FACULTY OF ENGINEERING
AND ARCHITECTURE

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FROM MACROMOLECULAR ARCHITECTURE TO FILM BLOWING PERFORMANCE OF L(L)DPE: AN OUTLOOK FOR RECYCLABILITY OF FLEXIBLES

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April 12, 2022

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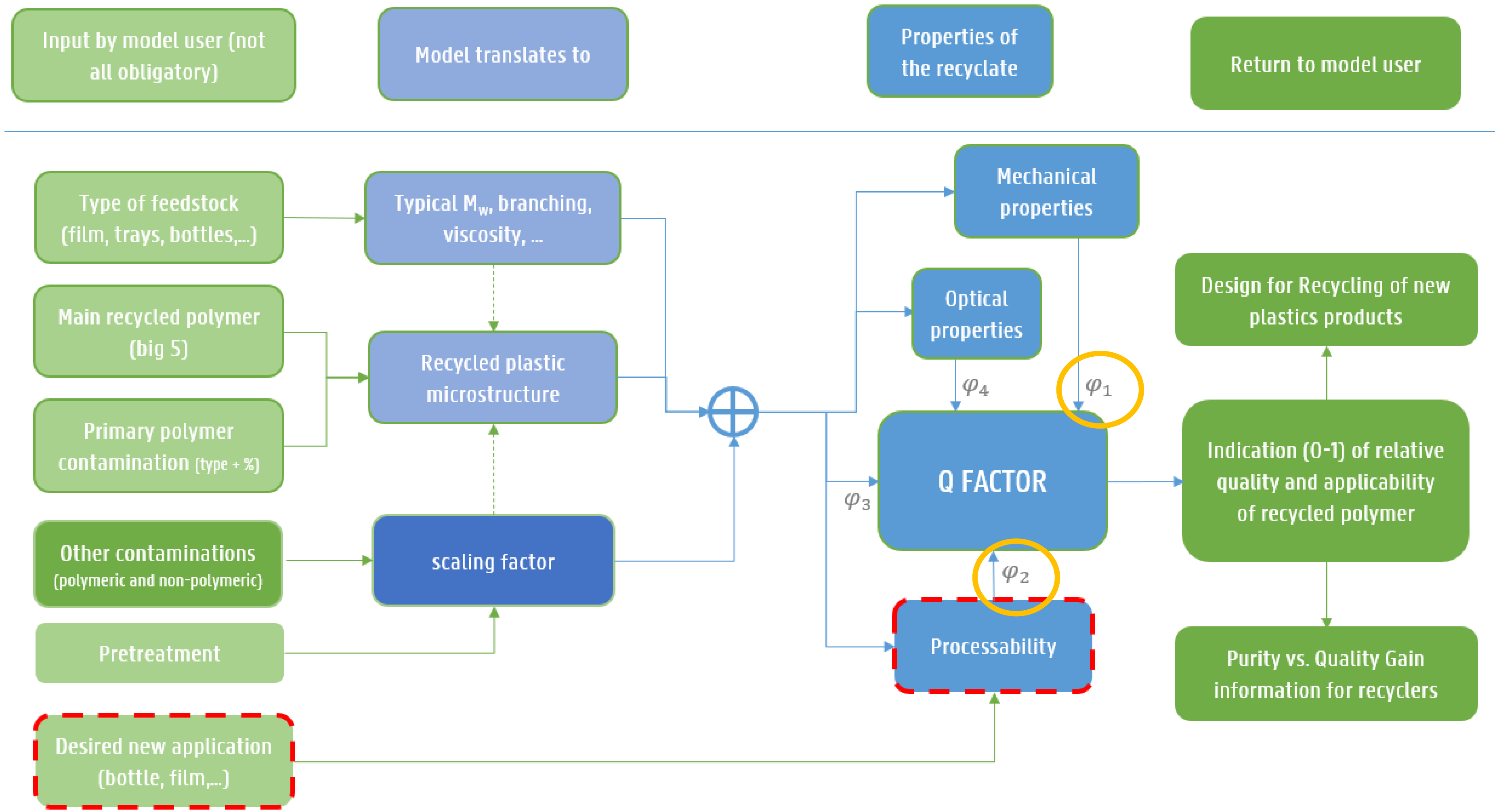
LCT DRIVING CHEMICAL TECHNOLOGY
Maastricht University
C-PlaNeT CIRCULAR PLASTICS NETWORK FOR TRAINING

RECYCLING QUALITY CONCEPT



RESEARCH QUESTION

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

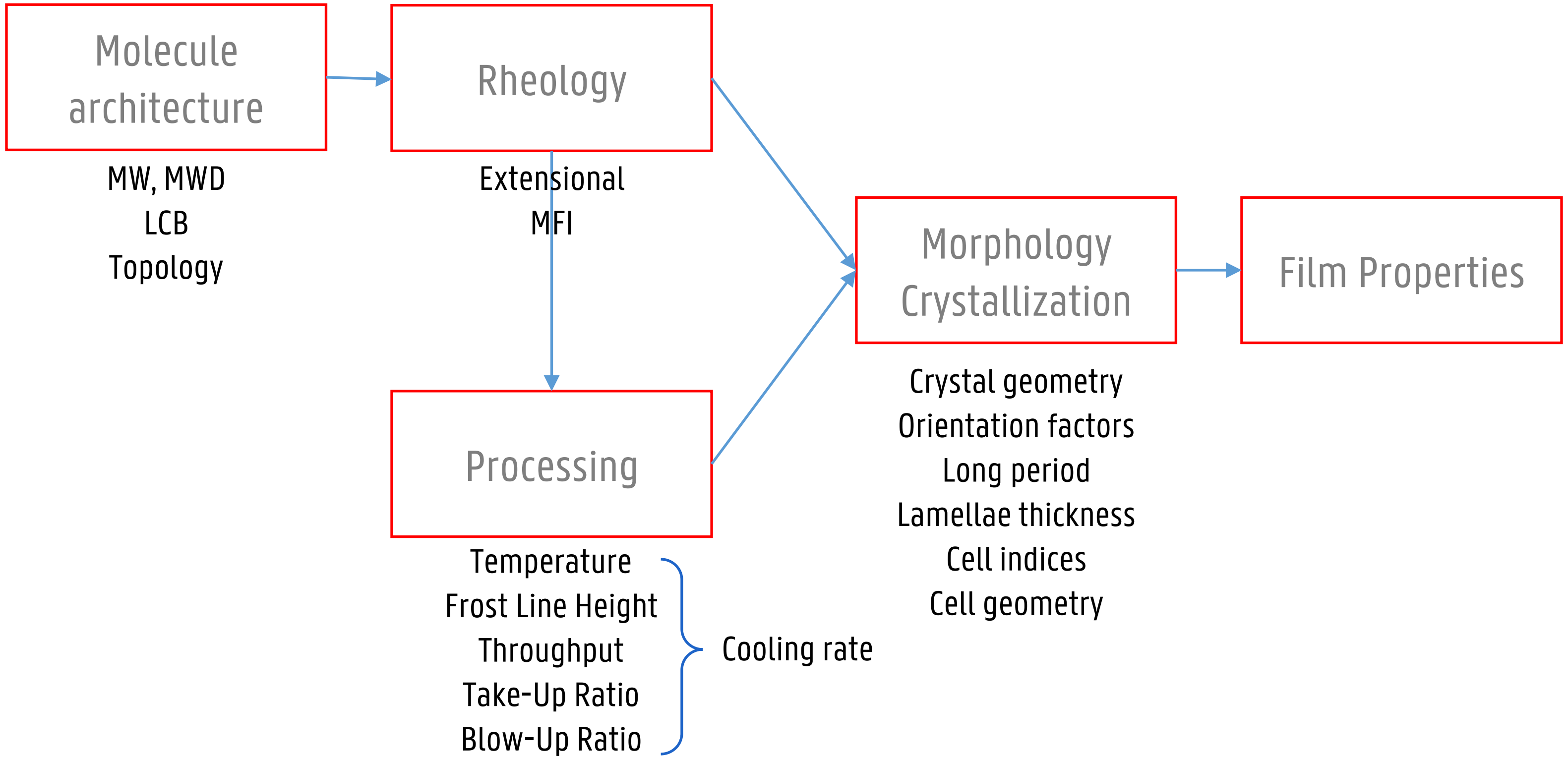
- Contaminations? For the moment, cross-polymer contaminations: other PEs, PP, PET, PS, and PA

$$\mathbf{RQ} = \frac{\text{Recycled Quality}}{\text{Virgin Quality}} = \varphi_1 \times \text{Properties} + \varphi_2 \times \text{Processability}$$

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. ϕ_1 and ϕ_2 coefficients should be assigned
3. RQ should be predictable for certain (distribution of) molecules/blends

PREDICTION OF RECYCLING QUALITY



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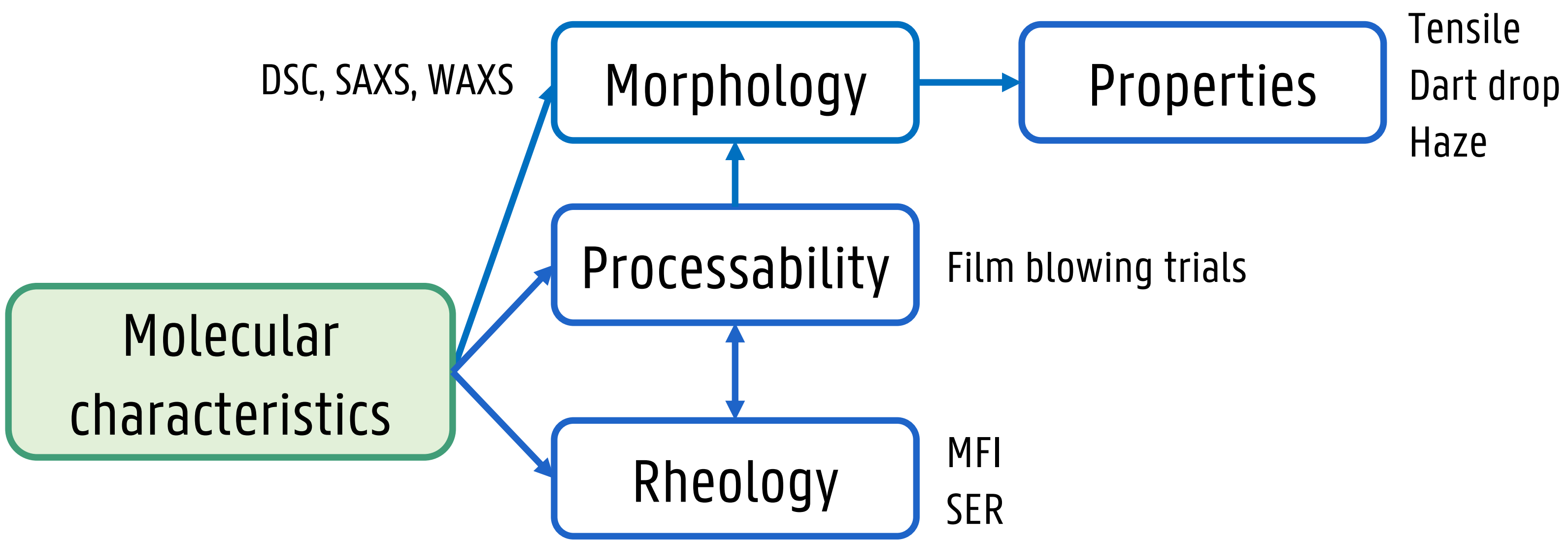
STRUCTURE OF THE EXPERIMENTS



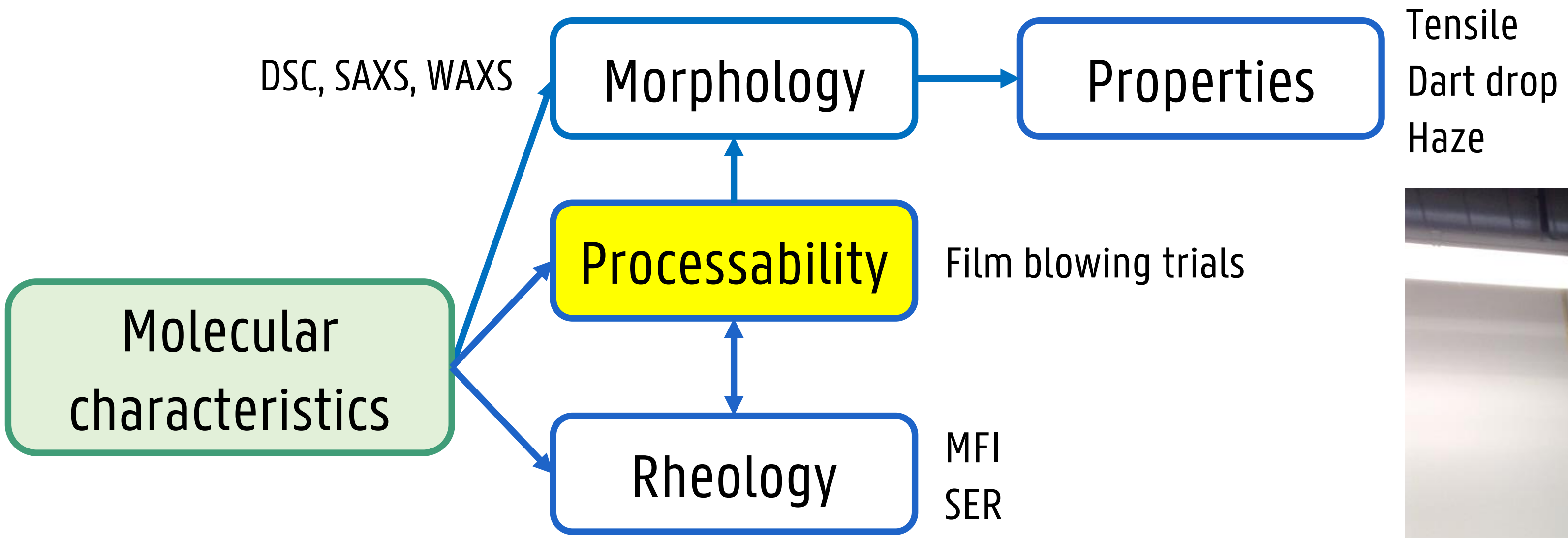
MATERIALS

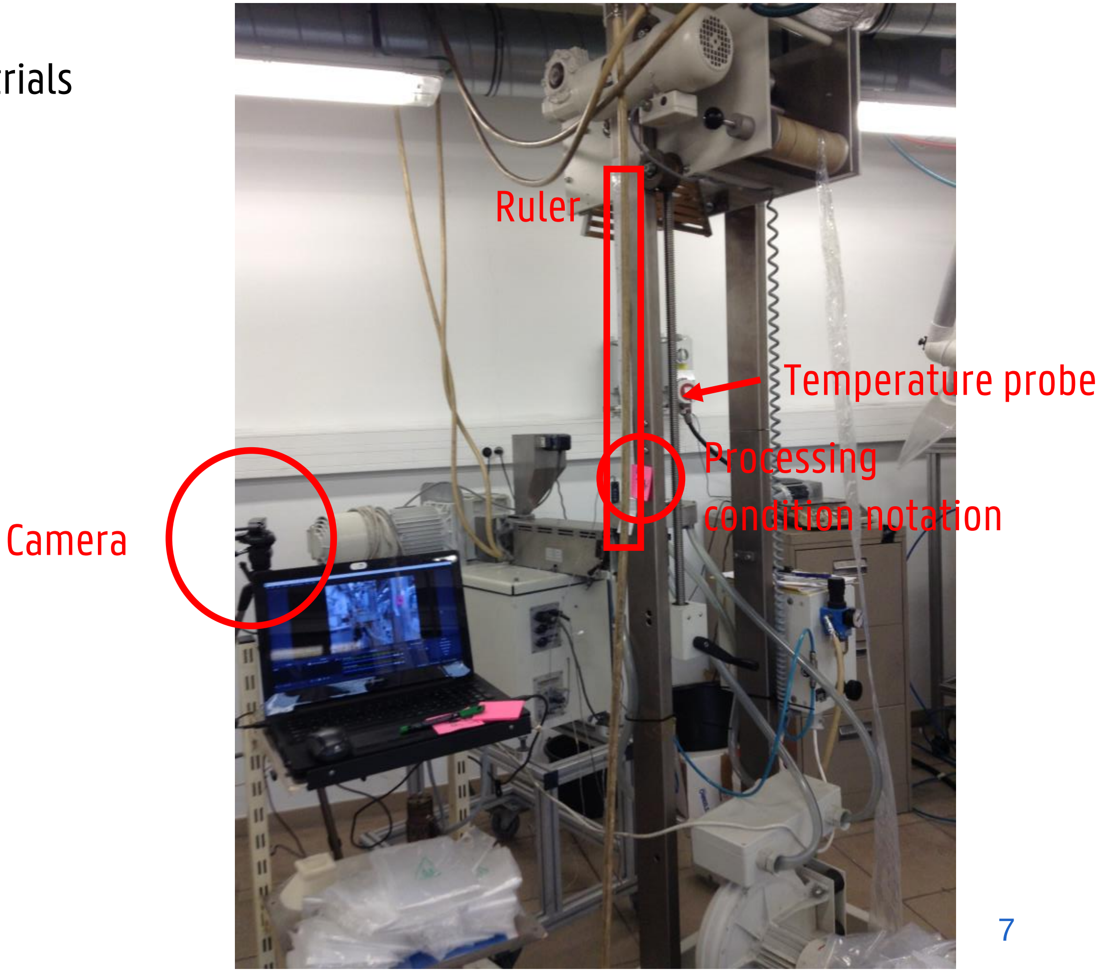
- 5 materials are tested
  - LDPE with high PDI
  - LDPE with medium PDI
  - LLDPE with low PDI

- Blend 21=20%L21+80%LL
- Blend 14=20%L14+80%LL

Grade	Mw [kg/mol]	Mn [kg/mol]	PDI	MFR [g/10min]
LDPE21	332	16	20,75	$1{,}58 \pm 0{,}02$
LDPE14	297	21	14,14	$0{,}96 \pm 0{,}01$
LLDPE4	125	30	4,17	$0{,}99 \pm 0{,}01$

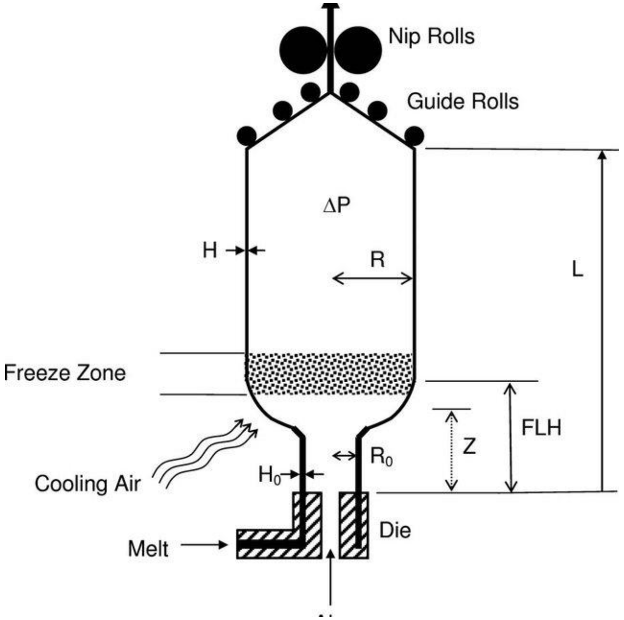
STRUCTURE OF THE EXPERIMENTS

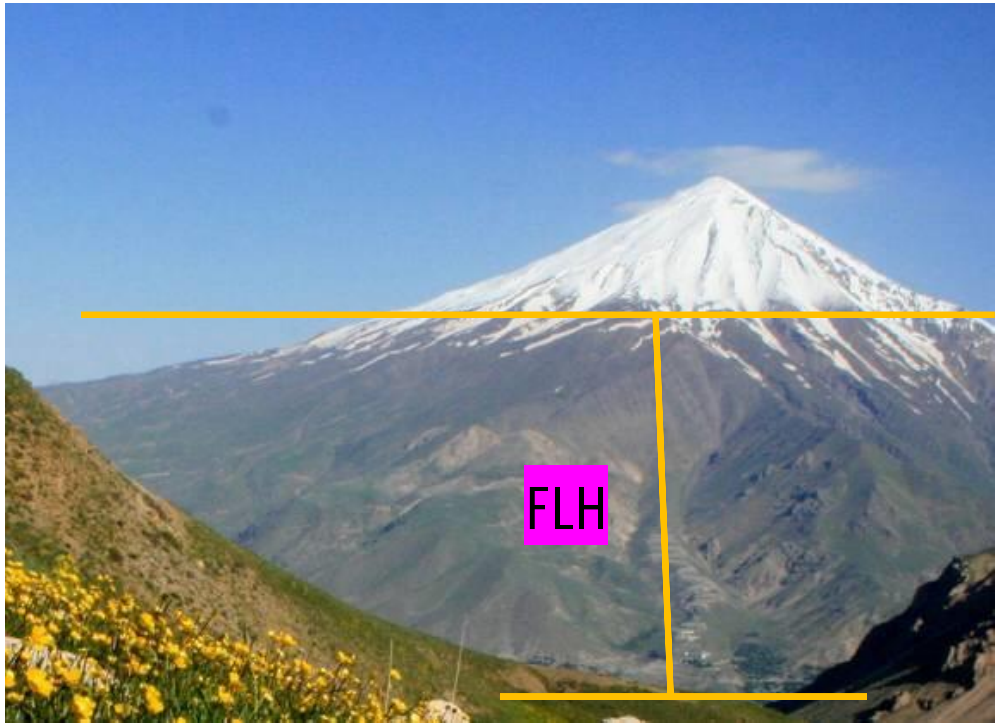




PROCESSING PARAMETERS: BUR, TUR, AND FLH

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





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FILM BLOWING

What is done?

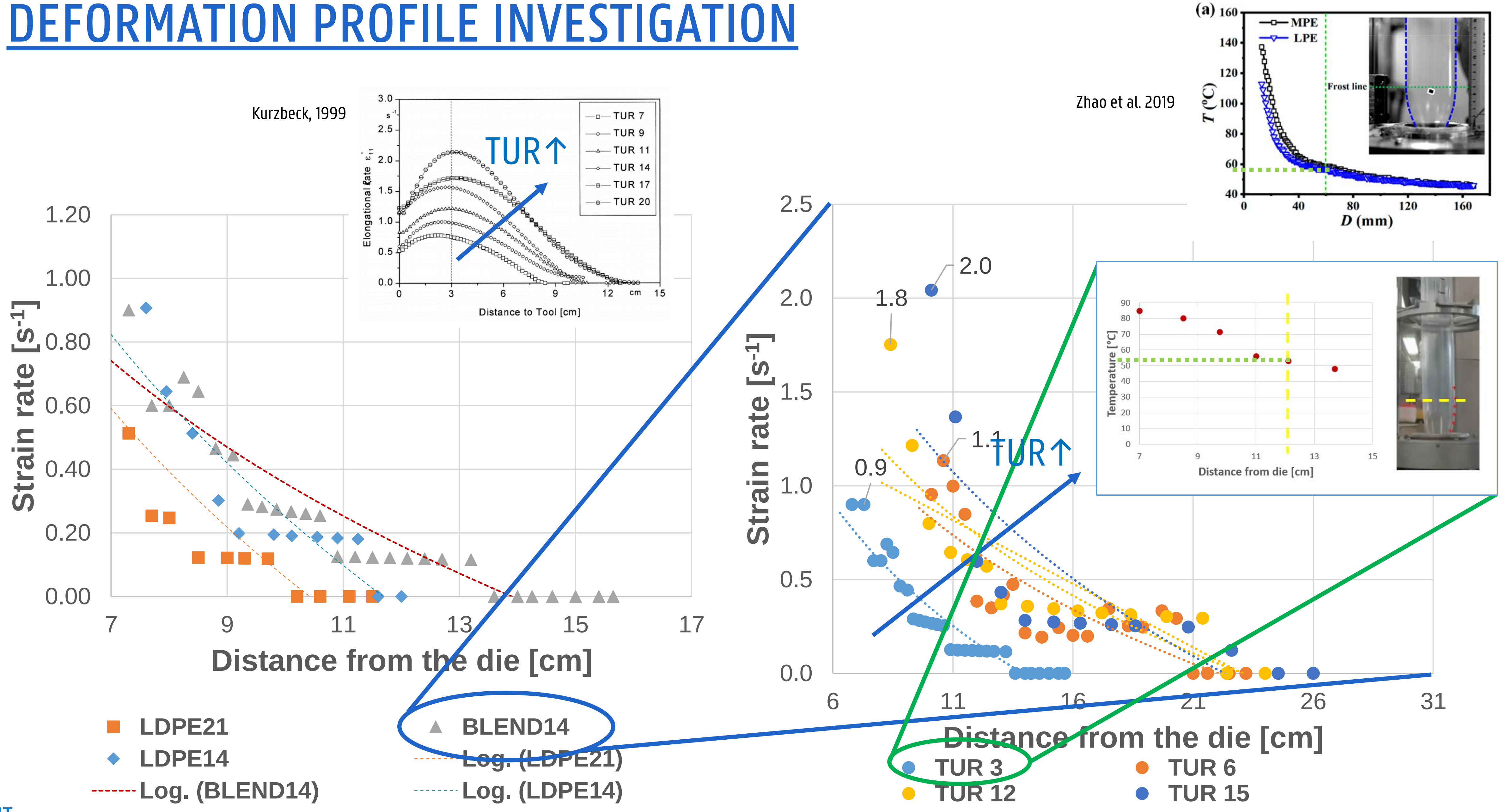
- Temperature: 180°C – 185°C – 190°C – 190°C
- Constant throughput of around 1,68 kg/h
- Constant cooling air flow
- Investigation of the processing window
  - 5 materials, each processed at 30 different conditions
    - 6 different BUR (1.5 – 2 – 2.5 – 3 – 4 – 5)
    - 5 different TUR (3 – 6 – 9 – 12 – 15)

What is measured?

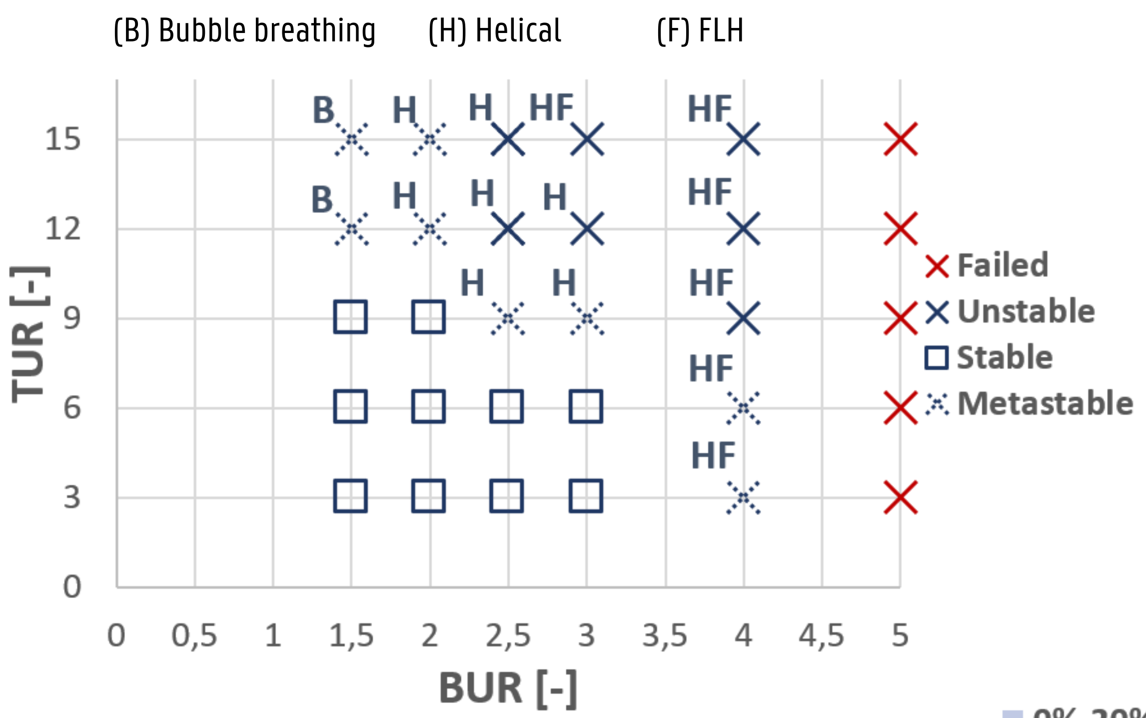
- If the condition was reachable?
- If stable? deformation profile…
- Type(s) of instability present?
- Quantified extent of stability?
  - Rate of geometrical evolutions over time

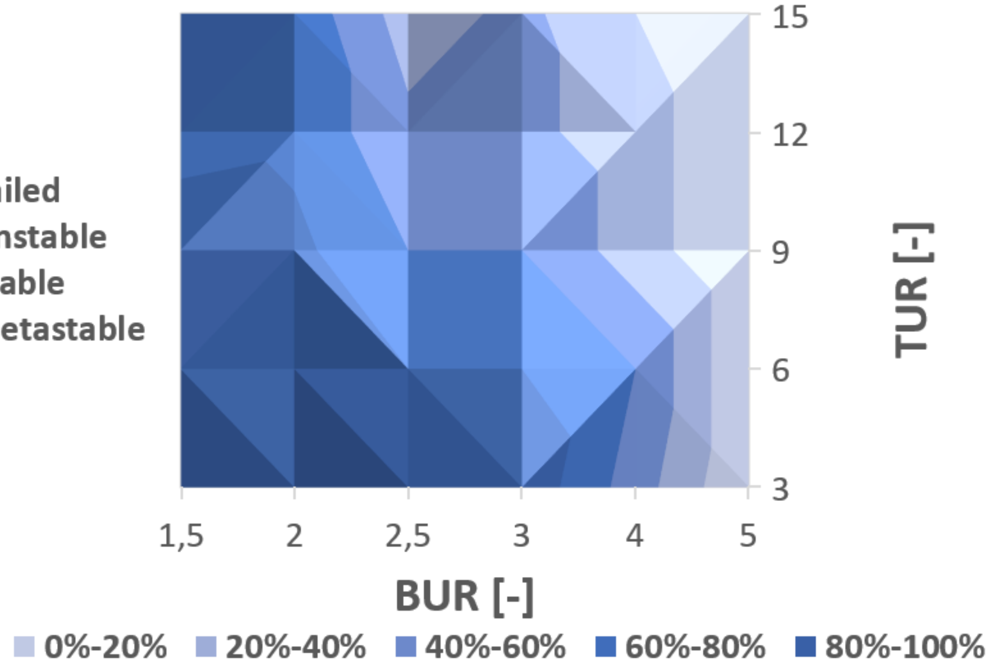
Materials	Screw speed [rpm]	I2 (dg/min)
LDPE21	50	1,58
BLEND21	80	-
LLDPE4	83	0,99
BLEND14	80	-
LDPE14	58	0,96

DEFORMATION PROFILE INVESTIGATION



PROCESSABILITY INVESTIGATION





Qualitative

Quantitative

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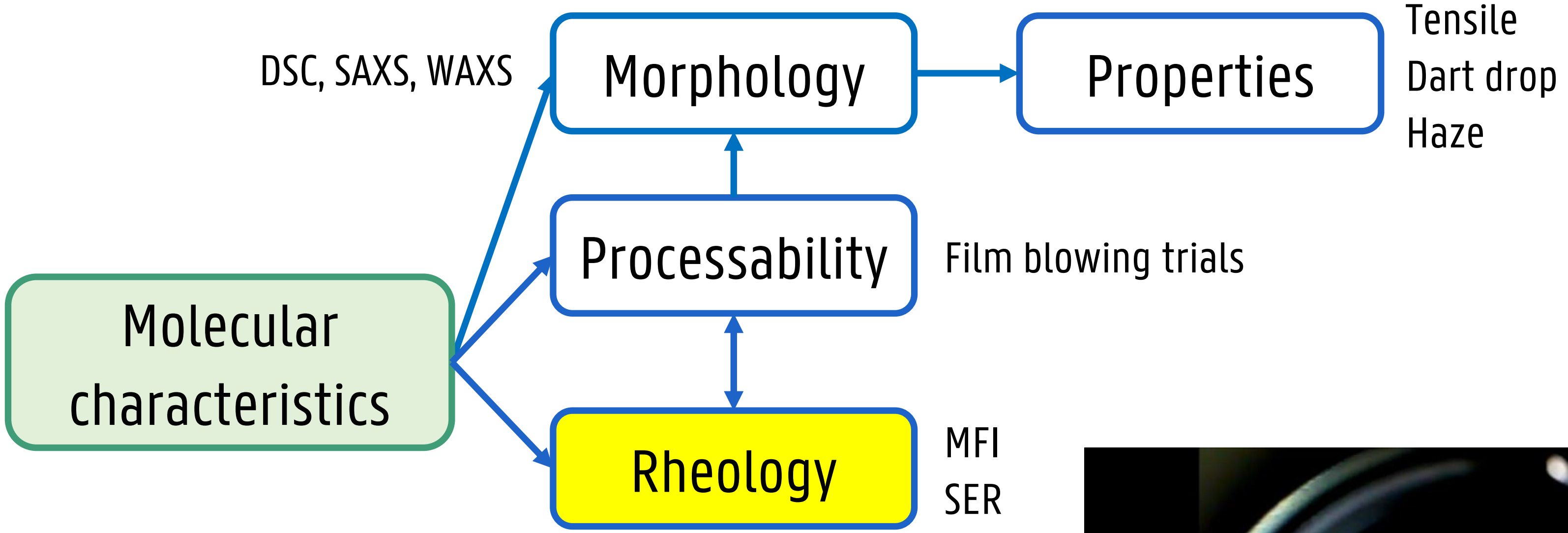
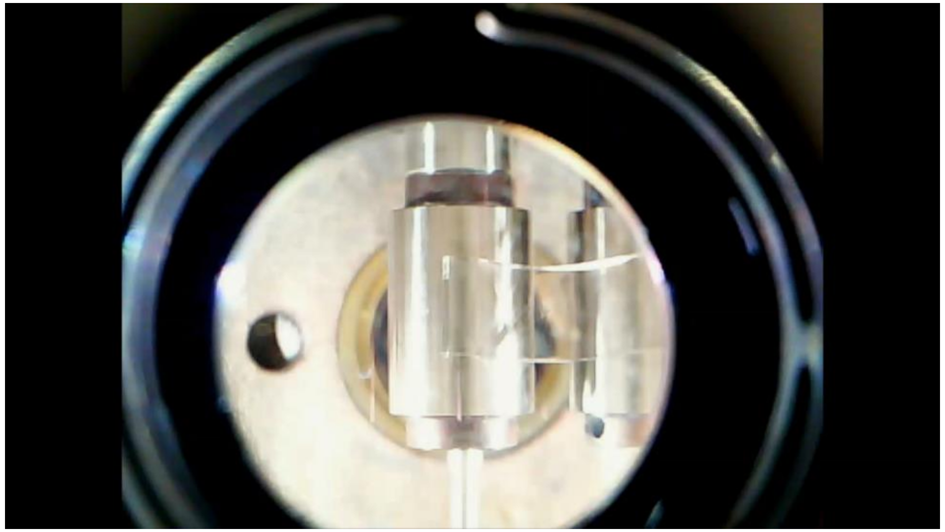
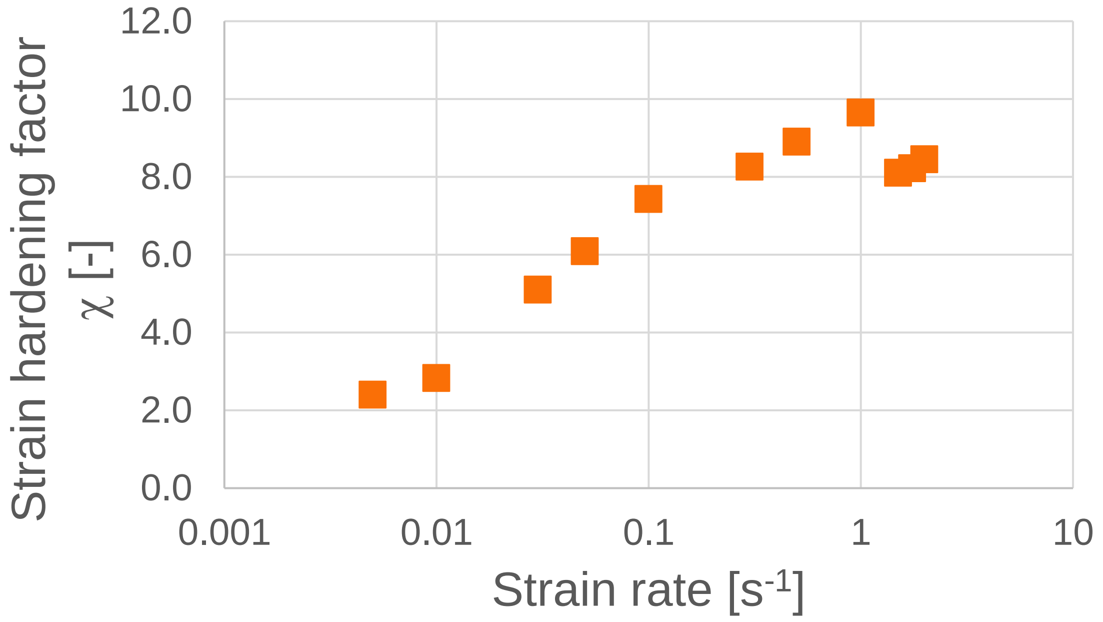




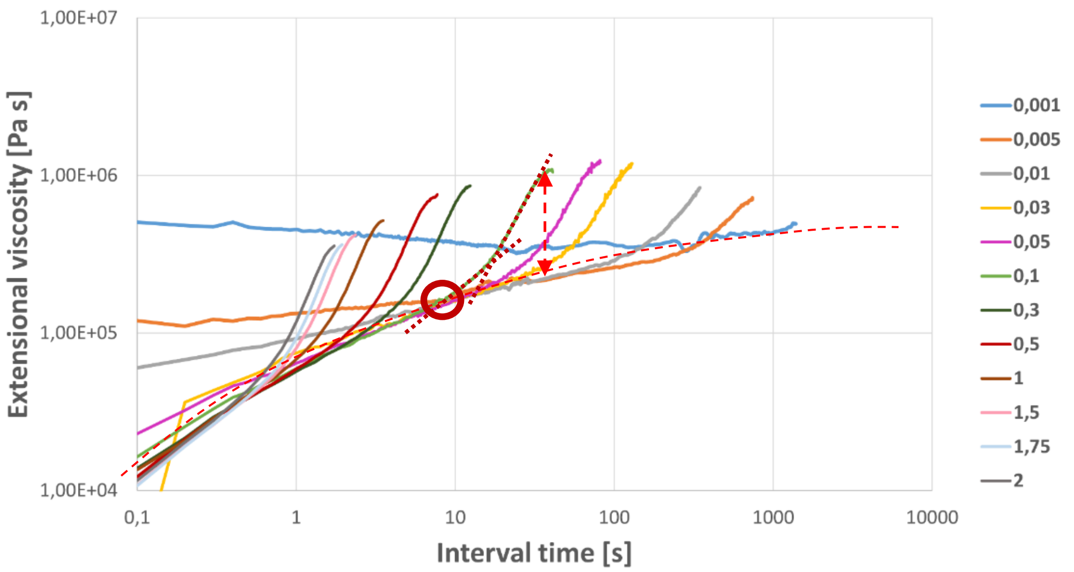
RHEOLOGY INVESTIGATION

- At two different temperatures, 130 and 150 °C
- At twelve different strain rates, 0,001 → 2 s^{-1}

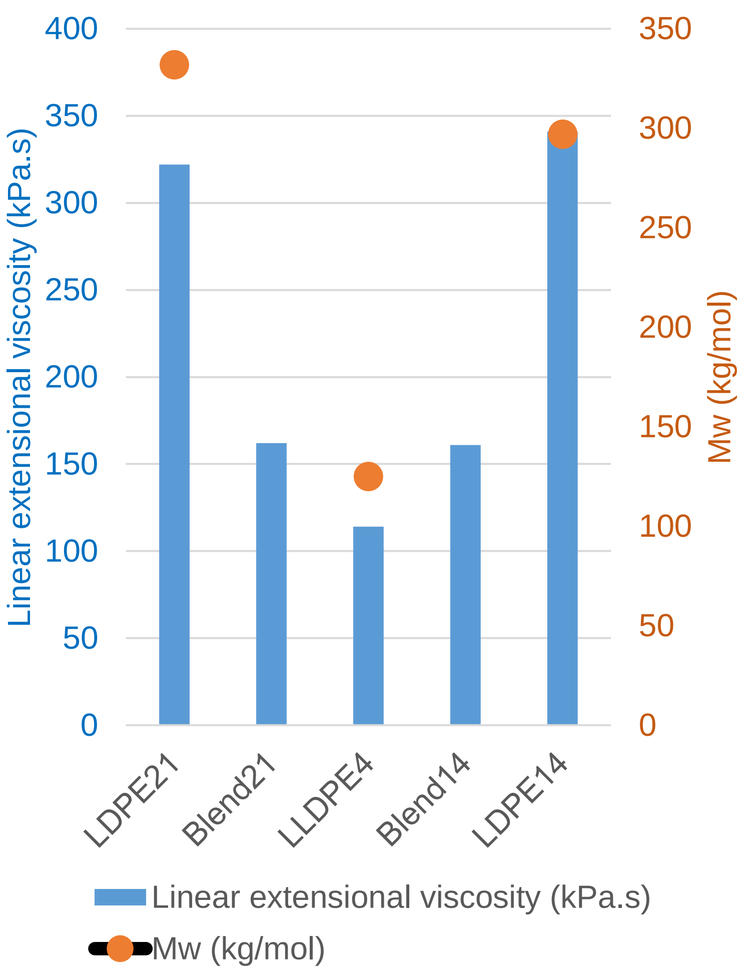
Grade	Mw [kg/mol]	PDI	MFR [g/10min]	LVE [kPa s]
LDPE21	332	20,75	1,58 ± 0,02	322

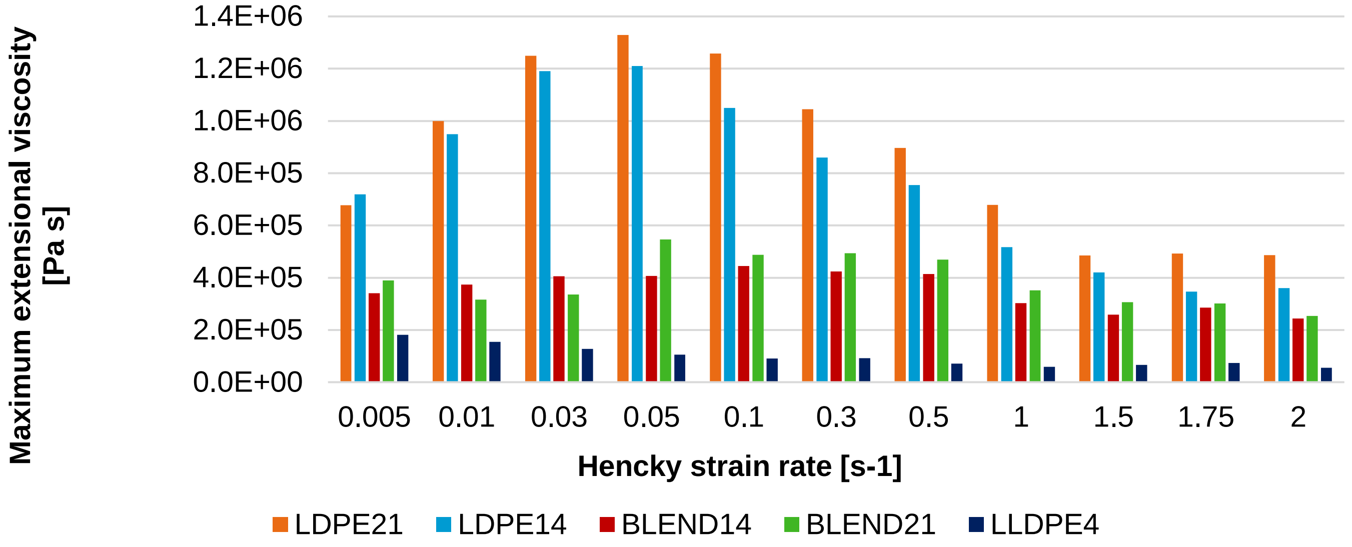


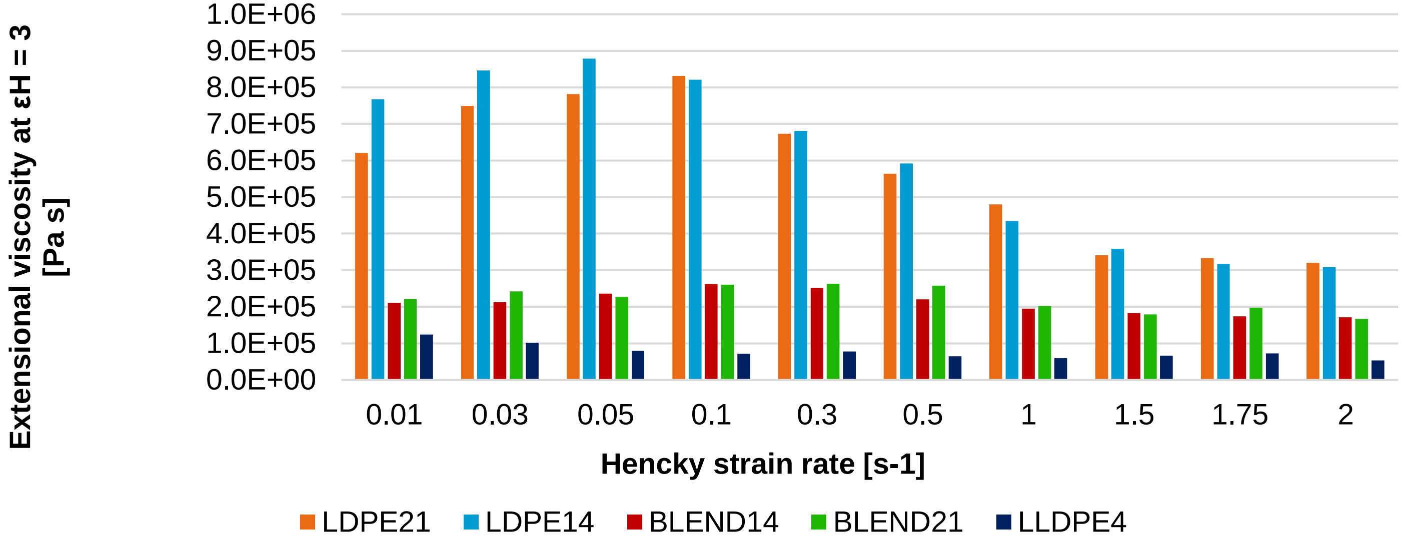
LDPE 21, 150 °C



EXTENSIONAL RHEOMETRY RESULTS AT 150 °C







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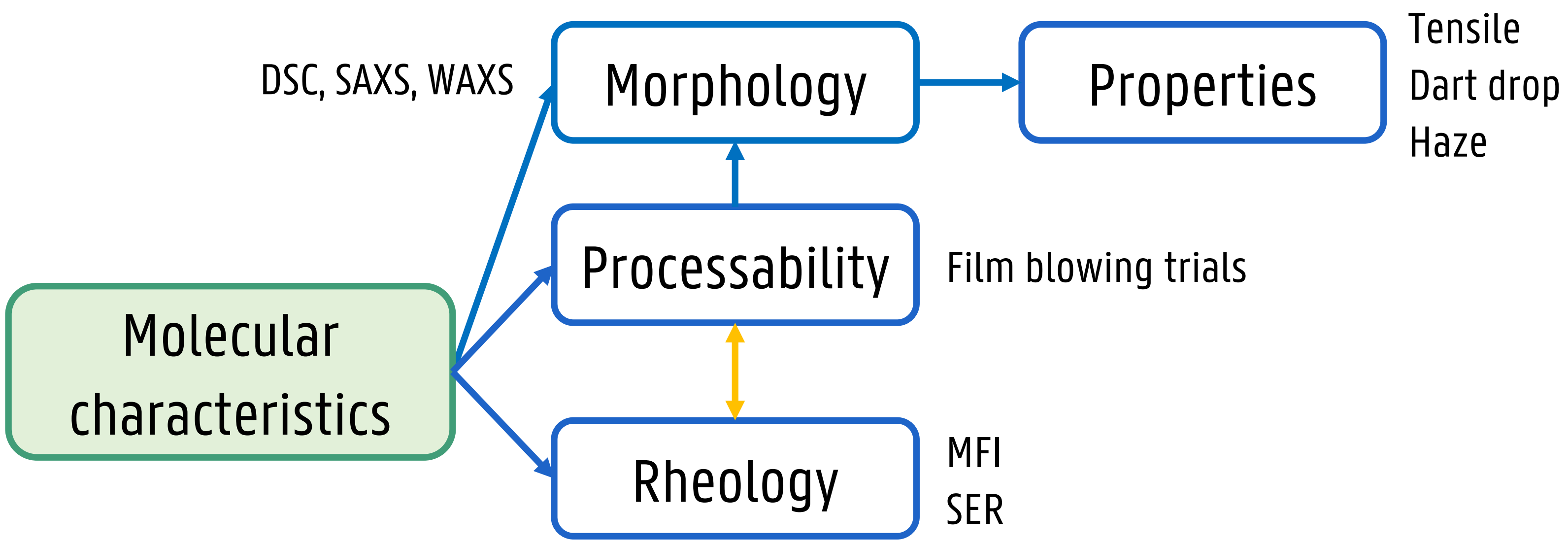
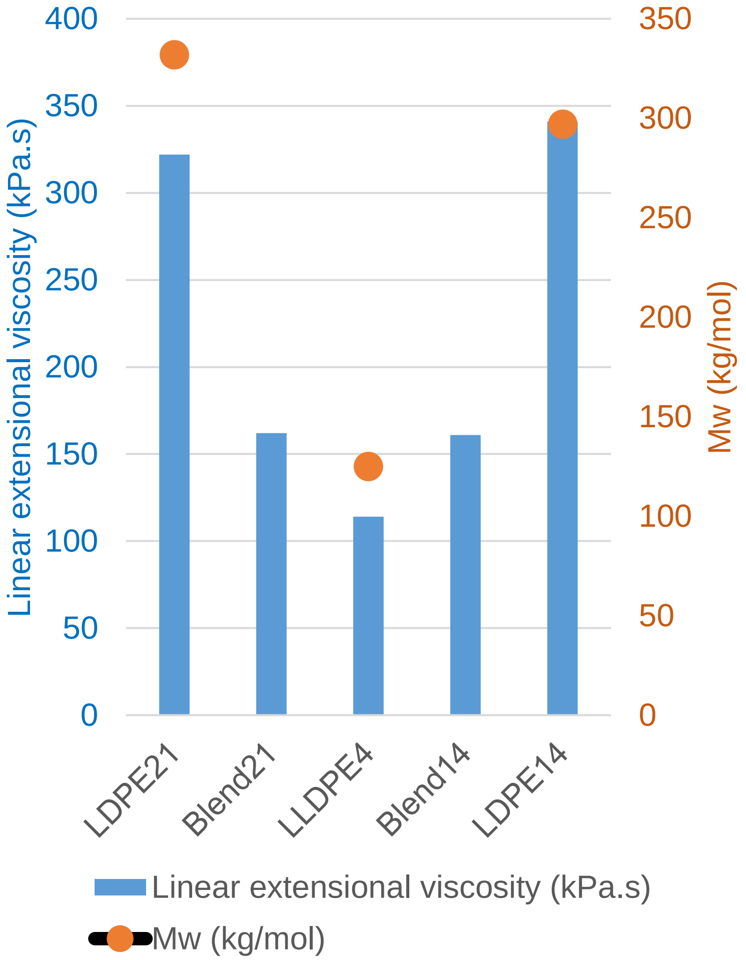
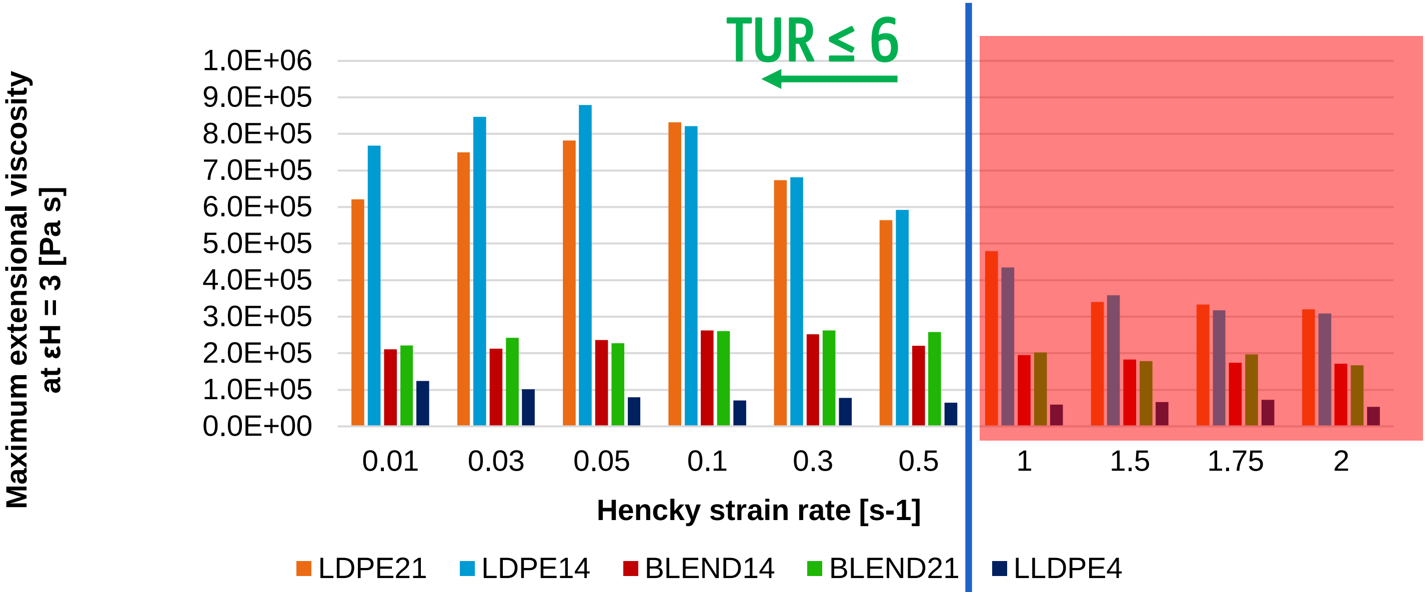
STRUCTURE OF THE EXPERIMENTS

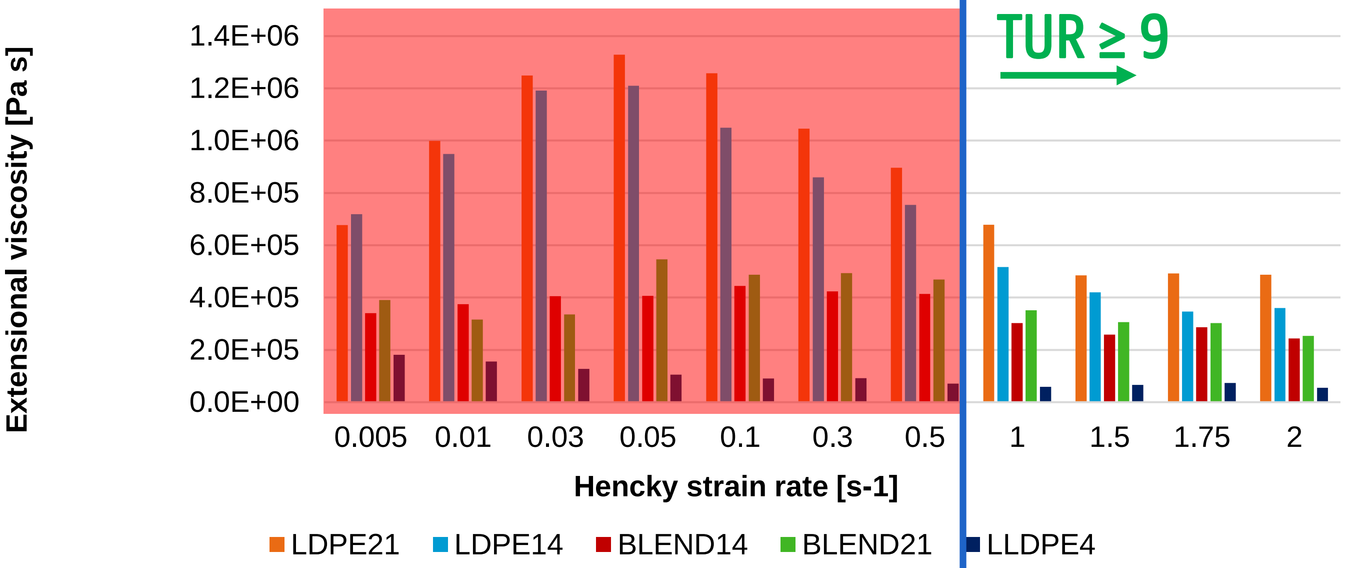


PROCESSABILITY FOR LDPES



For LDPEs





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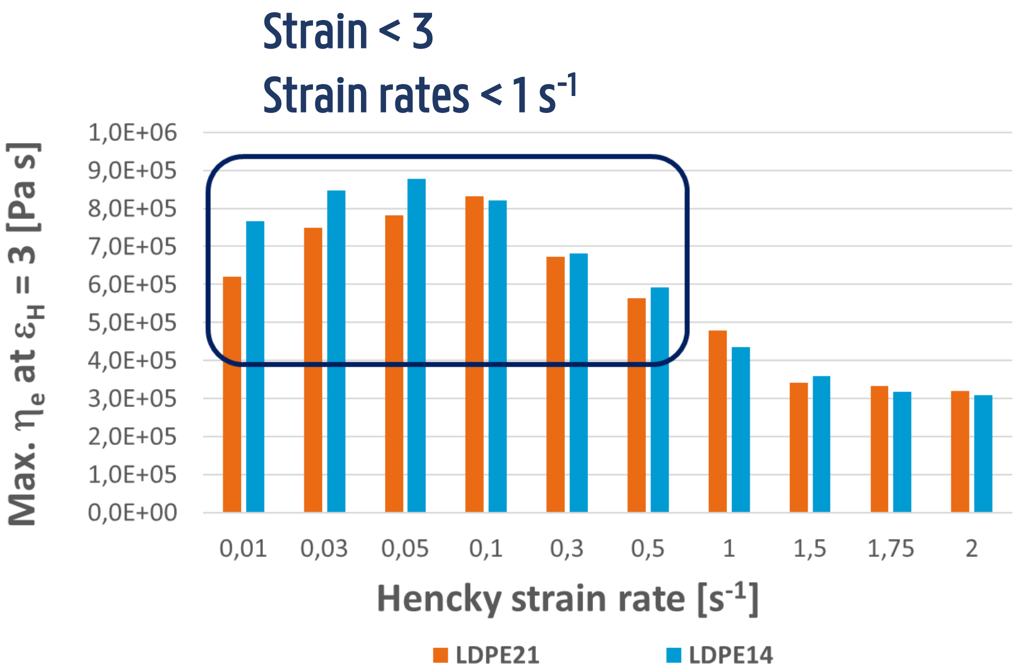
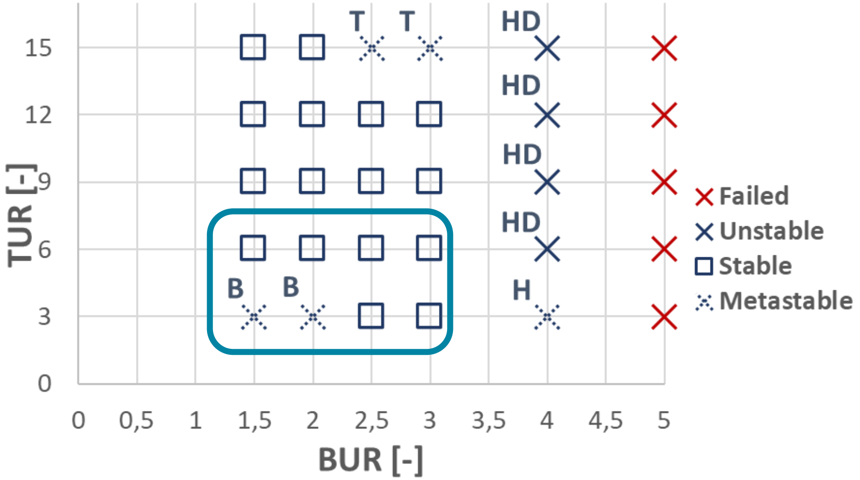
PROCESSABILITY OF LDPES LOW TUR

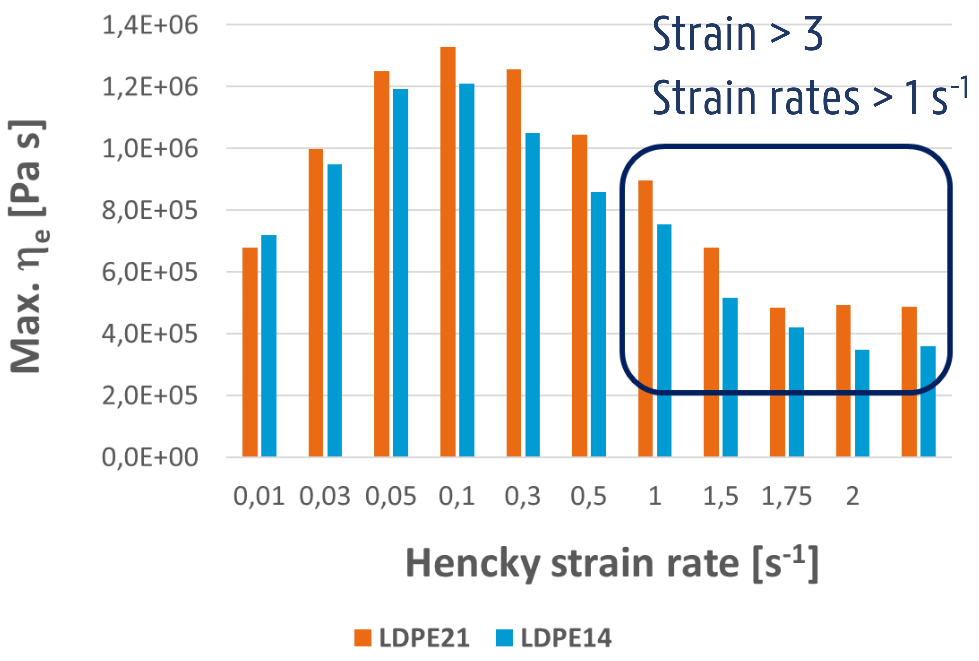
– LDPE14: higher LVE + high SHF ➔ highest η_e

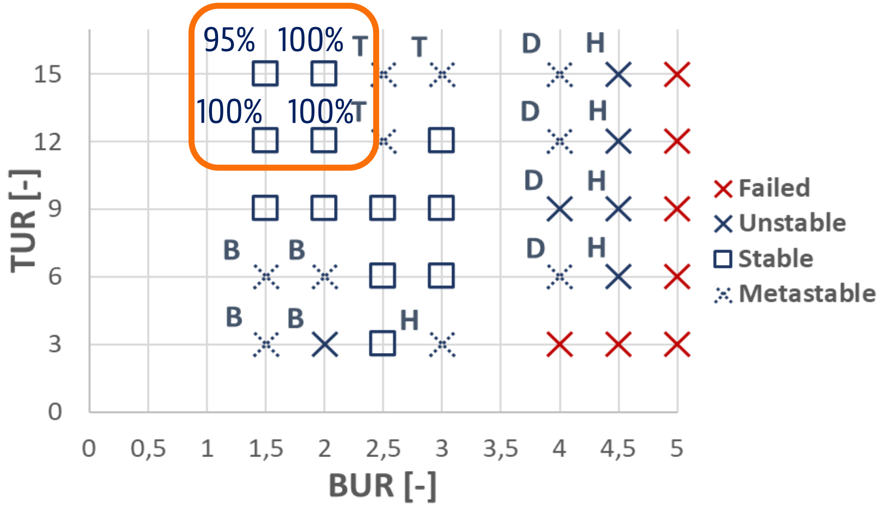


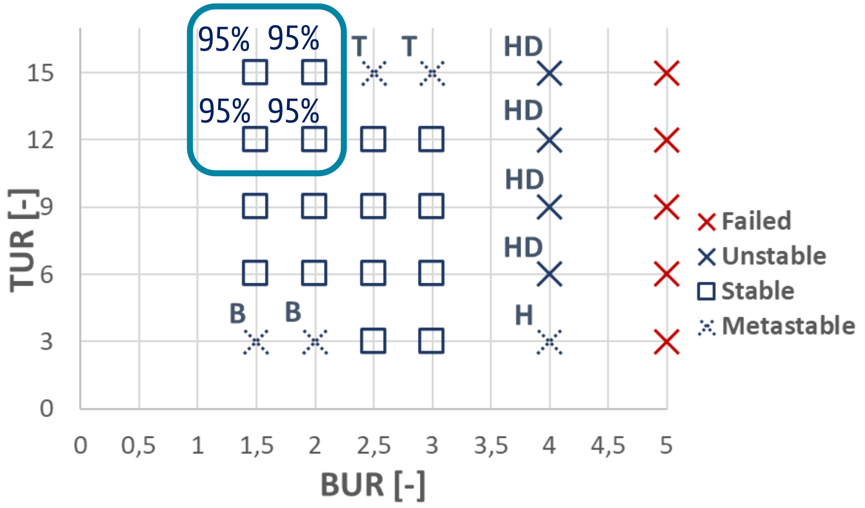


PROCESSABILITY OF LDPES HIGH TUR

– LDPE21: highest SHF → highest η_e







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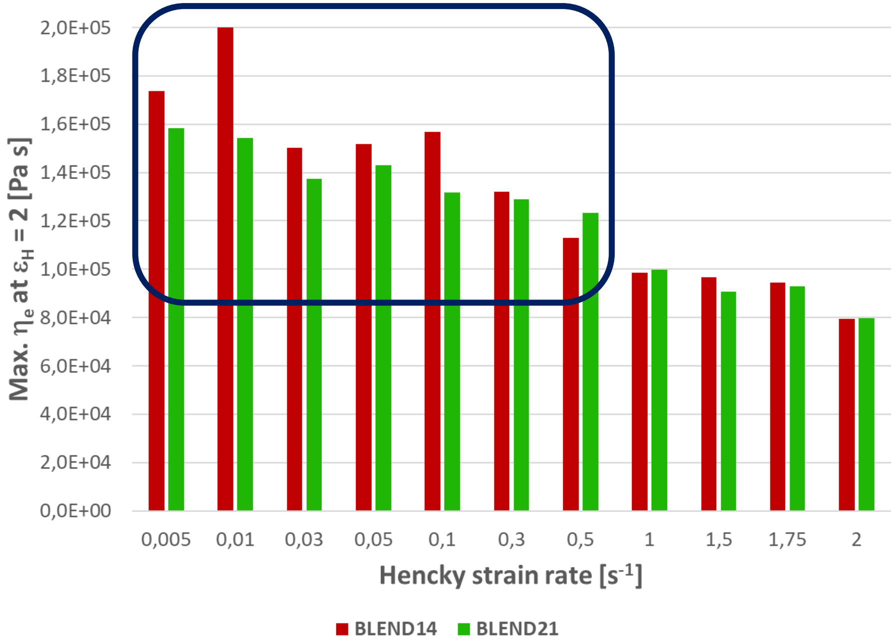
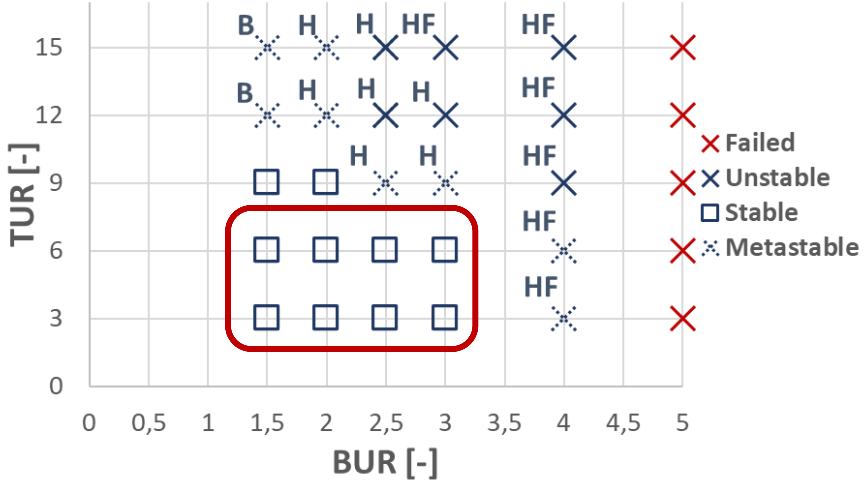
PROCESSABILITY OF BLENDS LOW TUR

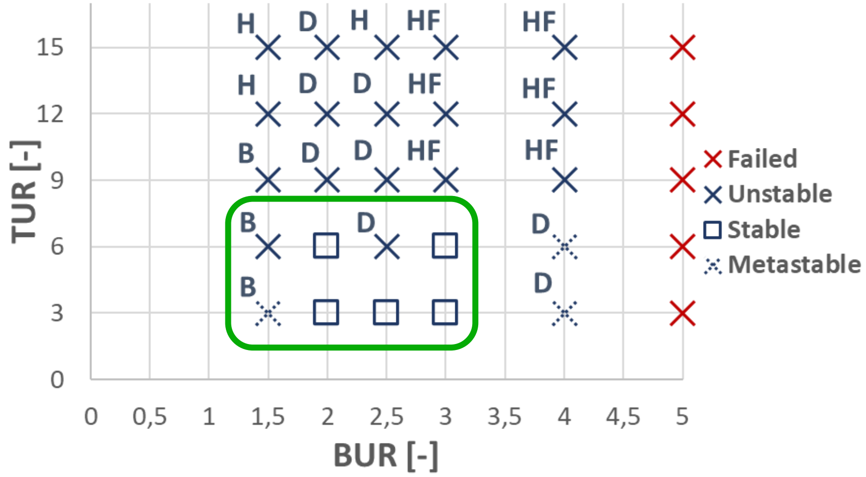
– BLEND14: earlier onset SH ➔ highest η_e

Strain < 2

Strain rates < 1 s^{-1}







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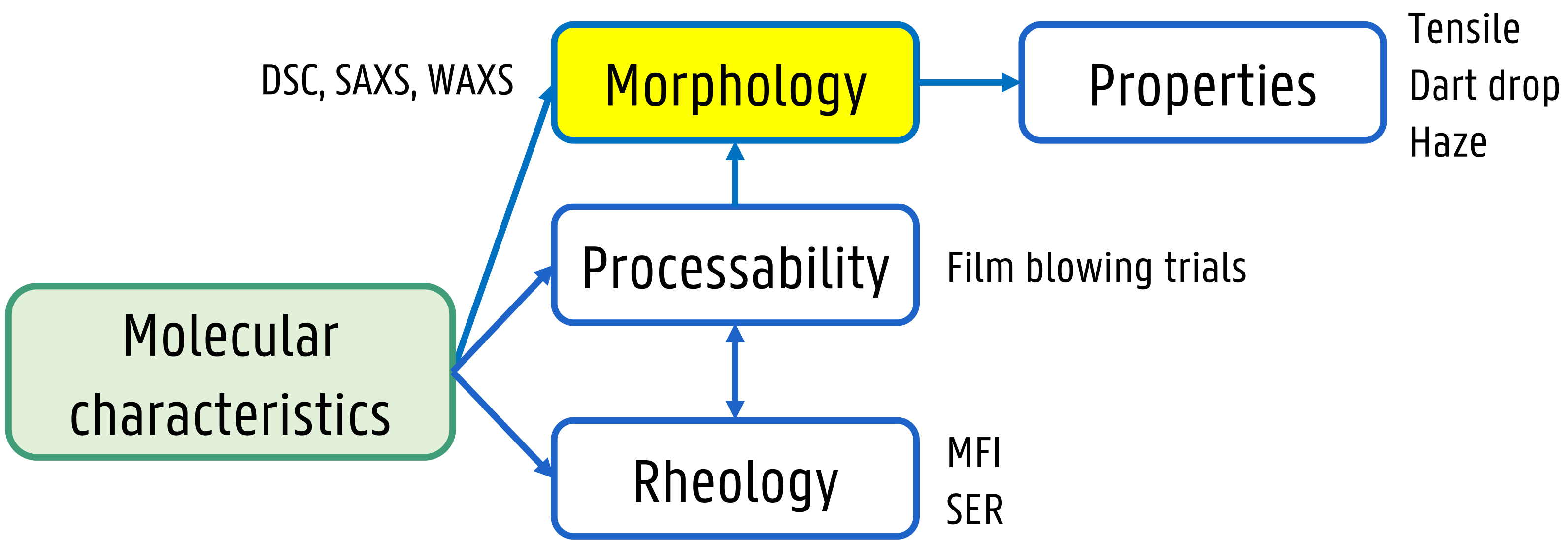
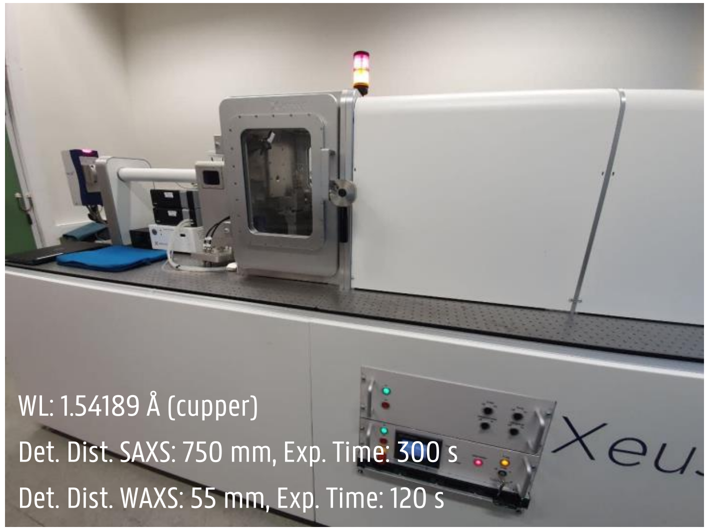
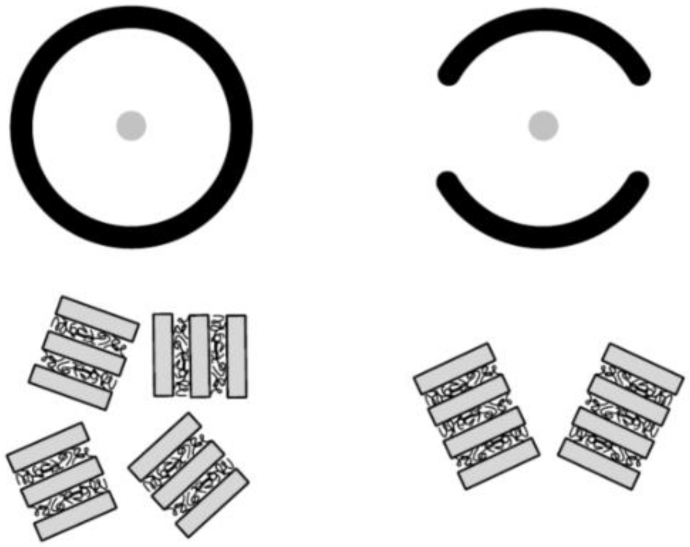
STRUCTURE OF THE EXPERIMENTS



X-RAY MORPHOLOGY RESULTS

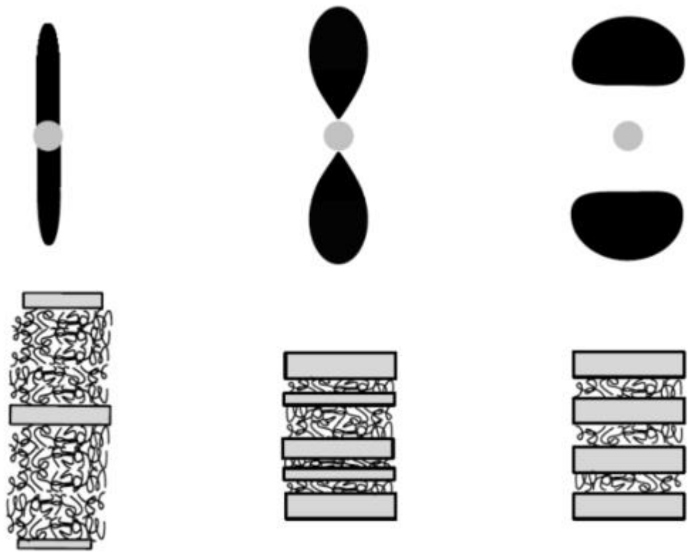




Debye-Sherrer ring from isotropic lamellar morphology

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

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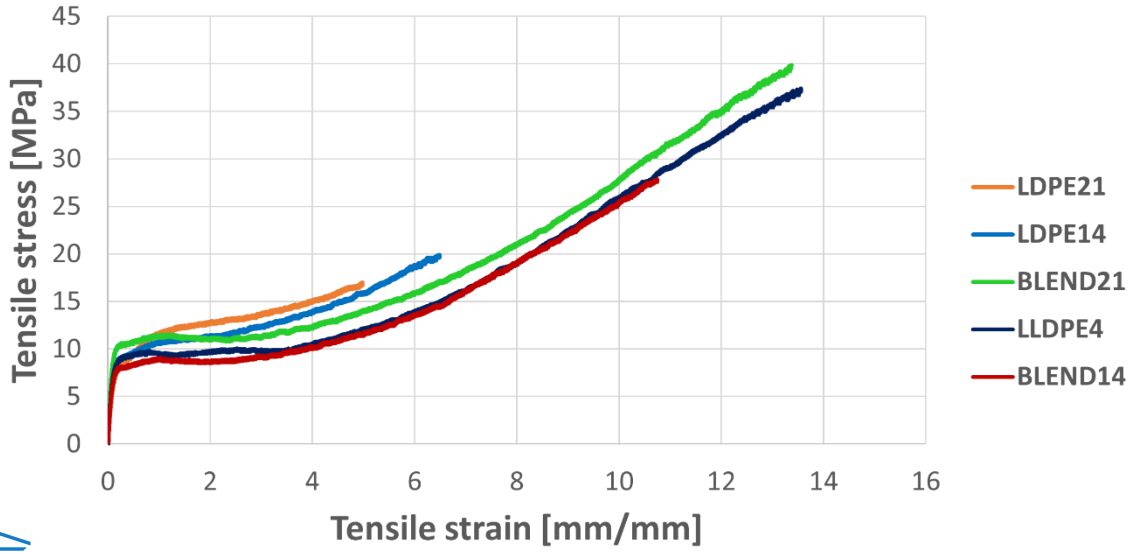
CONDITIONS FOR X-RAY INVESTIGATION

– **Stable Thick**

For all the materials the thickness of the stably produced films is measured.
The common condition (within all the five materials) which delivers the most stable bubble, and at the same time the highest thickness is chosen.

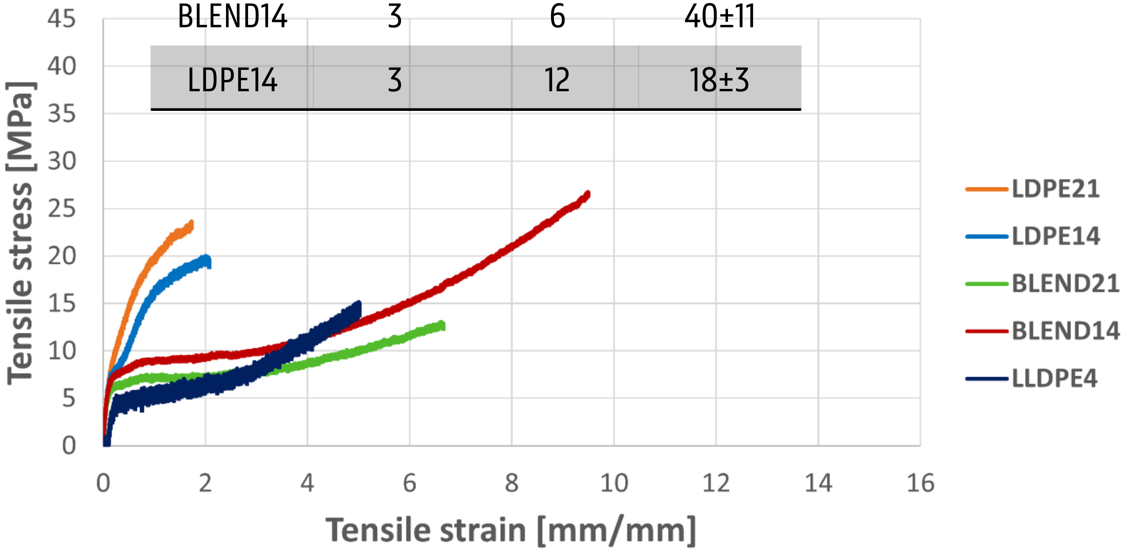
BUR 2.5-TUR 3, t˜70-75 µm



– **Stable Thin**

For all the materials the thickness of the stably produced films is measured. For each material, the thinnest stable film is chosen.

Materials	BUR	TUR	T (µm)
LDPE21	3	12	24±5
BLEND21	3	6	31±4
LLDPE4	3	9	14±4
BLEND14	3	6	40±11
LDPE14	3	12	18±3



MORPHOLOGICAL PARAMETERS

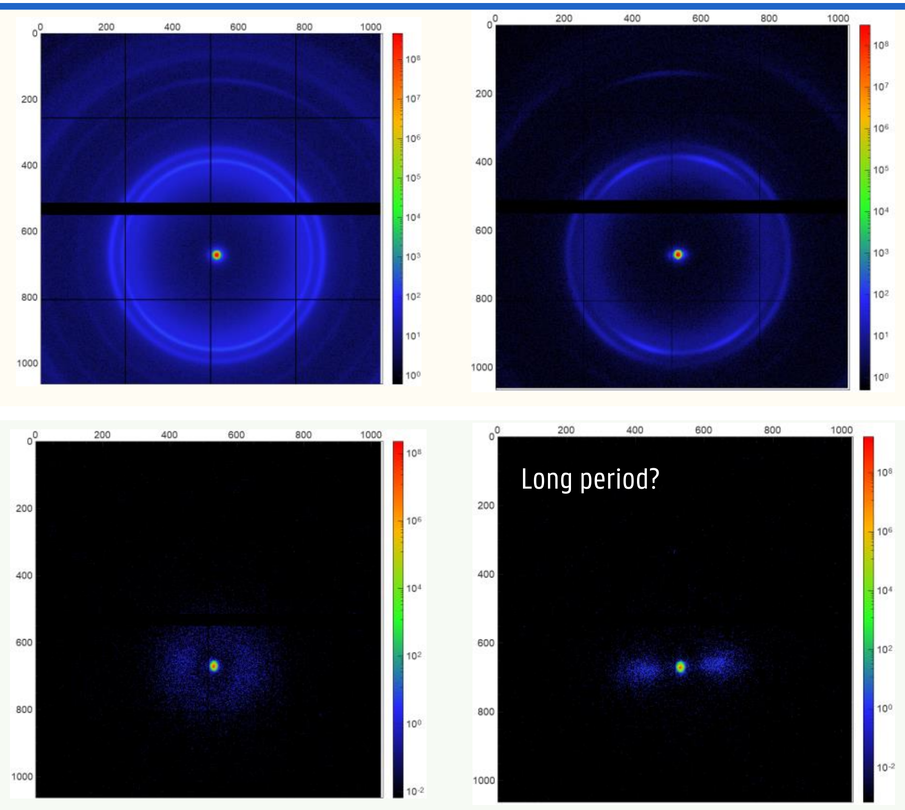
Increased strain rate

		Lamellar thickness	Orientation	Crystallinity	Crystallinity	Crystallinity
		l_C^{SAXS} $[nm]$	$1/_{FWHM}$ $[deg^{-1}]$	x_C^{SAXS} [%]	x_C^{WAXS} [%]	x_C^{DSC} [%]
LDPE 21	Thin	4.8	0.057 ▲	32 ▼	30 ▲	28 ▼
	Thick	4.5	0.015	33	29	32
Blend 21	Thin	4.2	0.040	34	32	32 ▼
	Thick					37
LLDPE 4	Thin	4.8	0.009 ▼	37 ▼	35 ▼	35 ▼
	Thick	4.9	0.014	39	36	40
Blend 14	Thin	4.2	0.011 ▼	37 –	33 –	37 ▼
	Thick	4.6	0.014	37	33	39
LDPE 14	Thin	3.9	0.031 ▲	36 –	35 ▼	34 ▼
	Thick	4.4	0.020	36	36	38

- films of lower overall crystallinity

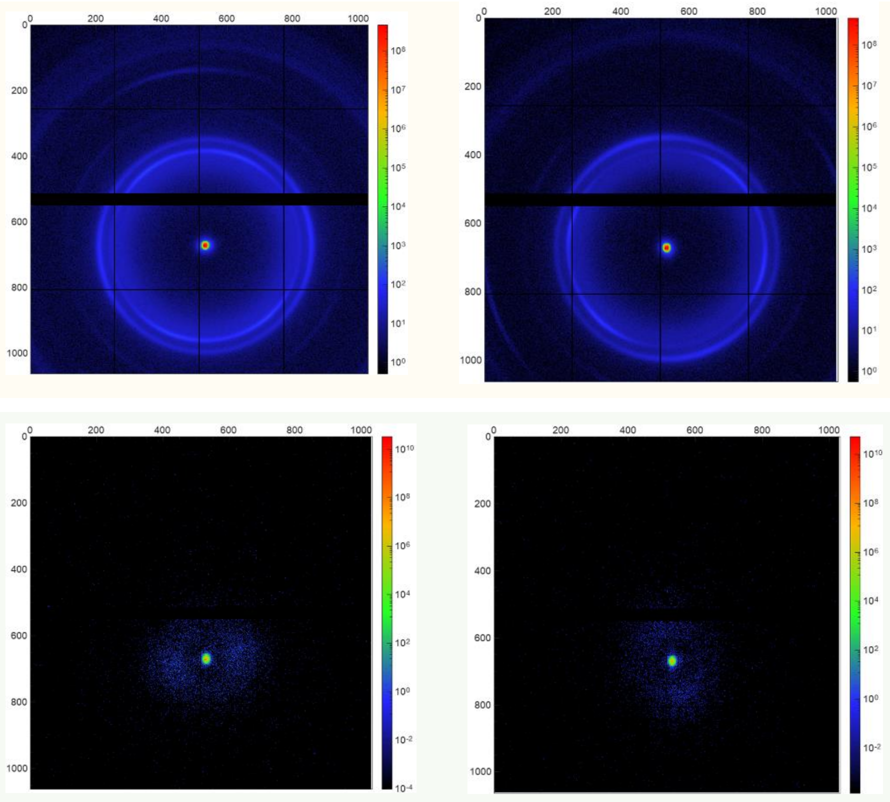
MORPHOLOGY OF LDPE21 VS LDPE14

LDPE21



Thick Thin

LDPE14



Thick Thin

WAXS

SAXS

Materials	BUR	TUR	T (µm)
LDPE21	3	12	24±5
LDPE14	3	12	18±3

		Lamellar thickness	Orientation	Crystallinity	Crystallinity	Crystallinity
		l_C^{SAXS} $[nm]$	$^1/_{FWHM}$ $[deg^{-1}]$	x_C^{SAXS} [%]	x_C^{WAXS} [%]	x_C^{DSC} [%]
LDPE 21	Thin	4.8	0.057	32	30	28
	Thick	4.5	0.015	33	29	32
LDPE 14	Thin	3.9	0.031	36	35	34
	Thick	4.4	0.020	36	36	38

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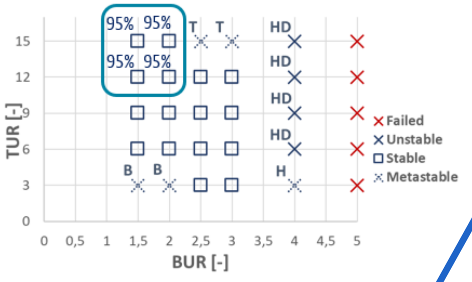
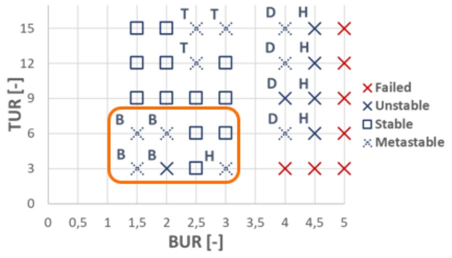
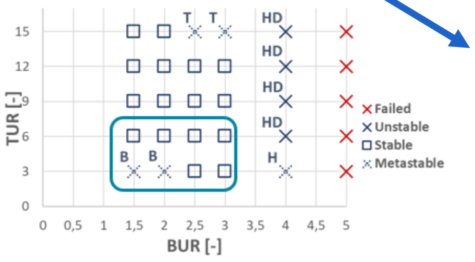
PROCESSABILITY FOR LDPES



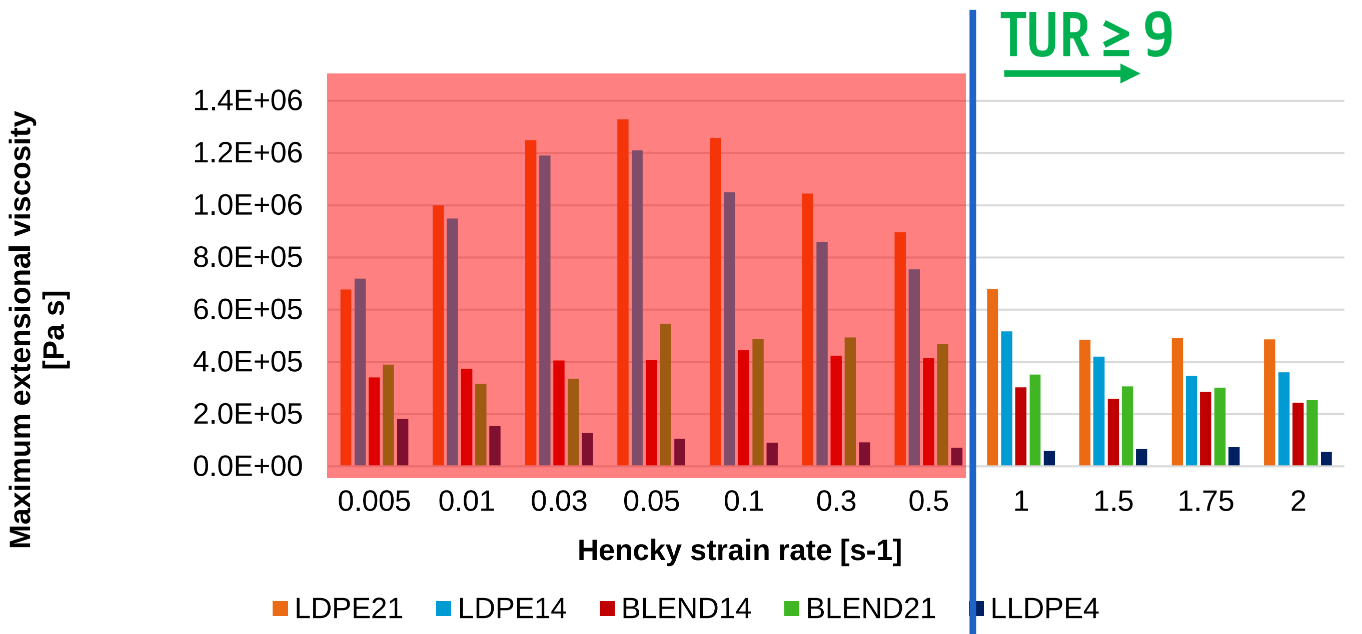
Orientation

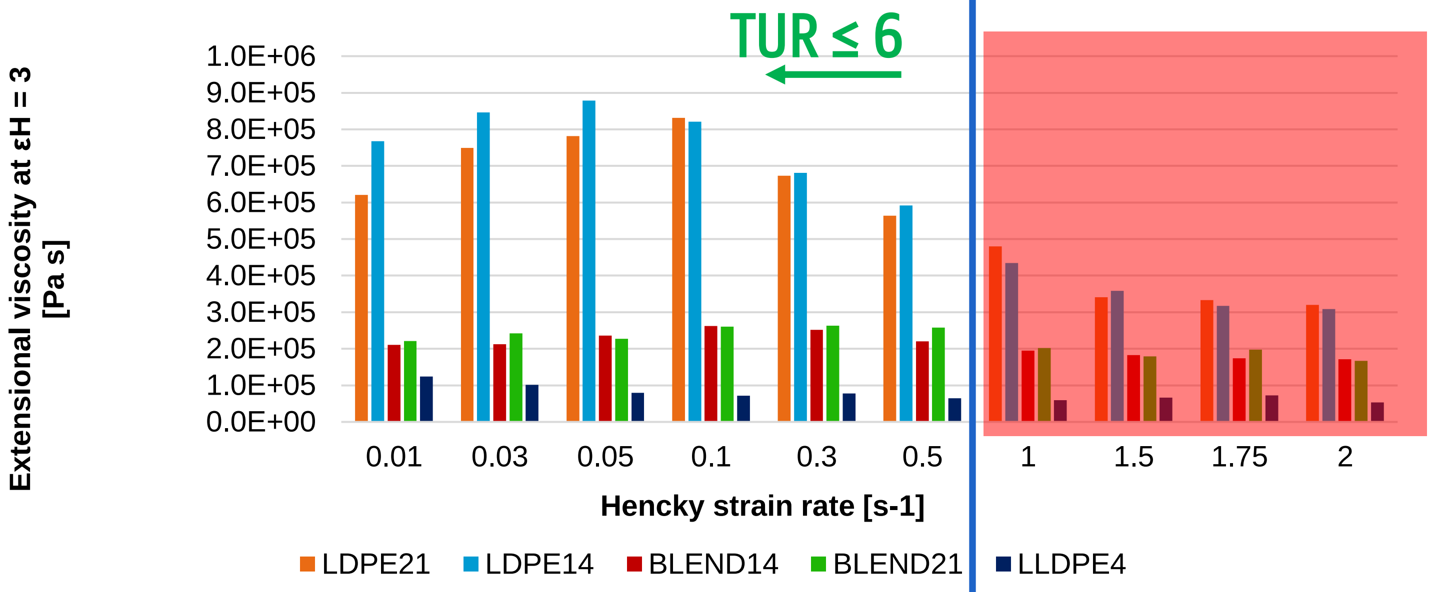
		$^1/_{FWHM}$ $[deg^{-1}]$
LDPE 21	Thin	0.057
	Thick	0.015
LDPE 14	Thin	0.031
	Thick	0.020





For LDPEs





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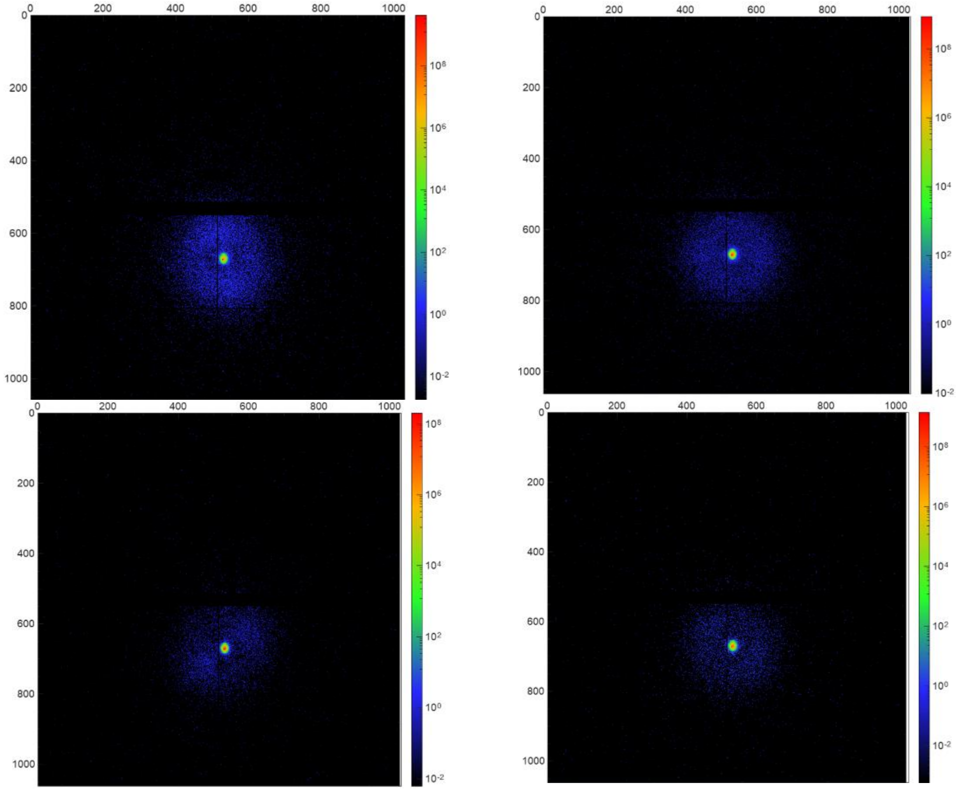
LLDPE4 VS BLEND14

		Lamellar thickness	Orientation	Crystallinity	Crystallinity	Crystallinity
		l_C^{SAXS} [nm]	$^1/_{FWHM}$ [deg^{-1}]	x_C^{SAXS} [%]	x_C^{WAXS} [%]	x_C^{DSC} [%]
LLDPE 4	Thin	4.8	0.009 ▼	37 ▼	35 ▼	35 ▼
	Thick	4.9	0.014	39	36	40
Blend 14	Thin	4.2	0.011 ▼	37 –	33 –	37 ▼
	Thick	4.6	0.014	37	33	39

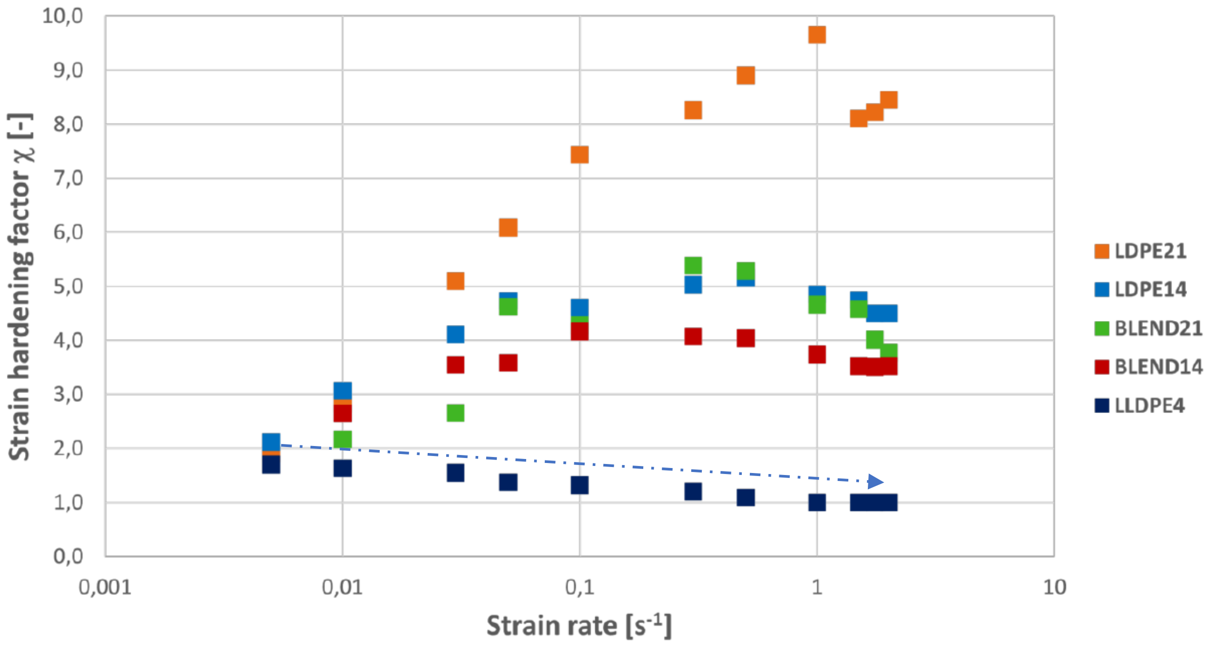
Blend14

LLDPE4



Thick

Thin



- Proves the presence of high molecular weight components in LLDPE

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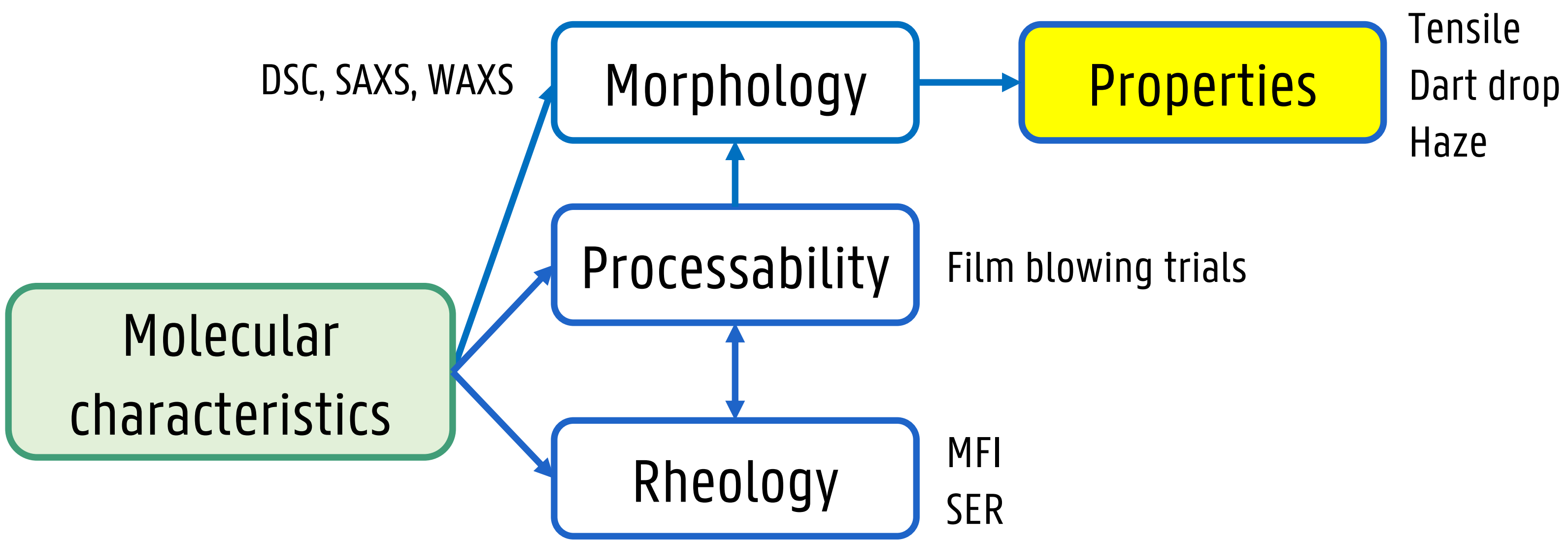
STRUCTURE OF THE EXPERIMENTS



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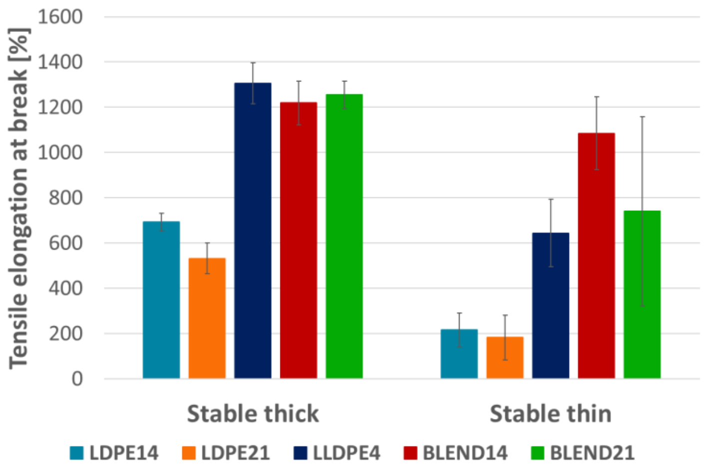
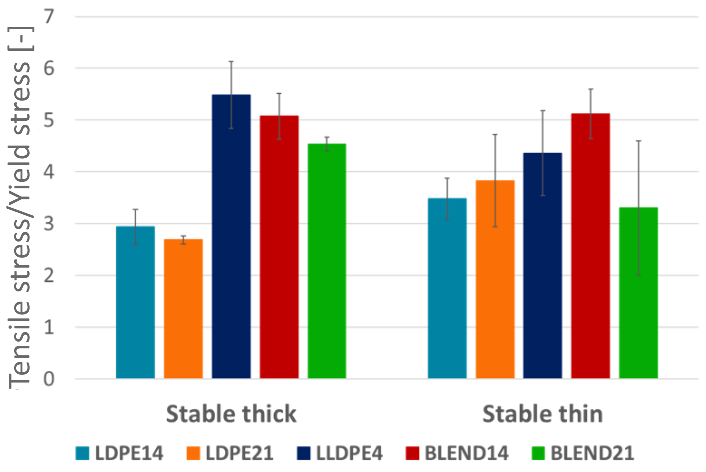
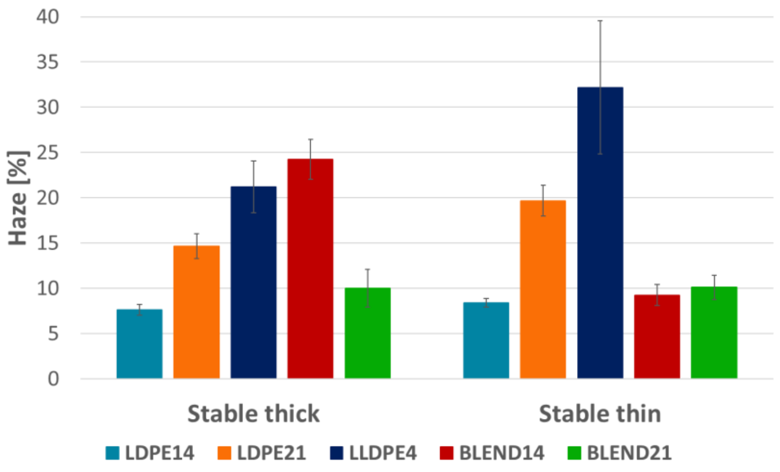
MECHANICAL PERFORMANCE OF LDPE21 VS LDPE14

- LDPE14 is more ductile in MD, due to its lower orientation
- For both LDPEs, the ductility degrades upon increasing the TUR
- Higher orientation leads to higher tensile strain hardening factor
- Higher crystal density leads to higher haze







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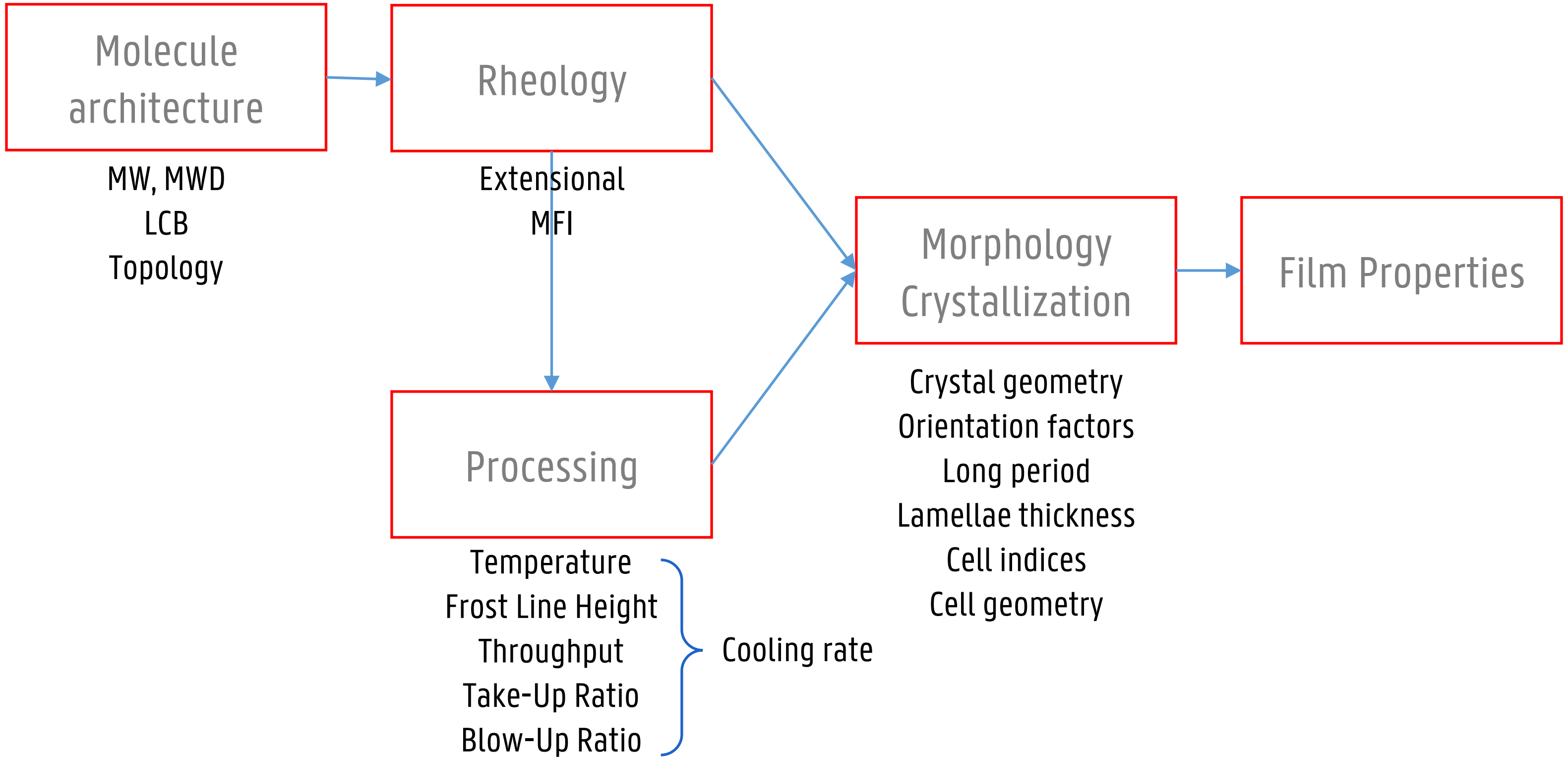
CONCLUSIONS

Can the closed loop (re)processability of L(L)DPEs be predicted by having an estimation over the macromolecular features??



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THANKS!

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FILM BLOWING INSTABILITIES

Draw resonance Instability

LDPE14 B4 T12

Helical instability

LDPE21 B4,5 T15

FLH instability

LLDPE4 B4 T12

Bubble tearing instability

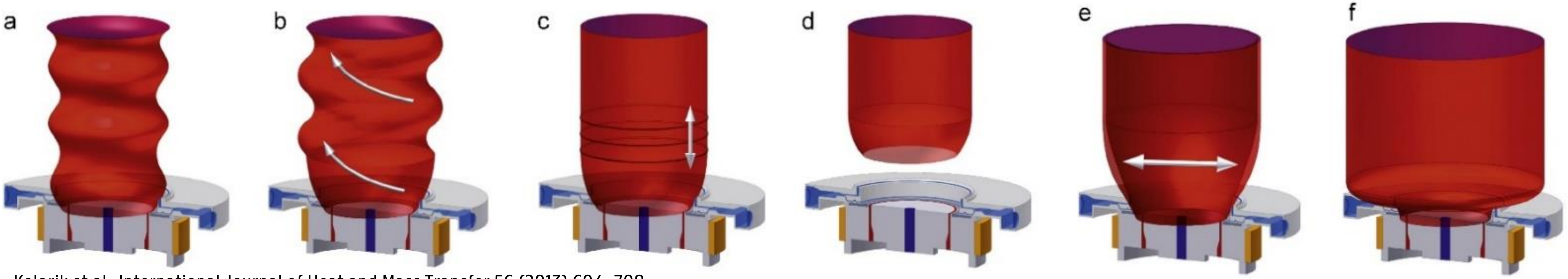
LDPE14 B3 T15

Bubble breathing instability

BLEND21 B2 T9

Bubble sag instability

LDPE21 B4 T6



Kolarik et al., International Journal of Heat and Mass Transfer 56 (2013) 694–708,
https://doi.org/10.1016/j.ijheatmasstransfer.2012.09.025

DEFORMATION PROFILE INVESTIGATION

- Strain rate in MD
  - Image analysis
- Frost line height
  - No further deformation beyond FLH
  - IR temperature probe
  - Clear to hazy transition

Bubble geometry

BUR 3, TUR 9

BLEND21

BLEND14

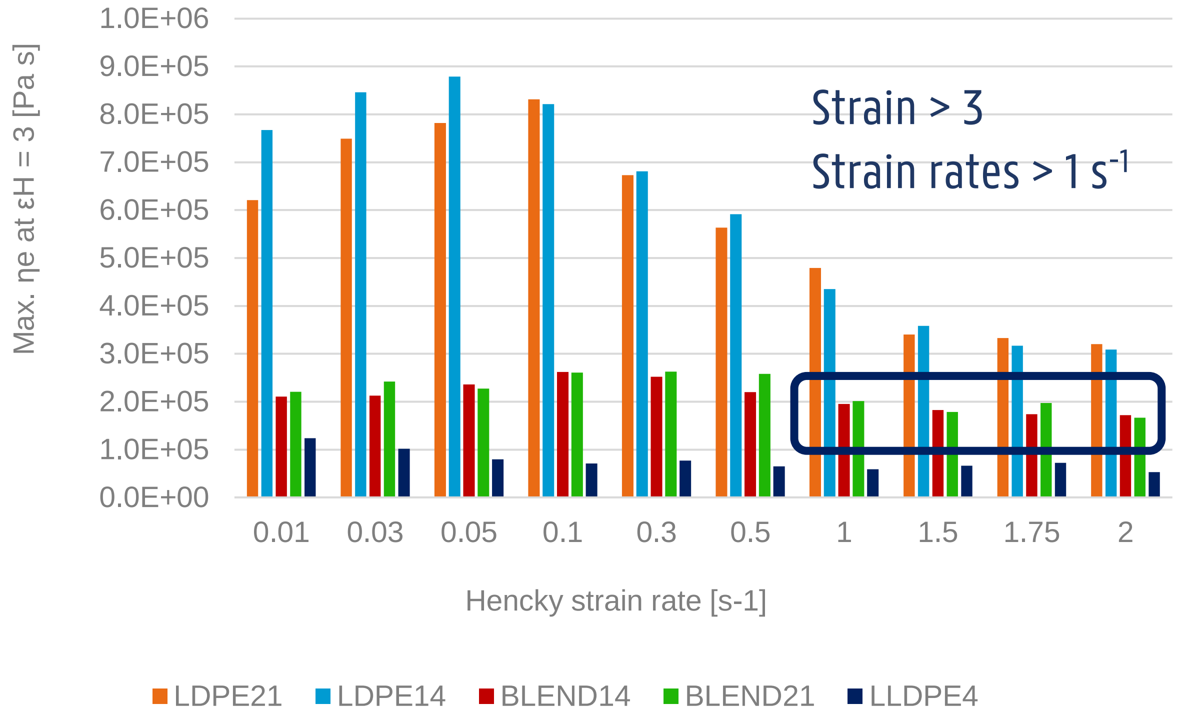
LLDPE4

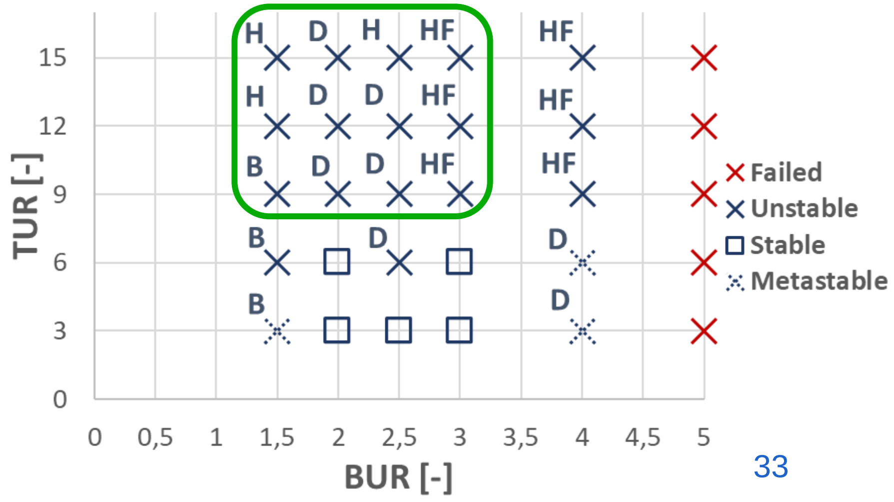
LDPE14

LDPE21

PROCESSABILITY OF BLENDS HIGH TUR

– BLENDs: high η_e ➔ stable bubble?





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