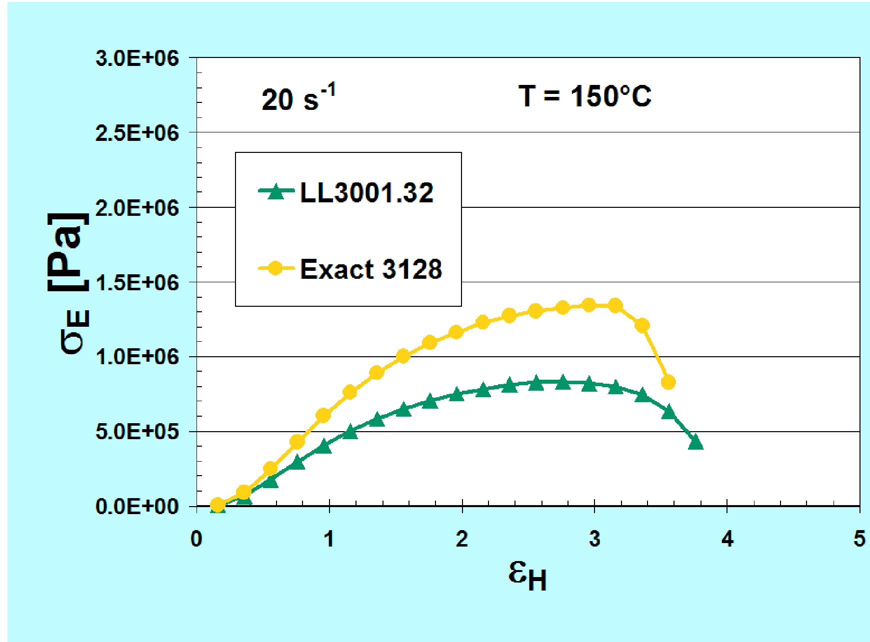
- Exit phenomenon - stress governed flow



Sharkskin Melt Fracture

- Exit phenomenon - stress governed flow





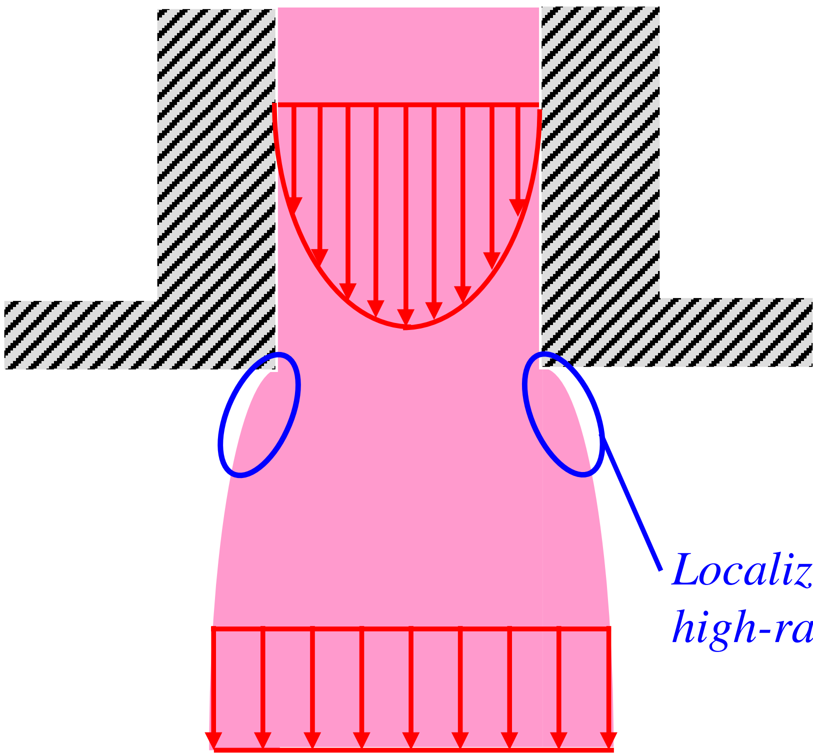
Critical Shear Rates for onset of...

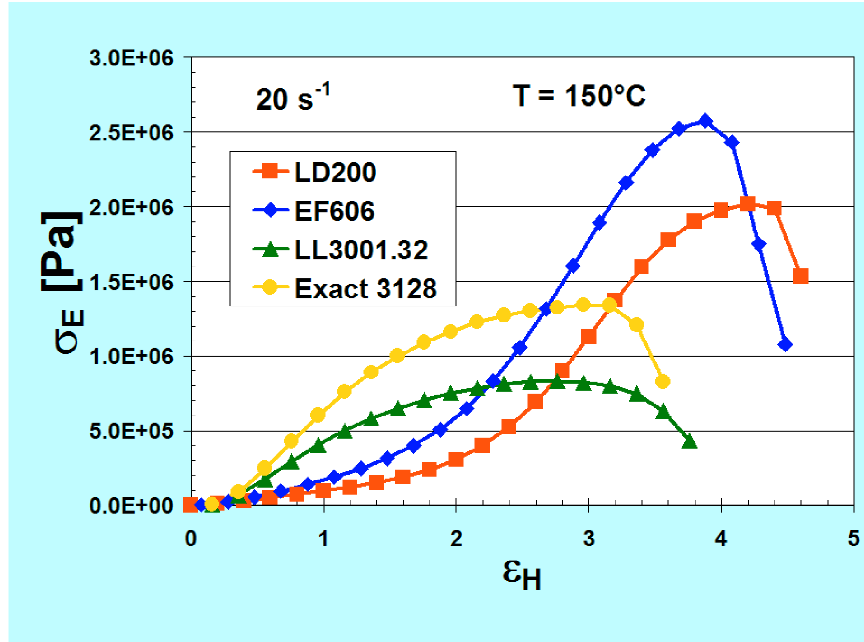
Polymer	*Sharkskin*
Exact 3128	20
LL3001.32	70

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

Sharkskin Melt Fracture

- Exit phenomenon - stress governed flow





Critical Shear Rates for onset of...

Polymer	*Sharkskin*
Exact 3128	20
LL3001.32	70
LD200	-
EF606	-

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

Part Ib: Experimental

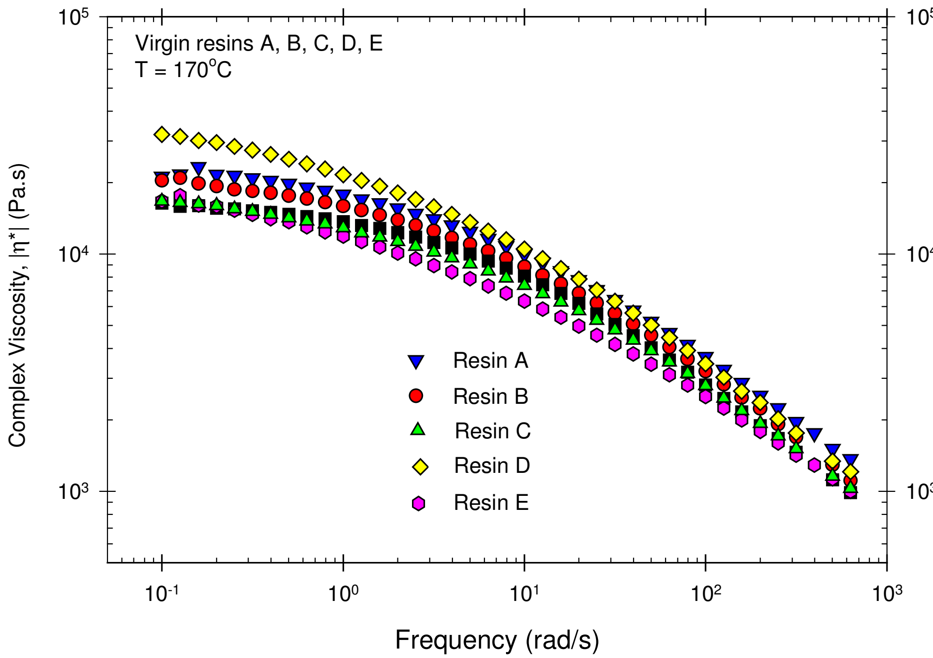
- Family of Z-N Polymers (Nova Chemicals)
  - 4 Film grade LLDPE
  - 1 Blow Molding grade HDPE

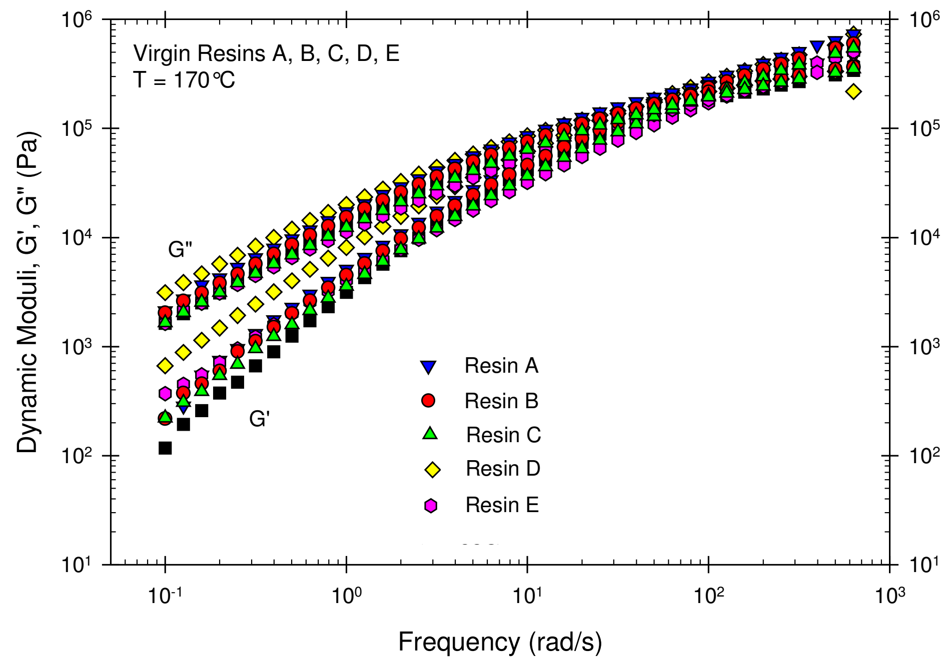
Resin	Commercial Nomenclature	Melt Index (g/10 min) (I_2)	Density (g/cm^3)	Co-monomer	Catalyst type	Process Technology	Application
A	PF-Y821-BP (LLDPE)	0.80	0.9230	Butene	Z-N	Unipol Gas	Film
B	TD-9022-D (LLDPE)	0.80	0.9195	Hexene	Z-N	Unipol Gas	Film
C	FP-120-F (LLDPE)	1.00	0.9218	Octene	Z-N	AST Solution	Film
D	FP-015-A (LLDPE)	0.55	0.9175	Octene	Z-N	AST Solution	Film
E	58G (HDPE)	0.95 (I_6)	0.9575	-	Z-N	SCLAIR Solution	Blow Molding

Part Ib: Experimental (cont.)

- LVE (SAOS)
  - Rheometrics System IV
- Extrusion/Processability
  - Rosand RH-2000
  - Capillary Die: D = 1 mm, L/D = 16, 180° entrance angle
- Extensional
  - SER-HV-A01 Universal Testing Platform hosted on a Rheometrics RDA-II
  - SER-HV-B01 Universal Testing Platform hosted on a Bohlin VOR

LVE Behavior: SAOS





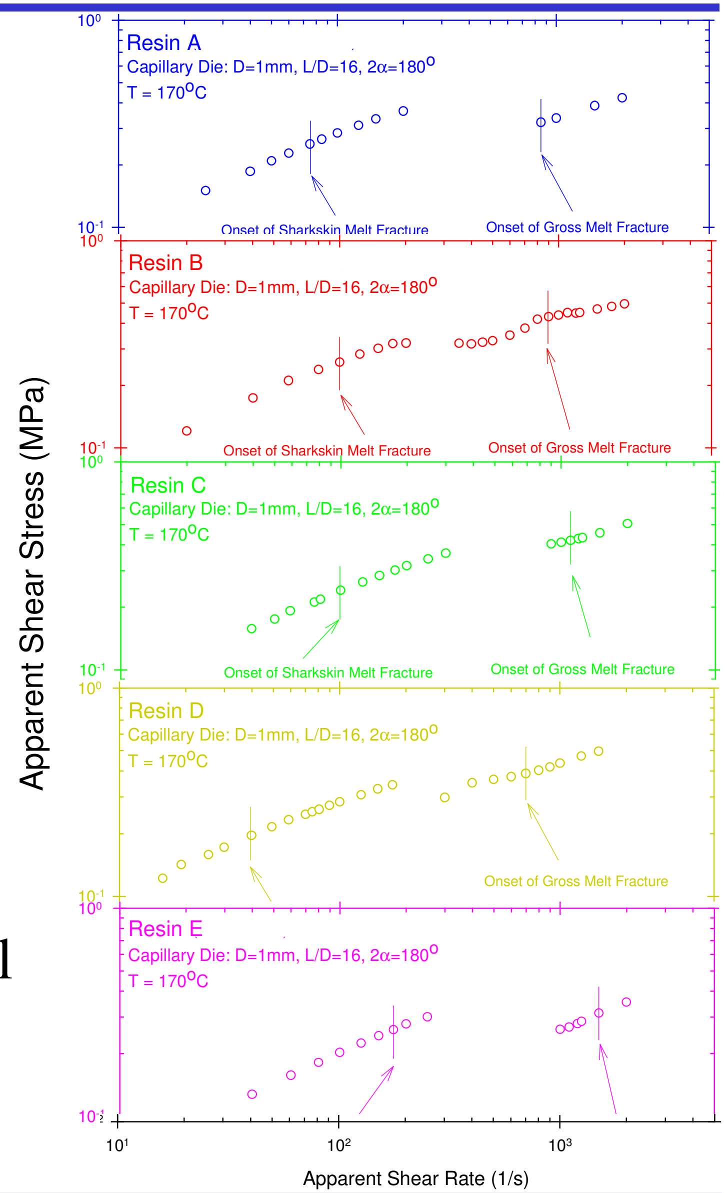
- With the exception of Resin D at low frequencies, the polymers exhibit very little difference in LVE behavior

Resin	η_0 (Pa-s) 170°C
A	2.91e4
B	2.27e4
C	1.84e4
D	3.92e4
E	2.33e4

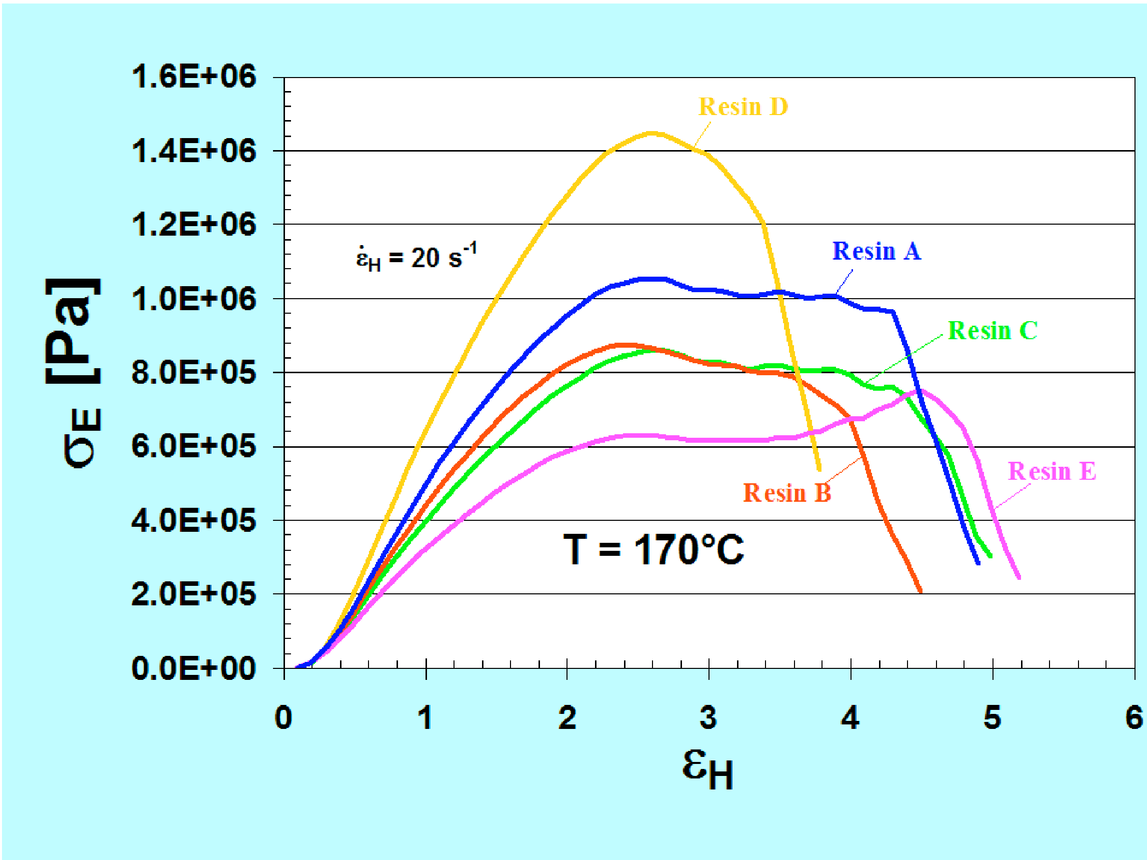
Melt Fracture Behavior

Resin		Critical shear rate (s^{-1}) and stress (MPa) for the onset of		
		Sharkskin	**Stick-slip**	**Gross melt**
A	Apparent shear rate	75	300	850
	Apparent shear stress	0.25	-	0.32
B	Apparent shear rate	100	225	900
	Apparent shear stress	0.26	-	0.43
C	Apparent shear rate	100	325	1100
	Apparent shear stress	0.24	-	0.42
D	Apparent shear rate	40	200	700
	Apparent shear stress	0.20	-	0.39
E	Apparent shear rate	175	300	1500
	Apparent shear stress	0.260	-	0.313

- Although the polymers exhibit similar LVE and flow curve behaviors, the critical shear rates for the onset of sharkskin and gross melt fracture vary greatly



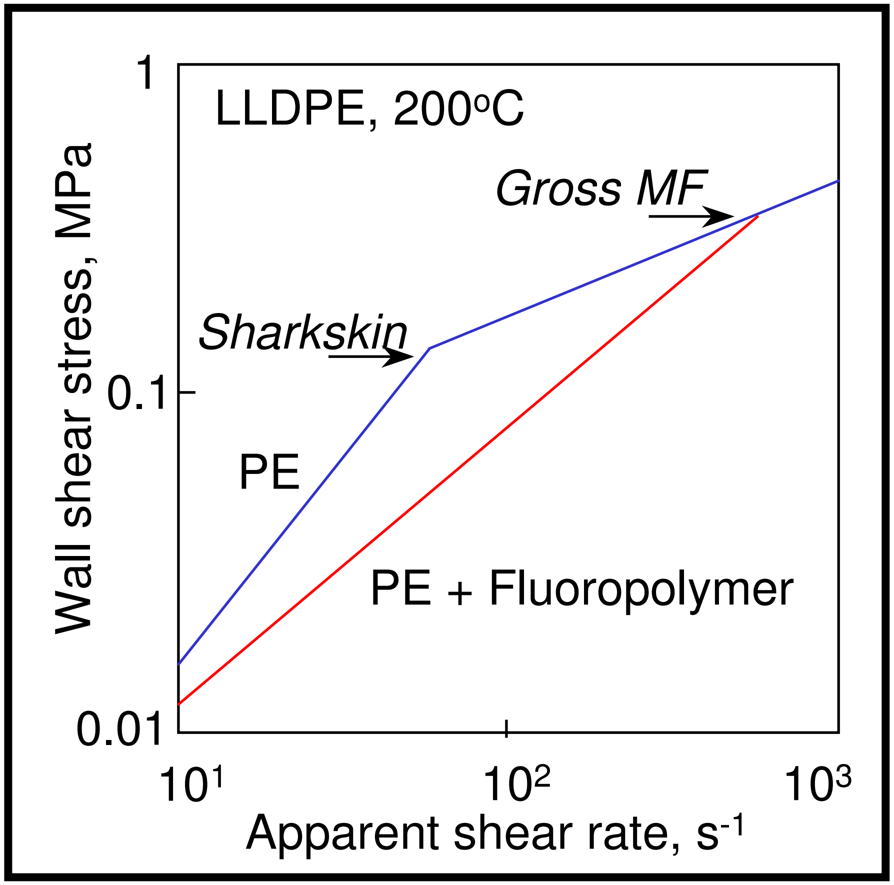
High-Rate Extensional Flow Behavior within a Family of ZN-LLDPE



Resin	Sharkskin Shear Rate (s^{-1})
D	40
A	75
B	100
C	100
E	175

- The onset of melt fracture behavior scales with the high-rate tensile stress growth behavior of the polymer melts

Part II: Gross Melt Fracture



- ***If slip promotion doesn't affect GMF, what does?***

  By what mechanism?

- 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**

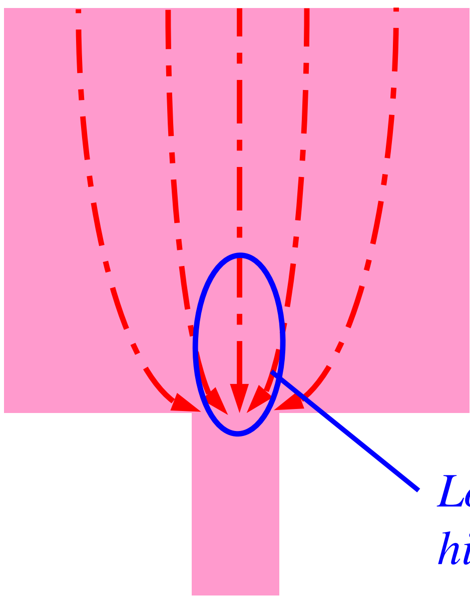
Part IIa: Experimental

- 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

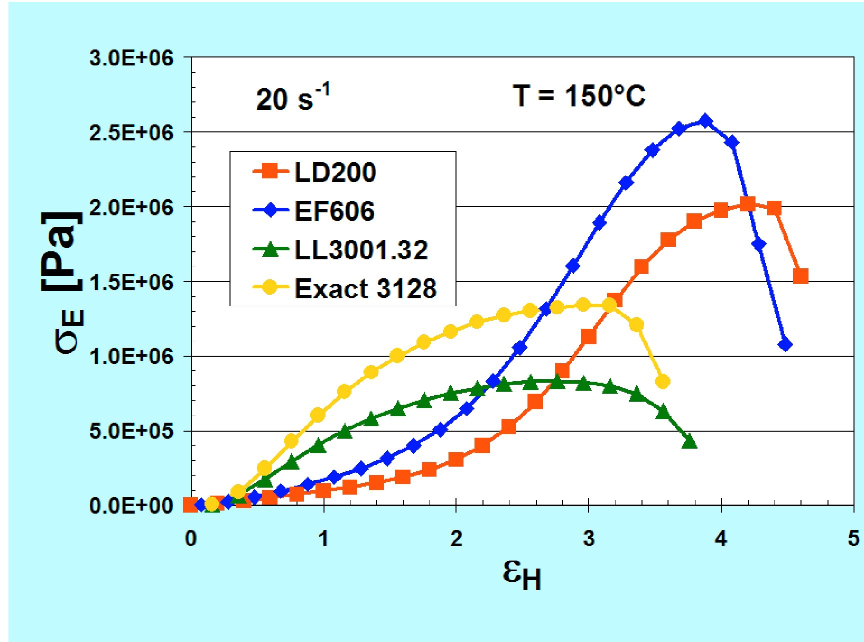
Gross Melt Fracture

- Entrance phenomenon
  - strain governed flow

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



Localized region of high stretch

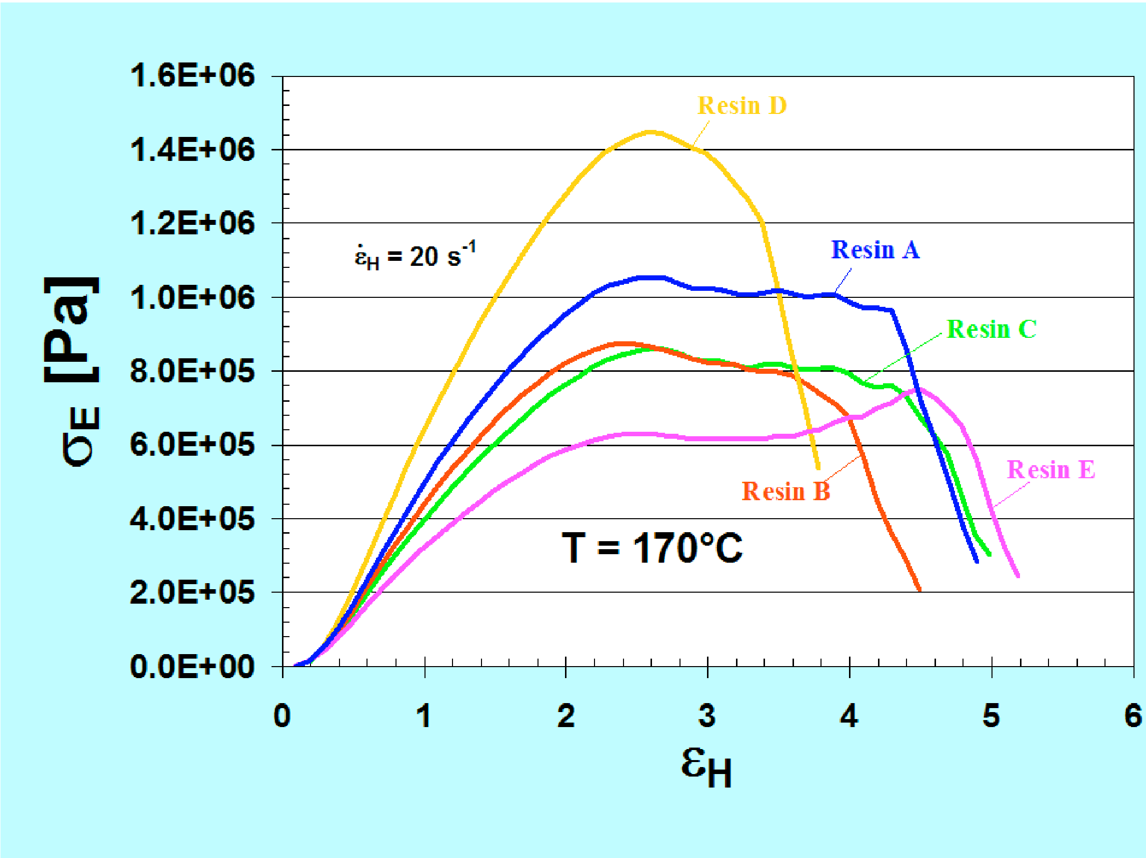


Critical Shear Rates for onset of...

Polymer	*Sharkskin*	*Stick-slip*	*Gross MF*
Exact 3128	20	120	420
LL3001.32	70	240	1400
LD200	-	-	270
EF606	-	-	50

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

High-Rate Extensional Flow Behavior

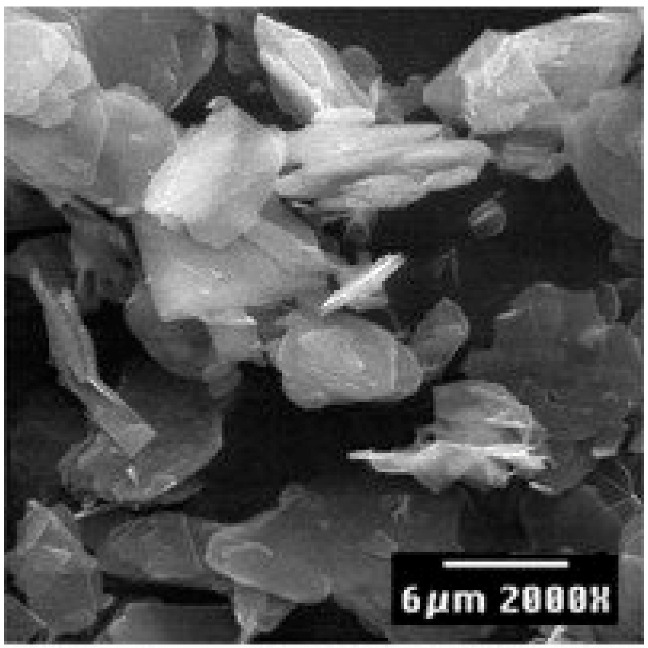


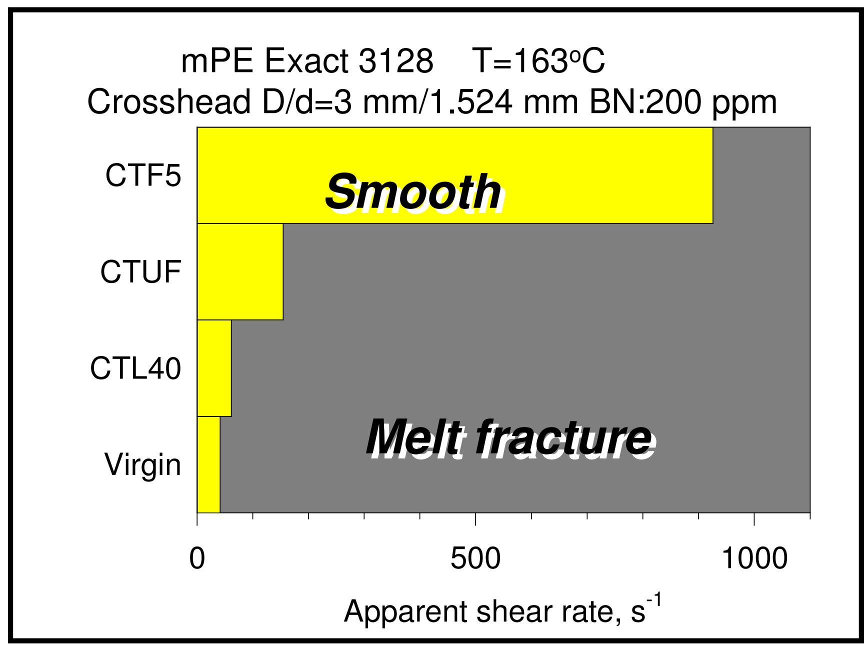
Resin	Sharkskin Shear Rate (s^{-1})	GMF Shear Rate (s^{-1})
D	40	700
A	75	850
B	100	900
C	100	1100
E	175	1500

- The onset of melt fracture behavior appears to scale with the high-rate tensile stress growth behavior of the polymer melts

Boron Nitride (BN) - GMF Suppressor

- 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



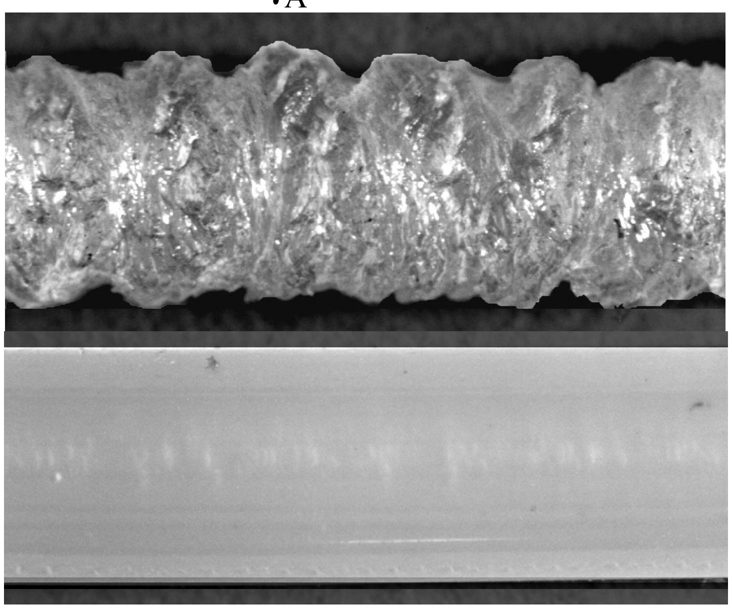


(h-BN: soft, graphite-like ceramic platelet particles)

By What Mechanism does BN Suppress GMF?

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

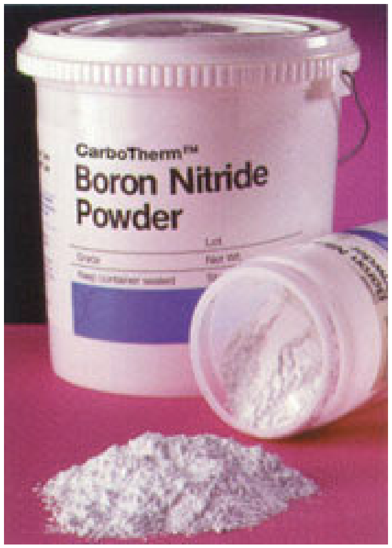
$\dot{\gamma}_A = 617\ s^{-1}$



m-LLDPE (Pure)

m-LLDPE + 0.1% BN

Part IIb: Experimental



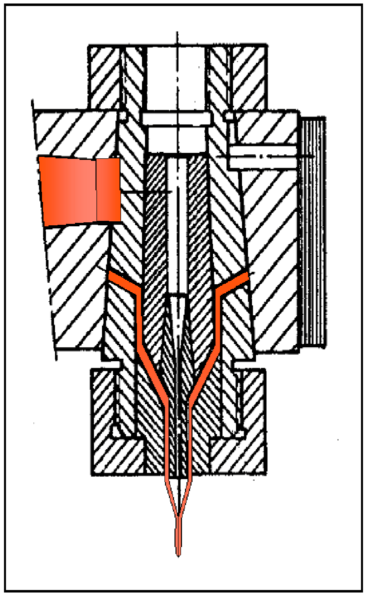
- BN Powders from Saint-Gobain Advanced Ceramics

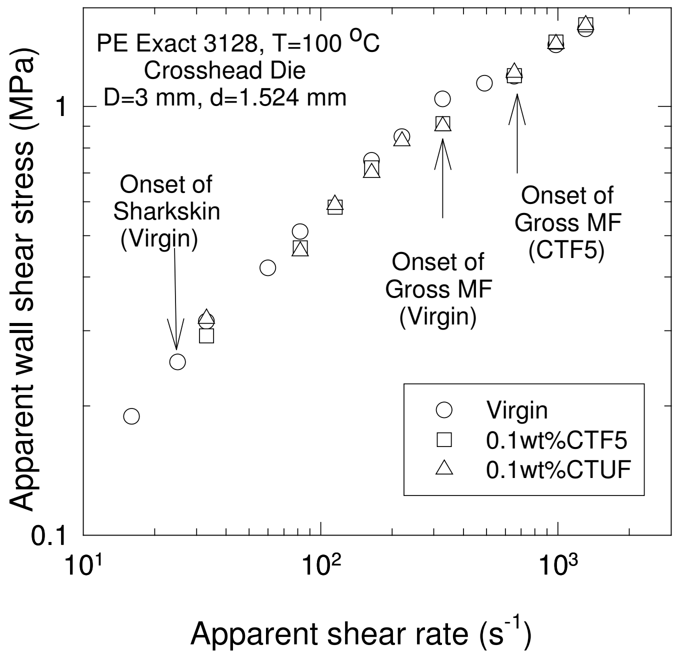
  (5-20 µm particle size) compounded at 0.1wt. %

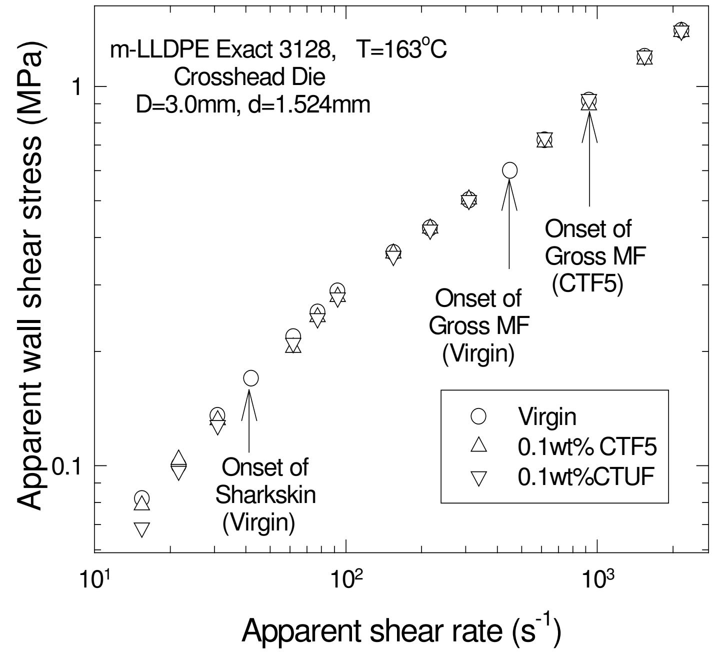
  - CarboTherm™ CTF5 (SE: 47.1 [11] mJ/m^2)
  - CarboTherm™ CTUF (SE: 63.4 [27] mJ/m^2)

- 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)

Exact 3128 Processing Behavior



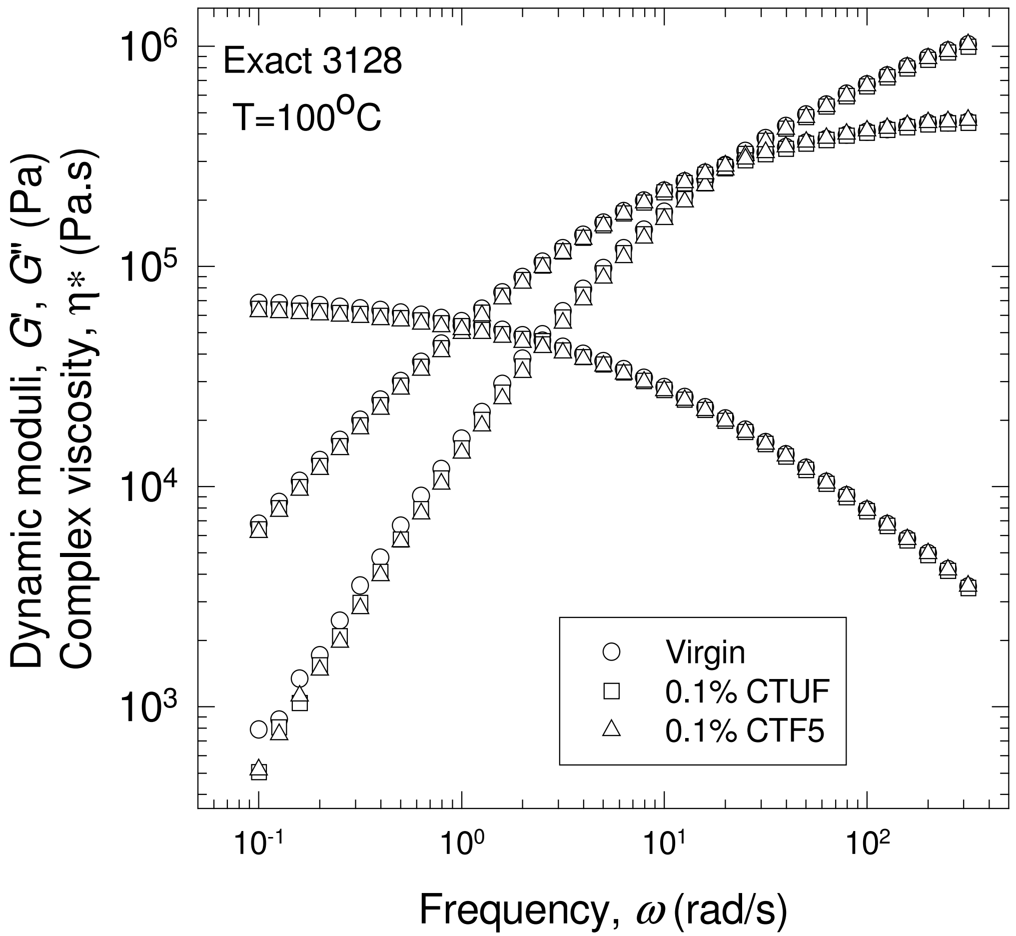




	Critical Shear Rates for the Onset of:			
	100 ℃		163 ℃	
	SS	GMF	SS	GMF
Exact 3128 (Virgin)	25	327	42	450
Exact 3128 + 0.1% CTUF	80	650	150	920
Exact 3128 + 0.1% CTF5	-	655	-	928

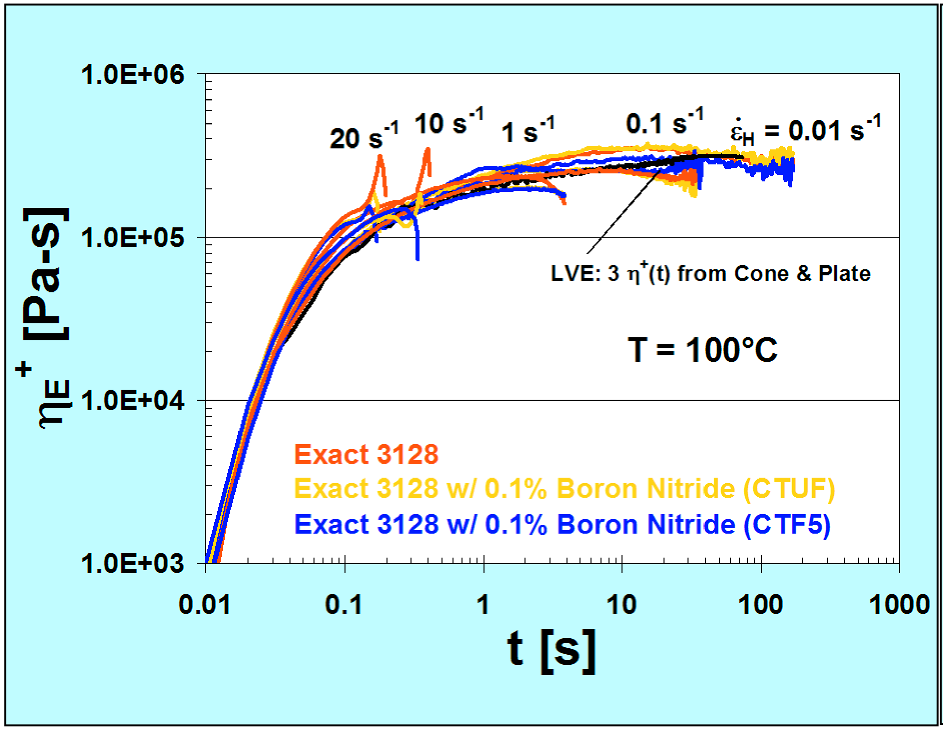
Despite displaying almost identical flow curves, the presence and type of BN appears to play a large role in melt fracture behavior

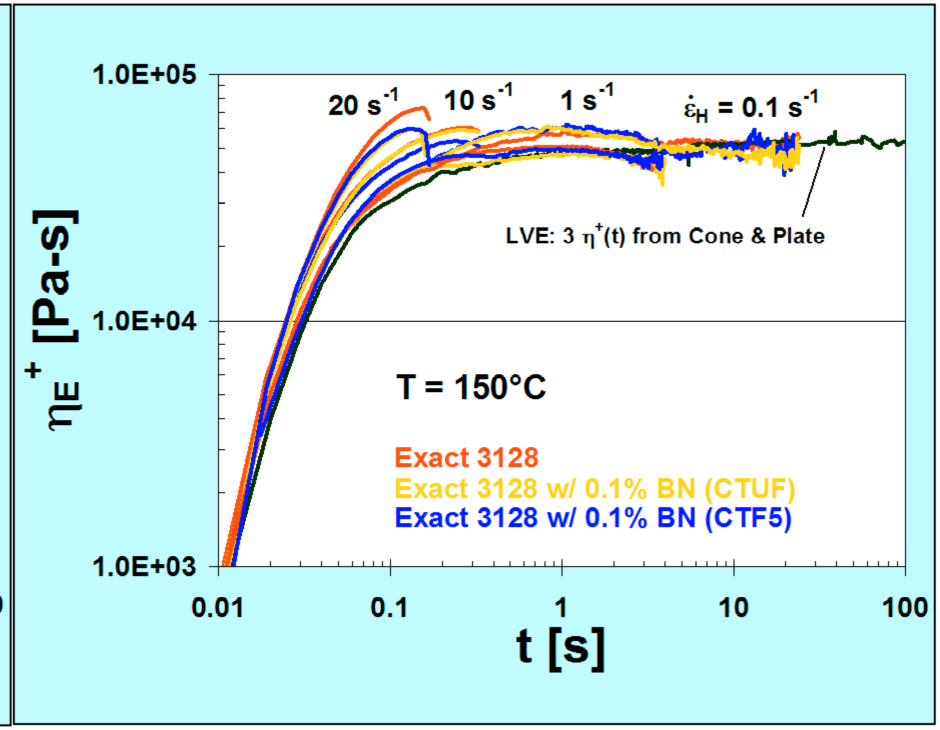
SAOS Exact 3128



LVE results from SAOS are incapable of revealing any unique information about the effect of BN on polymer behavior

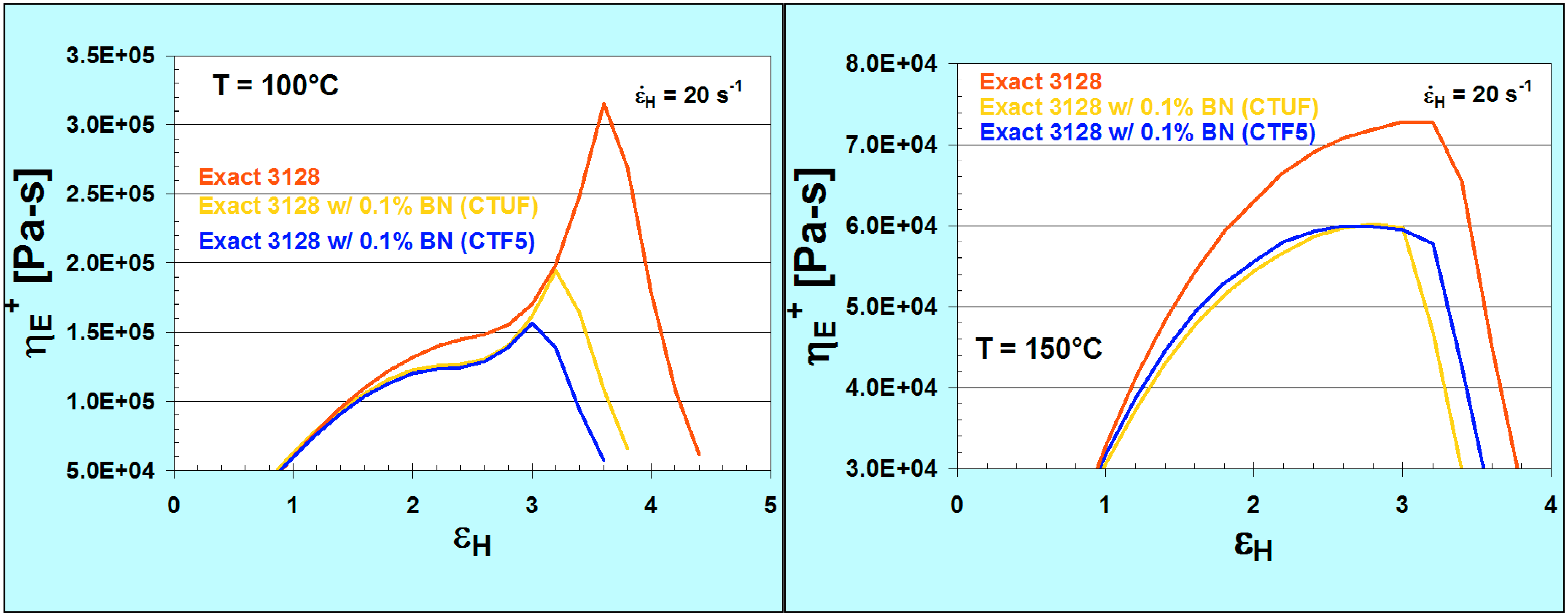
Tensile Stress Growth - Exact3128





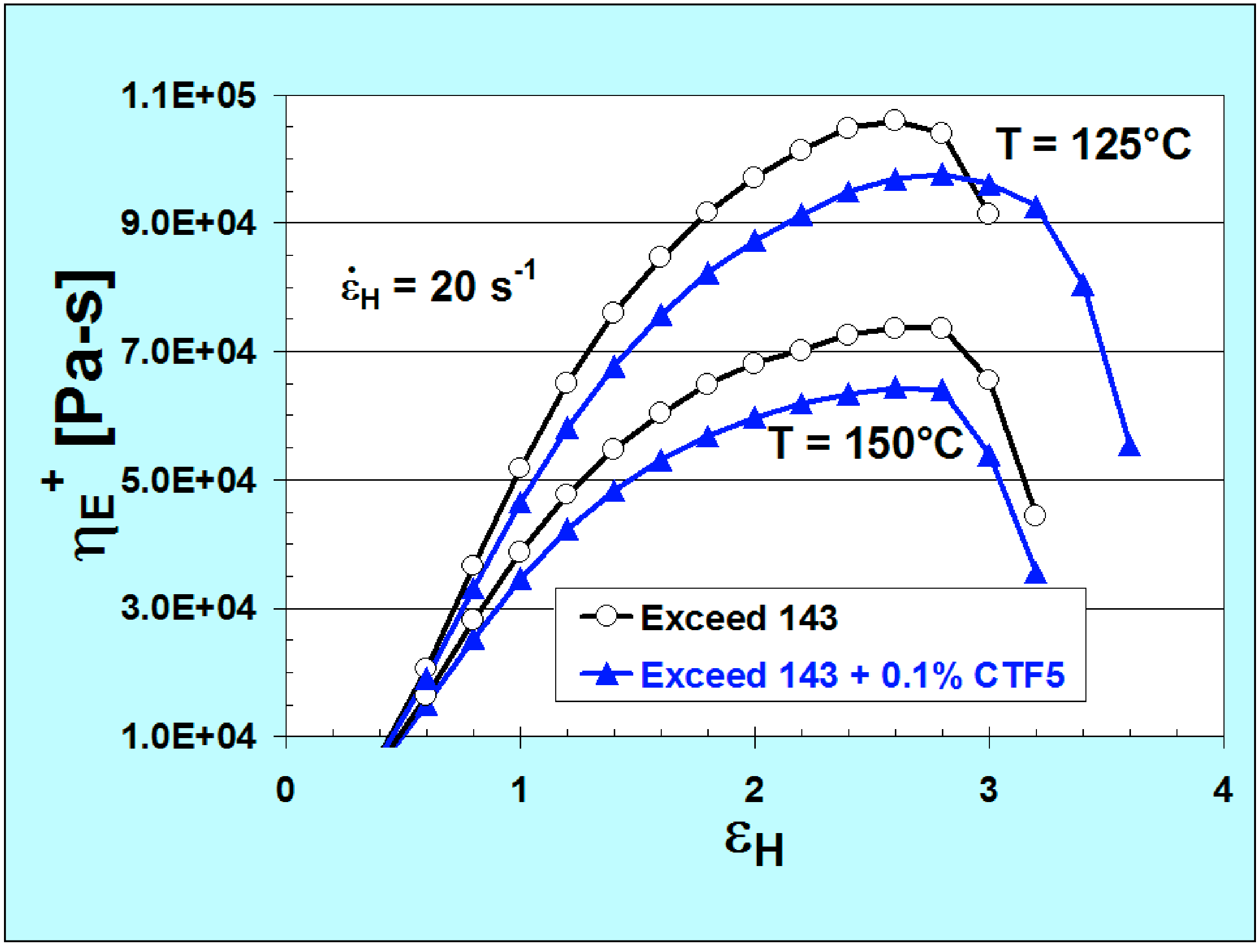
- As the rate of extension increases, the sample rupture transitions from a ductile to a brittle-type mode of failure, coinciding with rubbery behavior at short times
- Only at high extensional flow rates are differences in the polymers clearly evident

Exact 3128 High-Rate Extensional Flow



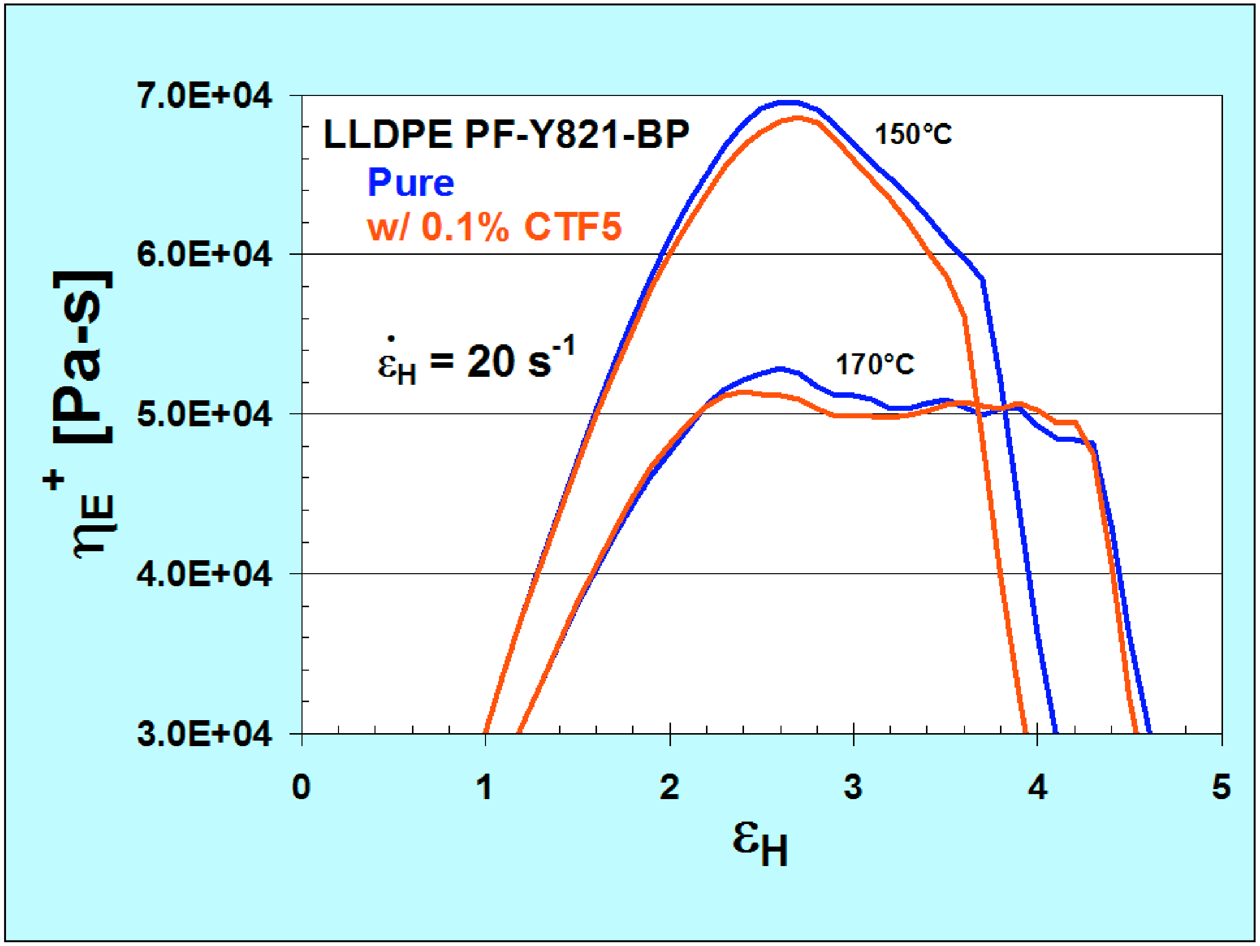
- Note that the BN-filled polymers exhibit subdued stress growth and peak stresses at high extensional rates
- These results suggest that the presence of BN serves as an energy dissipater/plasticizer that inhibits the elastic/rubber-like behavior of the m-LLDPE polymer at large deformations and rates

Exceed 143 High-Rate Extensional Flow



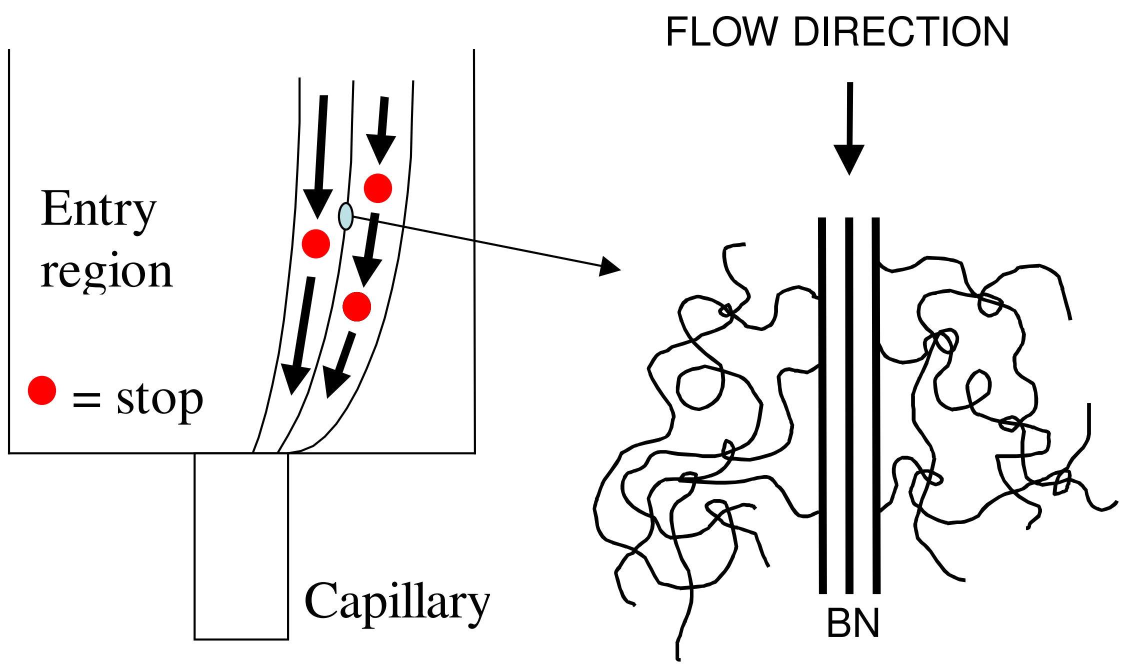
- The presence of BN appears to have a similar energy dissipation effect on Exceed 143 (m-LLDPE)

PF-Y821-BP High-Rate Extensional Flow



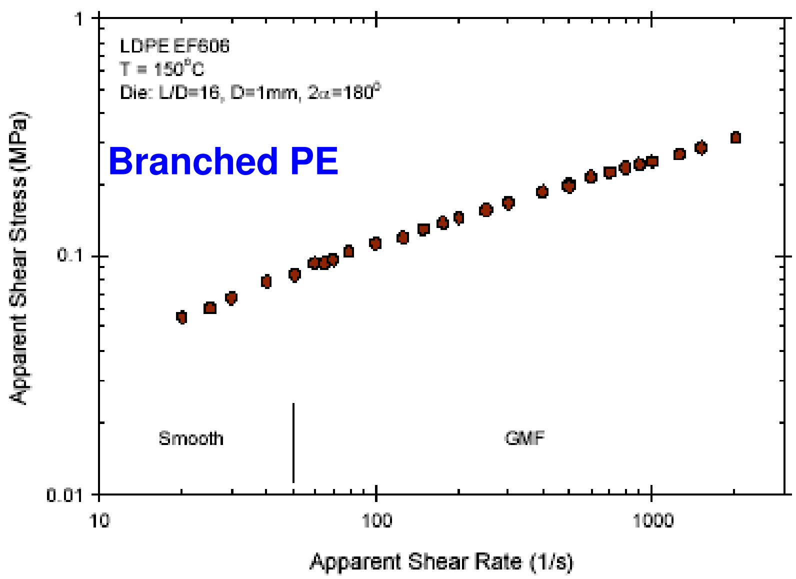
- The presence of BN also has a similar energy dissipation effect on PF-Y821-BP (ZN-type LLDPE)

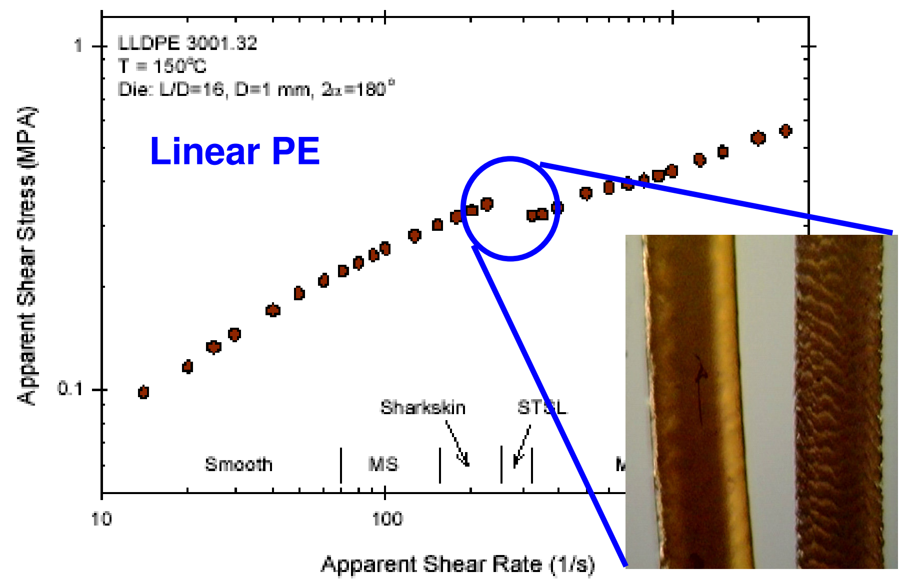
Mechanism of GMF Suppression by BN



- 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

Part III: Stick-Slip Flow Regime



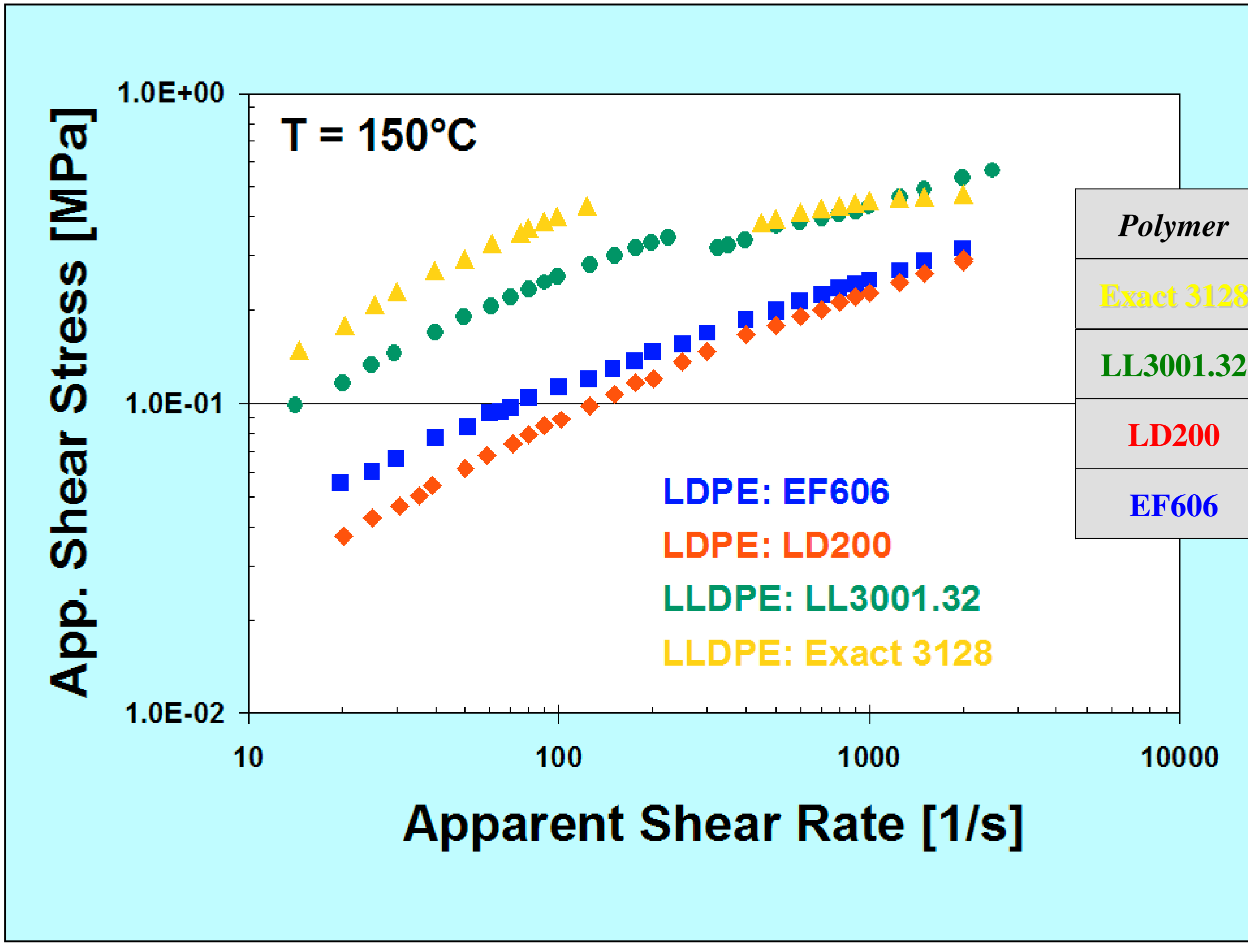


- Although this “stick-slip”, “spurt”, or “oscillating” melt flow instability regime has been studied at length over the past few decades from a phenomenological and symptomatic perspective, the cause of this melt flow behavior remains unclear.

Part III: 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

Capillary Extrusion Results

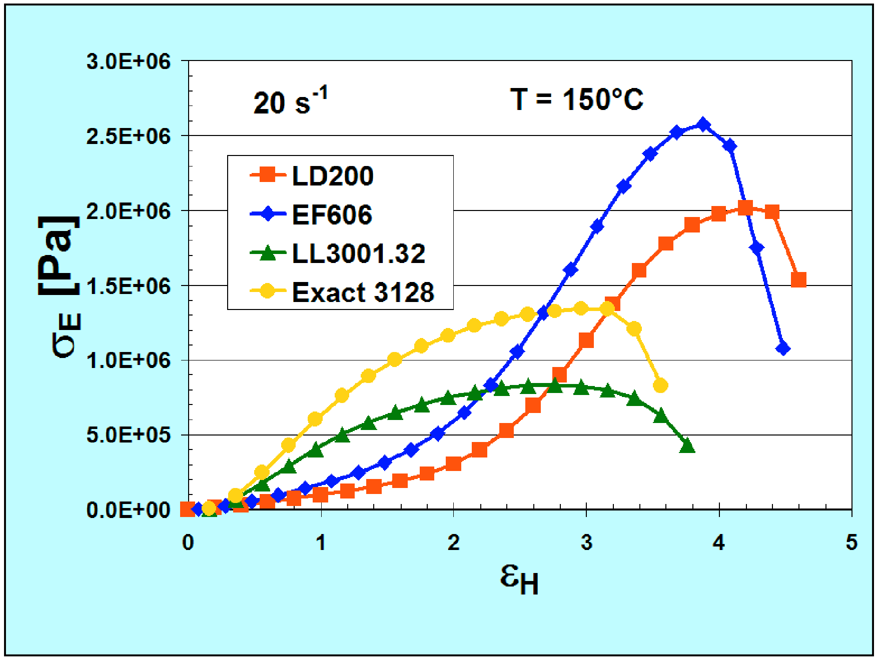


Critical Shear Rates for onset of...

Polymer	*Sharkskin*	*Stick-slip*	*Gross MF*
Exact 3128	20	120	420
LL3001.32	70	240	1400
LD200	-	-	270
EF606	-	-	50

- Exact 3128 exhibits a much large jump between branches of the flow curve than LL3001.32

High-Rate Tensile and Melt Flow Instability



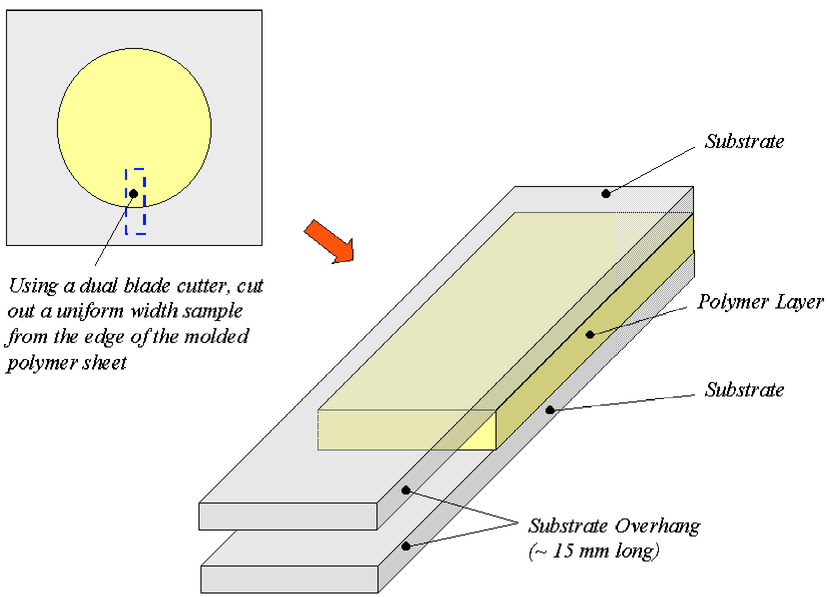
Critical Shear Rates for onset of...

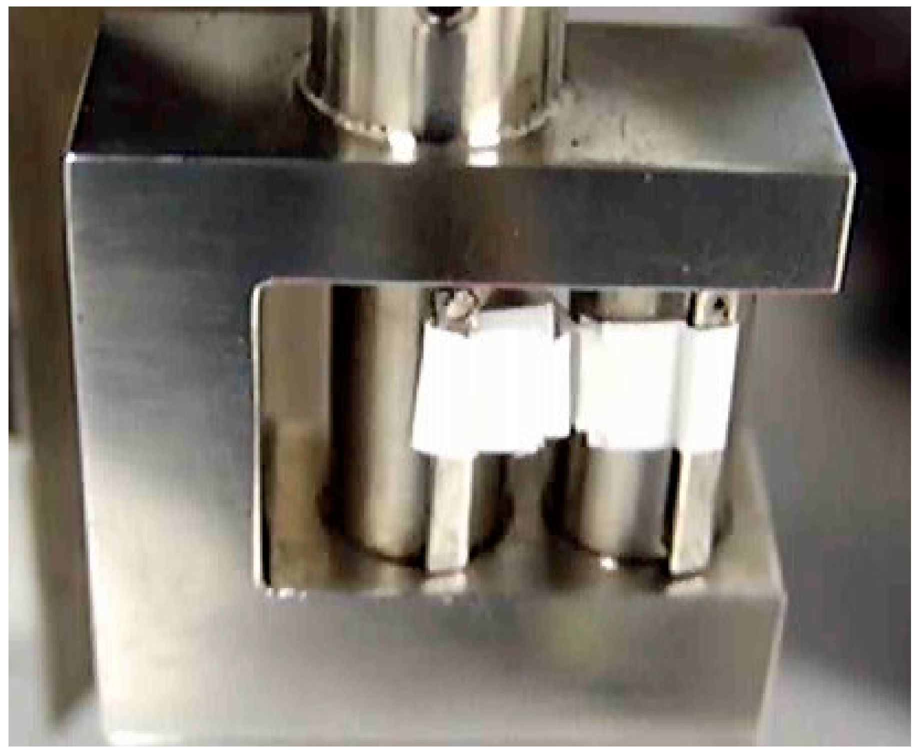
Polymer	*Sharkskin*	*Stick-slip*	*Gross MF*
Exact 3128	20	120	420
LL3001.32	70	240	1400
LD200	-	-	270
EF606	-	-	50

- Exact 3128 exhibits a steeper tensile stress growth rise than LL3001.32 at high rates of extension - approaching elastomeric behavior

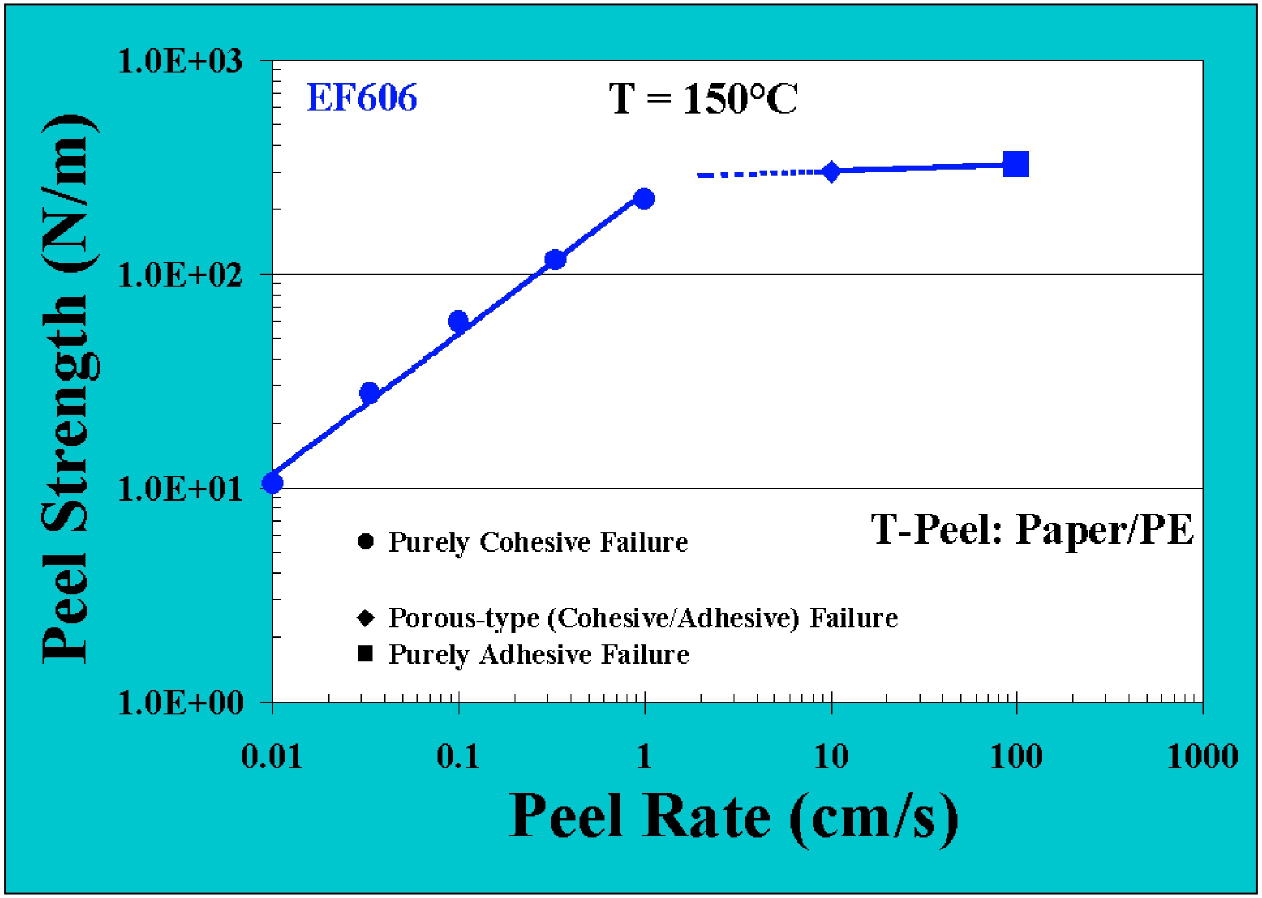
High-Rate Melt Adhesion Experiments

- 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



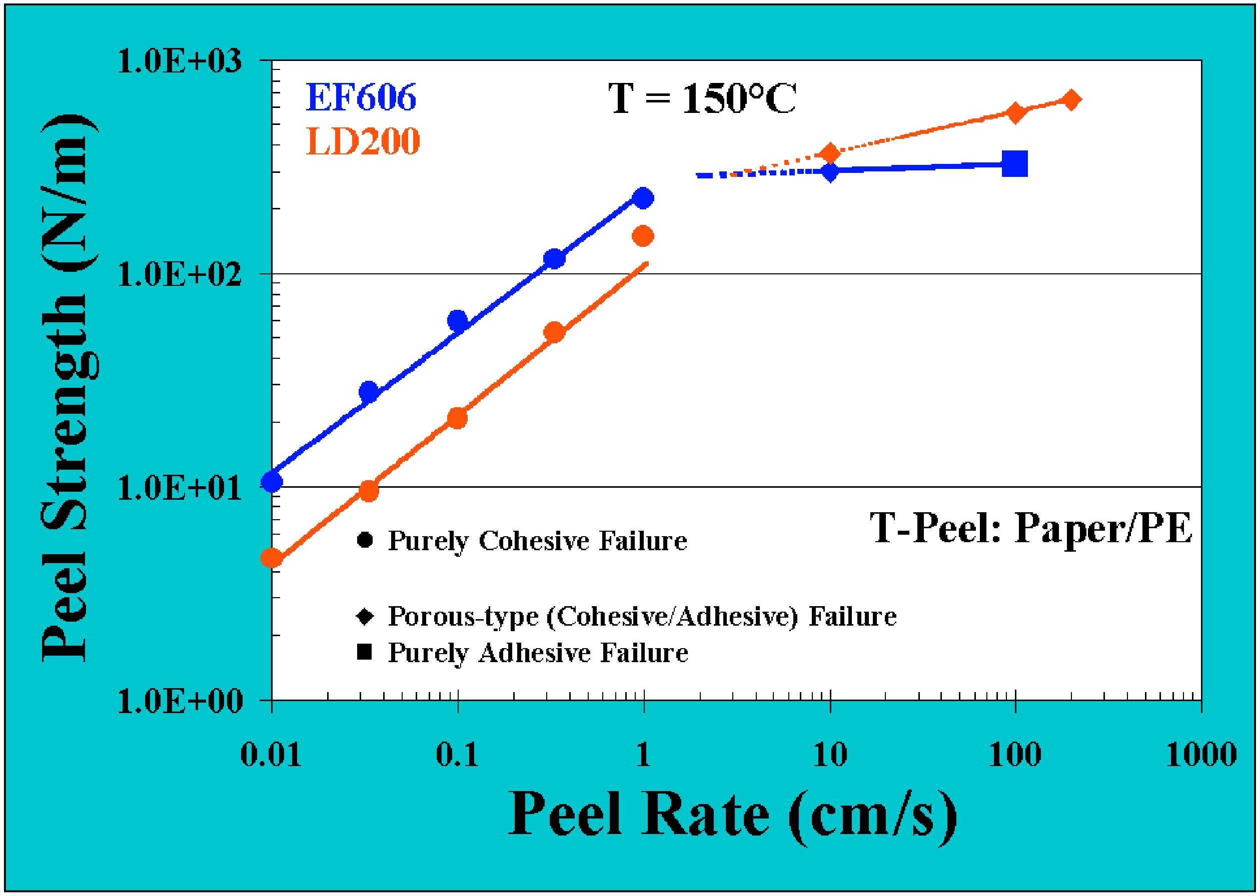


Peel/Melt Adhesion Data



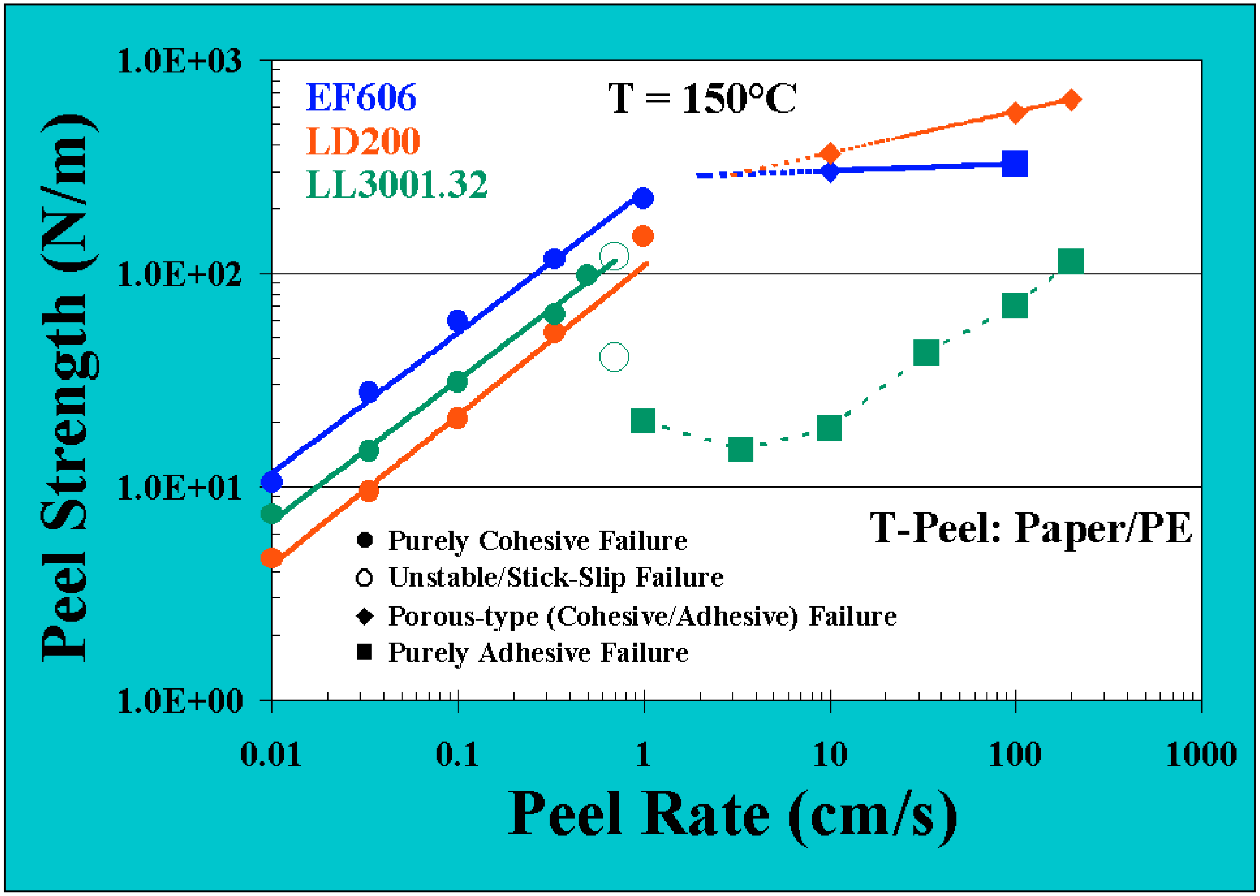
- The peel strength curve of the film grade LDPE (EF606) has very distinct regions of peel behavior as indicated
- Despite adhesive failure, peel strength always increases with rate

Peel/Melt Adhesion Data



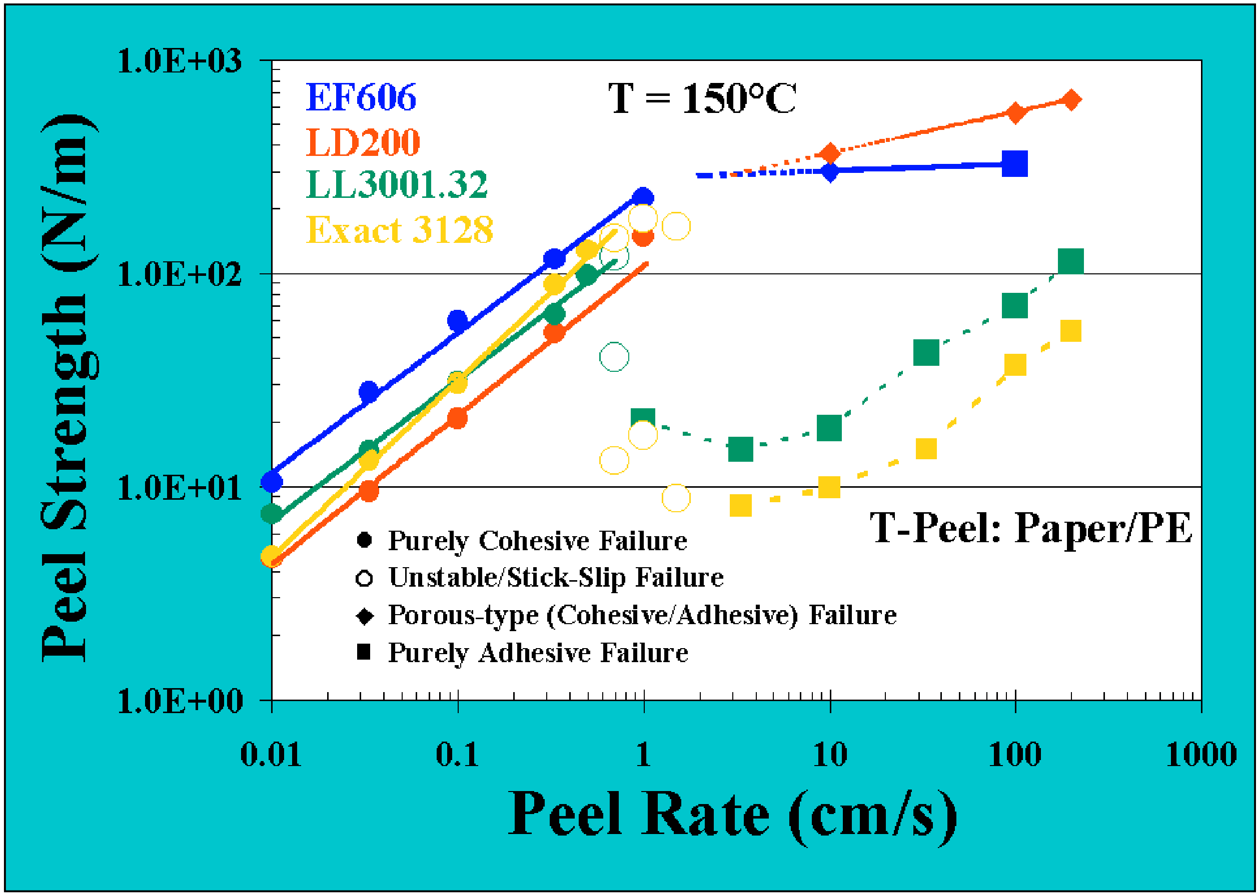
- The coating grade LDPE (LD200) also has a distinct “break” in the peel strength curve but exhibits superior peel strength to EF606
- LD200 does not exhibit adhesive failure

Peel/Melt Adhesion Data



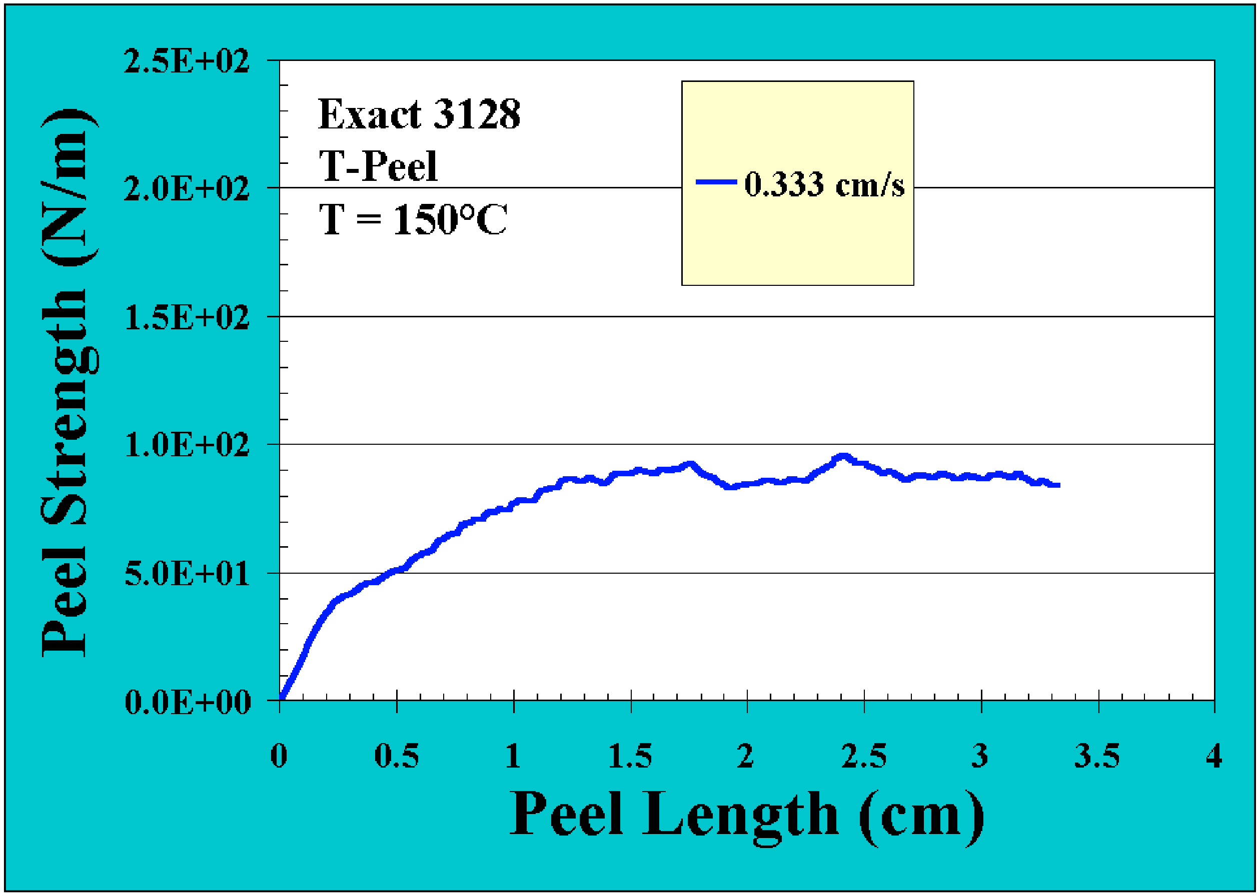
- The LLDPE (LL3001.32) exhibits an unstable region of peel behavior that appears qualitatively similar to stick/slip flow behavior
- Upon adhesive failure, peel strength drops dramatically

Peel/Melt Adhesion Data



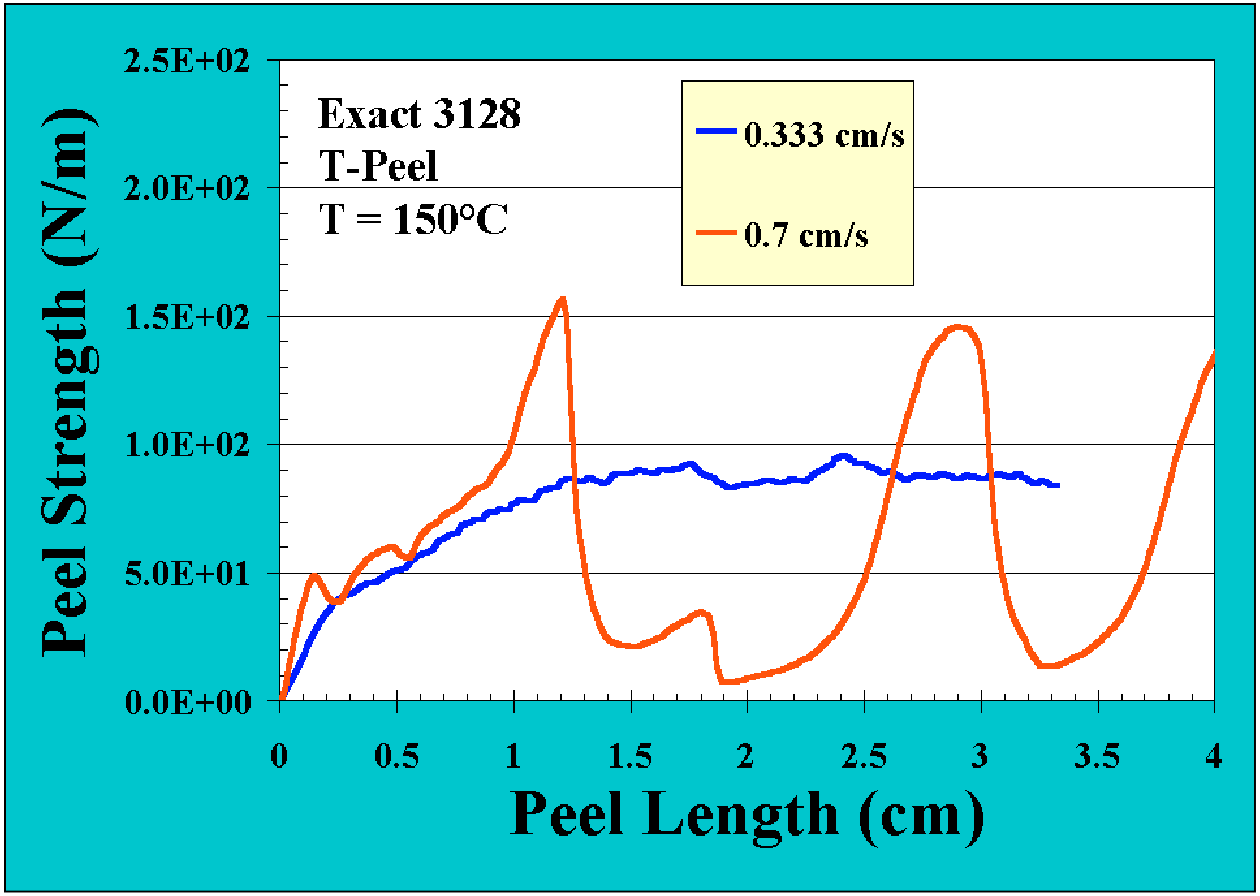
- Exact 3128 exhibits a larger region of peel instability that is very similar to its broad stick/slip flow region in extrusion
- Upon adhesive failure, peel strength decreases even more dramatically

Exact 3128 Peel Traces



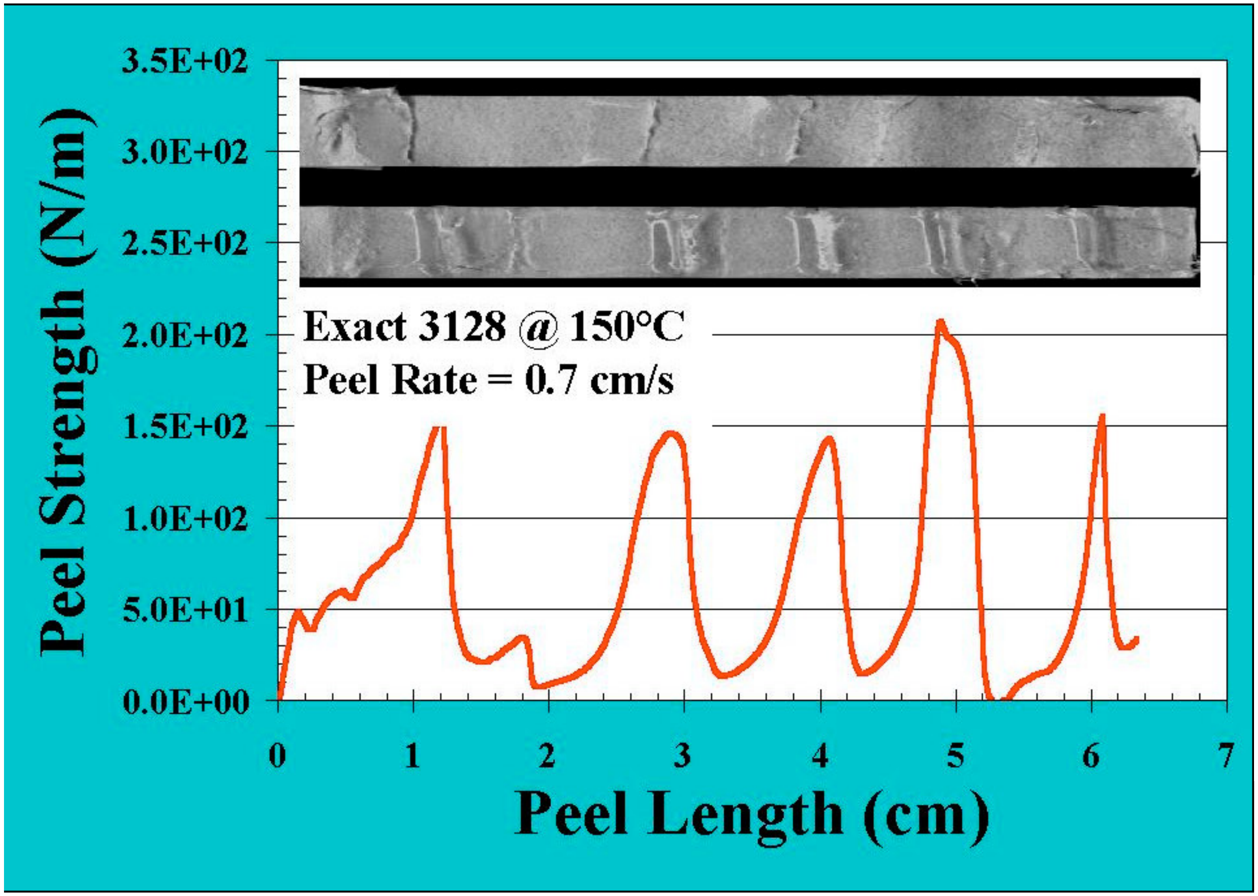
- At a peel rate of 0.333 cm/s, the peel strength trace for Exact 3128 is stable and the peel failure is purely cohesive.

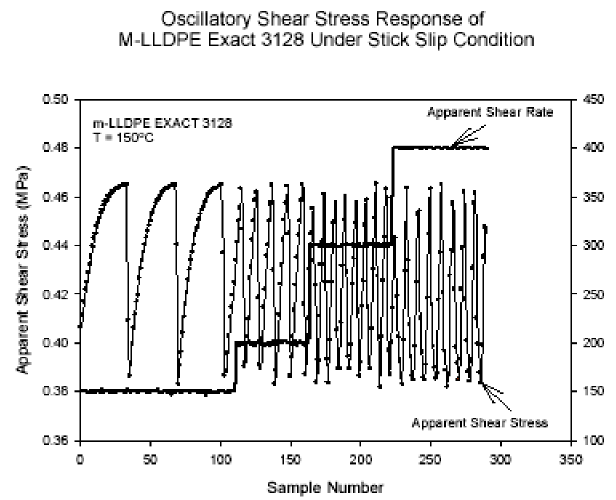
Exact 3128 Peel Traces



- 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.

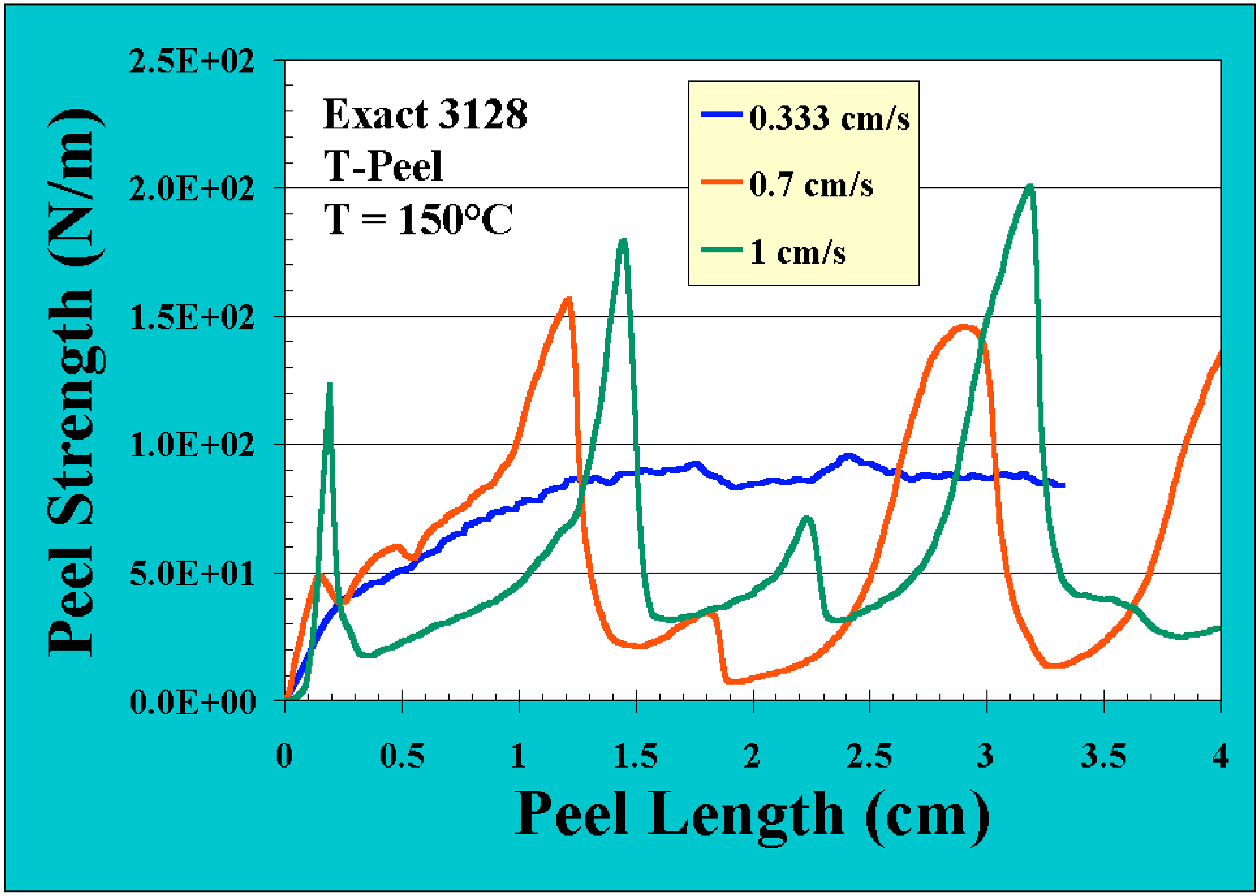
Exact 3128 Peel Traces





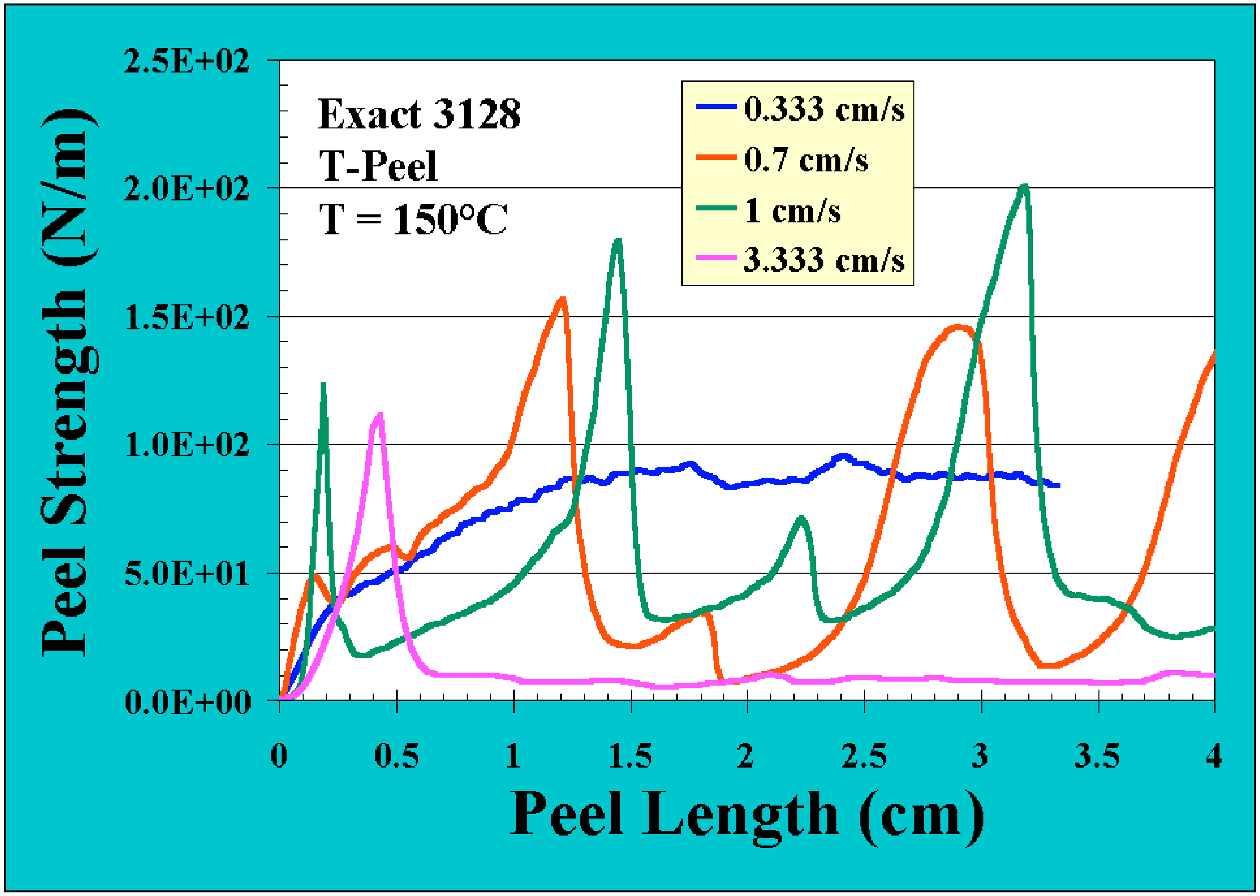
- The peaks in the peel strength trace correspond to cohesive modes of failure and are abruptly followed by troughs corresponding to adhesive modes of failure.

Exact 3128 Peel Traces



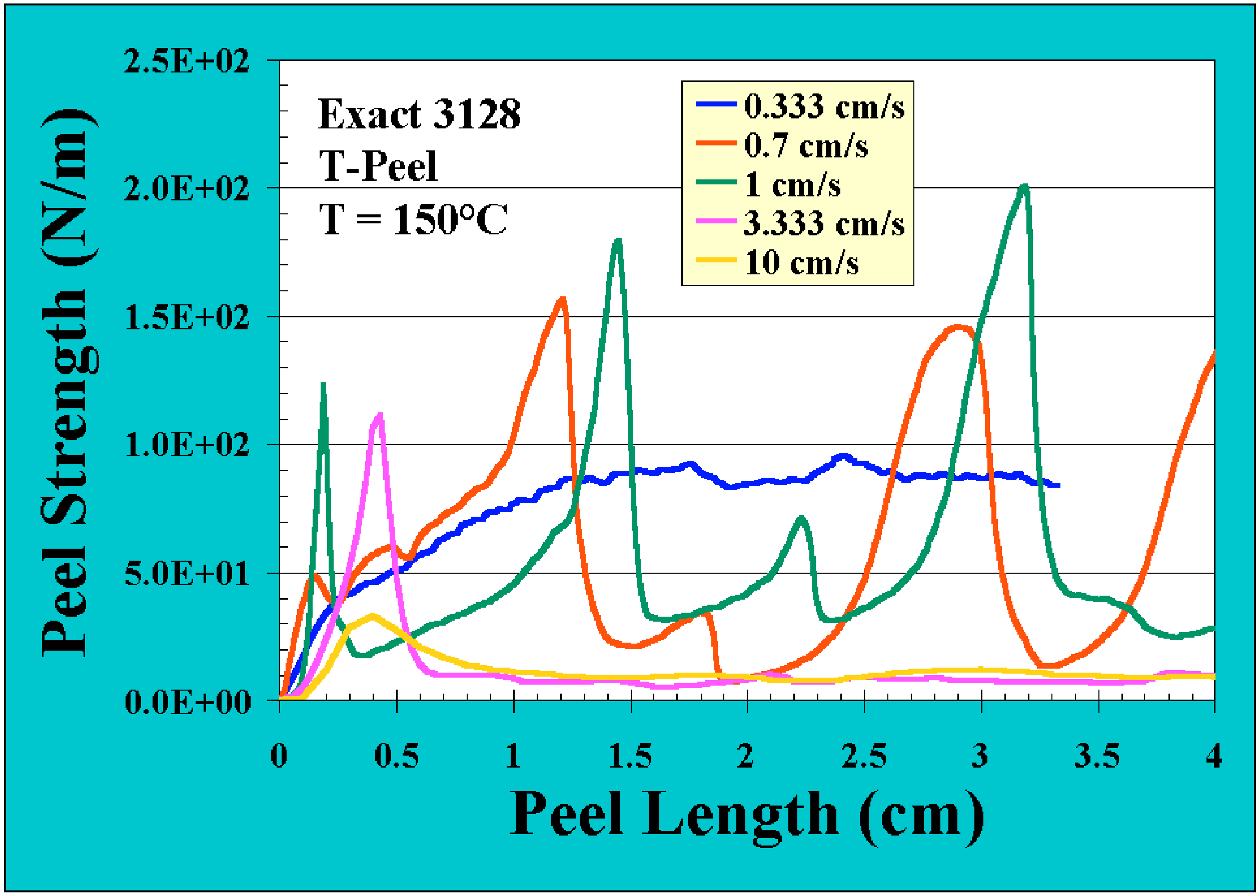
- At a peel rate of 1 cm/s, the peel strength trace and mode of failure remains unstable.

Exact 3128 Peel Traces



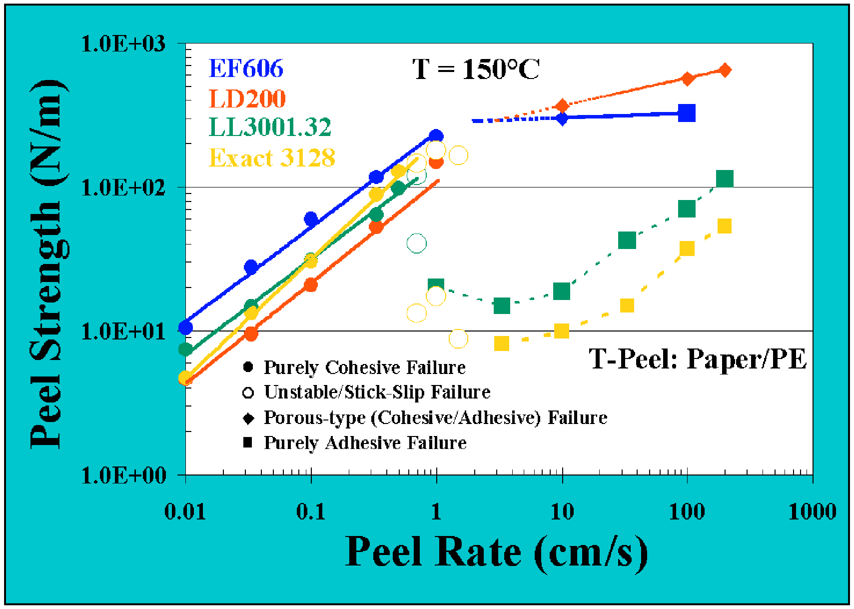
- At a peel rate of 3.333 cm/s, the peel strength trace exhibits a brief peak followed by a significant drop in signal that remains steady - the mode of failure is purely adhesive.

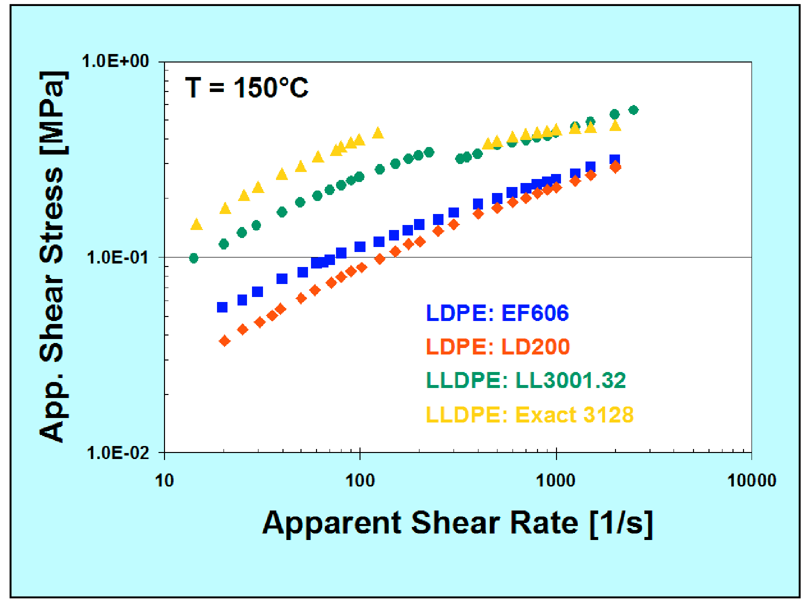
Exact 3128 Peel Traces



- 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.

Insight into Processing Behavior



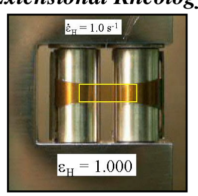


- These melt peel results with the SER appear quite promising as a fingerprint/laboratory predictor of melt processing behavior and may provide fundamental insight into the role of adhesion/slip in melt flow instabilities.

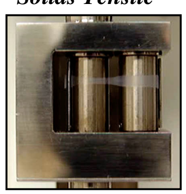
Summary

- Elucidated the role of high-rate melt tensile behavior on sharkskin melt fracture and the susceptibility of linear PE
- In comparing the extensional flow results with observed melt processing behavior, the mechanism of melt fracture suppression was elucidated with regard to elastic energy dissipation
- Unique melt peel results provide a characteristic fingerprint of melt processing behavior and elucidate the role of the work of adhesion on stick-slip flow instability

Extensional Rheology

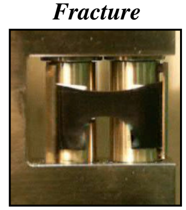


Solids Tensile



Peel/Adhesion

Fracture



Tear

Friction

SER Universal Testing Platform from Xpansion Instruments… Accept No Imitations.