Evaluation of ESCR of PE Resins Using Tensile Strain Hardening and Extensional Viscosity

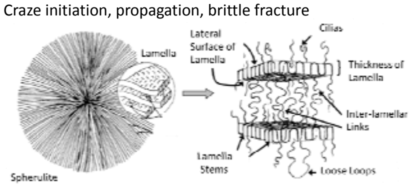
Institute for Polymer Research, University of Waterloo

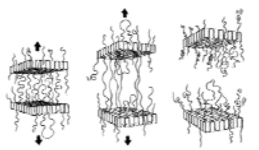
Pouyan Sardashti[1], Costas Tzoganakis[1], Maria Anna Polak[2], and Alexander Penlidis[1]

1: Department of Chemical Engineering, 2: Department of Civil Engineering, University of Waterloo

Environmental Stress Cracking Resistance (ESCR)

- **ESCR is the resistance to initiation of cracking and embrittlement of polymeric components; herein applied to polyethylene (PE) resins**
  - Main fracture mechanism involved in polymers (25% of all fractured polymers experience ESCR mechanism)
  - Function of different micromolecular properties (MW, MWD, SCB, etc.)
  - Occurs when polymers are subjected to low levels of stress over long periods of time, and aggressive environment
- **Mechanism: Slow Crack Growth (SCG)**
  - Polymer chain rearrangement to minimize stress
  - Craze initiation, propagation, brittle fracture





Need to identify the extent of entanglements

Objective: Evaluation of ESCR

- **Conventional Methods: Low accuracy, high uncertainty, long testing periods**
  - Notch Constant Load Test (NCLT), Pennsylvania Notch Test (PENT), Full Notch Creep Test (FNCT), Notched Pipe Test (NPT)
- **Potential Extensional Characterization Methods:**
  - Uniaxial Tensile Testing
    - Tensile Strain Hardening Stiffness Test (TSHS)
  - Rheological Techniques
    - Converging Flow Technique
    - Extensional Rheometry

Correlation between strain hardening and extent of entanglements

Materials

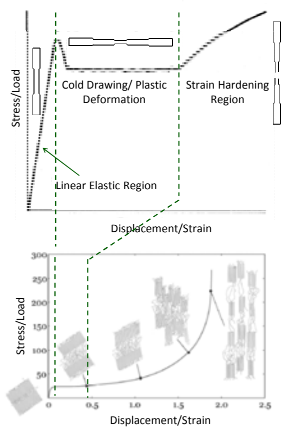
- HDPE: High Density Polyethylene (HD 8660.29, ExxonMobil)
- LLDPE: Linear Low Density Polyethylene (LL 8550.24, ExxonMobil)

Resin	Density (g/cm^3)	ESCR (h)	Differential Scanning Calorimetry (DSC): Crystallinity (%)	Melting Point (°C)	Lamella Thickness (nm)
HDPE	0.942	35	56.1	127.5	4.2
LLDPE	0.936	15	48.4	125.5	3.6

ESCR: Notch Constant Load Test (NCLT)
Lamella Thickness: Gibbs-Thomson Equation and DSC Analysis

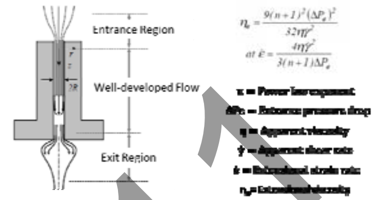
Methodology

- **Mechanical Approach:**
  - **Tensile Strain Hardening Stiffness Test (TSHS)**

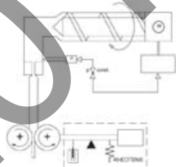


- A potential standard test for evaluation of ESCR
- Evaluation of ESCR from simple testing in a reliable and more practical fashion

- **Rheological Approach:**
  - **Converging Flow Technique:**

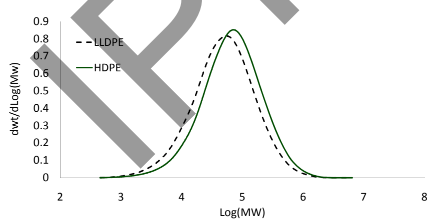


  - **Extensional rheometers:**
    - Sentmanat Extensional Rheometer (SER)
    - Rheotens (Fiber Spinning)



- Relationship between melt strain hardening and ESCR
- Insight into the influences of chain entanglements on ESCR

RESULTS



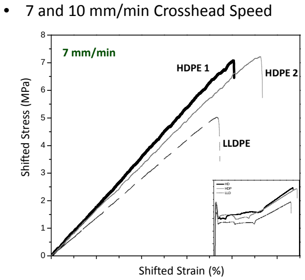
Resin	Gel Permeation Chromatography (GPC): M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI M_w/M_n	NMR: SCB (/1000C)
HDPE	25,236	118,501	336,312	4.70	1.8
LLDPE	18,334	90,101	279,526	4.91	3.5

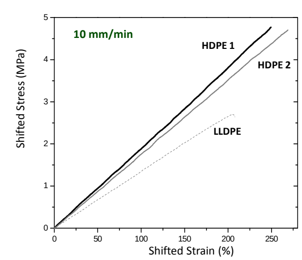
NMR: Nuclear Magnetic Resonance
SCB: Short Chain Branching

- Tensile Strain Hardening Stiffness Test (TSHS)
  - Room Temperature
  - 7 and 10 mm/min Crosshead Speed

Hardening Stiffness (HS)= $\frac{1}{n}\sum \frac{\sigma_{i+1}-\sigma_i}{\varepsilon_{i+1}-\varepsilon_i}$

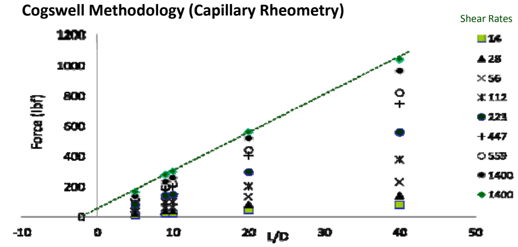
	HD	LLD
HS (MPa)	0.019	0.013

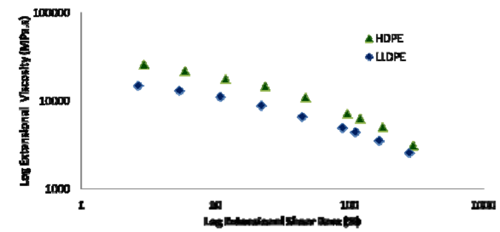




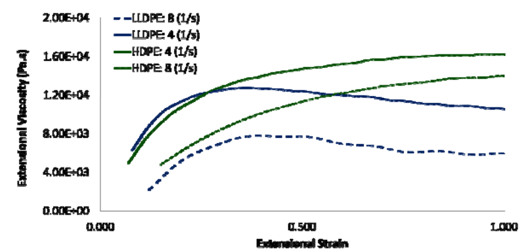
Results

- **Converging Flow Technique: Evaluation of Extensional Viscosity Using Cogswell Methodology (Capillary Rheometry)**





- **Extensional Rheometry: Sentmanat Extensional Rheometer (SER)**



Future Steps

- Investigation of the validity of the techniques on a broader ranger of PE resins (ESCR between 50 and 800 hours)
- Optimization of the TSHS test based on specimen dimensions and crosshead rates
- Development of a standard test for evaluation of the ESCR of PE resins

REFERENCE

- Cheng, J.; Polak, M.; Penlidis, A. J. Macromol Sci. Pure & Appl Chem 2008, 45, 599.
- Cogswell, F. N. J.Non-Newtonian Fluid Mech 1972, 12, 64.
- Cheng, J. J. Mechanical and Chemical Properties of High Density Polyethylene Effects of Microstructure on Creep Characteristics; PhD Dissertation, Dept of Chem Eng, University of Waterloo: Waterloo, Ont., 2008.
- Wright, D. C. 1996. Environmental Stress Cracking of Plastics, Smithers Rapra Technology, 1996.
- Bernnat,A., Wagner,M.H. Prog Trends Rheol V, Proc Eur Rheol Conf. 5th , 1998.