FACULTY OF ENGINEERING
AND ARCHITECTURE

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C-PLANET

NTE 1 – ESR11 – MICROTEACHING 3

Amir Bashirgonbadi

Sept. 9, 2020

GHENT UNIVERSITY

Centre for Polymer and Material Technologies

C-PlaNeT
CIRCULAR PLASTICS NETWORK FOR TRAINING

AMIR BASHIRGONBADI

- Graduated as MSc materials engineer
  @ KU Leuven
- Then, I served as a Sales Engineer in a polymer compounding company, in Iran
- PhD: ESR 11, started in May

I WORK ON FILMS!

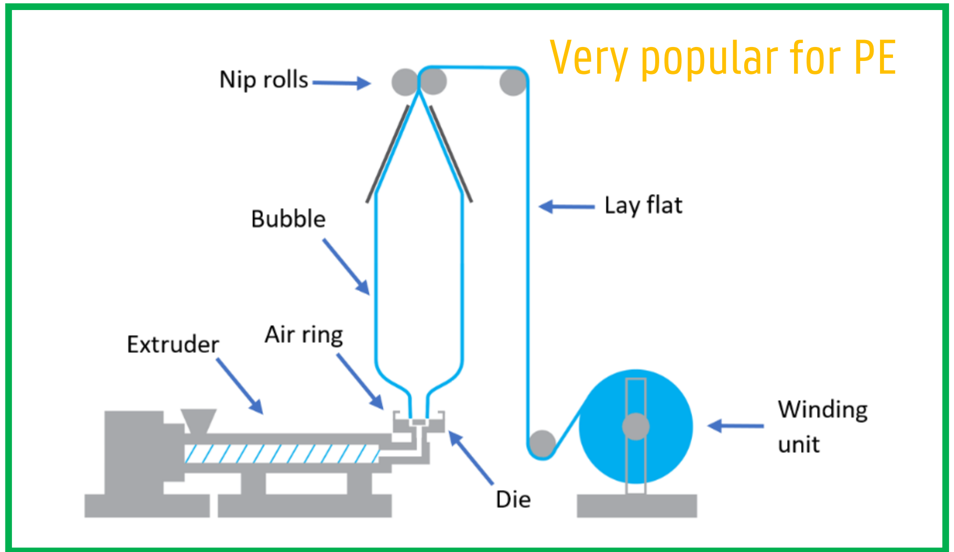
— Where are they used?

And millions of more applications!

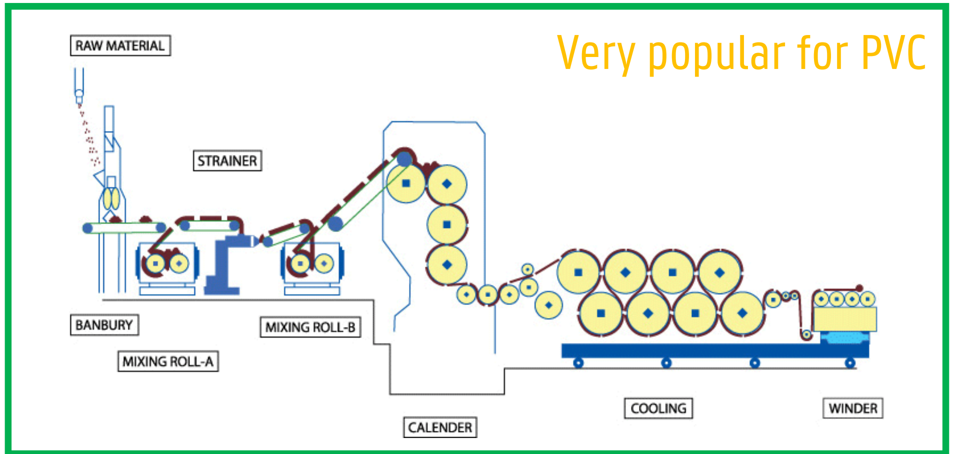
HOW ARE THEY PRODUCED?

- Very different techniques!

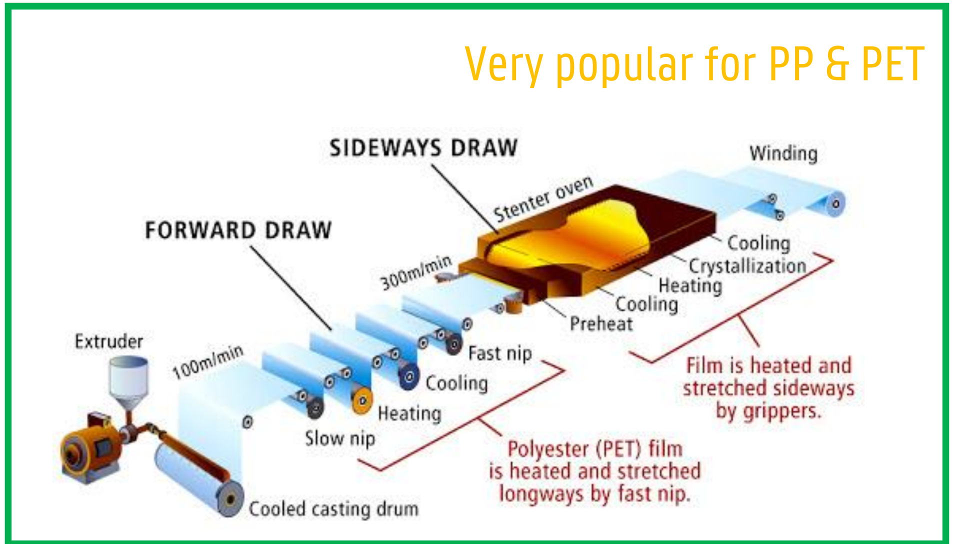
  For example these three:



Film blowing



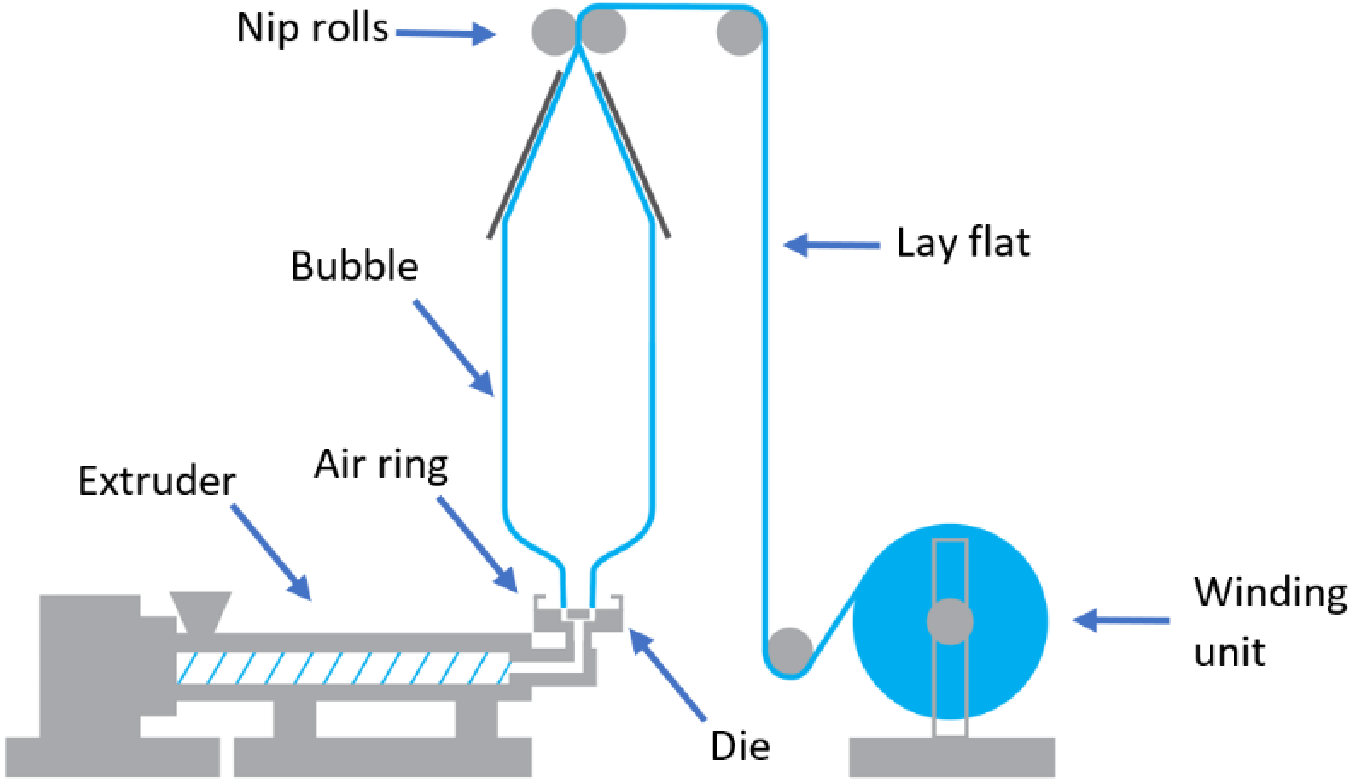
Film calendaring



Film casting

FILM BLOWING PROCESS PARTS

- Or: Tubular film extrusion



RESEARCH QUESTION

How can we quantify (and enhance) the Recycling Quality of the contaminated polyethylenes in film blowing applications?

- Contaminations? For the moment, cross-polymer contaminations: other PEs, PP, PET, PS, and PA

RQ = α×(Blowability) + β×(Properties)

Objective: to be able to make a choice of film-blowable contaminated PEs

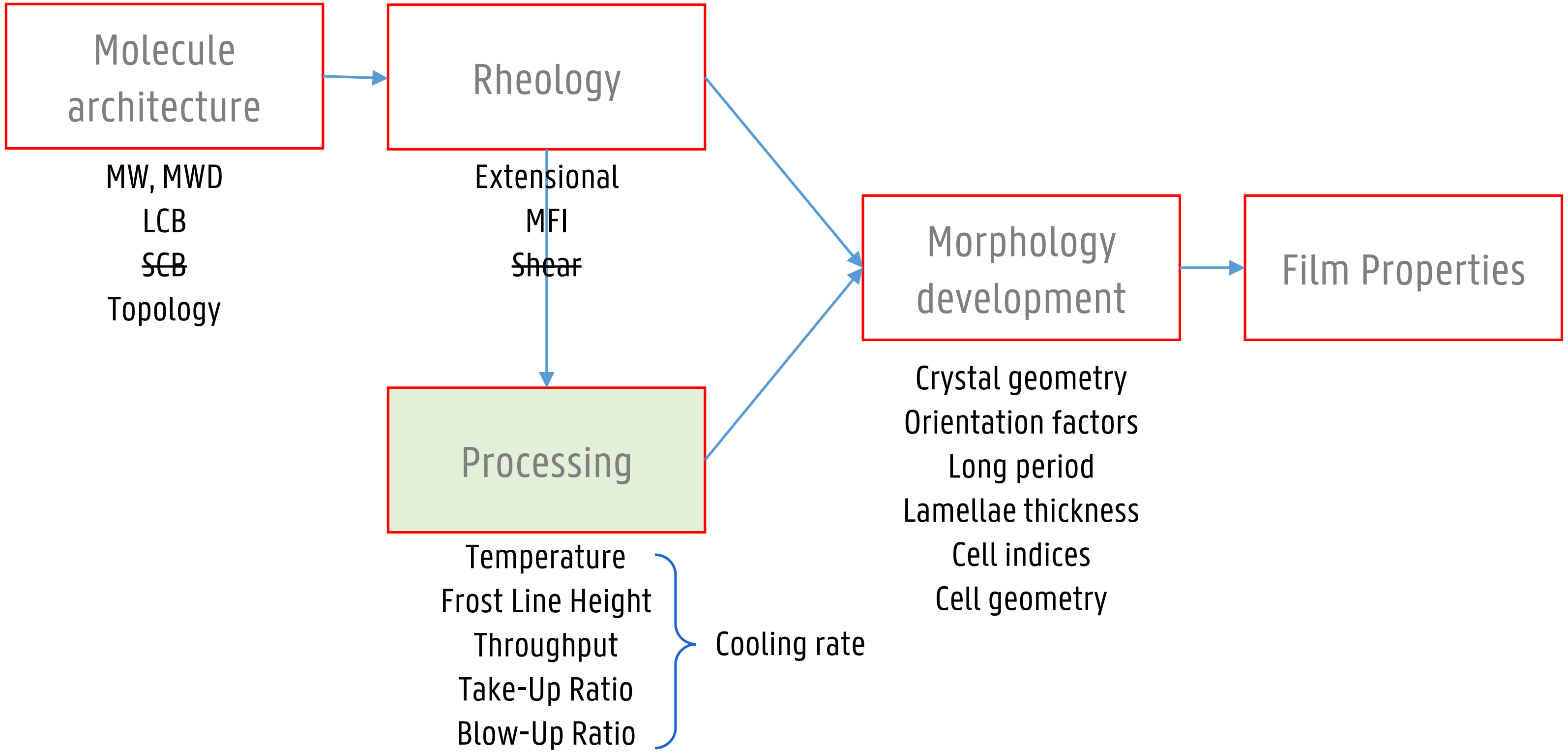
1. A technique to define and measure blowability needs to be developed
2. Alpha and Beta coefficients should be assigned
3. RQ should be predictable for certain (distribution of) molecules/blends

IS IT EASY TO MAKE FILMS FROM RECYCLED PLASTICS?

Challenges:

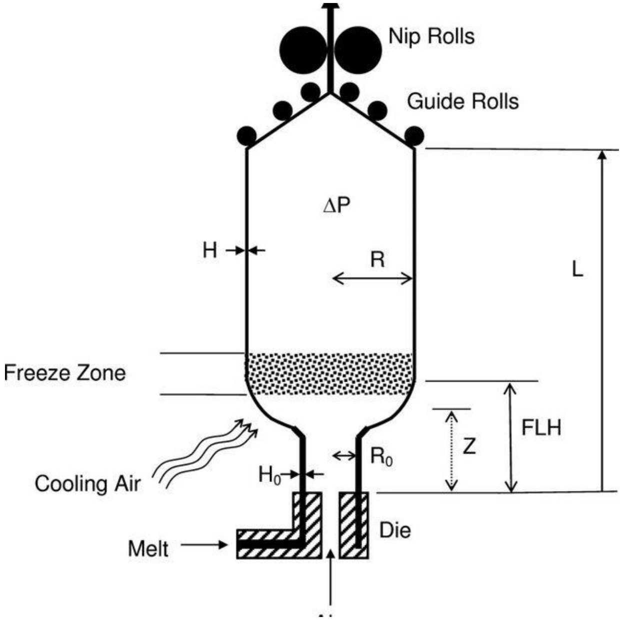
- Flow behavior
- Phase morphology
- Mechanical properties
- Aesthetics and smell
- Food-contact limitations

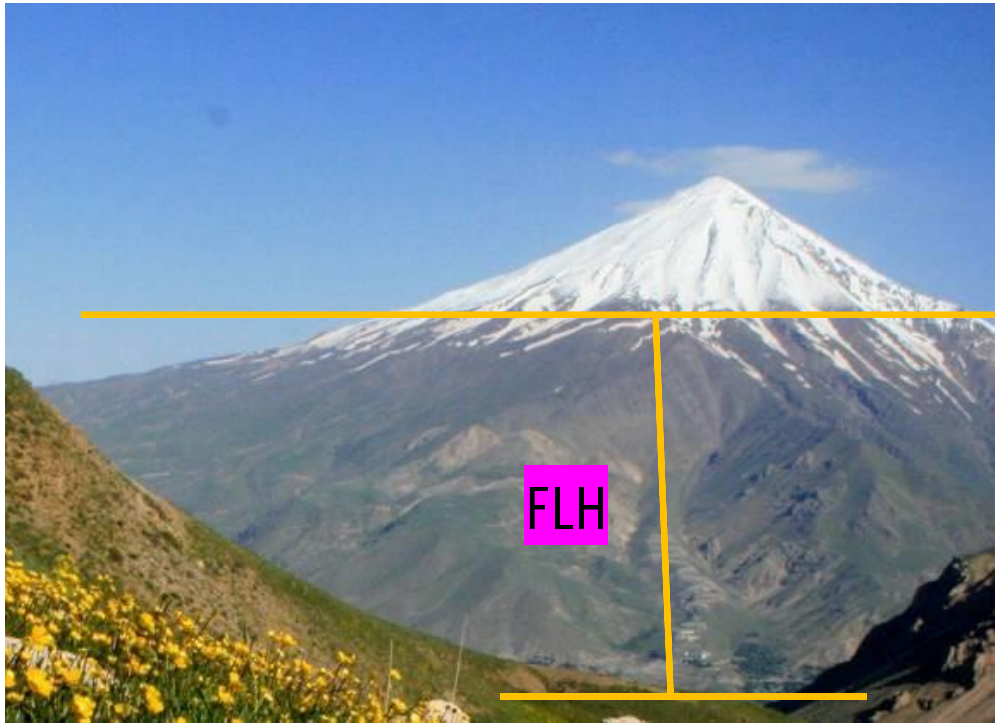
AN OVERVIEW OF THE FILM BLOWING PROCESS



PROCESSING PARAMETERS: BUR, TUR, AND FLH

BUR: Blow up ratio, **TUR**: Take up ratio, **FLH**: Frost line height





Mount Damavand, 5610m high, back in my hometown

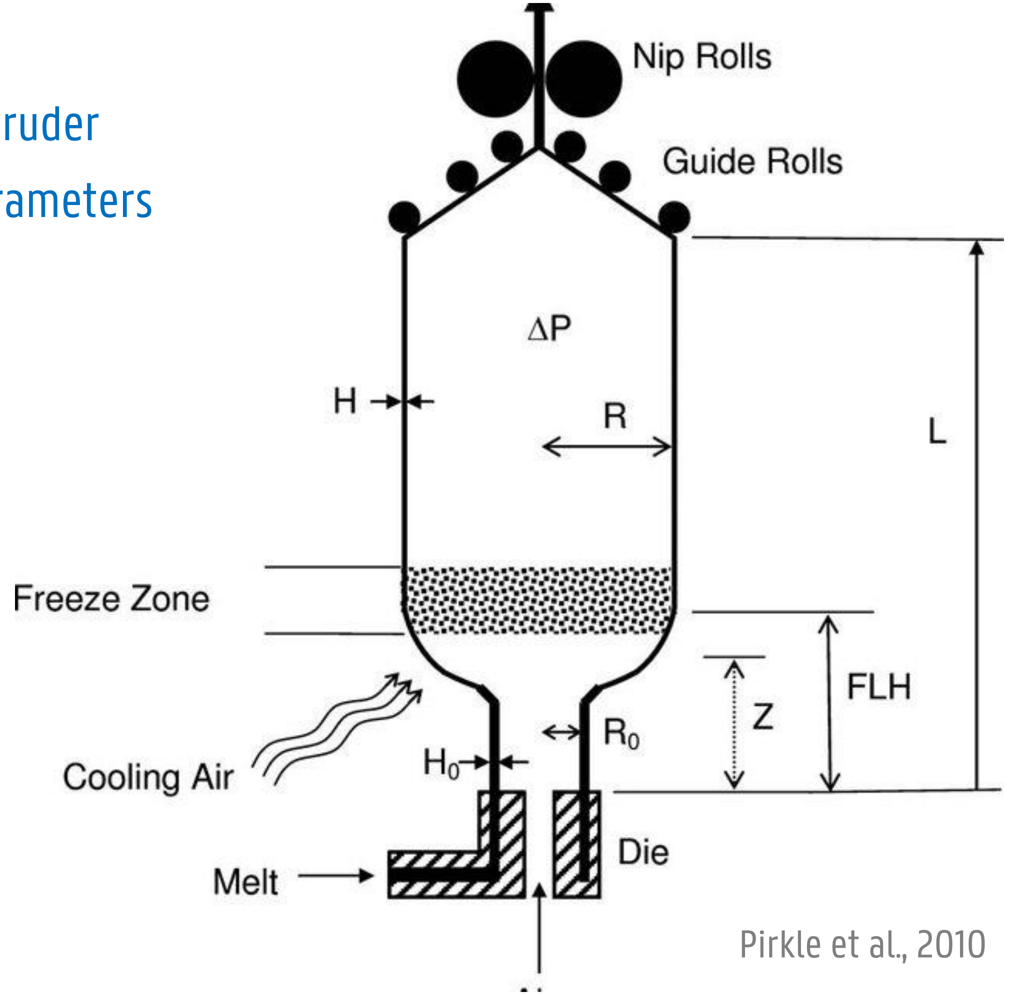
FILM BLOWING PROCESS VARIABLES

Main parameters in this process are as follows:

1. Melt temperature, which is controlled by the extruder heating elements.
2. Throughput, which is controlled by the rotation speed of the extruder screw.

Extruder parameters

3. Blow up ratio, which is the ratio of the radius of the inflated bubble to the diameter of the die
4. Take up ratio, which is the ratio of the vertical speed of the material coming out of the die to the linear speed of the nip roller
5. Frost line height, which is the height from the die surface where the polymer is frozen and is not deformable anymore, and is controlled by the cooling unit.



Pirkle et al., 2010

PROCESSING WINDOW

More than 20 min

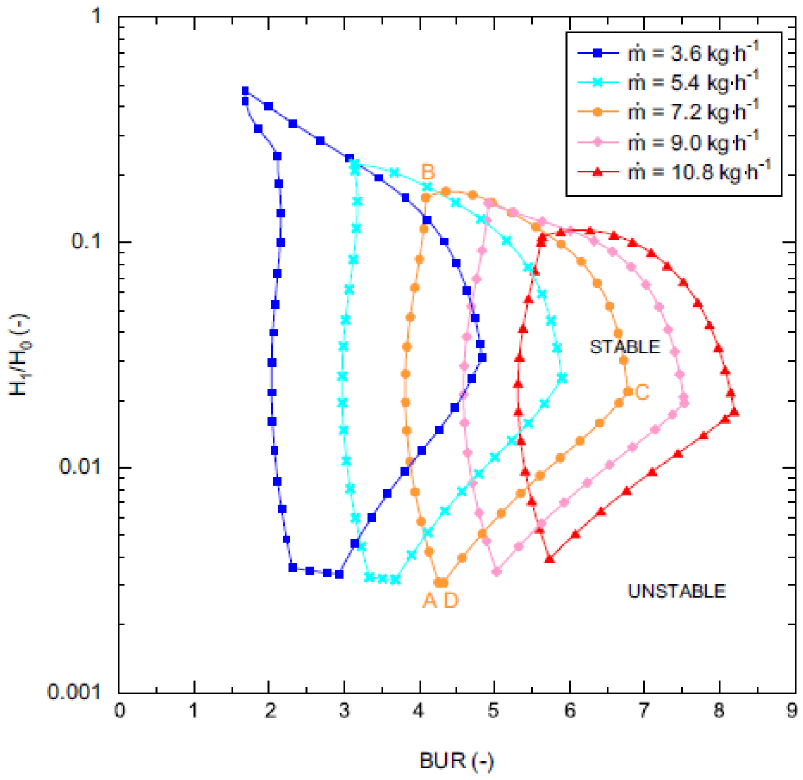
Lower than 180C

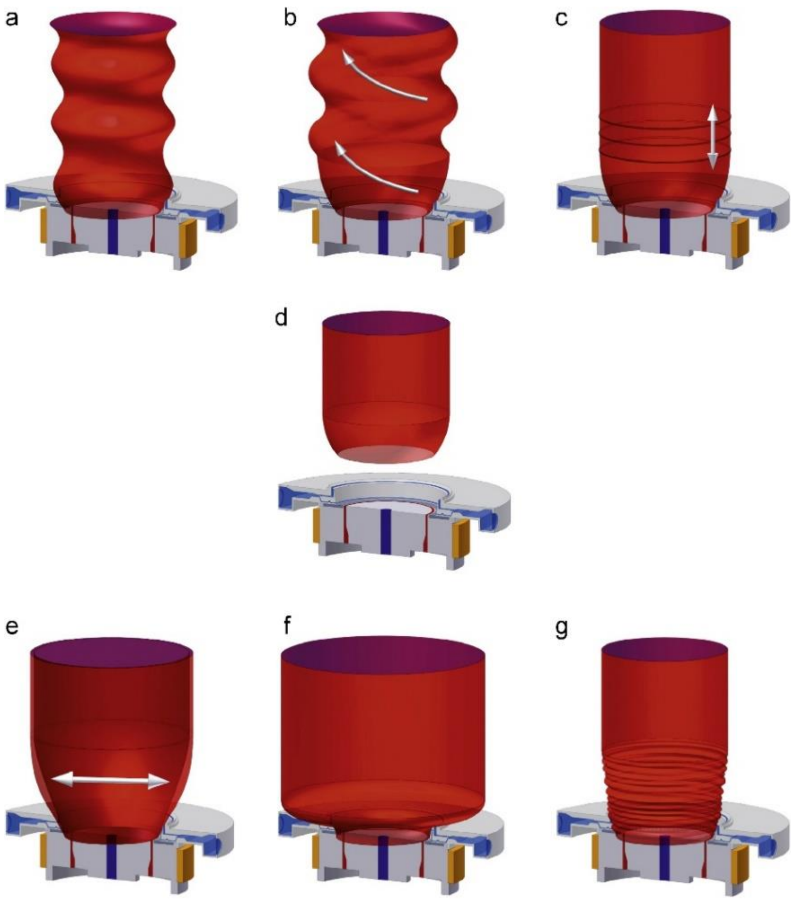
Higher than 240C

Less than 15 min

BUBBLE STABILITY – DIRECT METHODS

- Current definitions:
  - Bubble instabilities
  - Processing window





Roman Kolařík PhD Thesis, 2012

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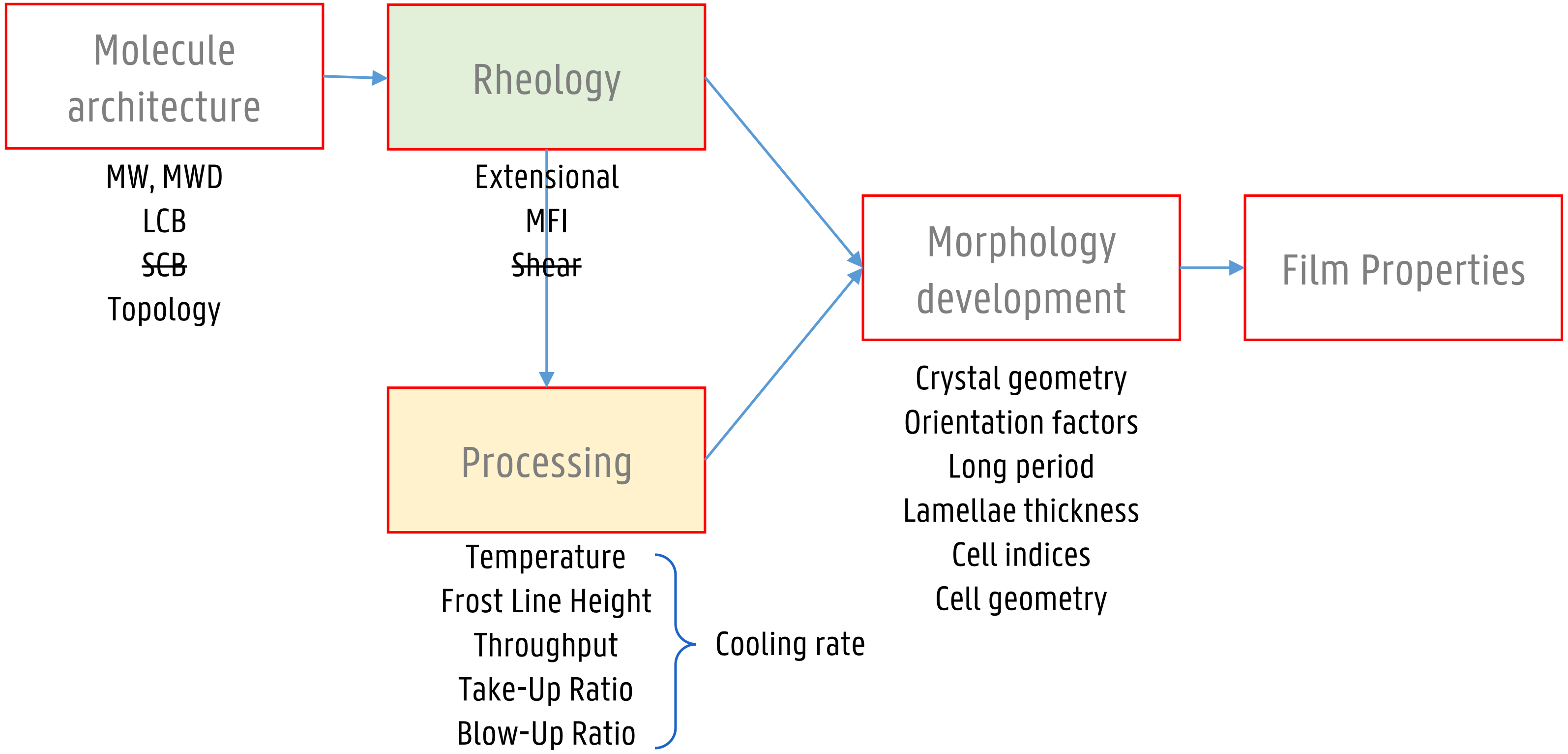
FILM BLOWING PROCESS



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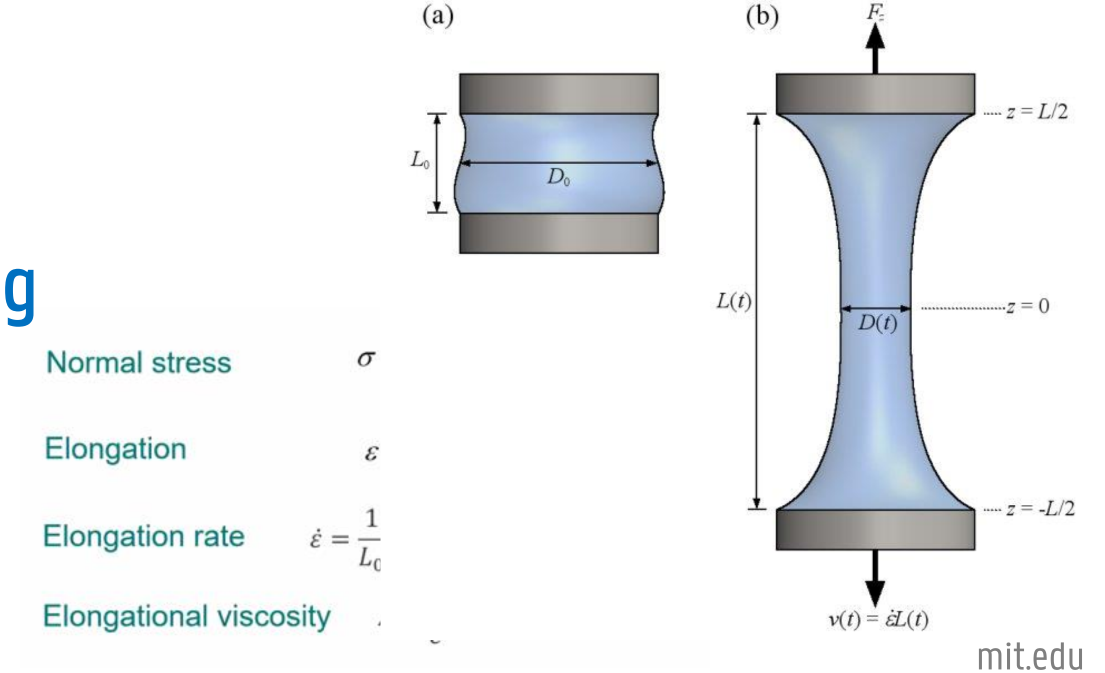
SHEAR VISCOSITY OR EXTENSIONAL VISCOSITY?

- Shear deformation

wiki.anton-paar.com

- Extensional deformation
  - This is what we see in processes like film blowing



mit.edu

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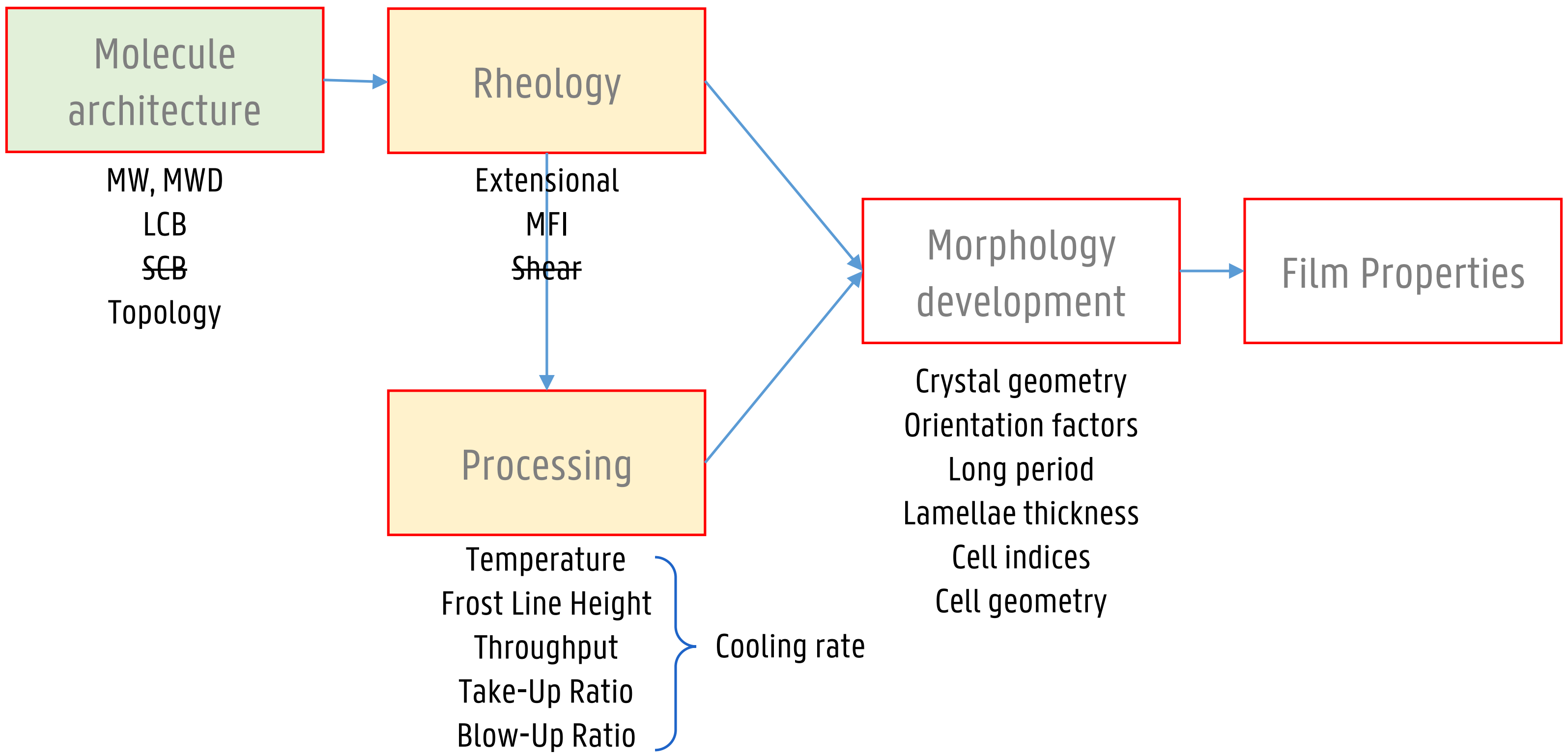
FILM BLOWING PROCESS



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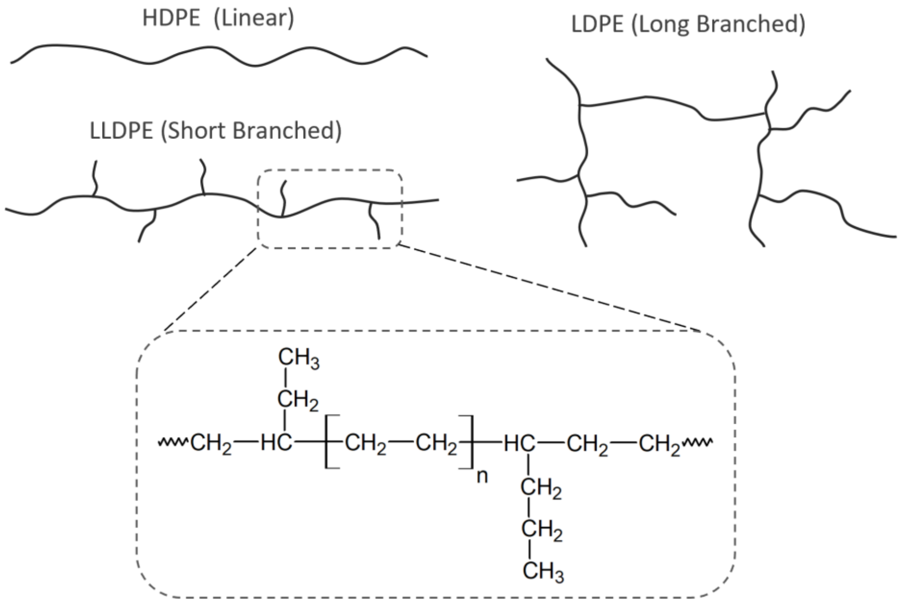
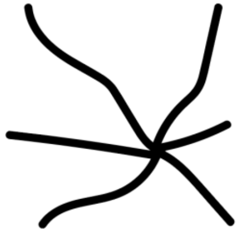
DIFFERENT POLYETHYLENES



TOPOLOGIES

Tree-like

Linear



Star-like

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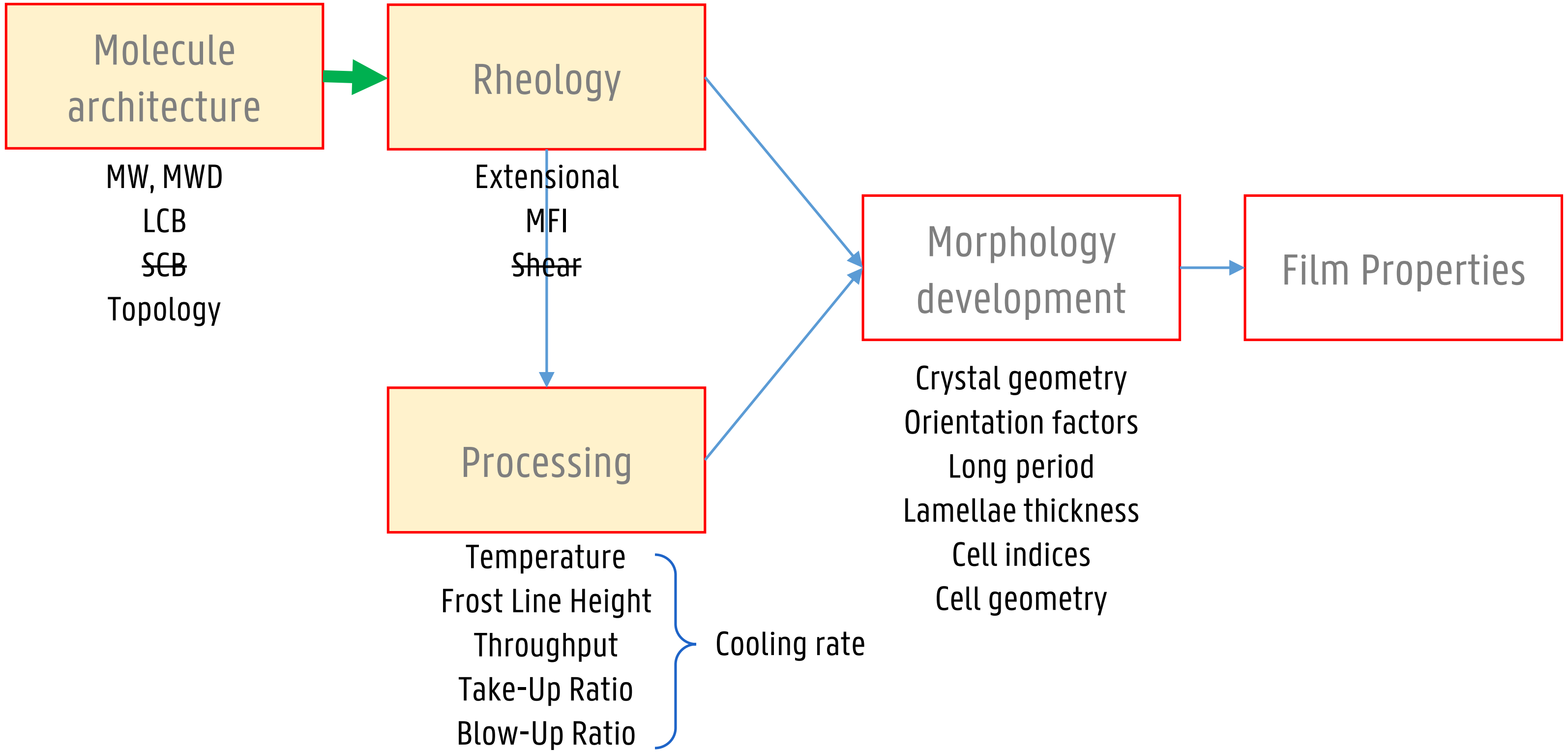
FILM BLOWING PROCESS



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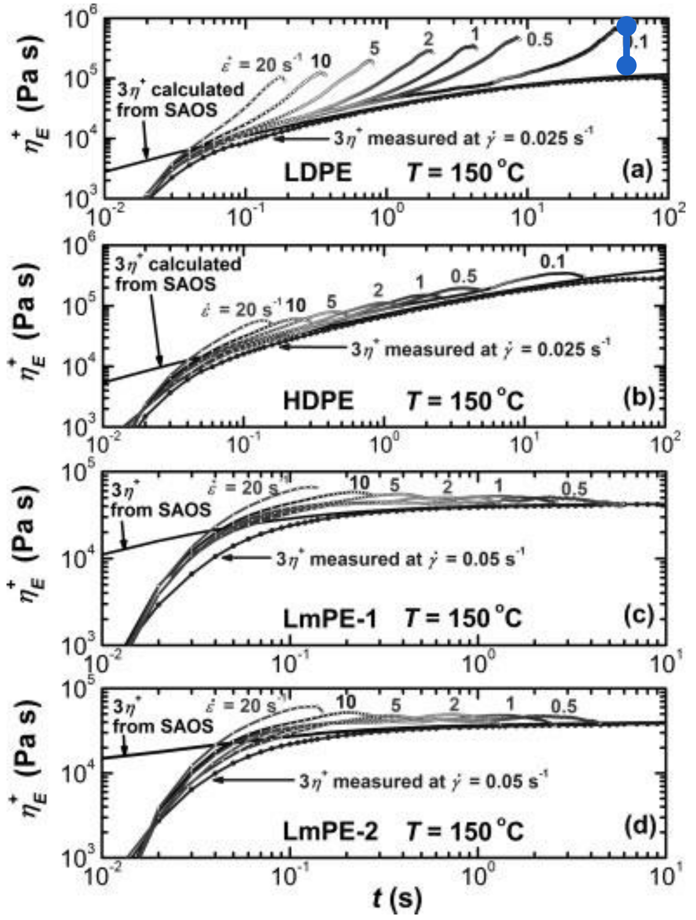
SHEAR VS EXTENSIONAL VISCOSITY

- Branched PEs exhibit strain hardening, while linear PEs stick to their linear viscoelastic behavior



Strain hardening factor

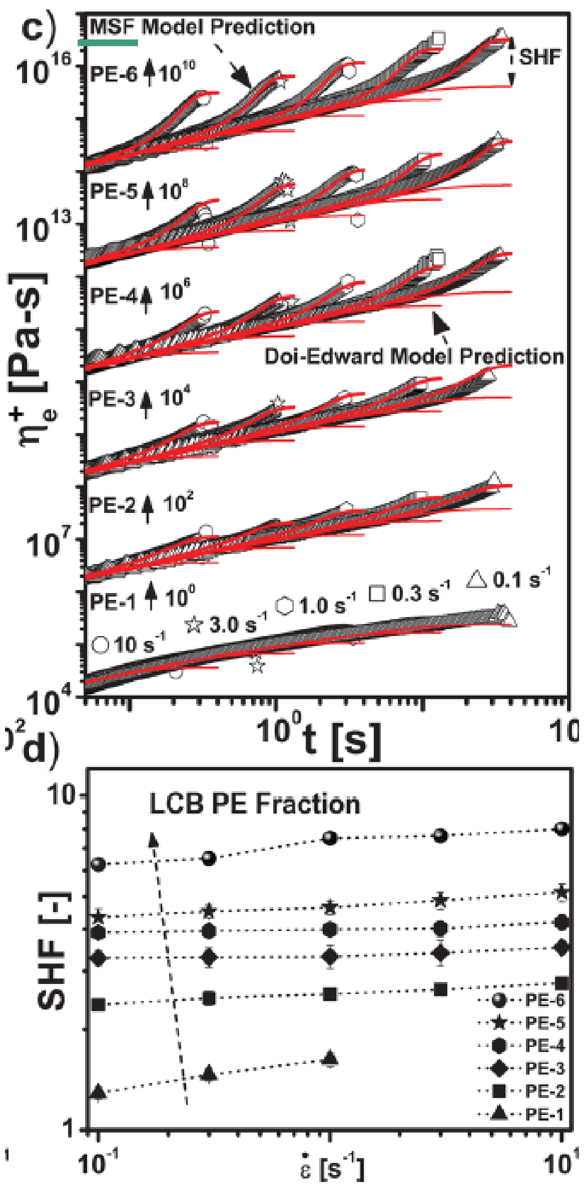
EXAMPLE OF RHEOLOGY VS MOLECULAR ARCHITECTURE

Four Behaviors:

- 1: Strain rate ↑ - Strain hardening no difference
- 2: Strain rate ↑ - Strain hardening ↓
- 3: Strain rate ↑ - Strain hardening ↑
- 4: Strain rate ↑ - No strain hardening

Typical for metallocene catalyzed PE

Molecular stress function

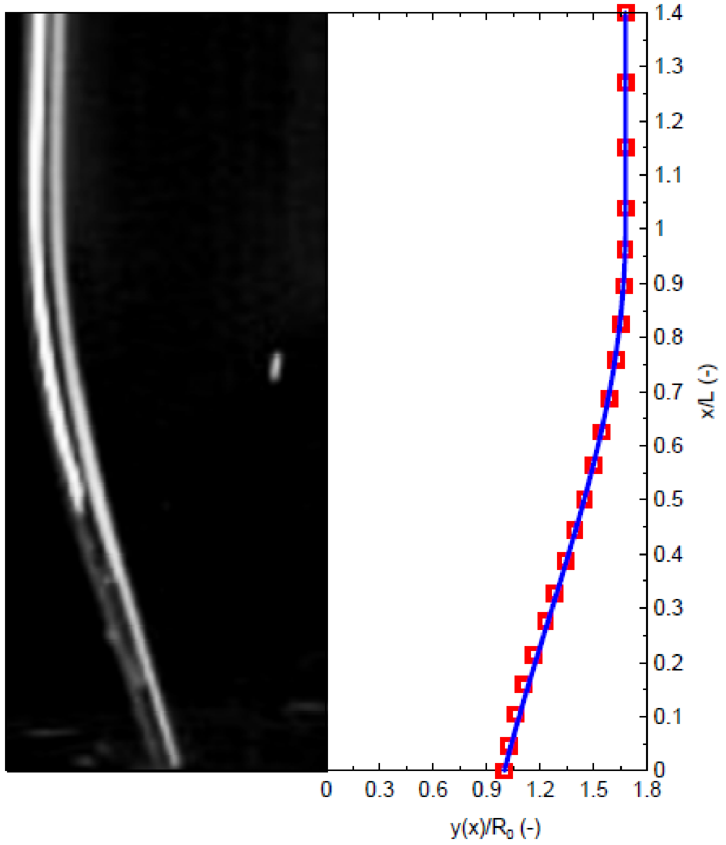


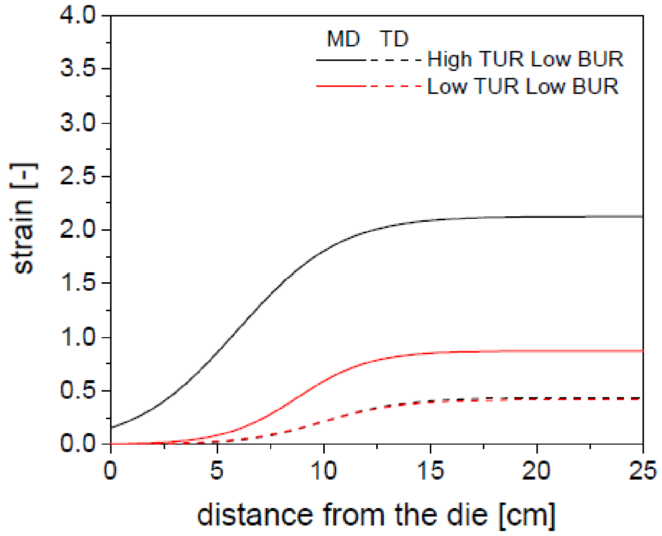
SHF indicates Network Strength

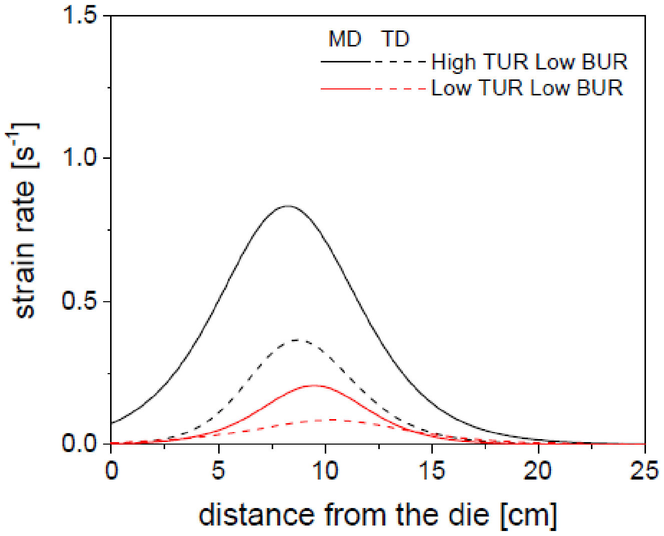
A high network strength implies that the applied stress cannot disrupt the network to soften the material.

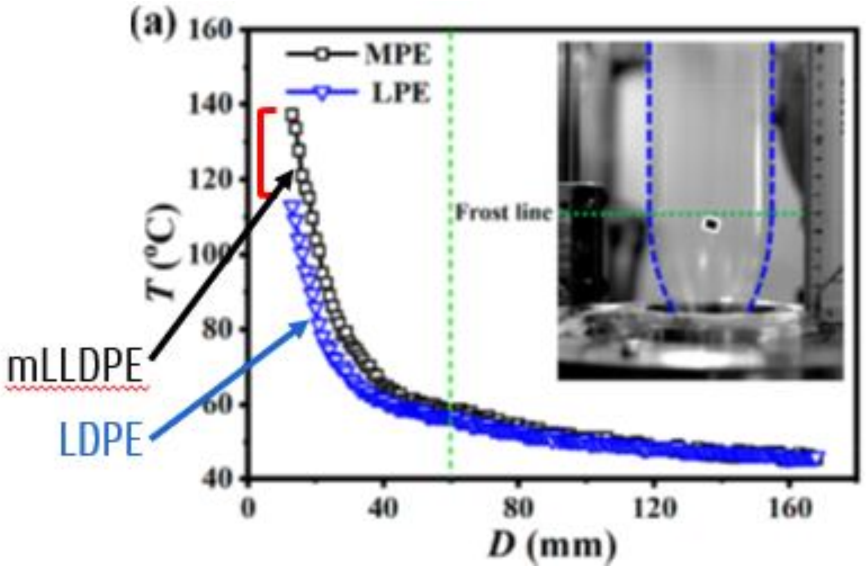
J. Rheol. 47, 619 (2003)

DIFFERENT STRAINS AND STRAIN RATES AT DIFFERENT TEMP.



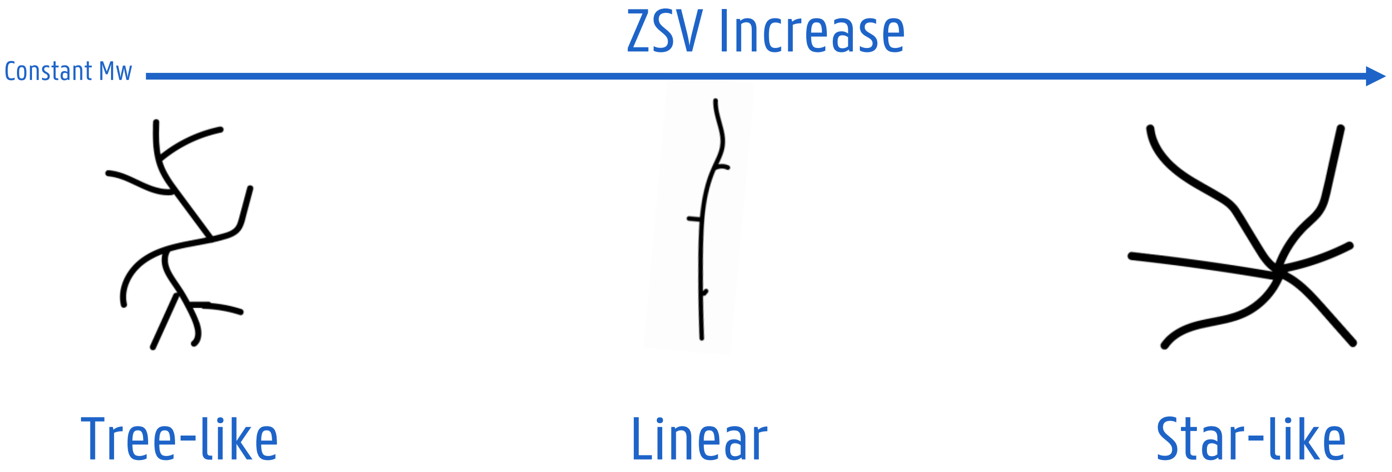


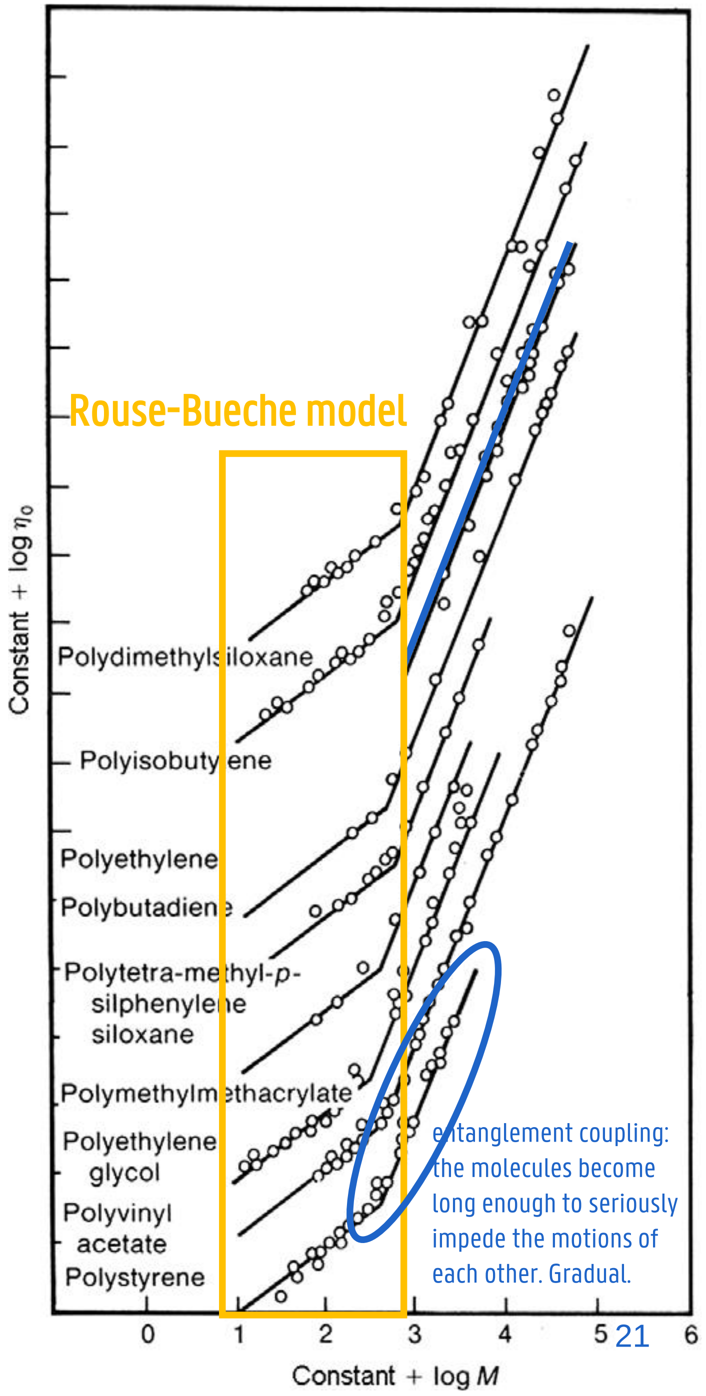




MOLECULAR TOPOLOGY AND MW VS ZSV

- For linear PE (at 190C): $\eta_0^L = 10^{-14.25} M_w^{3.6}$
- Star-like topology will have higher ZSV
- Tree-like topology will have lower ZSV





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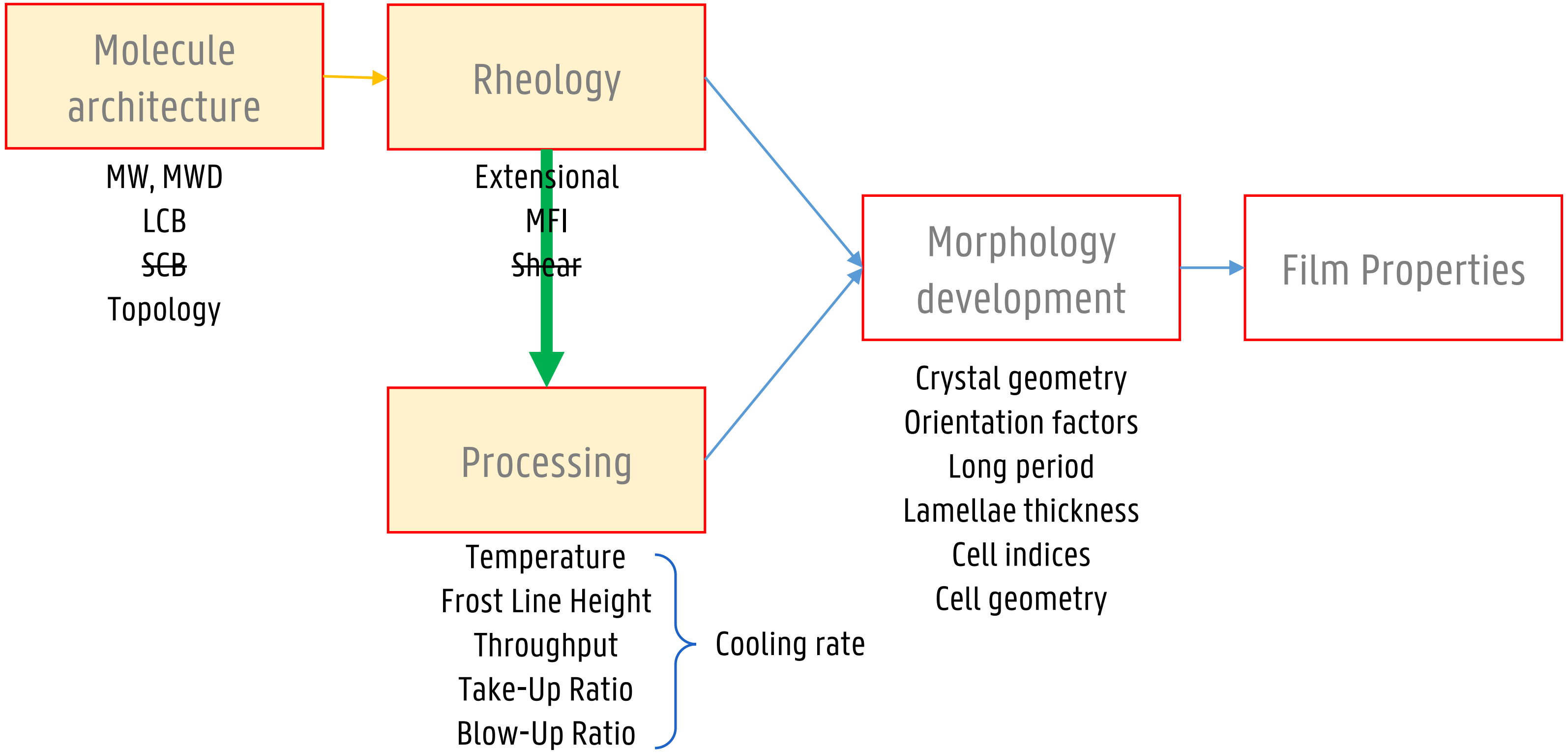
FILM BLOWING PROCESS



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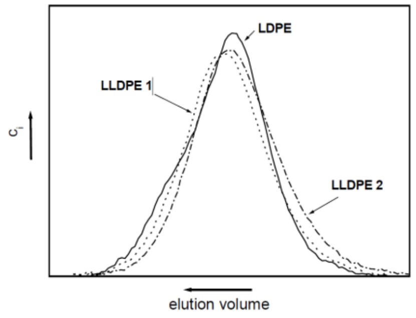
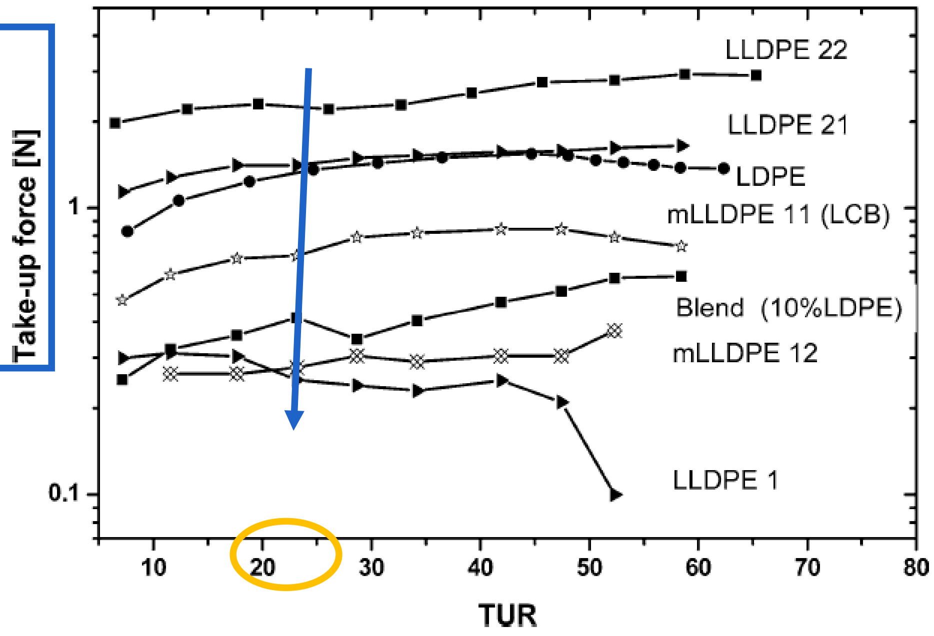
BUBBLE STABILITY - INDIRECT METHOD 2



The bubble stability is the better the higher the take-up force.



Take-up force as a function of take-up ratio for various polyethylenes

- stability at given processing parameters
- easiness to reach a stable state of processing
- duration of stability and width of stability window.

	LLDPE 22	LLDPE 21	LDPE	mLLDPE 11	LLDPE/LDPE 90/10	mLLDPE 12	LLDPE 1
F[N] at TUR = 25	2.2	1.5	1.4	0.7	0.4	0.3	0.2
$3\eta_0$[Pa s] at 150 °C	32×10^4	11×10^4	3.5×10^4	4.3×10^4	1.6×10^4	3×10^4	1.5×10^4
μ[Pa s] at $\dot{\varepsilon}_0 = 0.5\ s^{-1}$ $\varepsilon_H = 3$ and $T = 150$ °C	$\sim50\times10^{4a}$	$\sim10\times10^{4a}$	10×10^4	7×10^4	2.1×10^4	3×10^4	1.5×10^4
μ_s[Pa s] at 150 °C	n.m.	n.m.	20×10^4	8×10^4	3.5×10^4	3×10^4	1.5×10^4
Bubble stability	+ +	+ +	+	+	+ -	-	– –

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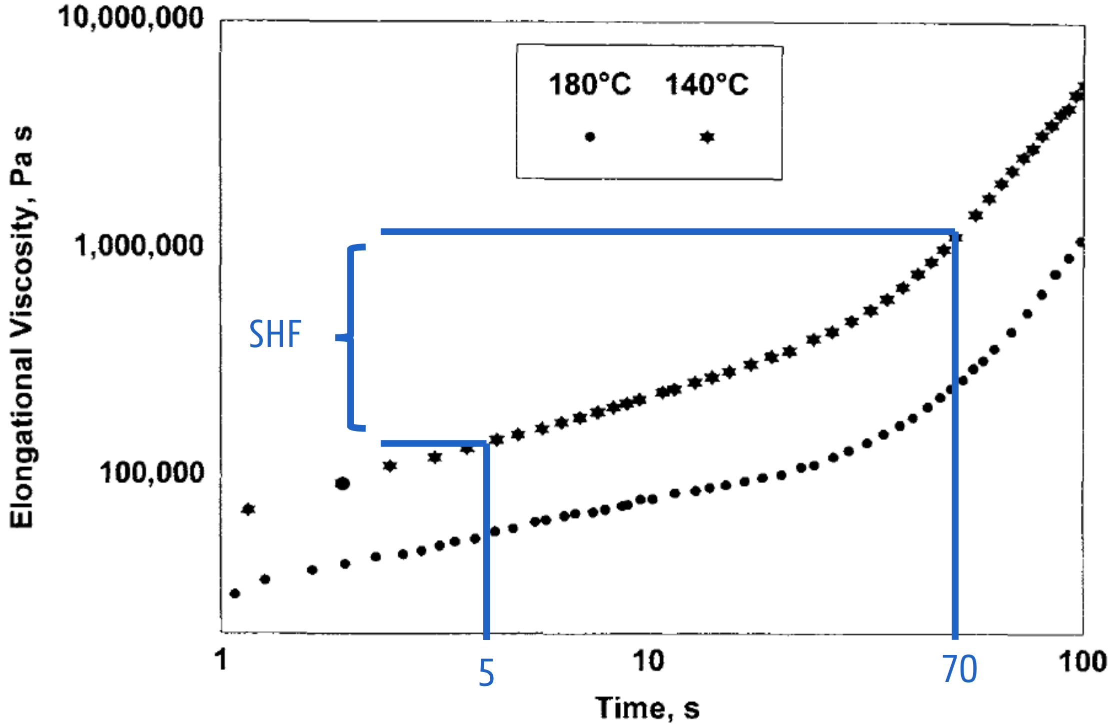
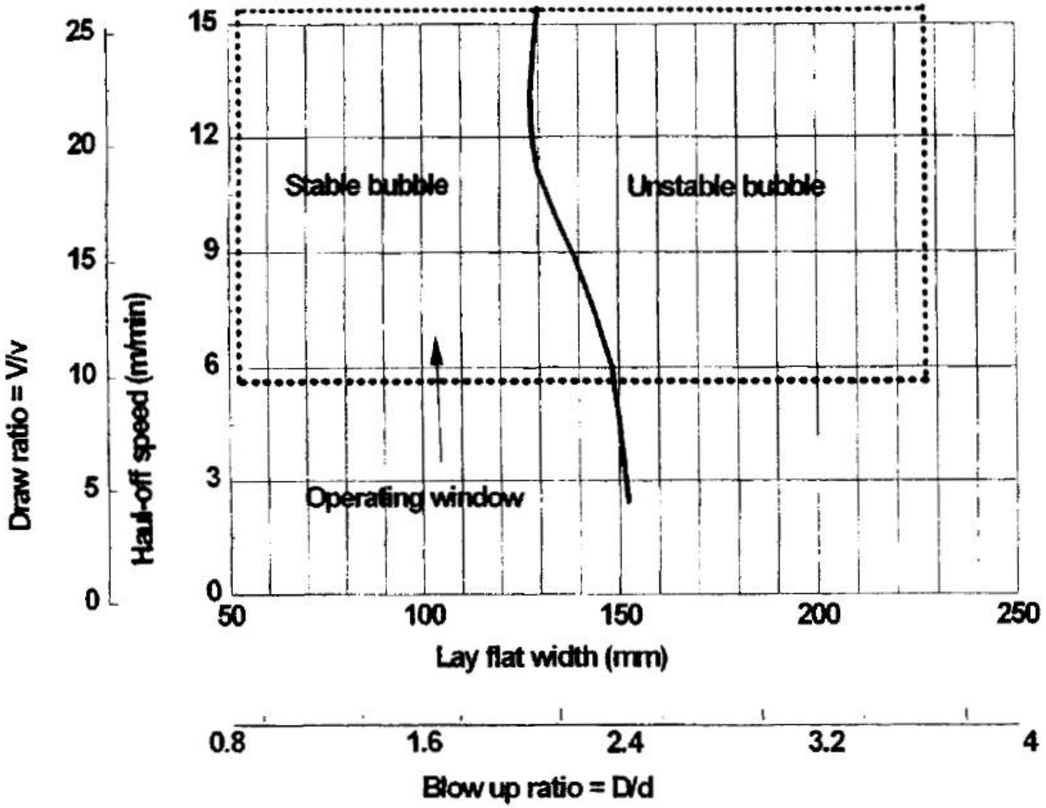
Rheol Acta (2005) 45: 14–22

BUBBLE STABILITY - DIRECT METHOD

POLYMER ENGINEERING AND SCIENCE, OCTOBER 1998, Vol. 38, No. 10



Elongational viscosity of LDPE at two temperatures, elongational deformation rate 0.05 1/s



Polymer Grade	Strain Hardening Parameter (SHP)		
	SHP at 140°C		SHP at 180°C
LLDPE	3.4	↑	4.4
LDPE	17.0	↓	7.8
90% LLDPE/10% LDPE	3.9	↑	5.0
80% LLDPE/20% LDPE	5.0	↑	6.5

robustness

Polymer Grade	Size of Operating Window (SOW)		
	SOW at 180°C (%)		SOW at 220°C (%)
LLDPE	49	↓	not measurable
LDPE	100	-	99
90% LLDPE/10% LDPE	66	↑	69
80% LLDPE/20% LDPE	85	↑	88

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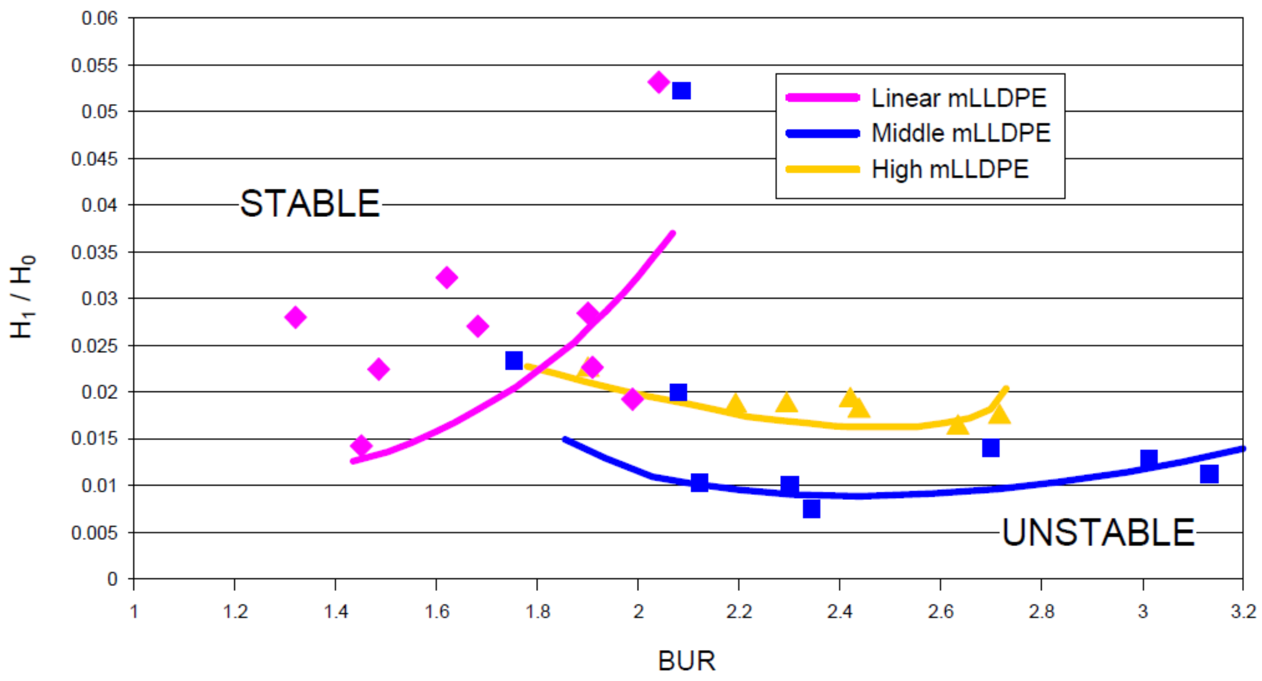
BUBBLE STABILITY CRITERIA – IDENTICAL PARAMETERS

No sharp transition stable-unstable?

Scattered measurements?



FLH 180mm and temperature 190°C

Roman Kolařík PhD Thesis, 2012

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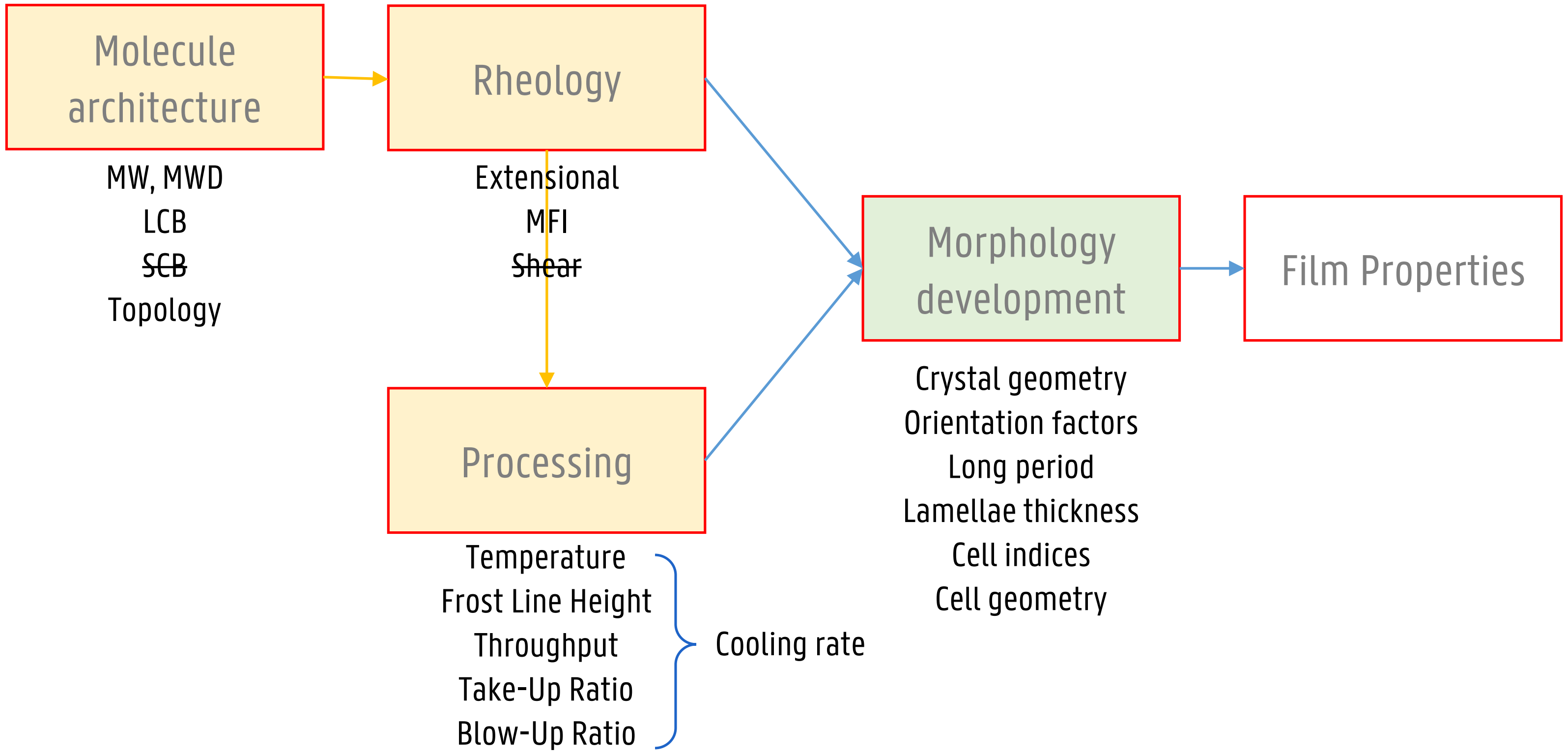
FILM BLOWING PROCESS



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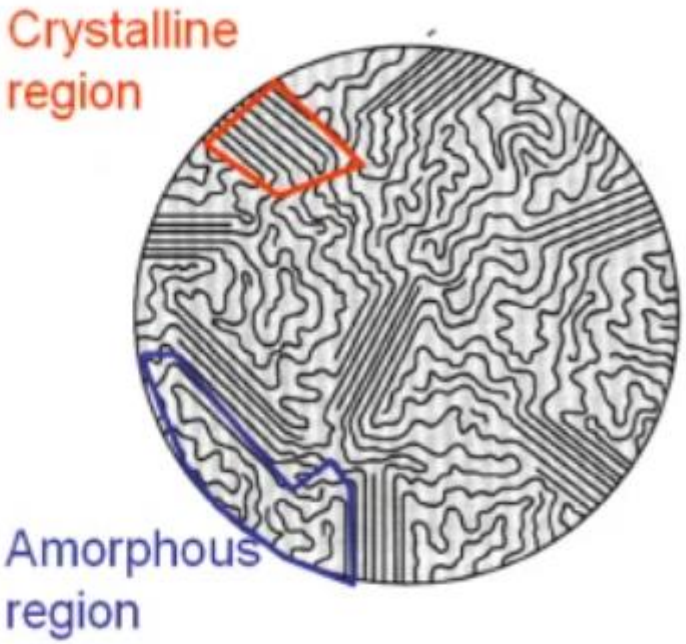
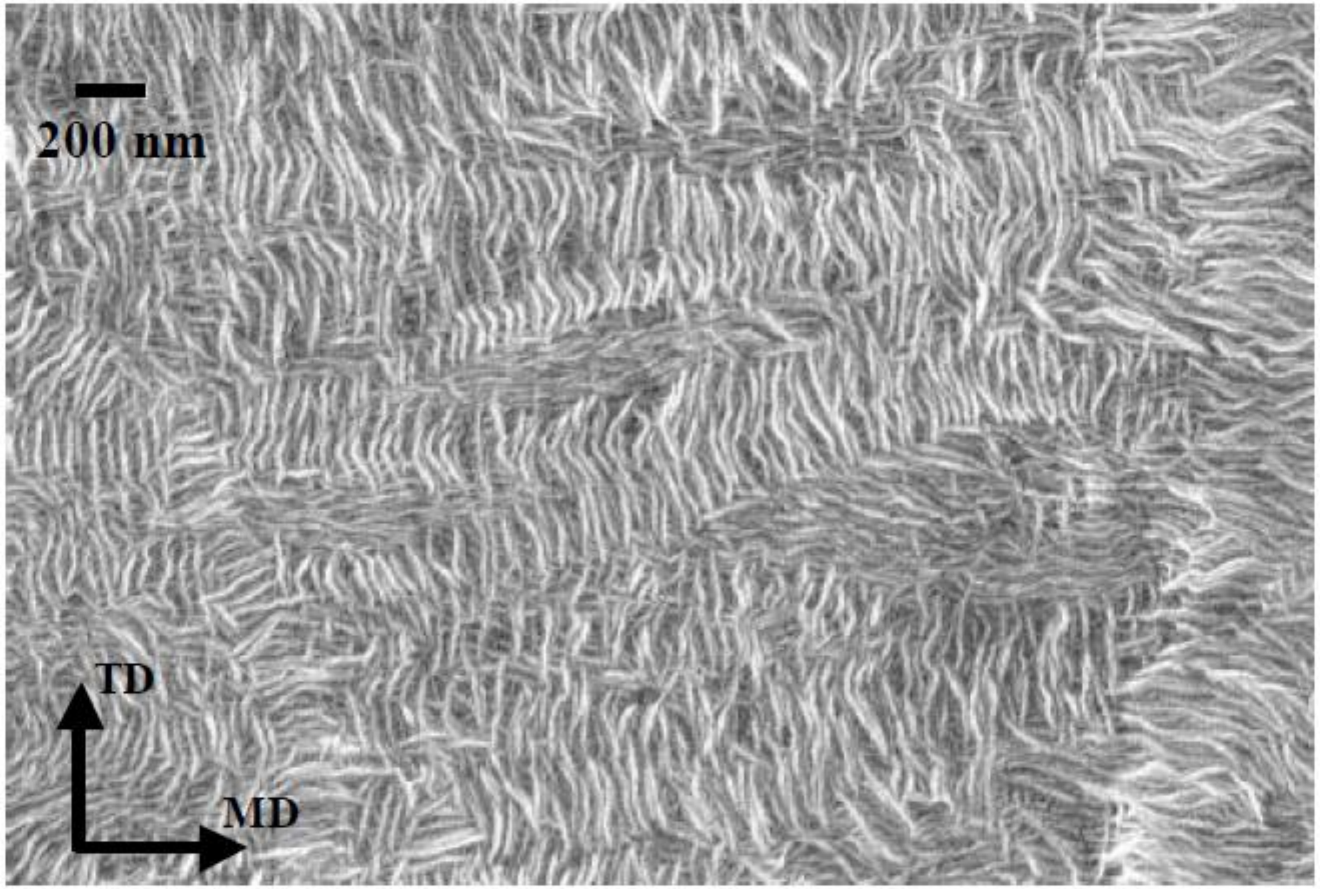
ORIENTATION OF LAMELLA STRUCTURES - SEM



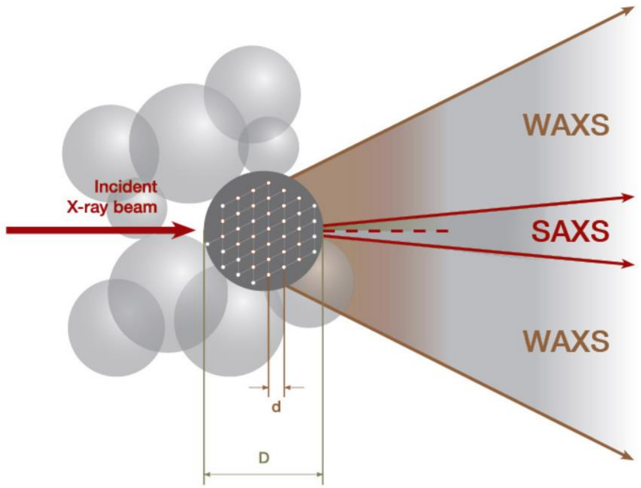


50,000 X

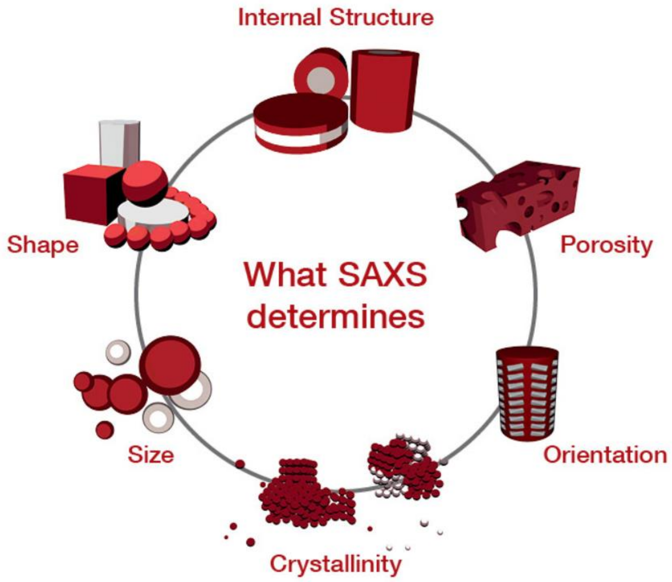
MORPHOLOGY CHARACTERIZATION

SALS, Raman Spectroscopy, Birefringence.

- WAXS:
  - Orientation of crystals
  - Crystalline content
  - Lamellar thickness
  - Average crystal size

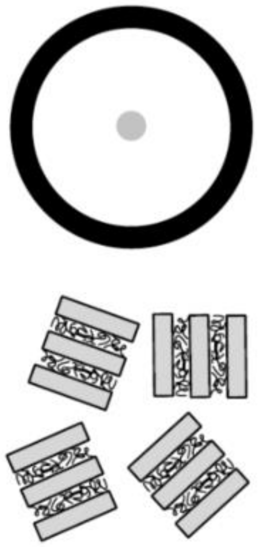


- SAXS:
  - Linear crystallinity
  - Orientation of lamellas
  - Lamellar thickness
  - Long period

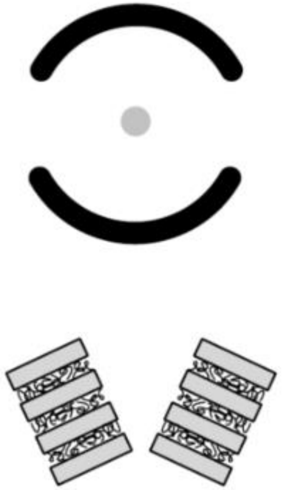


XRD RESULTS

How to interpret the results?

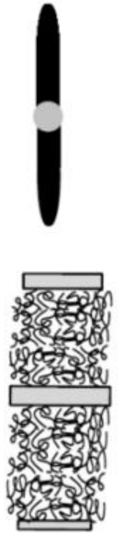


Debye-Sherrer ring from isotropic lamellar morphology



Meridional arcs from lamellae with many orientations along machine direction

WAXS



Meridional streaks from lamellae oriented in machine direction with different lateral sizes and thicknesses and with very high correlation lengths

Tear drop pattern from oriented lamellae with irregular thicknesses and distances

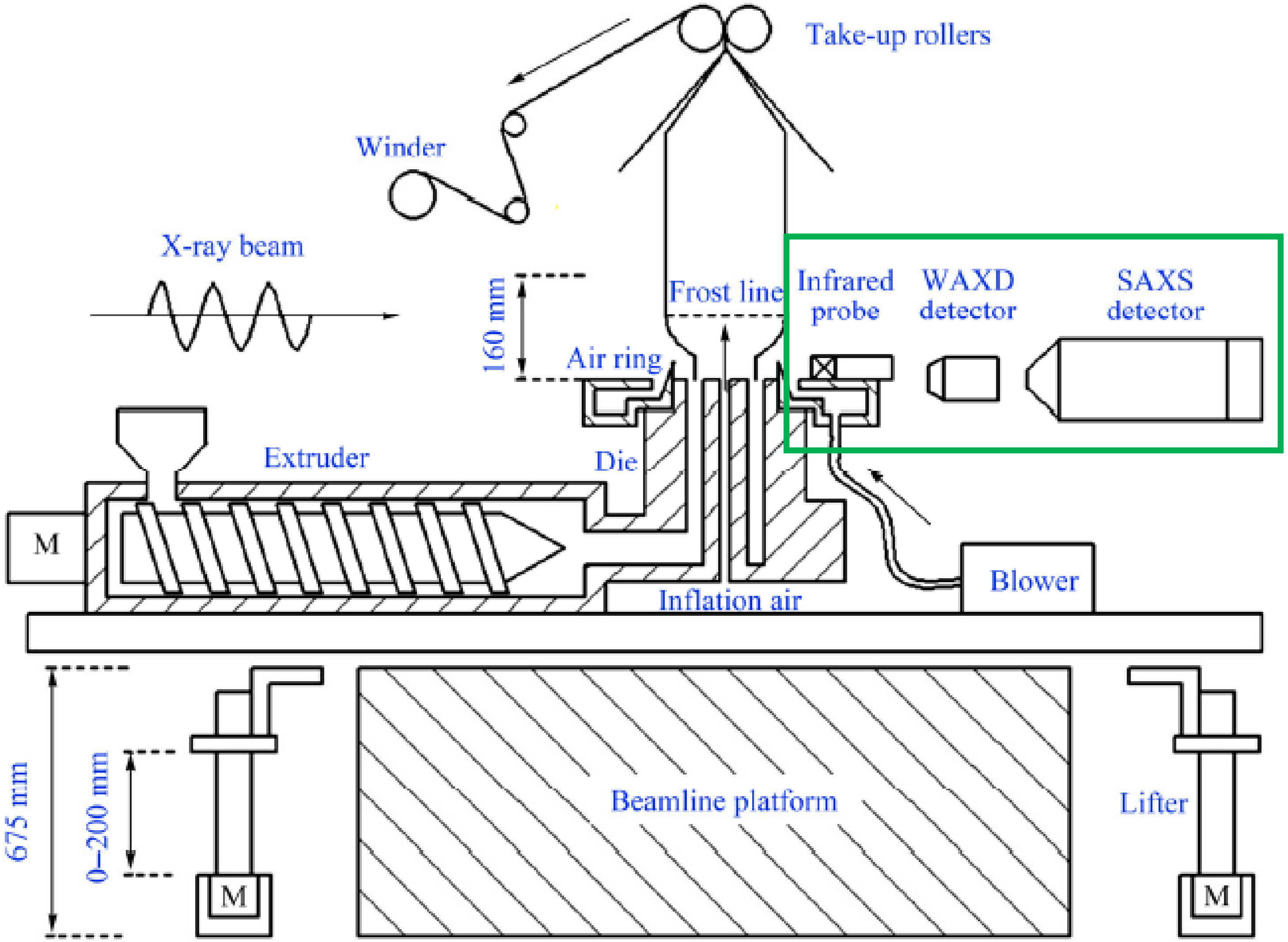
Meridional lobes from oriented regularly spaced lamellae with uniform thickness

SAXS

Troisi et al., 2016

ONLINE INVESTIGATION OF THE MORPHOLOGY

Film blowing setup, with adjustable height, exposes the bubble to the X-ray radiation at different points



Chinese Journal of Polymer Science Vol. 35, No. 12, (2017), 1508–1516

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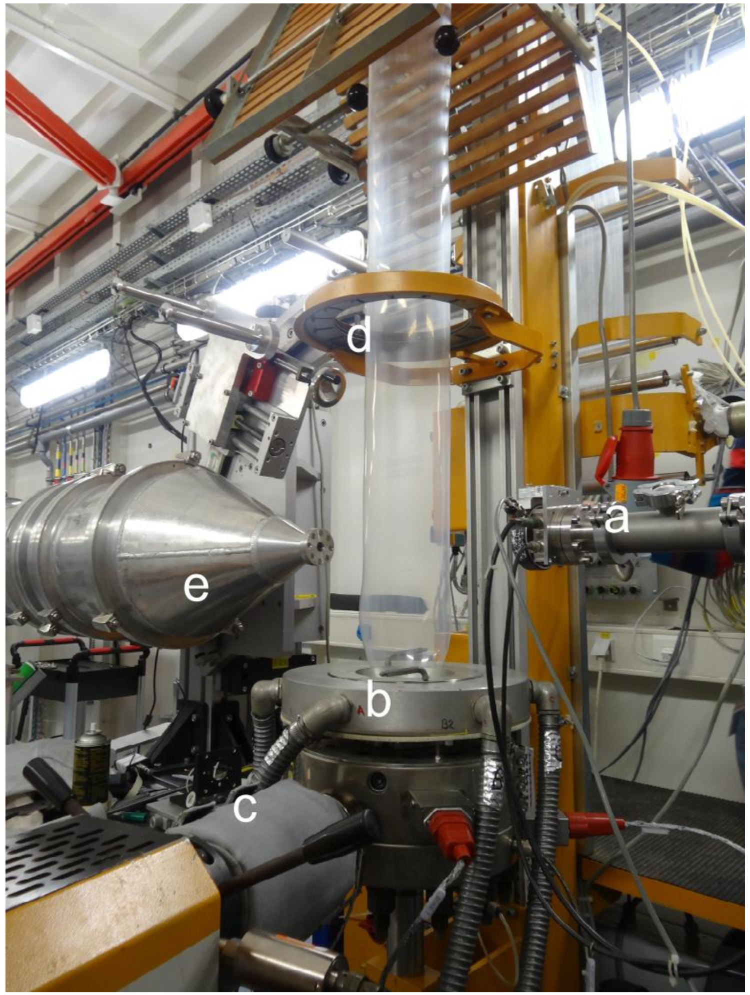
STRUCTURE DEVELOPMENT – ONLINE XS

Offline/Online

1997, On-Line Birefringence Measurement in Film Blowing of a Linear Low Density Polyethylene

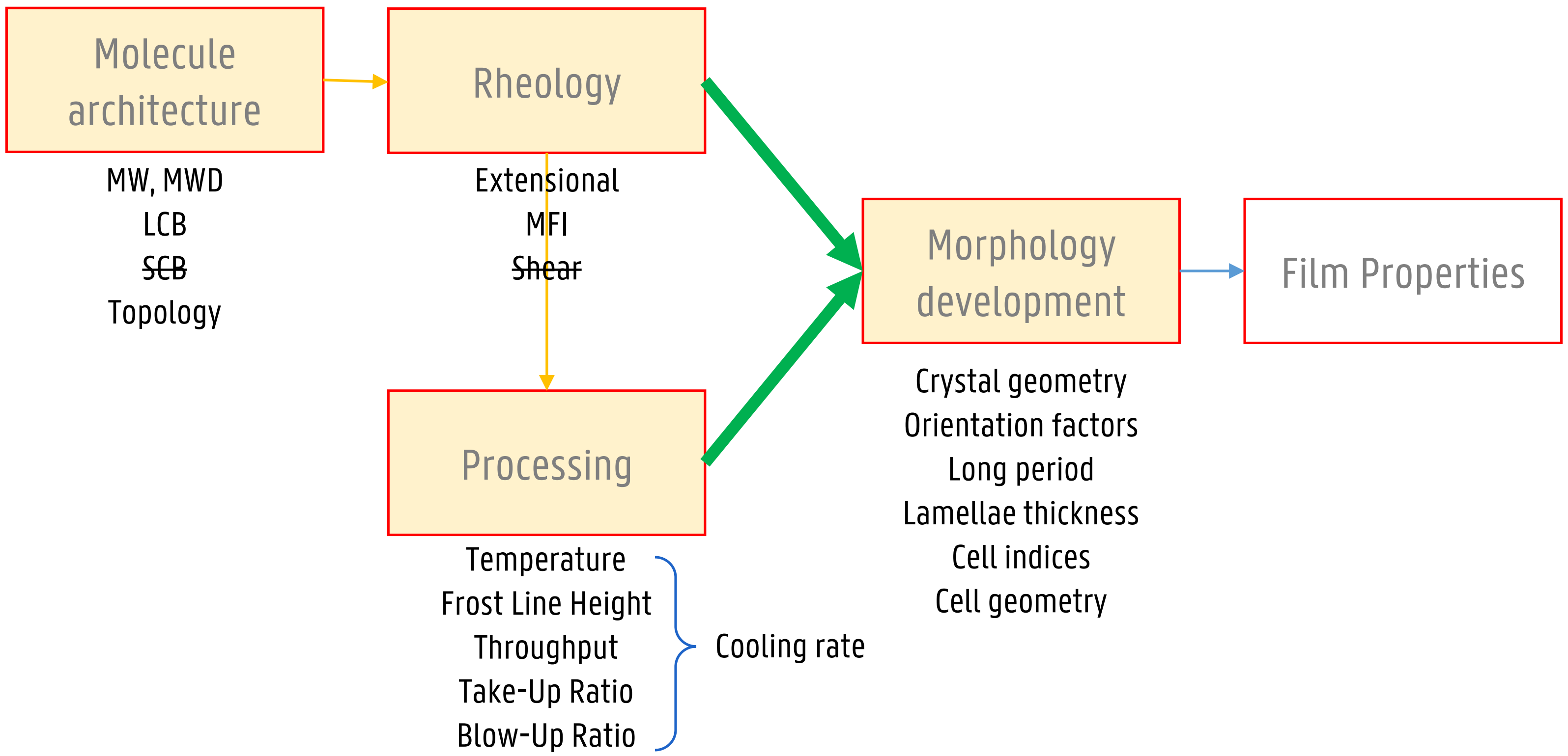
China
Chinese Journal of Polymer Science Vol. 35, No. 12, (2017), 1508–1516



Dutch Belgian Beamline BM26B at the European Synchrotron Radiation Facility (ESRF, Grenoble, FR)

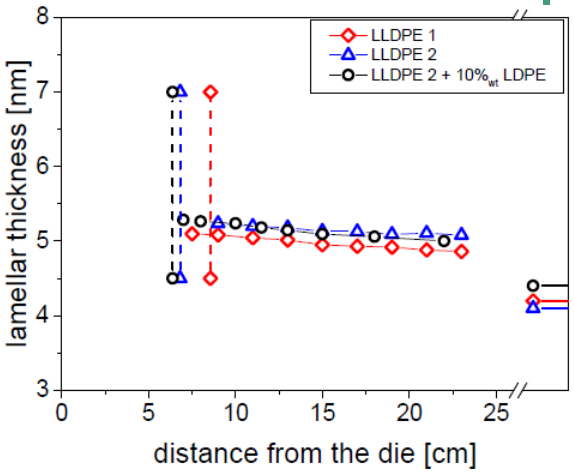
E.M. Troisi, M. van Drongelen, H.J.M. Caelers, G. Portale, G.W.M. Peters
Eindhoven University of Technology
European Polymer Journal 74 (2016) 190–208

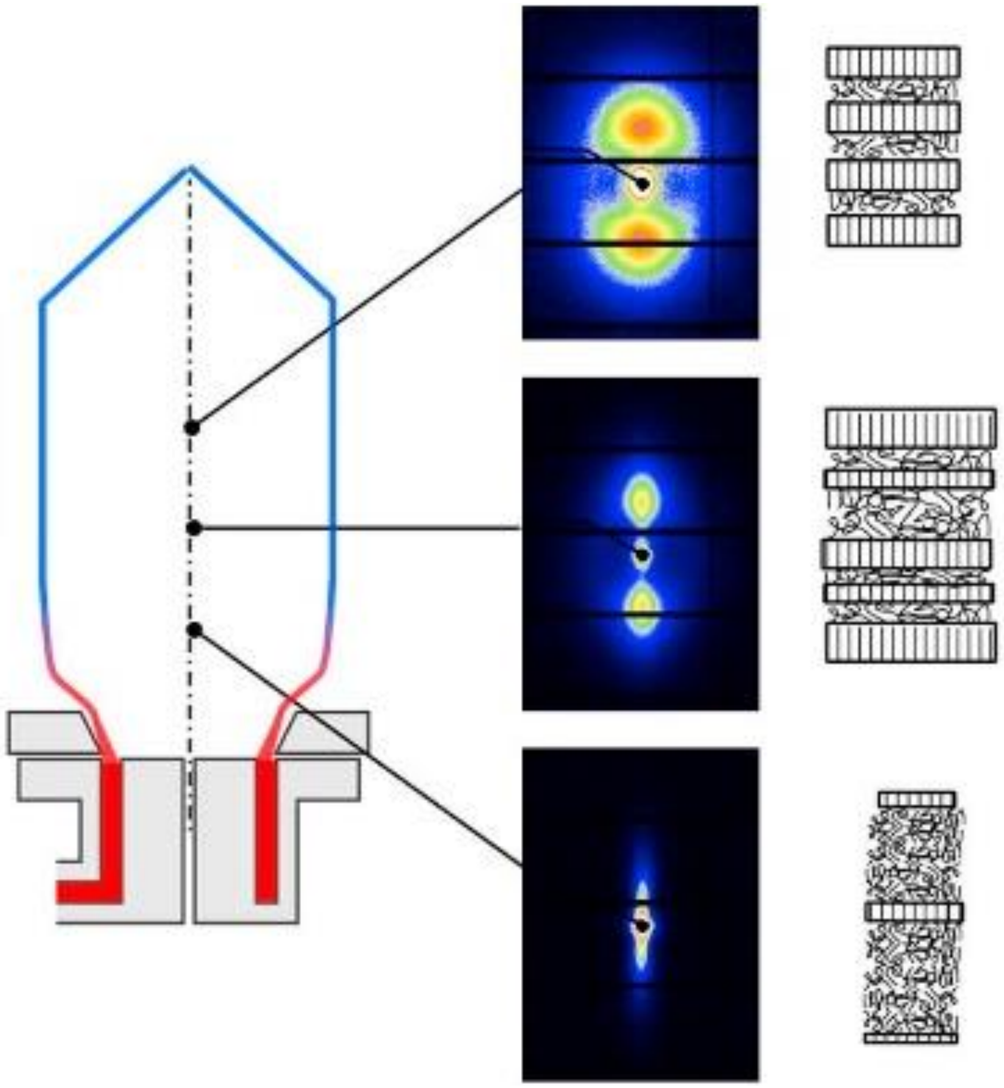
FILM BLOWING PROCESS



MORPHOLOGY DEVELOPMENT ALONG BUBBLE

- Crystallinity ↑
- Orientation: Consistent



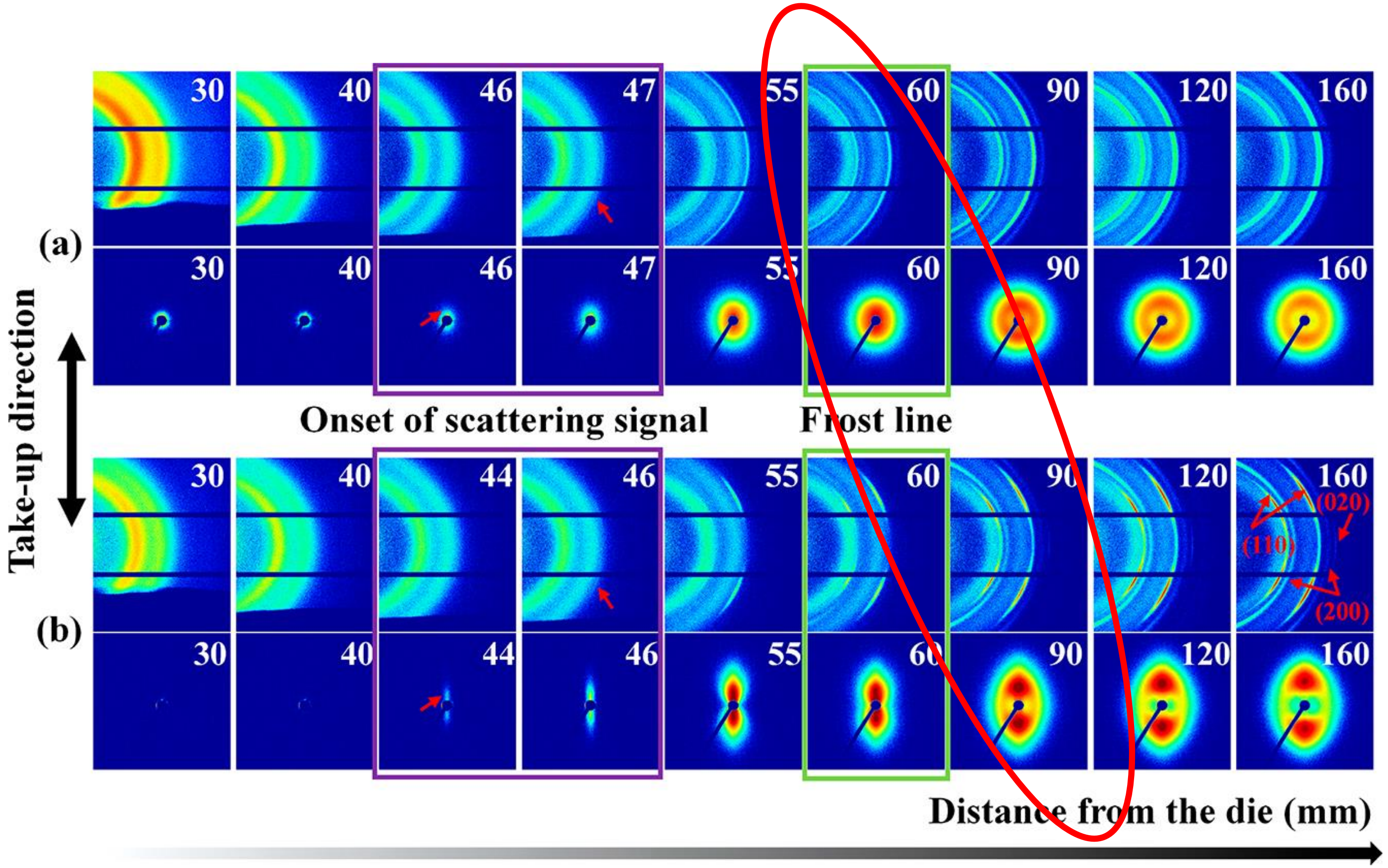


Flow induced crystallization

Troisi et al., 2016

POLYMER EFFECT ON MORPHOLOGY

Linear polymers tend to develop non-oriented structures,
while branched polymers exhibit oriented morphologies

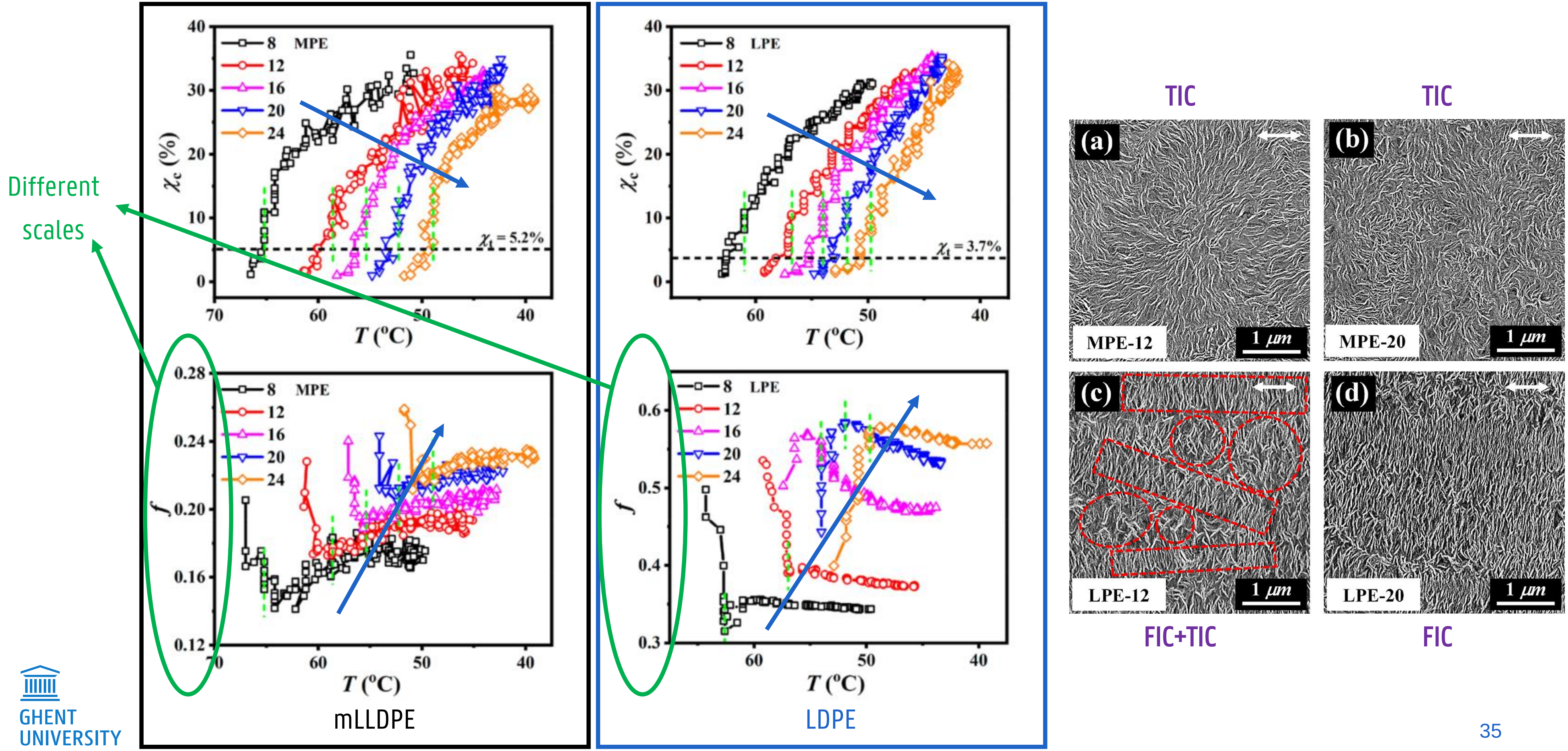


mLLDPE

LDPE

Chinese Journal of Polymer Science Vol. 35, No. 12, (2017), 1508–1516

MORPHOLOGY VS TUR



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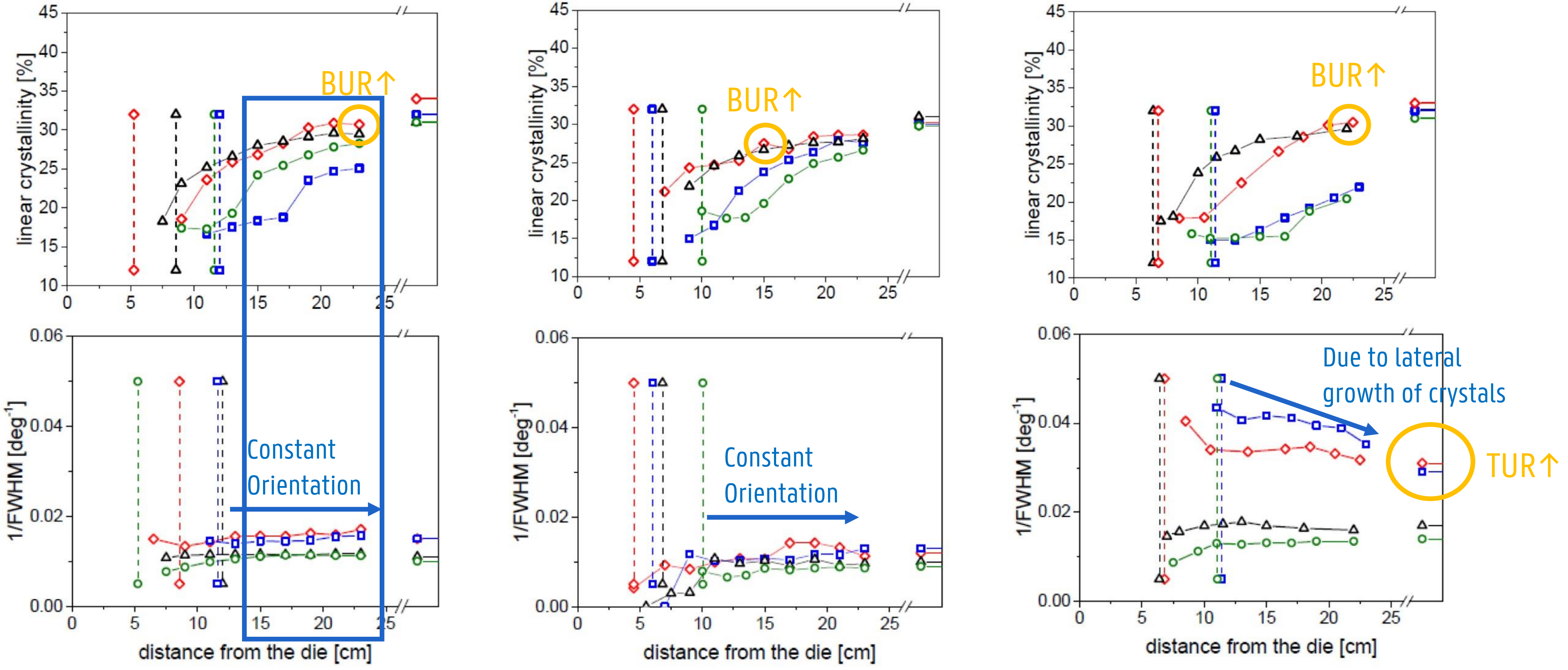
ORIENTATION AND XC EVOLUTION

	Mw (kg/mol)	PDI
LLDPE1	94	3.9
LLDPE2	108	2.4
LDPE	217	5.9



LLDPE1 LLDPE2 LLDPE2+10%LDPE

thinner lamellae form within the template of already formed and oriented lamellae → Average lamellar thickness

Troisi et al., 2016

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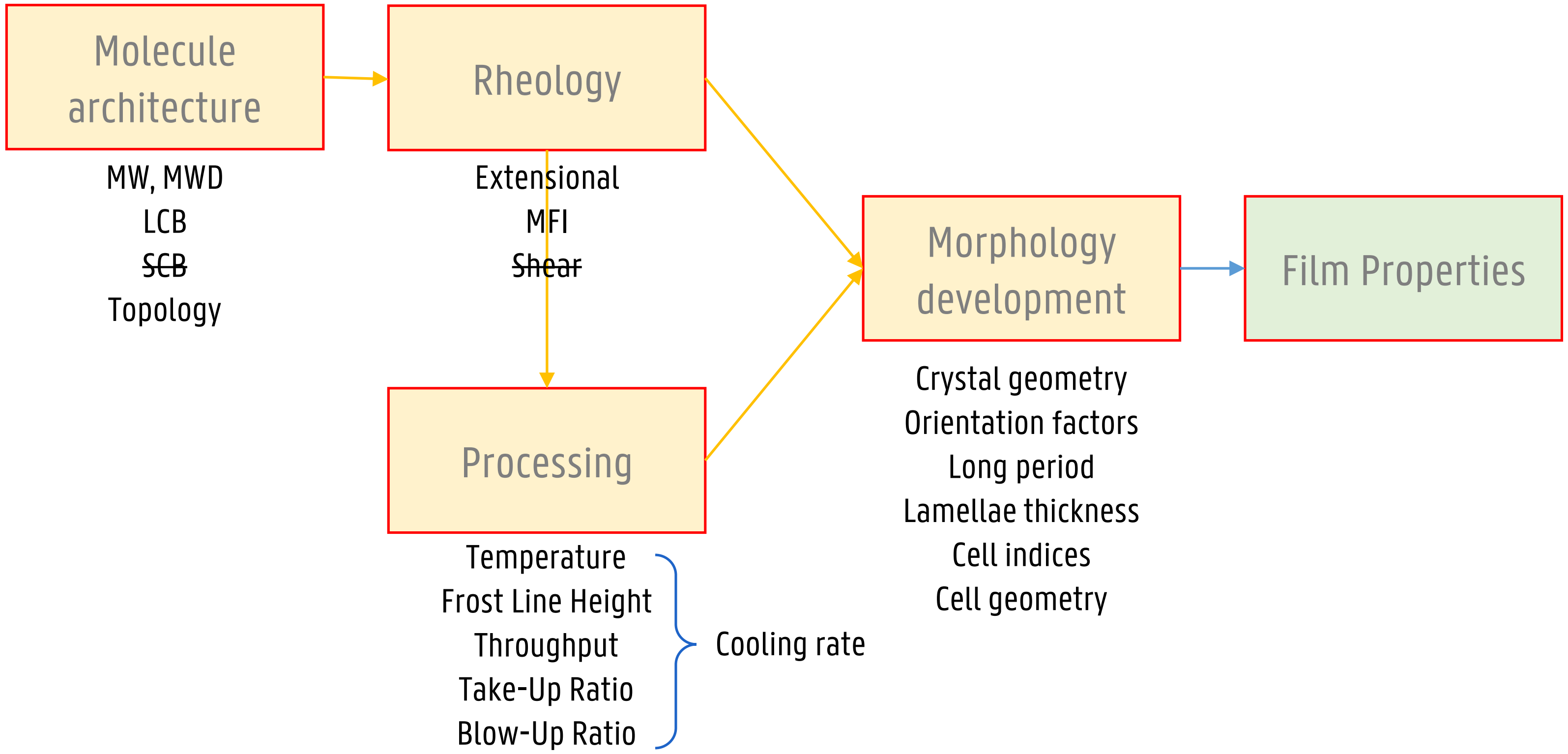
FILM BLOWING PROCESS



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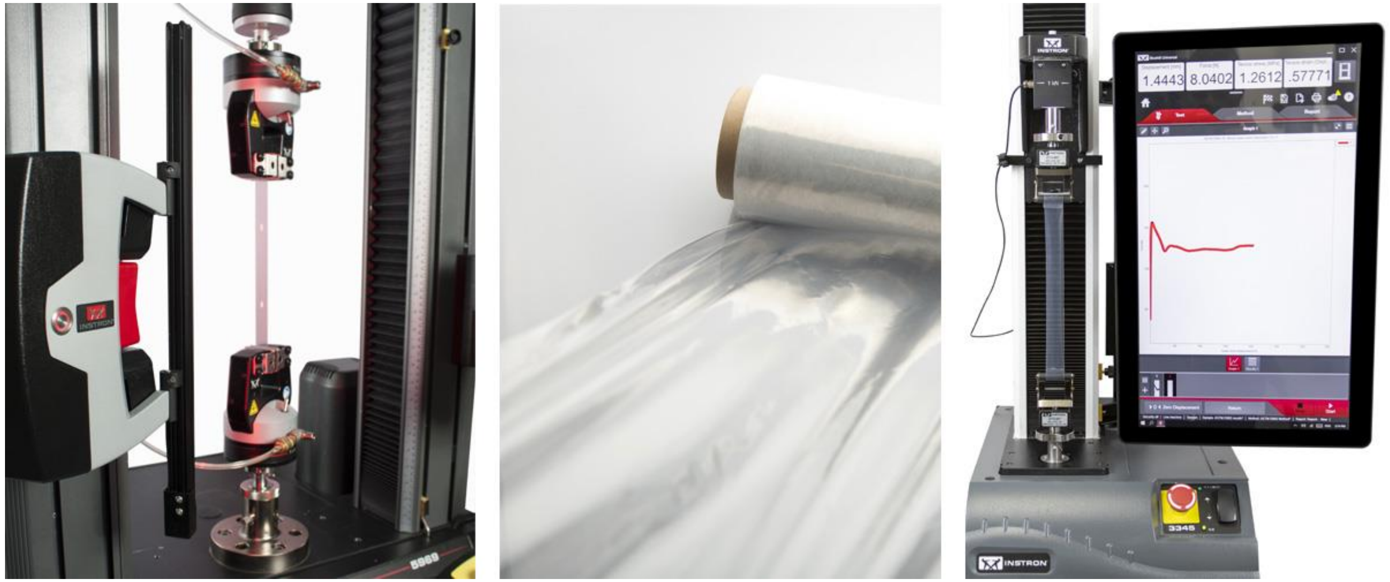
FILMS MECHANICAL PROPERTIES



instron.us

Static loading condition
Tensile testing

labthink.com

Dynamic loading condition
Dart drop testing

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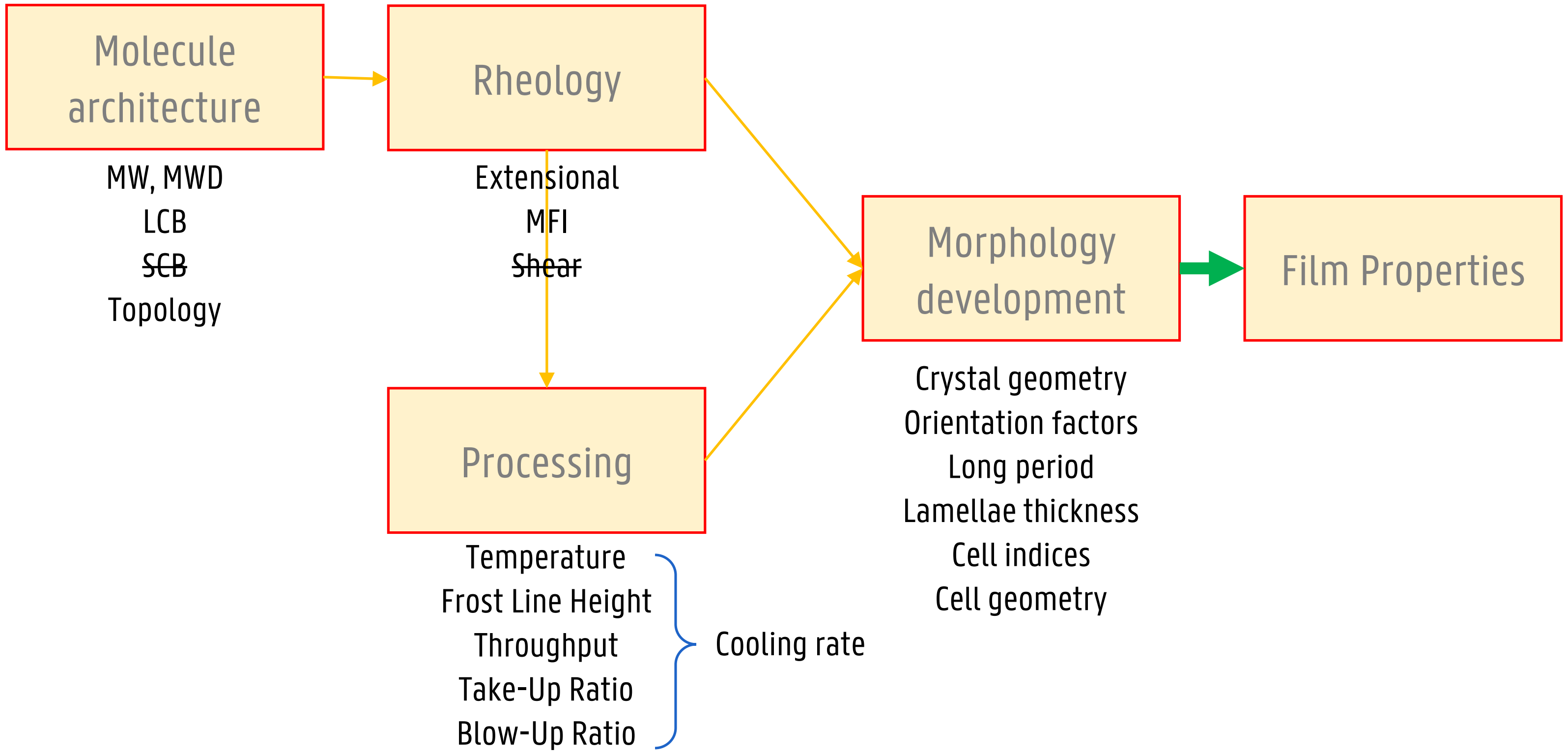
FILM BLOWING PROCESS



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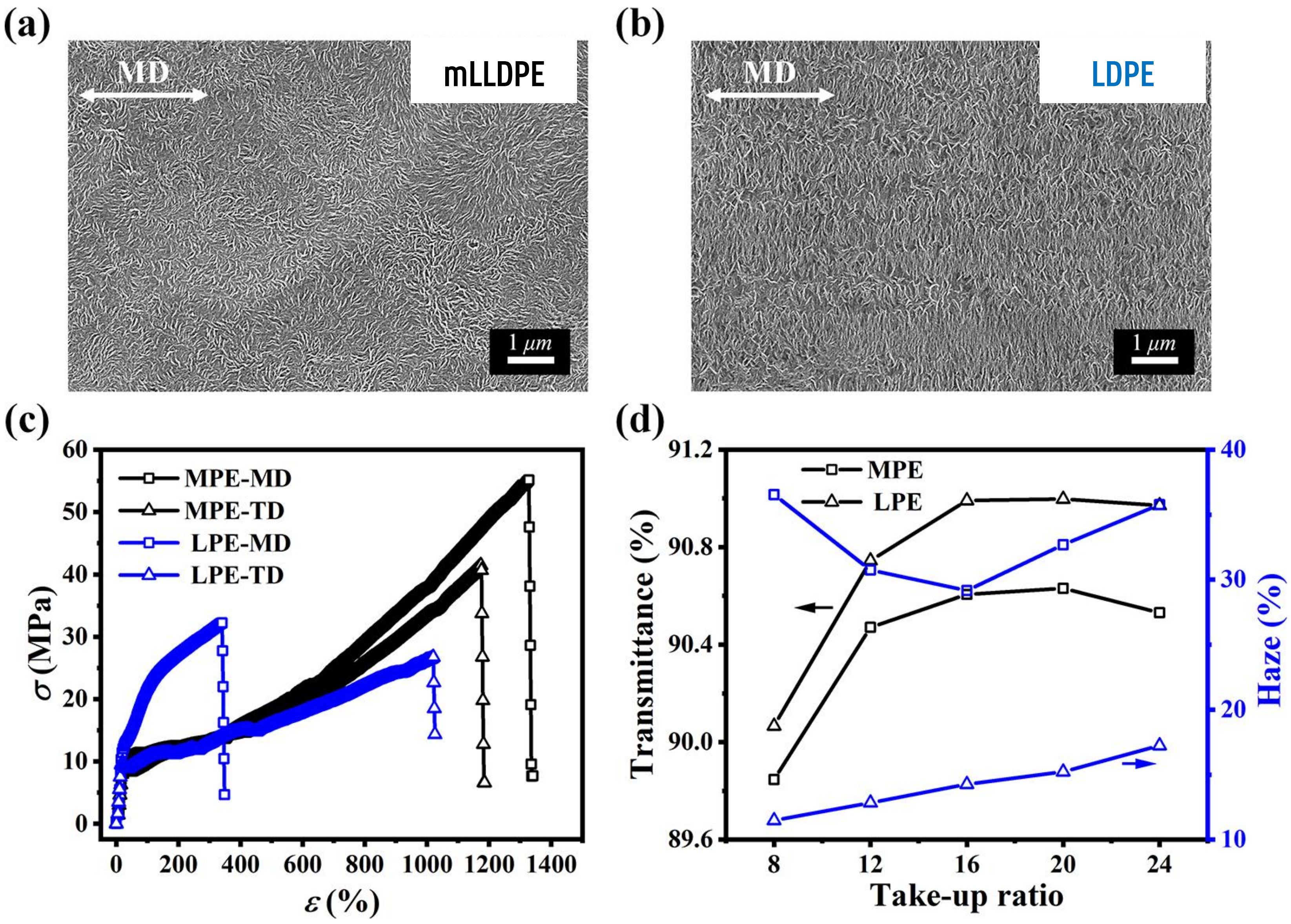
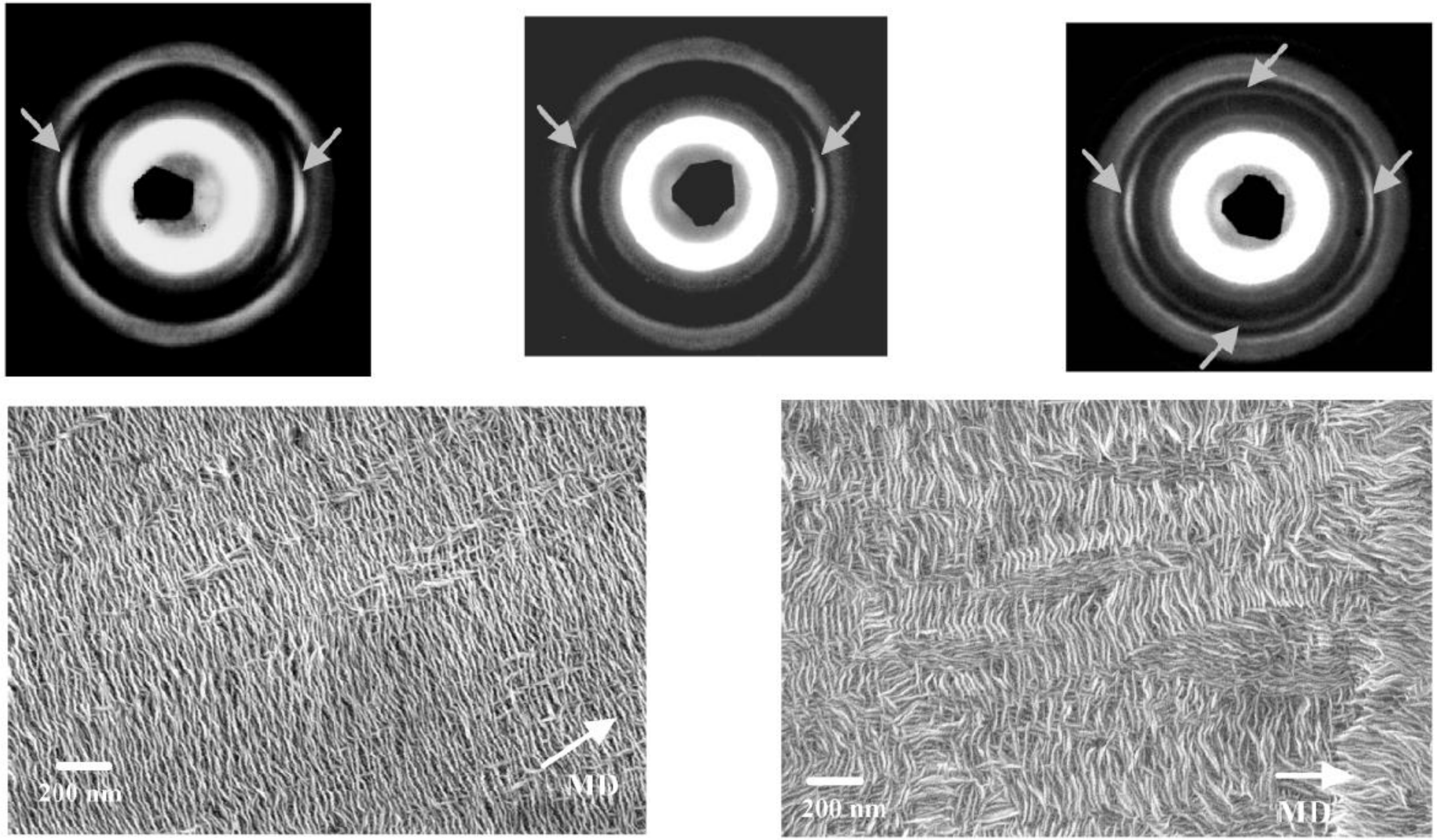
ANISOTROPIC PROPERTIES, POLYMER EFFECT



Branched PE:
Lower mechanical properties, higher anisotropy, higher optical properties, and better processability

FLH VS CRYSTALLINE STRUCTURE



MD Orientation is decreased

Godshall, 2003

FLH ↑

- MD tear ↑
- TD tear ↓
- Dart impact ↑

Cooling rate↓:

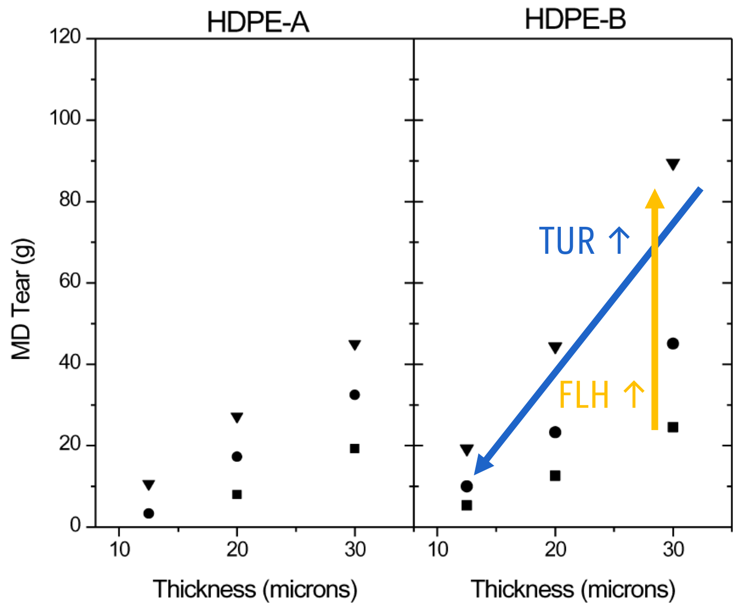
UTS ↓

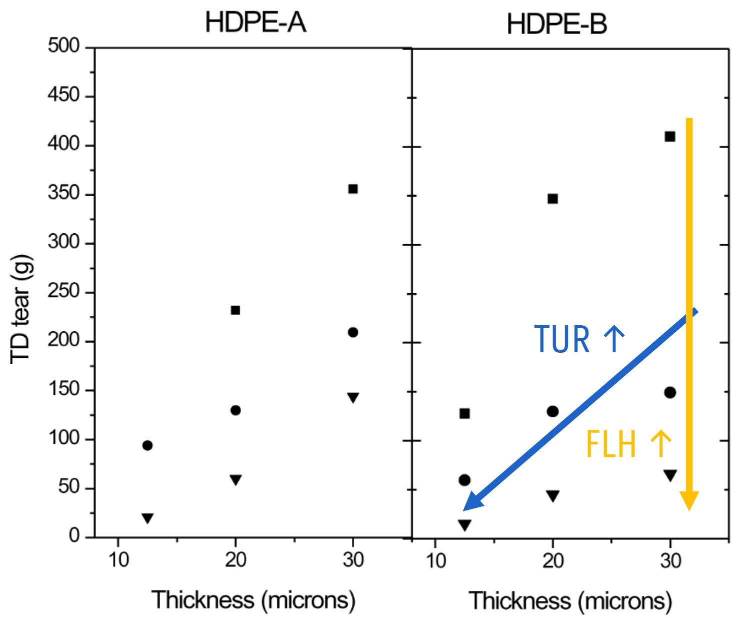
E ↓ or consistent

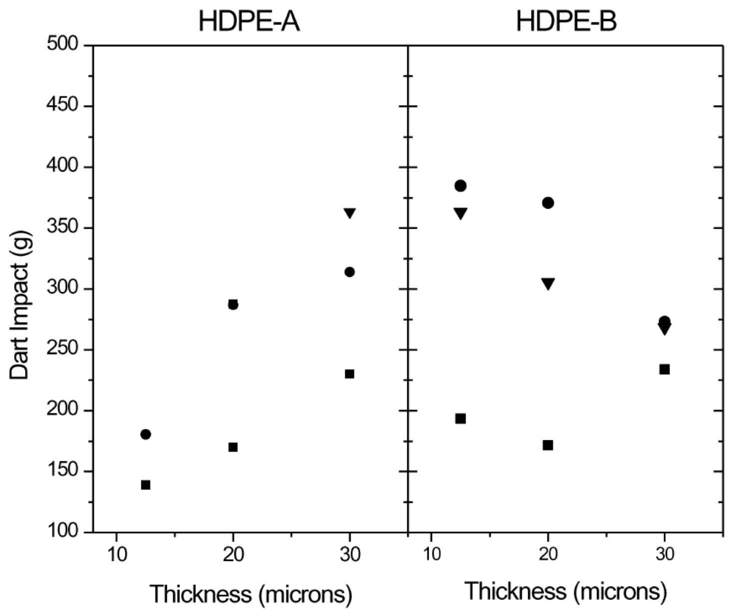
MECHANICAL PROPERTIES VS TUR

In linear PE:

As the FLH increases, MD Tear increases, and TD Tear substantially degrades, dart drop resistance is mixed!







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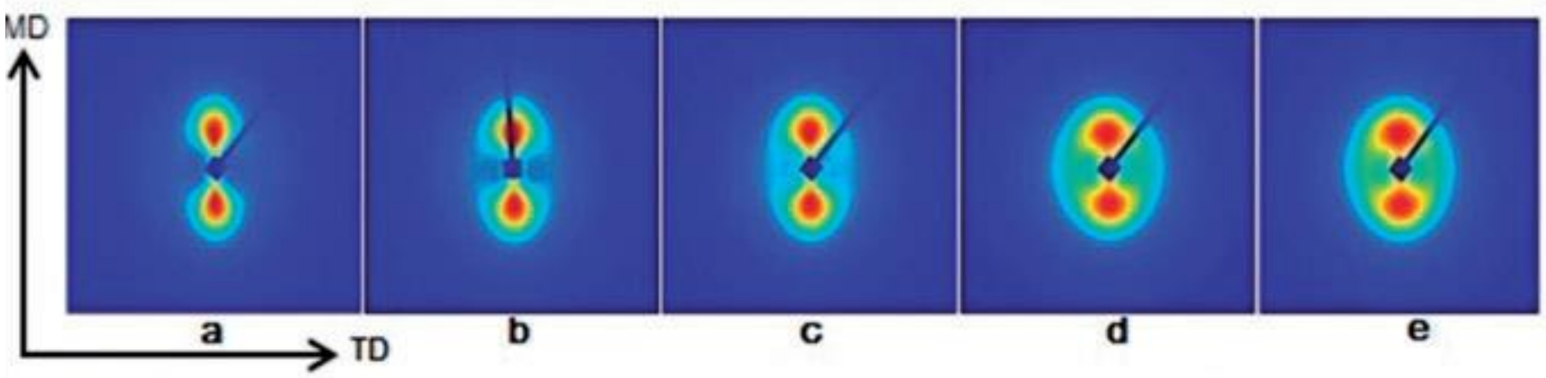
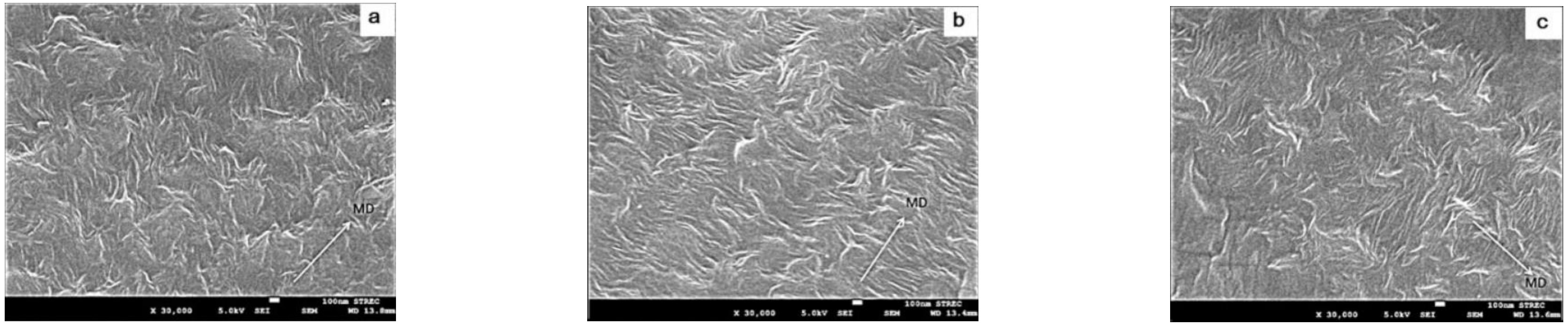
BUR VS CRYSTALLINE STRUCTURE

Not very different mechanical properties but different barrierity as a result of BUR changes for linear PE





BUR ↑

Constant thickness

- WVTR ↑
- OTR ↑

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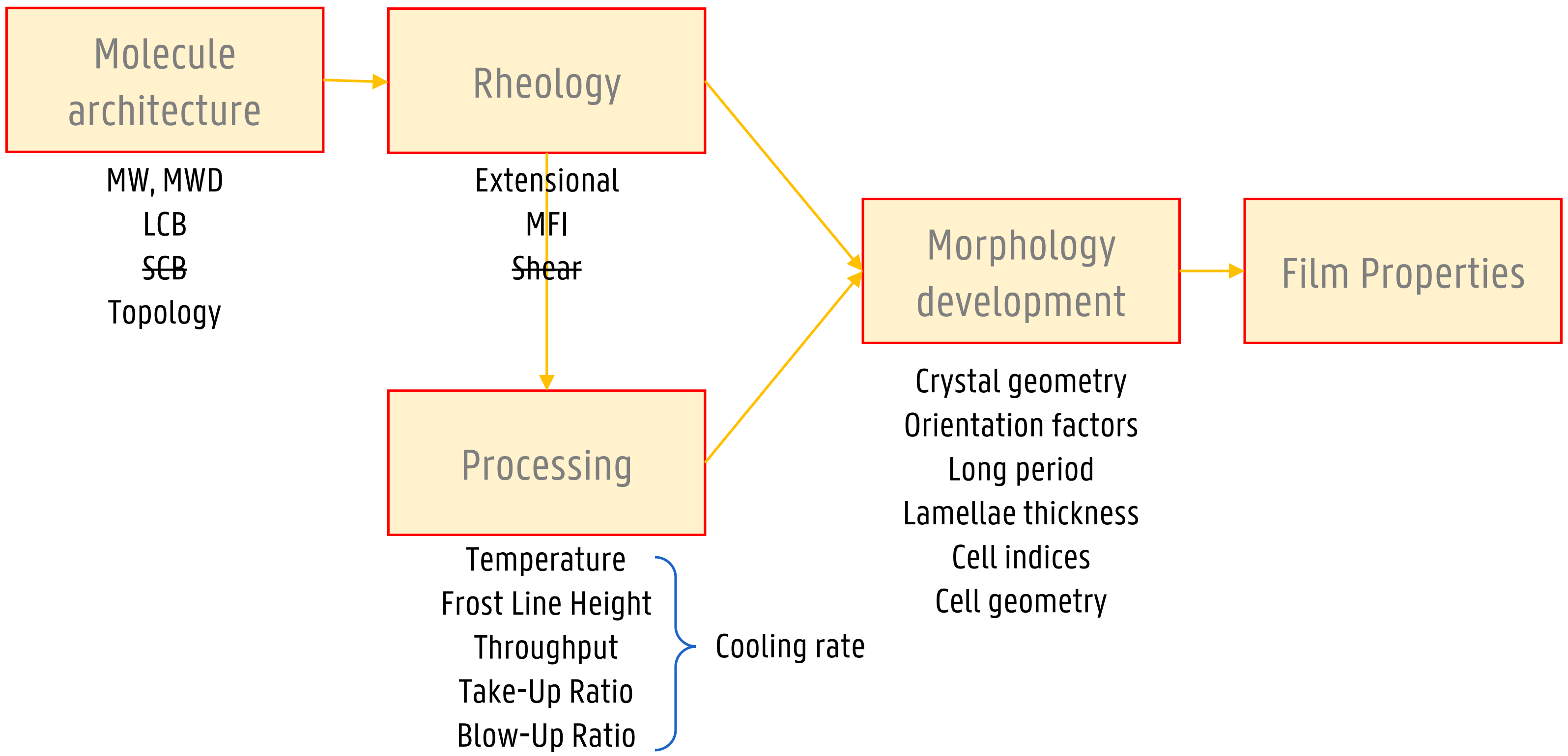
SUMMARY



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ESR 11 EXPERIMENTS PLANNING - MATERIAL

- A choice of film blowing grade PEs are made available.
  - 3 LDPEs: Different in MW and LCB content
  - 3 LLDPEs: Different in comonomer type and content but at the same MW
  - 2 HDPEs: Different in PDI but at the same MW

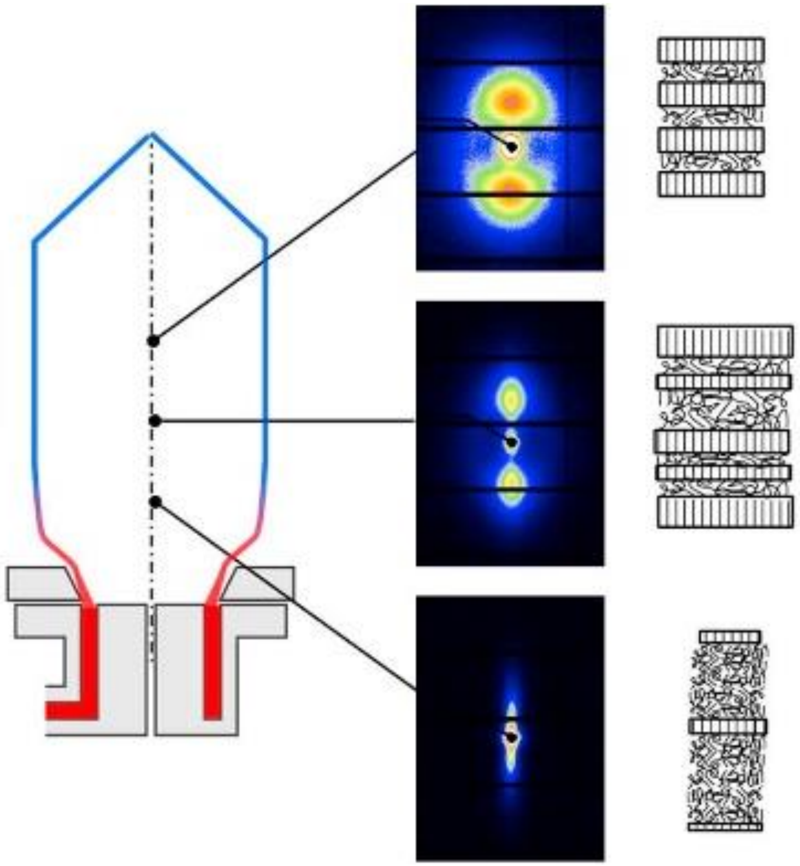
Grade	MW	LCB content	Info
LDPE 1	A	D	Topology and MWD are known
LDPE 2	A	C	Topology and MWD are known
LDPE 3	B	C	Topology and MWD are known

Grade	MW	Comonomer type	Comonomer content	Info
LLDPE 1	H	I	K	MWD is known.
LLDPE 2	H	I	L	MWD is known.
LLDPE 3	H	J	L	MWD is known.

Grade	MW	PDI	Info
HDPE 1	E	F	MWD is known.
HDPE 2	E	G	MWD is known.

ESR 11 EXPERIMENTS PLANNING - TECHNIQUES

- Characterization of material MFI and Melt density at different temperatures
- Extensional viscometry at different temperatures and strain rates to examine the rheology at different stages through processing (before FLH)
- Film blowing trials at different processing parameters to draw processing windows for different material systems
- Mechanical testing at both static and dynamic loadings, tensile tests, puncture resistance, dart drop test, Elmendorf test, sealability tests, and other tests?
- In- and off-process SAXS and WAXS studies and SEM characterizations of morphology
- Rheotens Viscometry
- Color, Haze, and gloss measurements
- Surface roughness characterizations and AFM
- Other tests?



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Thanks for your attention.

Questions?

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