Improvement of the Hardening Stiffness Test as an Indicator of Environmental Stress Cracking Resistance of Polyethylene Resins

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Long term mechanical behaviour of polyethylene (PE) is of great importance especially in cases where structural integrity is required. In order to predict the mechanical behaviour of PE, it is necessary to fully understand the micromolecular structure of the employed resins. In this study, evaluation of several micromolecular properties of PE will be conducted. These properties influence an important performance indicator of PE for structural applications, namely the environmental stress cracking resistance (ESCR). ESCR in PE resins occurs through a slow crack growth mechanism under low applied stresses and long periods of time. This property is usually assessed by unreliable and time consuming testing methods such as the notch constant load test (NCLT) or bent strip test (BST) on notched PE specimens in the presence of an aggressive fluid and elevated temperatures. In this work, it was tried to find relationships between micromolecular structure and material response, mainly molecular weight properties and short chain branching content to strain hardening behaviour of PE resins, through mechanical experiments. Inter-lamellar entanglements are believed to be the main parameter controlling slow crack growth of PE. Extent of entanglements and entanglement efficiency will be investigated by monitoring the strain hardening behaviour of PE resins in solid state through a uniaxial tensile test. The hardening stiffness (HS) test suggested by Cheng et al. [1] for prediction of ESCR was refined and improved to cover a broader range of PE resins, along with easier sample preparation, and faster testing. This test will offer a more reliable and consistent ESCR picture without the drawbacks of the subjective notching process and presence of aggressive fluids.

Experimental

In this study, a range of commercially available rotomolding and pipe grades of LLDPE and HDPE were selected. These resins were selected according to their ESCR values, reported in their product data sheets. The ESCR values were reported from a bent strip test (BST). The objective was to select group of resin that offered ESCR values between 8 and 1000 hours. The material properties are summarized in Table 1. The tensile tests were performed at room temperature on an Instron 3365 machine. The specimens were prepared by punching compression moulded plaques prepared at the following condition: compression molding at 195 ºC±5 ºC and 10,000 lbf, followed by 24 hour cooling at room temperature in the mold. The HS was obtained by measuring the slope of the strain hardening section of the load-displacement curve. The test specimens were pulled until complete failure was obtained

Table 1: PE resin properties used in this study

PE Grade	Resin Type	Density (kg/m^3)	Melt Index (g/10 min)[a]	Mn (kg/mol)	Mw (kg/mol)	Mz (kg/mol)	PDI	Comonomer	SCB /1000C[b]
LLDPE 1	Rotomolding	936	6.8	15.4	71.8	252.0	4.65	Hexene	4.2
LLDPE 2	Rotomolding	938	3.3	20.8	82.0	232.0	3.94	Hexene	7.5
LLDPE 3	Rotomolding	937	5.0	18.0	74.6	191.0	3.98	Hexene	13.3
LLDPE 4	Rotomolding	932	5.2	15.1	76.6	286.0	5.08	Hexene	22.3
HDPE 1	Rotomolding	948	5.0	18.7	77.9	349.0	4.17	Hexene	1.6
HDPE 2	Rotomolding	942	2.0	25.24	118.5	336.0	4.70	Hexene	0.9
HDPE 3	Pipe	958	----	10.4	217.9	1244.2	20.90	Butene	7.0
HDPE 4	Pipe	955	----	5.9	315.4	2129.3	53.30	Butene	11.8

A d-optimal factorial design was selected to investigate the significance of specimen dimensions, strain rate, and the molecular weight of PE resins on HS. Three levels of strain rate, specimens' thickness, gauge length and width were selected and tensile tests were performed on three different HDPE resins.

Results and Discussions

Effect of Molecular Properties on ESCR obtained by NCLT and BST

ESCR results obtained from the NCLT and BST are shown in Table 2. The ESCR values reported are mean averages over several replicates (15-20). Although both NCLT and BST tests are used to measure the creep rupture of plastics under an aggressive environment, they are fundamentally different from each other. During an NCLT experiment, a constant load (15 % of resin's yield strength) is applied to notched samples, and time to a complete failure is measured. On the other hand, BST applies a constant deformation to notched polymer samples and time to failure (50 or 100 % failure or creation of crack) is recorded. As a result, deviations in reported ESCR values from both tests were expected. In this study however, the deviation between the measured ESCR from the two tests were large. This deviation was clearly obvious for LLDPE resins, especially for resins with higher SCB content, but considerably lower for HDPE, especially for resins experiencing either very high or very low ESCR. Despite the differences between the reported ESCR values by two tests, ESCR of HDPE increased with Mw. On the other hand, no correlation between the SCB content of the ESCR of the resin was obtained, alluding the domination of Mw on the ESCR of HDPE. This behaviour was completely reversed for LLDPE. No correlation between Mw and ESCR was found as ESCR of LLDPE 2 was lower than LLDPE 3-4. A trend between the SCB and ESCR of the LLDPE resin obtained from the BST was found, indicating the dominance of SCB of the LLDPE when relatively similar LLDPE (in terms of Mw) are compared. The inconsistency between the ESCR values of BST and NCLT suggested the lack of sensitivity of the NCLT to subtle molecular structures such as SCB and molecular weight differences. Further, it was suggested that the test condition for the NCLT may have been too harsh (notch depth of 40 % nominal thickness) for LLDPE resin and caused premature failure. Because of the constant applied strain in BST, HDPE with various densities (as a result of different crystallinity) and hence different stiffness, go under higher applied loads than needed for the test. This tends to develop heterogeneous crack initiation and propagation, resulting in a premature failure of the HDPE. LLDPE on the other hand, due to lower stiffness, performs well when subjected to BST as crack initiation and growth are relatively more smooth and homogeneous. Therefore, NCLT should be considered for HDPE and BST for LLDPE, when ESCR conventional testing methods are required.

Table 2: ESCR values reported by NCLT and BST

PE Grade	ESCR by NCLT (h)[a]	St. Dev (h)[b]	ESCR by BST (h)[c]	HS (N/mm)	St. Dev (N/mm)
LLDPE 1	12.00	1.53	60	0.249	0.012
LLDPE 2	57.10	6.73	150	0.336	0.007
LLDPE 3	22.63	3.96	190	0.269	0.001
LLDPE 4	180.00	67.20	650	0.300	0.005
HDPE 1	8.36	2.09	8	0.214	0.002
HDPE 2	27.19	9.30	50	0.352	0.002
HDPE 3	872.10	338.00	1000	0.536	0.009
HDPE 4	3000	---	1000	0.550	0.015

a: notch constant load test (performed in our laboratories), b: Standard deviation, c: bent strip test (provided by the manufacturer)

Evaluation of specimen's dimension and strain rate on hardening stiffness

It was intended to identify the effects of specimen's dimension and strain rate on hardening stiffness of the PE resins. This was done in order to create a more practical and informative tensile test for the evaluation of HS. An experimental was constructed and tensile tests at different strain rates were performed on specimens with different dimensions and molecular weights. In this case, Mw (A), strain rate (B), width (C) and thickness (C), along with some of their interactions (AE, DE) were found to be the significant factors. Gauge length had no significant effect on the HS. All significant main factors had positive relationship with HS, from which, molecular weight, thickness, and width were the most significant ones. It was suggested that in order to amplify the effect of molecular structure (Mw, SCB, etc.) on HS, the effect of specimen's dimension, namely, thickness and width should be minimized. Further, the strain rate and gauge length should be properly selected to make the test easier, faster, and more practical. The effect of thickness and width (the interaction plot obtained at highest Mw and strain rate) on HS is shown in Figure 1(a). As the thickness of the specimens increased, the effect of width on HS becomes more pronounced. This trend suggested that a thickness of 0.6 mm should be selected in order to minimize the effect of width on HS, for widths between 3-6 mm (slope of the line represent the effect on HS). If width of the specimen is selected between 6-12 mm, then thicknesses between 0.6-1.8 mm should be selected to minimize the effect of width on HS (where slope is the lowest). Figure 1(b), similarly shows the relationship between Mw and HS at various specimens' widths. The idea was to select the condition at which the effect of Mw on HS is maximized. The slope of the lines for widths of 6-12 mm is very similar, suggesting that any width selected in that range would maximize the effect of Mw on HS, however, for simplicity of the test it is recommended to use lower values. Widths below 6 mm also reflect the effect of Mw on HS, however to a smaller extent. It should be noted that a minimum width to thickness ratio of 8 is recommended when constructing dog bone shaped specimens. In this study, it was decided to keep the thickness to its lowest value of 0.6 mm (to minimize the effect of width) and width to a value of 5 mm. Further, for practicality and ease of testing, it was decided to keep the gauge length at 16 mm (lowest value), and strain rate at 10 mm/min (highest rate).Figure 2, is a representation of this finalized test specimen. It should be mentioned that any width and thickness selection that follows the above mentioned criteria can be used (it is recommended to use thinner specimens).

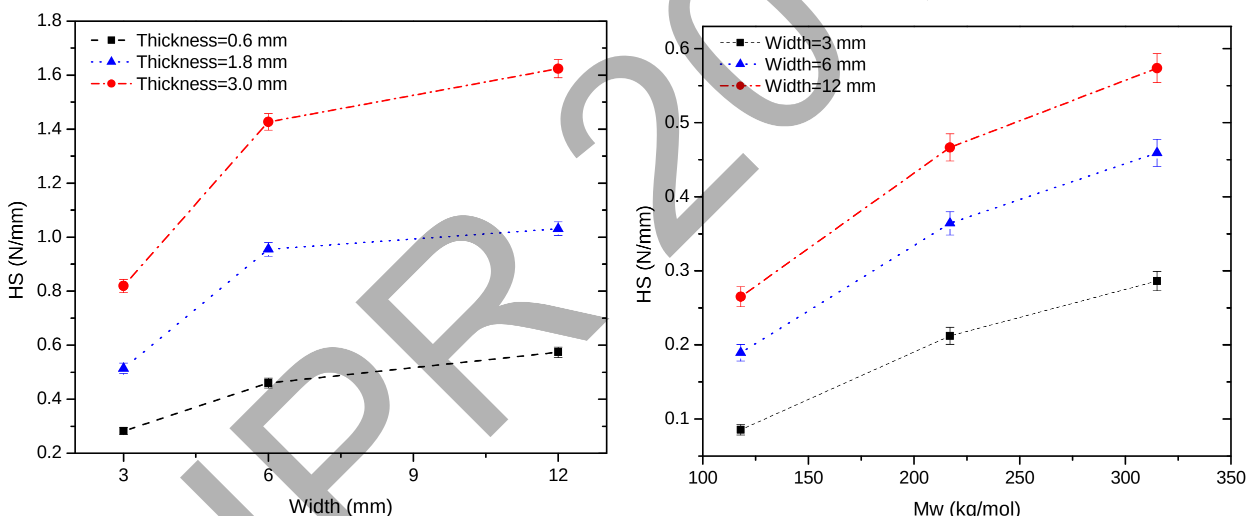

Figure 1: (a) Effect of width on HS at various thicknesses, (b) Effect of Mw on HS at different widths

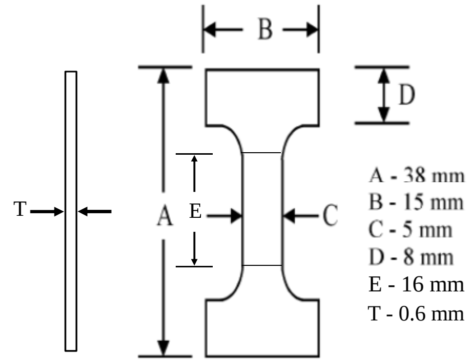

Figure 2: Specimens' dimension used in this study

HS data obtained from the tensile testing on specimens designed in previous section of this study are shown in Table2. As expected, there exists an increasing trend in ESCR of HDPE as HS values increased, representing a higher resistance in polymer towards slow crack growth. This trend once again, verified that the hardening stiffness can be used as a measure of ESCR of HPDE resins. Compared to Cheng et.al.'s work, HS values obtained in this study were recorded in a more practical, reproducible, and reliable fashion (low standard deviation as reflected in Table2). It is also believed that the effect of molecular structure is more readily reflected on HS due to minimization of the effect of specimens' shape on HS.

References

(1) Cheng, J. J. *Mechanical and chemical properties of high density polyethylene effects of microstructure on creep characteristics*; University of Waterloo: Waterloo, Ont., 2008.

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Environmental Stress Cracking Resistance (ESCR)

2 [3,4,10]

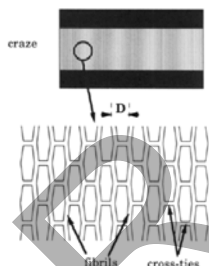
- Resistance to initiation of cracking and embrittlement
  - Function of different micromolecular properties
  - Mechanism: Slow crack growth (SCG)
- Polymers subjected to:
  - Bulk inhomogeneity (scratches, voids, etc.)
  - Low levels of stress (much lower than yield stress)
  - Long periods of time
  - Environmental conditions
- Craze initiation, propagation, brittle fracture


Failure Mechanism (SCG via craze failure)

3 [7,8]

Failure governed by network of effective entanglements in the strain hardened fibril

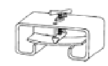
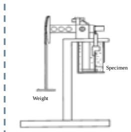
Resistance to craze propagation and failure is primarily determined by the **strain hardening response of fibrils and hence of the material**



Challenges in Prediction of ESCR

4 [4]

- Conventional testing
  - Low accuracy, high uncertainty
  - Long testing periods
- Micromolecular variables vs. ESCR
  - Single factor analysis
  - Narrow property range
- Processing factors vs. ESCR
  - Limited knowledge
  - Poor estimation

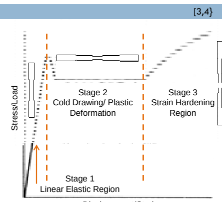



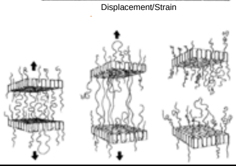
Hardening Stiffness (HS) as a Measure of ESCR

5 [3,4]

- Based on a suggestion by Cheng et al. (2009)
- Uniaxial tensile test performed at:
  - Room temperature, 0.5 & 7 mm/min
  - No notching process/ aggressive environment
  - Evaluation of strain hardening behaviour
  - HS as the extent of entanglements

Correlation between HS and ESCR





Research Objectives

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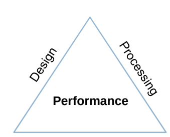
- Meaningful relationship between ESCR and molecular properties of PE resins
- Development of practical tests for evaluation of ESCR in a reliable fashion
- Evaluation of effect of processing factors on ESCR
- Modification of ESCR of PE resins



Resin Selection

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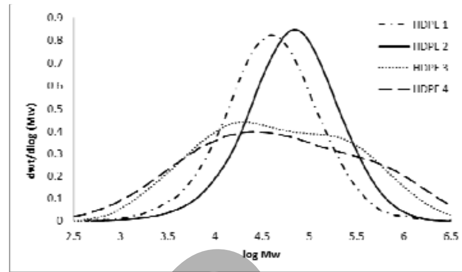
Grade	PE	Remarks	ESCR (h)
HDPE	HDPE 1	Rotomolding, Hexene Copolymer	8
	HDPE 2	Rotomolding, Hexene Copolymer	50
	HDPE 3	Pipe, Butene Copolymer	1000
	HDPE 4	Pipe, Butene Copolymer	>1000
LLDPE	LLDPE 1	Rotomolding, Hexene Copolymer	60
	LLDPE 2	Rotomolding, Hexene Copolymer	150
	LLDPE 3	Rotomolding, Hexene Copolymer	190
	LLDPE 4	Rotomolding, Hexene Copolymer	650

ESCR values taken from a BST

MW Distributions

8



PE Resin Properties

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PE Grade	Density (kg/m³)	Melt Index (g/10 min)	Mn (kg/mol)	Mw (kg/mol)	Mz (kg/mol)	PDI	SCB /1000C
LLDPE 1	936	6.8	15.4	71.8	252.0	4.65	4.2
LLDPE 2	938	3.3	20.8	82.0	232.0	3.94	7.5
LLDPE 3	937	5.0	18.0	74.6	191.0	3.98	13.3
LLDPE 4	932	5.2	15.1	76.6	286.0	5.08	22.3
HDPE 1	948	5.0	18.7	77.9	349.0	4.17	1.6
HDPE 2	942	2.0	25.24	118.5	336.0	4.7	0.9
HDPE 3	958	----	10.4	217.9	1244.2	20.90	7.0
HDPE 4	955	----	5.9	315.4	2129.3	53.30	11.8

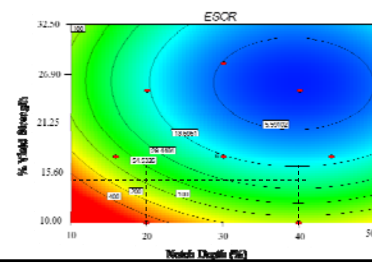
NCLT vs. Bent Strip Test (BST)

10

- Stress level: 15% of PE yield strength
- Notched depth: 40% of specimen thickness
- 20 specimens per resin type @ 50 °C

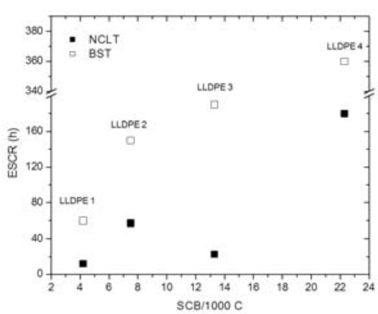
Notch Depth (%)	Stress Level (%)
20.00	10.00
40.00	25.00

PE Grade	ESCR by NCLT (h)	ESCR by BST (h)
LLDPE 1	12.00	60
LLDPE 2	57.10	150
LLDPE 3	22.63	190
LLDPE 4	180.00	650
HDPE 1	8.36	8
HDPE 2	27.19	48
HDPE 3	872.10	1000
HDPE 4	>1000	>1000



Molecular Properties vs. ESCR

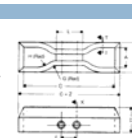
11



Refinement of the Hardening Stiffness Test

12

- Selected resins: HDPE 2-4
- Factors: Mw, strain rate, gauge length, width, and thickness
- Levels selected according to ASTM D412 & D638



Study Type: Factorial	Design Type: D-optimal		
Design Model: 2nd order interaction			
Factors		Levels	
A: Mw (kg/mol)	118	218	315
B: Strain rate (mm/min)	0.5	5	10
C: Gauge Length (mm)	16	33	60
D: Width (mm)	3	6	12
E: Thickness (mm)	0.6	1.8	3

Refinement of the Hardening Stiffness Test

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Analysis of Variance

Source	Sum of Squares	df	Mean Square	F value	p-value	
Model	3.33	16	0.21	97.40	< 0.0001	significant
A-MW	0.81	2	0.40	189.34	< 0.0001	
B-Speed	0.025	2	0.013	5.95	0.0052	
D-Width	0.81	2	0.40	188.43	< 0.0001	
E-Thickness	1.26	2	0.63	294.65	< 0.0001	
AE	0.053	4	0.013	6.24	0.0005	
DE	0.076	4	0.019	8.93	< 0.0001	
Residual	0.092	43	2.136E-03			
Lack of Fit	0.082	39	2.115E-03	0.9	0.6328	not significant
Pure Error	9.362E-03	4	2.340E-03			
Total	3.42	59				

Refinement of the Hardening Stiffness Test

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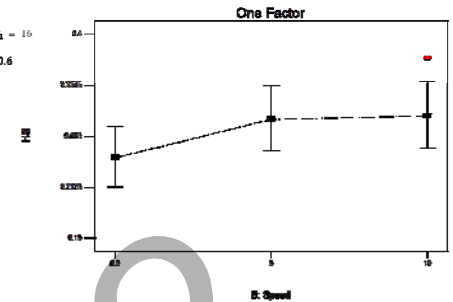
X1 = B: Speed

Actual Factors
A: MW = 118
C: Gauge Length = 16
D: Width = 6
E: Thickness = 0.6



Specimen's Dimensions and Rate of Test: Final Selection

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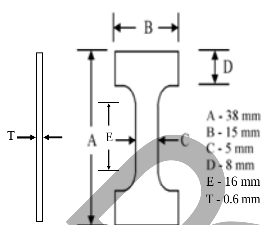
- Specimen Dimensions:
  - Gauge length: 16 mm
  - Width: 6 mm
  - Thickness: 0.6 mm
- Strain Rate: 10 mm/min



Hardening Stiffness and ESCR

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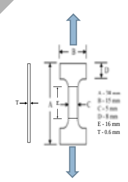
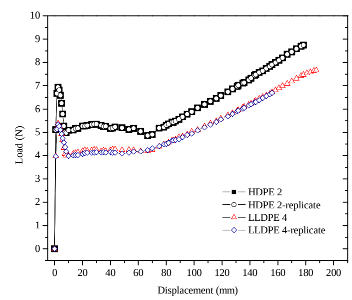
- Tensile tests performed at:
  - Room temperature
  - 10 mm/min

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





Hardening Stiffness and ESCR

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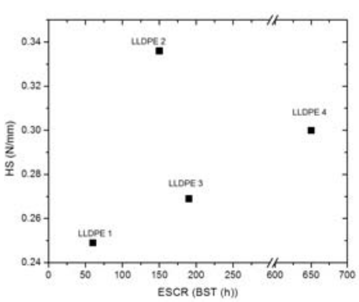

St. Dev

PE Grade	Mw (kg/mol)	SCB /1000C	ESCR (h)
LLDPE 1	71.8	4.2	60
LLDPE 2	82	7.5	150
LLDPE 3	74.6	13.3	190
LLDPE 4	76.6	22.3	650

Effect of SCB on HS

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- Central composite design (Face-centered)
- Selected resin: LLDPE 1, LLDPE 3, LLDPE 4 (Similar Mw, different SCB)
- Strain rate: 0.1, 2.5, 5.0 mm/min

	Type	SCB/ 1000C	Strain Rate (mm/min)	SCB/ 1000C	Strain Rate (mm/min)
1	Center	0	0	13.25	2.55
2	Axial	0	0	13.25	0.1
3	Factorial	+1	+1	22.3	5
4	Center	0	0	13.25	2.55
5	Axial	+1	0	22.3	2.55
6	Factorial	+1	-1	22.3	0.1
7	Factorial	-1	+1	4.2	5
8	Axial	0	+1	13.25	5
9	Center	0	0	13.25	2.55
10	Center	0	0	13.25	2.55
11	Factorial	-1	-1	4.2	0.1
12	Axial	-1	0	4.2	2.55
13	Center	0	0	13.25	2.55

Significance of SCB on HS

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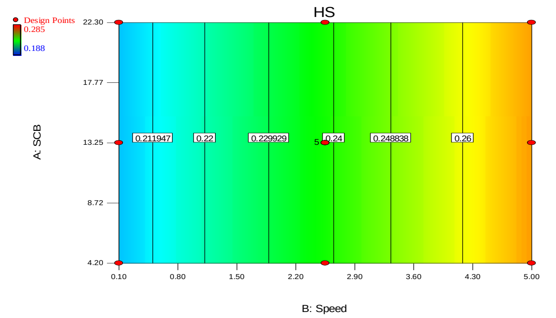

HS Correction

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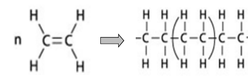
- Number of branching points (m)
  - Unitless number
  - Product of Mw and SCB



$$\text{Number of branching points } (m) = \frac{SCB \times Mw}{M_m}$$

Mw → Weight average MW

M_m → Monomer MW

$$cHS = HS \times m$$

ESCR vs. cHS

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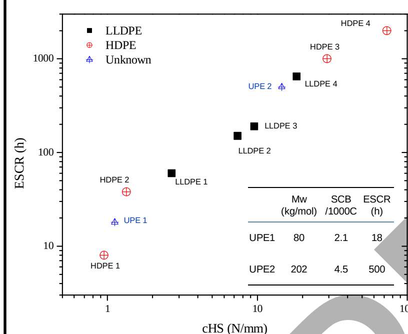


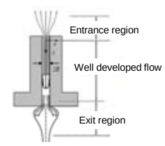
	Mw (kg/mol)	SCB /1000C	ESCR (h)
UPE1	80	2.1	18
UPE2	202	4.5	500

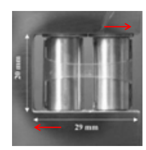
- Better reflection of Mw and branching on ESCR
- Clear comparison between different types of PE
- Better property mapping between ESCR and cHS
- Reliable measure for ranking PE with different structural characteristics
- Verified by using unknown PE resins (UPE1 and UPE2)

Ongoing Research: Extensional Rheological Characterization

22 [5,6,9]

- Evaluation of extensional (elongational) viscosity
  - Effect of micromolecular properties on strain hardening behaviour in melt state
- Converging flow techniques
  - Cogswell approach
  - Use of capillary rheometers
- Extensional rheometry approach
  - Extensional rheometers: SER





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Thank you

Questions?

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Additional Slides

Failure Mechanism

26 [1,2,7]

- Energy needed to create crazes: (Argon) $\Gamma(\gamma, v_e) = \gamma + \frac{1}{4} v_e U d$

γ = van der Waals cohesive energy between molecules
v_e = Effective entanglement density
U = Energy needed to fracture a covalent chain
d = End to end distance between the effective entanglements

- Energy for Craze-Crack transition: (Brown-Kramer) $G_{1c} \propto (\Sigma_e f_c)^2$

G_{1c} = Energy release rate for crack opening
Σ_e = Network density (number of load bearing chains per unit volume)
f_c = Force needed to break one molecular chain

Rheological Characterization

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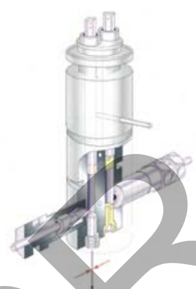
- Capillary Rheometry
  - Shear viscosity vs. shear rate
  - Shear rates: 14-1400 (s^{-1})
  - Temperature: 190 °C
  - Correction for non-Newtonian behaviour
  - Entrance pressure drop calculation

$$\eta_e = \frac{9(n+1)^2(\Delta P_e)^2}{32\eta\dot{\gamma}^2}$$
$$at\ \dot{\varepsilon} = \frac{4\eta\dot{\gamma}^2}{3(n+1)\Delta P_e}$$



- Selected Resins:
  - LLDPE 2-4

Ongoing Research:
Effect of Temperature on Lamella Lateral Surface Area (LLSA)

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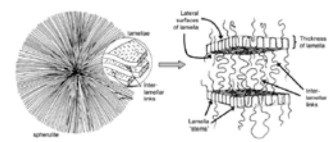
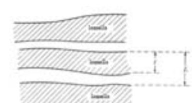
- Controlled cooling:
  - Quenching
  - 1°C/min
  - Slow cooling



- Annealing:
  - Different temperatures: 100 °C and 90 °C
  - Different time periods:1 h, 5 h, and 10 h
- Characterizations:
  - WAXS, SAXS, HS



Molecular Properties and ESCR

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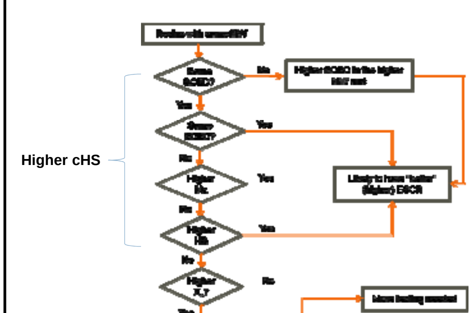
	Property change	Effects	ESCR
MW	↑	•Increases chain entanglements •Increases tie-molecule concentration •Increases lamella lateral surface area •Increases crystallinity and strength	↑
MWD	↑	•Improves processability •Increases chain entanglements	↑
SCB	↑	•Increases chain entanglements •Reduces chain slippage	↑
SCBD	Related to SCB	•Higher SCB content in the high MW end of the MWD increases inter-lamellar link formations	↑
LCB	↑	•Increases chain entanglements •HDPE generally does not have sufficiently high levels of LCB to affect its ESCR	↑

Selecting Resin with Higher ESCR

30



BST vs. NCLT

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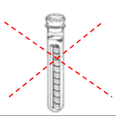
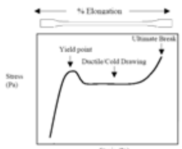
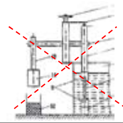
- BST:
  - HDPE:
    Impose high stress conditions (related to modulus)
    Heterogeneous crack propagation (number and position)
  - LLDPE:
    Lower modulus results in lower applied stresses: more uniform crack propagation

BST: LLDPE
NCLT: HDPE (lower applied stress)
Need for a better measure of ESCR







Sensitivity of LLDPE to Notch Depth and % Yield Strength

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- Central composite design
- PE: LLDPE 1, ESCR: 55h, BST: condition A: thickness 3mm, notch depth: 20%

Notch Depth (%)	Stress Level (%)
20.00	10.00
40.00	25.00

NCLT should be performed at 20 % notch depth for LLDPE