Learning from Shear and Extensional Rheology of a few Extrusion Coating Polyethylenes

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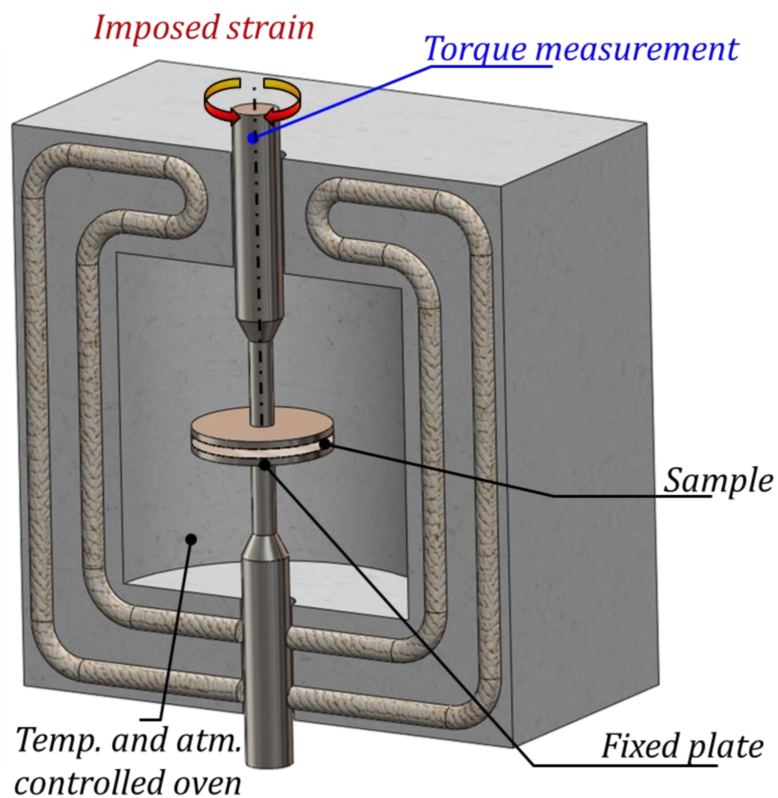
Introduction

- This presentation is the start of on-going work to determine the relationship between **polymer molecular structure & polydispersity / rheology / process-ability / final properties**
- Rheometry is a powerful tool to investigate the macromolecular structure of polymer melts and recent tools have been used to characterize a few extrusion coating grade resins
- Ultimate goal: to be able to **model** or **predict** through correlations between rheology and processing data:
  - Neck-in
  - Process Stability

Shear rheology: dynamic measurements

- Rotational Rheometer

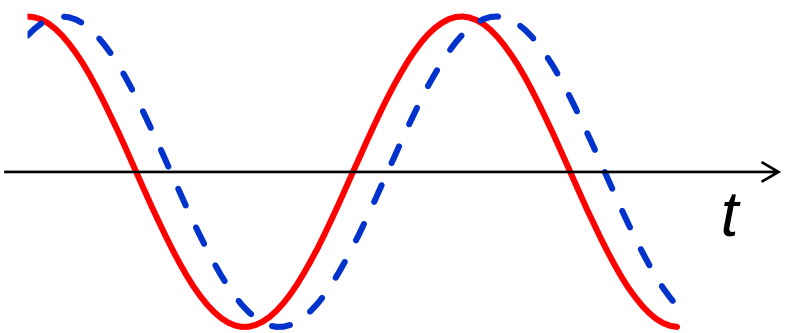


Dynamic strain is imposed:

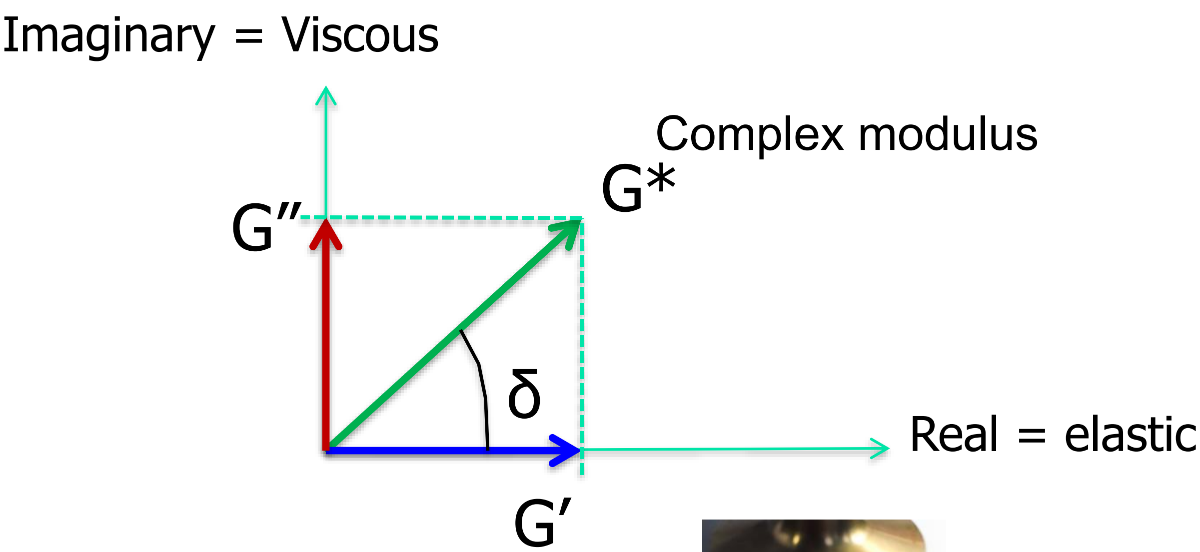
$$\gamma^* = \gamma_0 \exp(i\omega t)$$

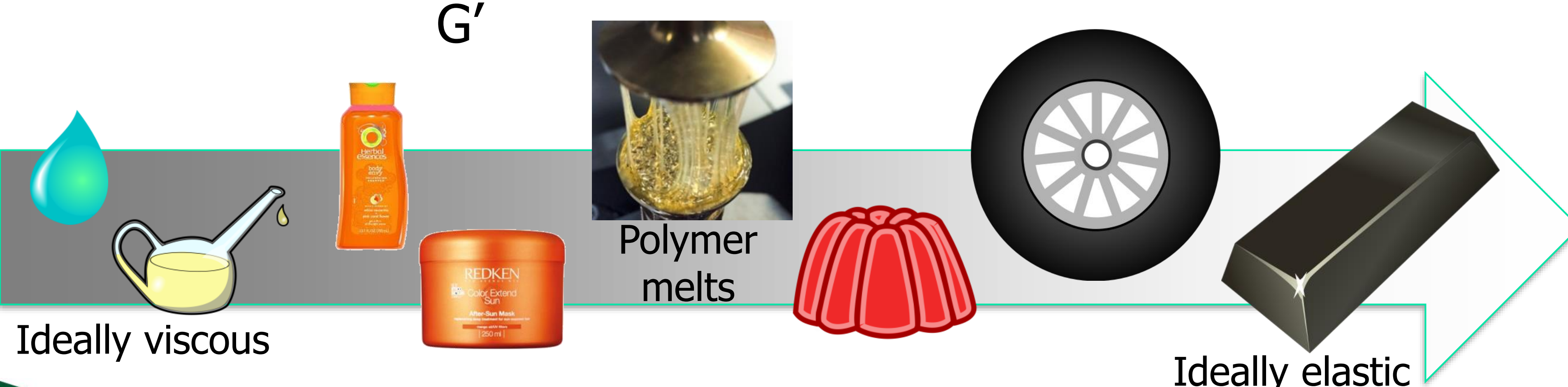
Delayed Shear stress response :

$$\tau^* = \tau_0 \exp i(\omega t + \delta)$$



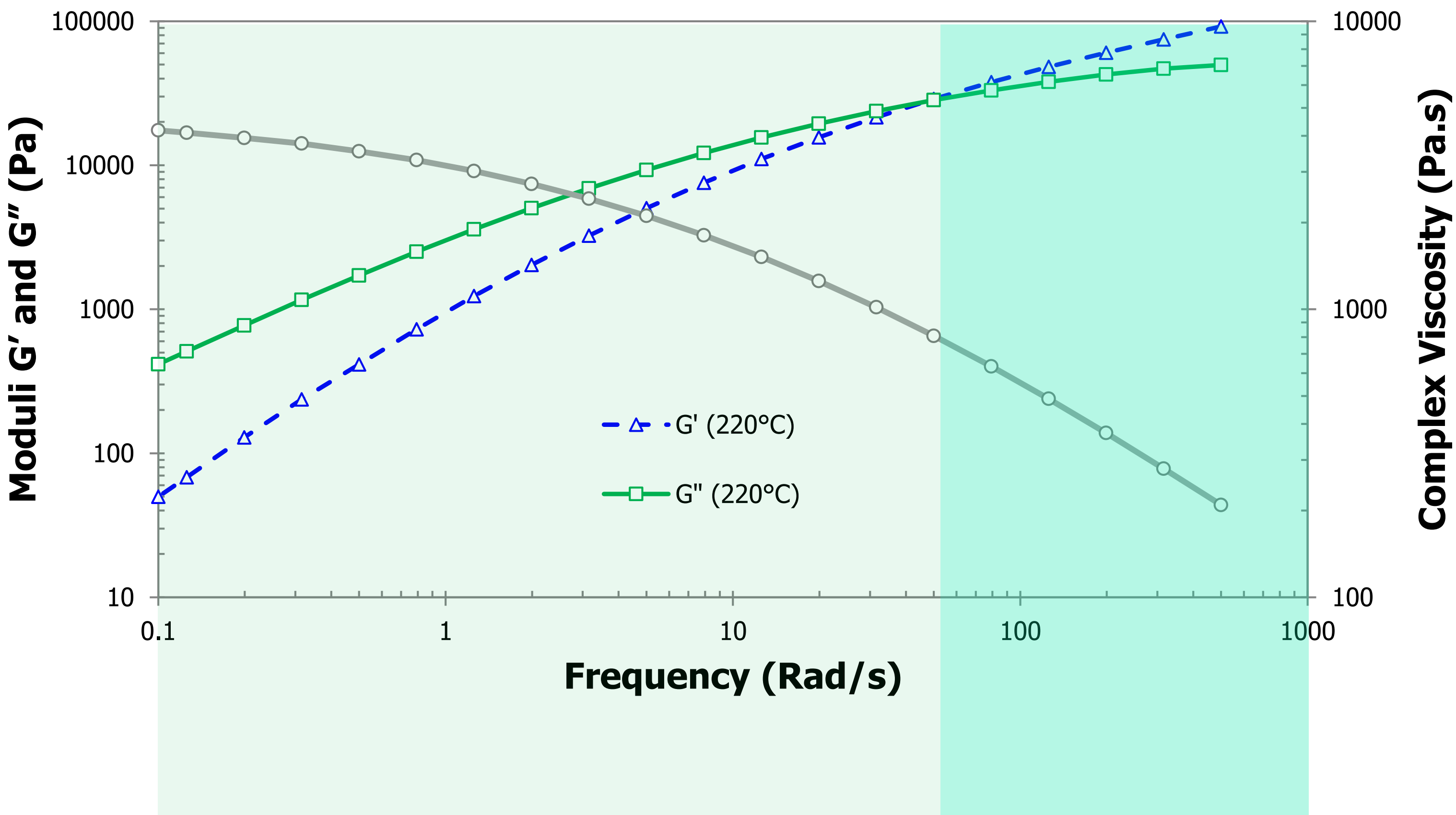
Shear rheology: dynamic measurements





Shear rheology: dynamic measurements

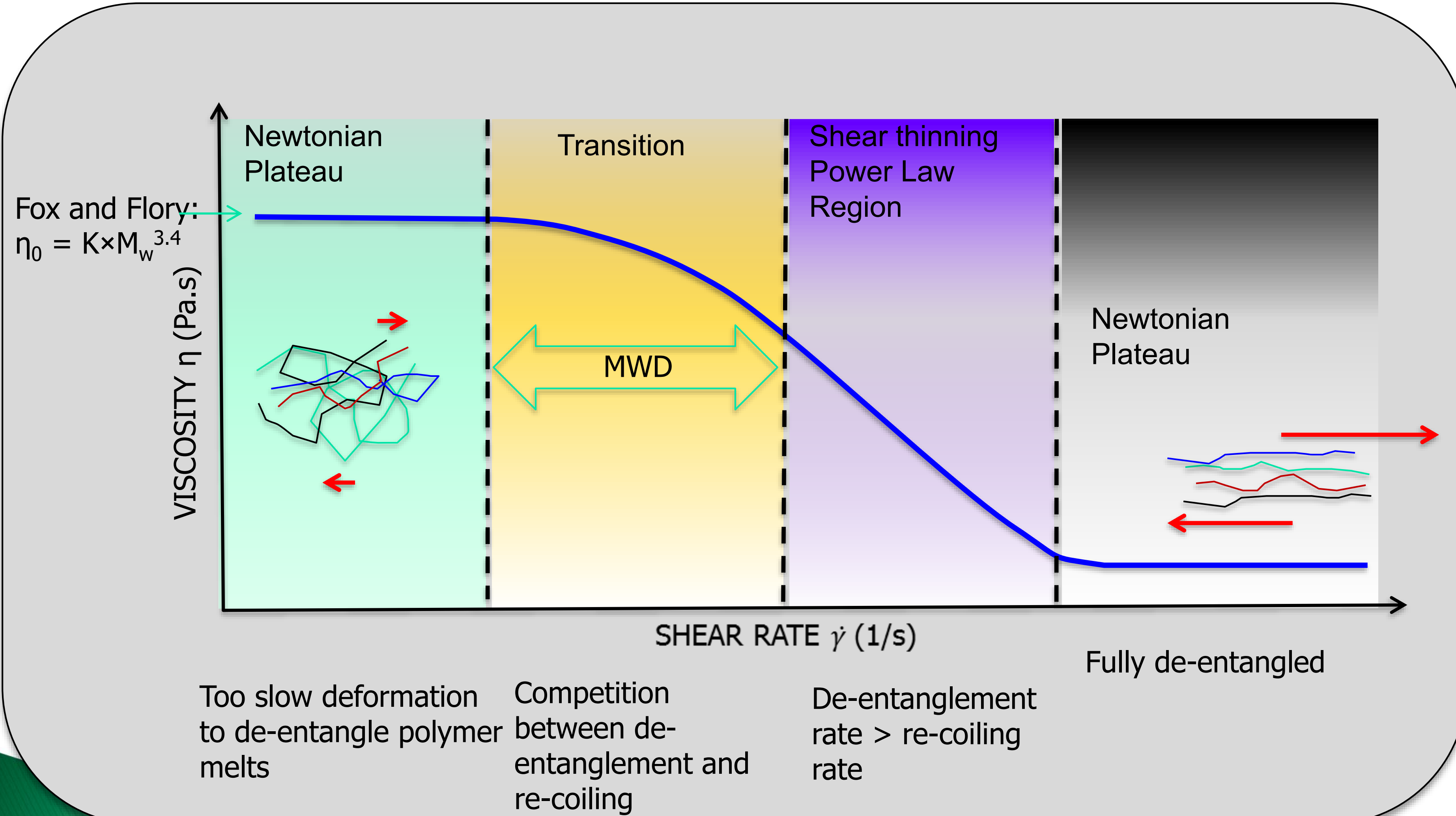
Frequency sweep in linear viscoelastic region (LVR)



Low frequency: G″>G′ (viscous dominant)

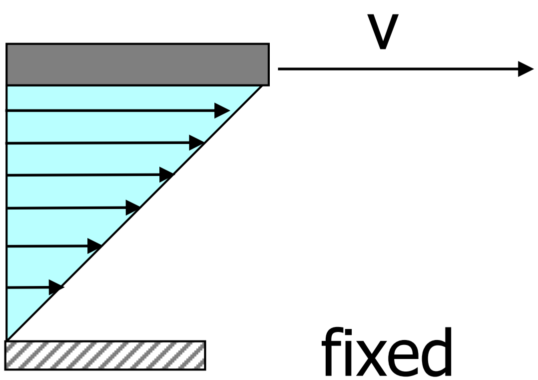
High frequency: G′>G″ (elastic dominant)

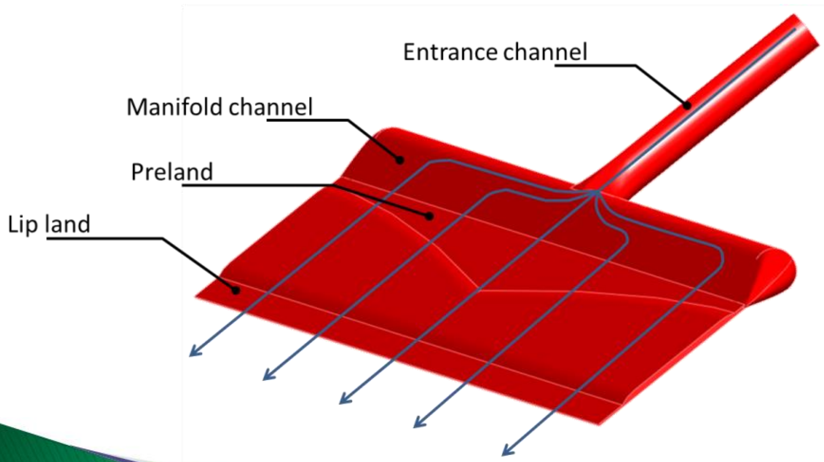
Shear rheology: dynamic measurements



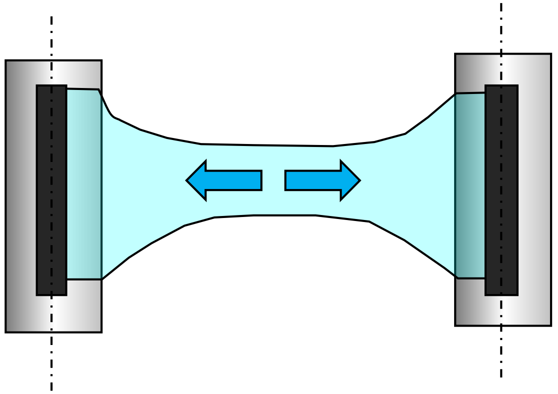
Elongational Viscosity – Neck in behavior

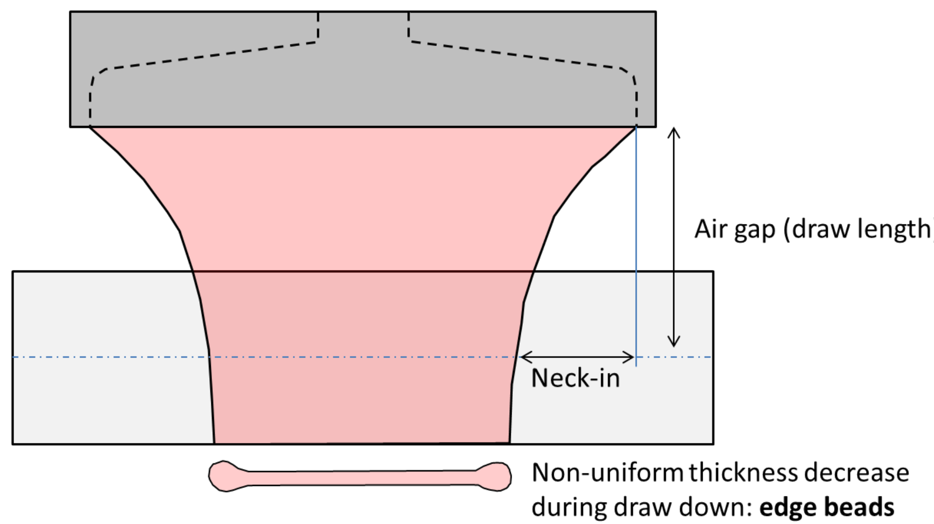
- Shear flow





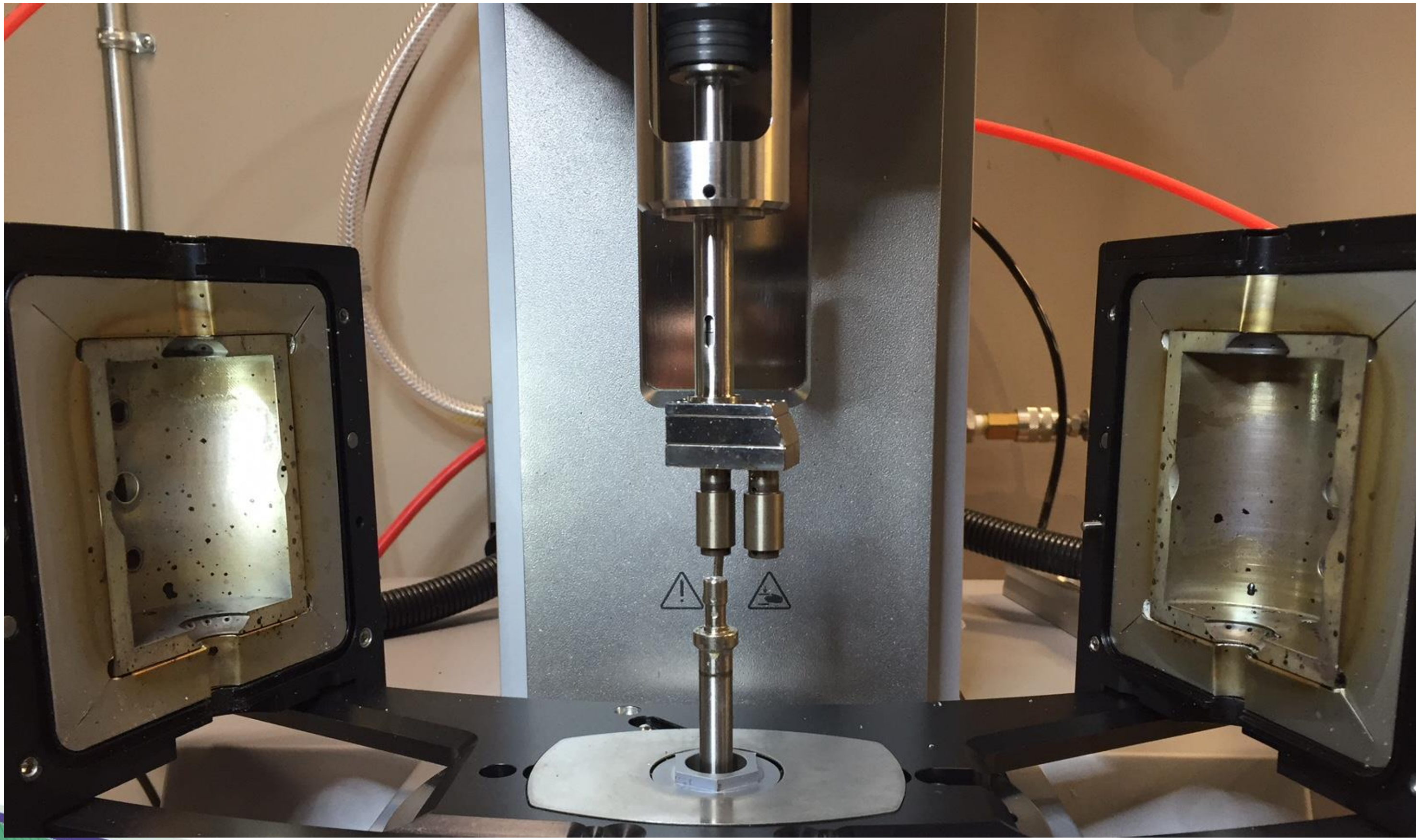
- Extensional flow





Elongational Viscosity measurement

- Sentmanat Extensional Rheometer (SER)



Elongational Viscosity measurement

- Sentmanat Extensional Rheometer (SER)

Polymers

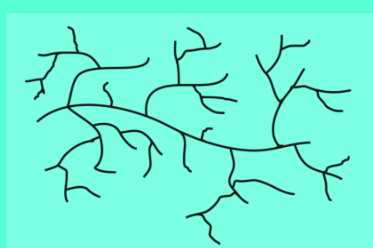
- Tested materials:

Name	Commercial name	Type	Density (g/cm^3)	MFI (g/10 min)	Comment
LD1	Chevron Phillips Marflex 1017	Autoclave LDPE	0.917	7.0	Reference material
LD2	Westlake Chemical EC808AA	Autoclave LDPE	0.917	7.0	Similar to reference
m-PE	ExxonMobil Exceed 0019XC	m-PE	0.918	19	Molecular structure and molecular weight
LD3	Chevron Phillips Marflex 1019	Autoclave LDPE	0.917	16	Similar molecular weight as 0019XC?

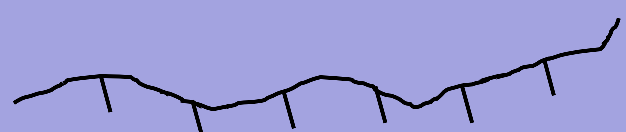
Molecular structure

- Extrusion Coating resins tested:

- LDPE:
  - Broad molecular weight distribution
  - Long and short chain present
  - High degree of long chain branching (LCB)
  - Branch spacing is irregular
  - Some short chain branching

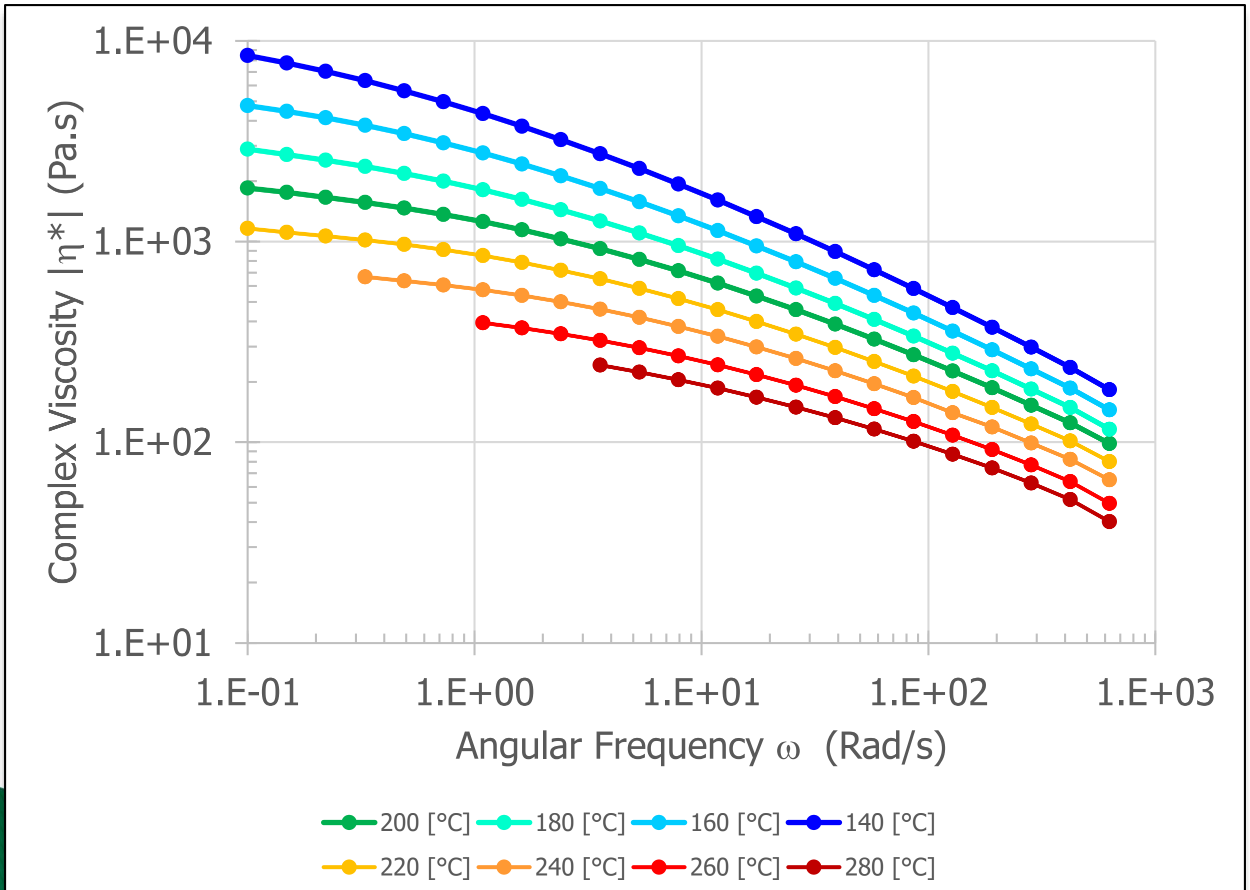


- m-PE:
  - narrow molecular weight distribution
  - Chain branching could be anything – but usually short chain branching from co-monomer butane, hexane, octane -LLDPE structure
  - Branch spacing is very regular



Results

- Reference: **LD1**
  - Autoclave LDPE - density= 0.917 g/cm^3 , MFI = 7 g/10 min

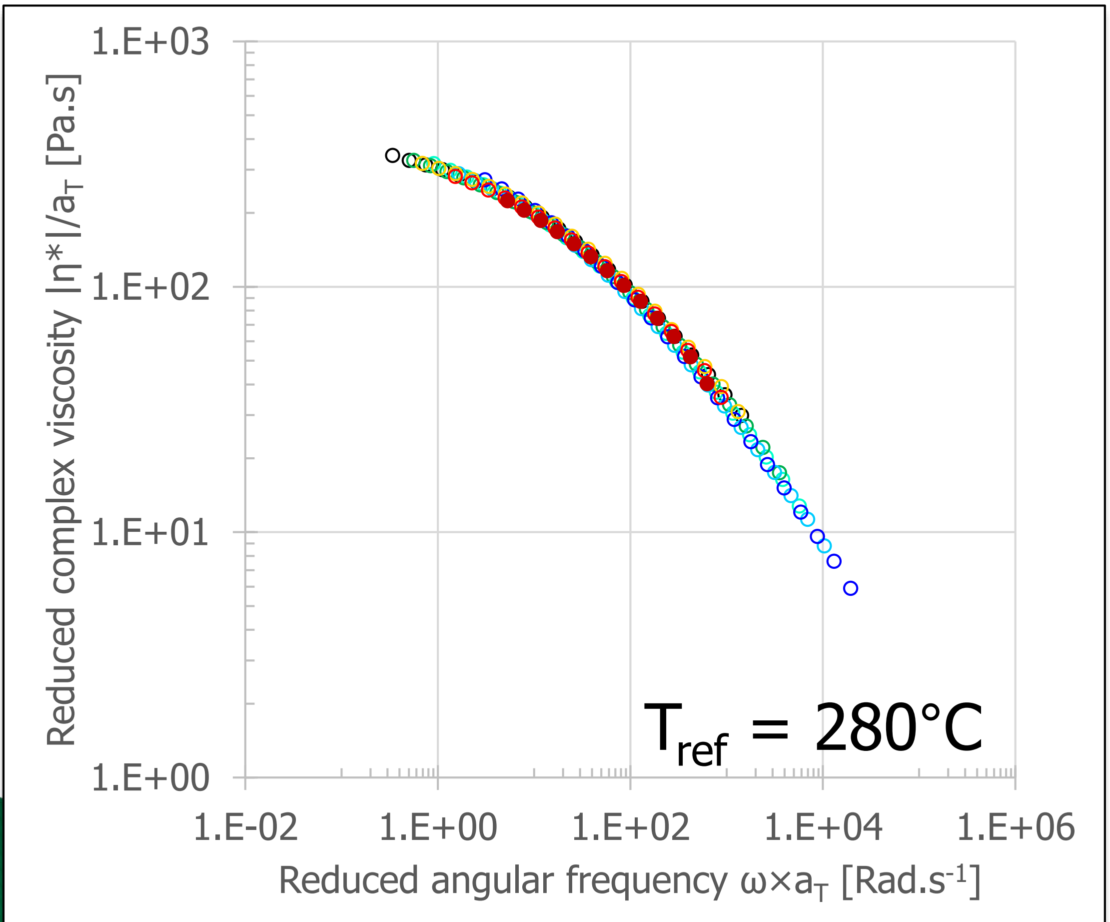


Complex viscosity at several different temperatures: excellent data

Difficult measurements at temperatures > 240°C at low frequencies due to degradation (despite N_2 atmosphere) resulting in increase of viscosity at low frequency

Results

- Reference: **LD1**
  - Autoclave LDPE - density= 0.917 g/cm^3 , MFI = 7 g/10 min

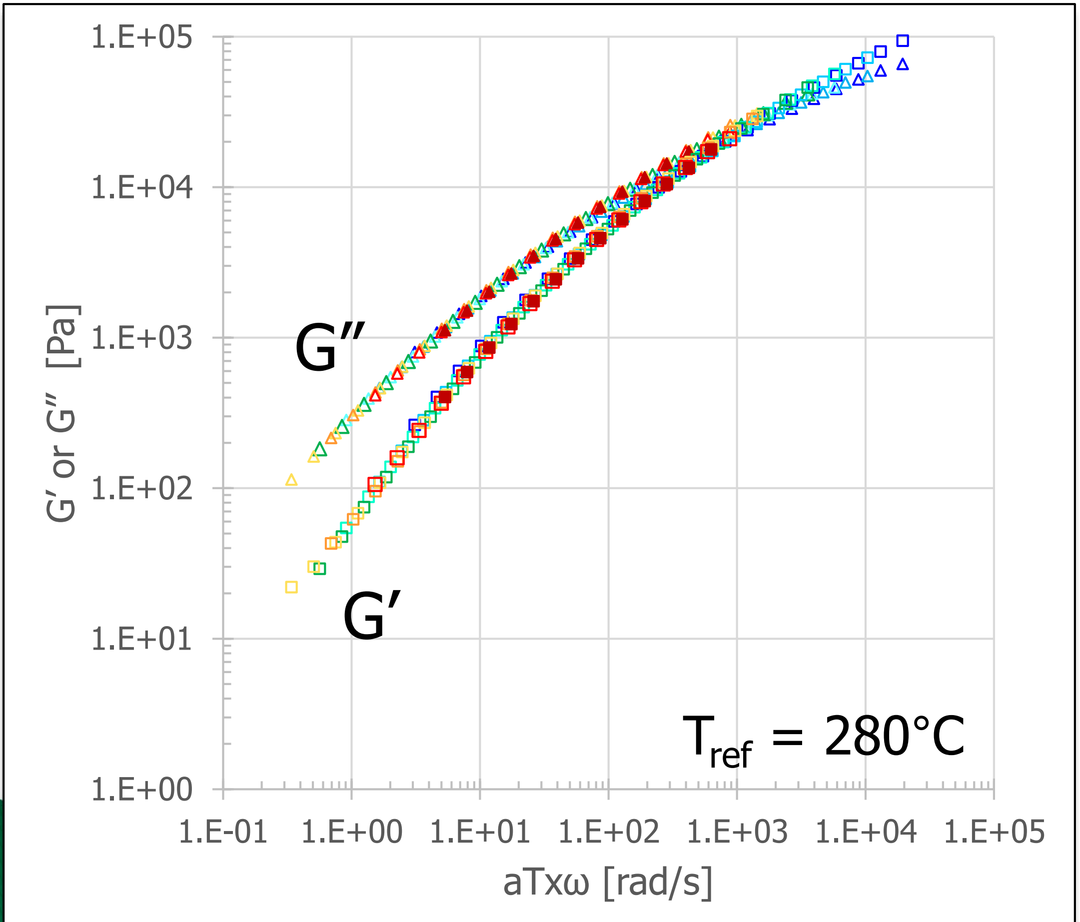


Viscosity master curve at 280°C

- time-temperature superposition (TTS): excellent superposition quality
- Zero-shear viscosity is not fully determined (Newtonian Plateau not reached)
  - ⇒ LCB
  - ⇒ Broad molecular weight distribution
- Strong shear thinning
  - Large entanglement density

Results

- Reference: **LD1**
  - Autoclave LDPE - density= 0.917 g/cm³ , MFI = 7 g/10 min



G′ and G″ master curves at 280°C, after applying time-temperature superposition: excellent superposition quality

The melt a truly a viscoelastic material

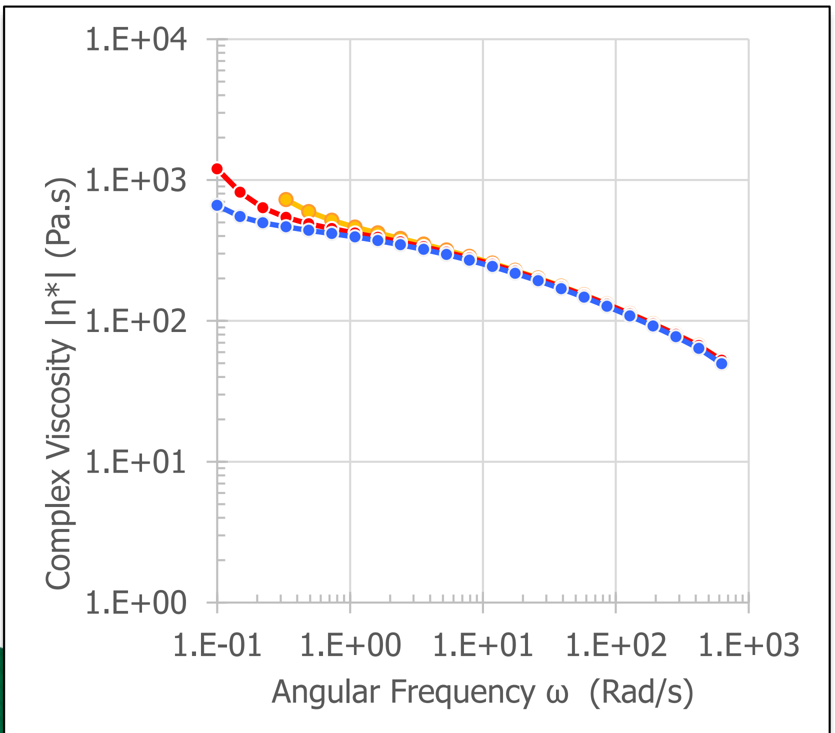
G″>G′ on majority of the frequency range: at this temperature the melt is viscous dominant

Cross over point at about 1,000 rad/s

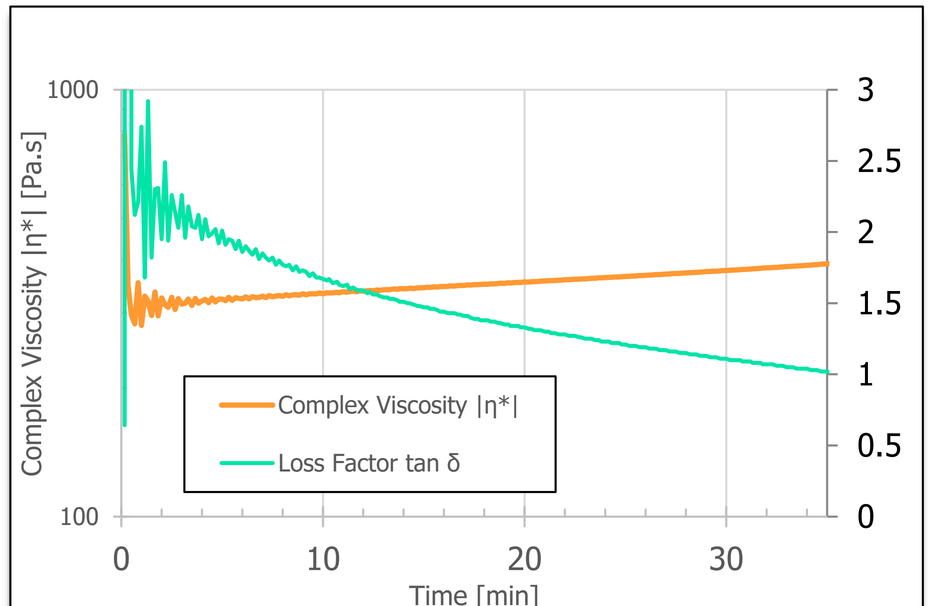
Results

- Reference: **LD1**
  - Autoclave LDPE - density= 0.917 g/cm^3 , MFI = 7 g/10 min
  - Thermal stability under N_2 atmosphere

Measurement repeats at 260°C



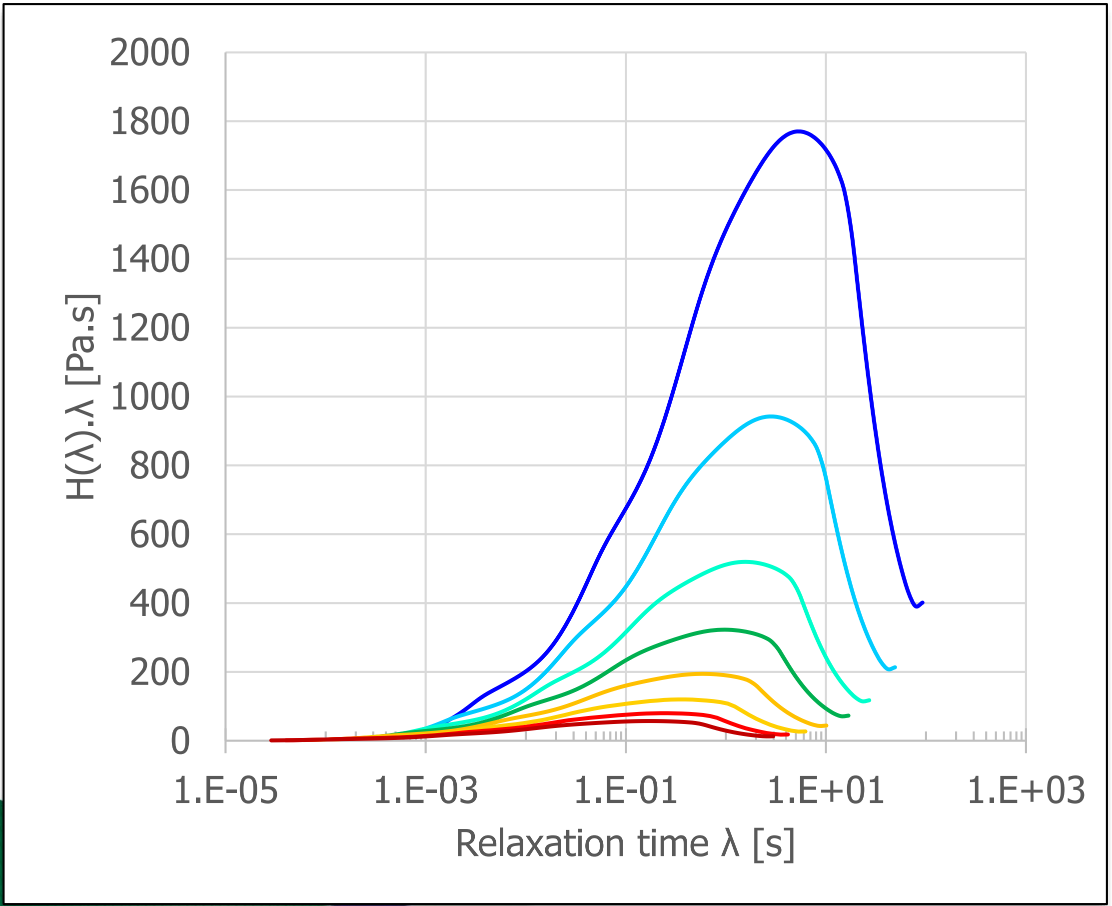
Time sweep at 1 rad/s and 280°C



Over time: increase of complex viscosity and melt elasticity near processing temperature

Results

- Reference: **LD1**
  - Autoclave LDPE - density= 0.917 g/cm^3 , MFI = 7 g/10 min



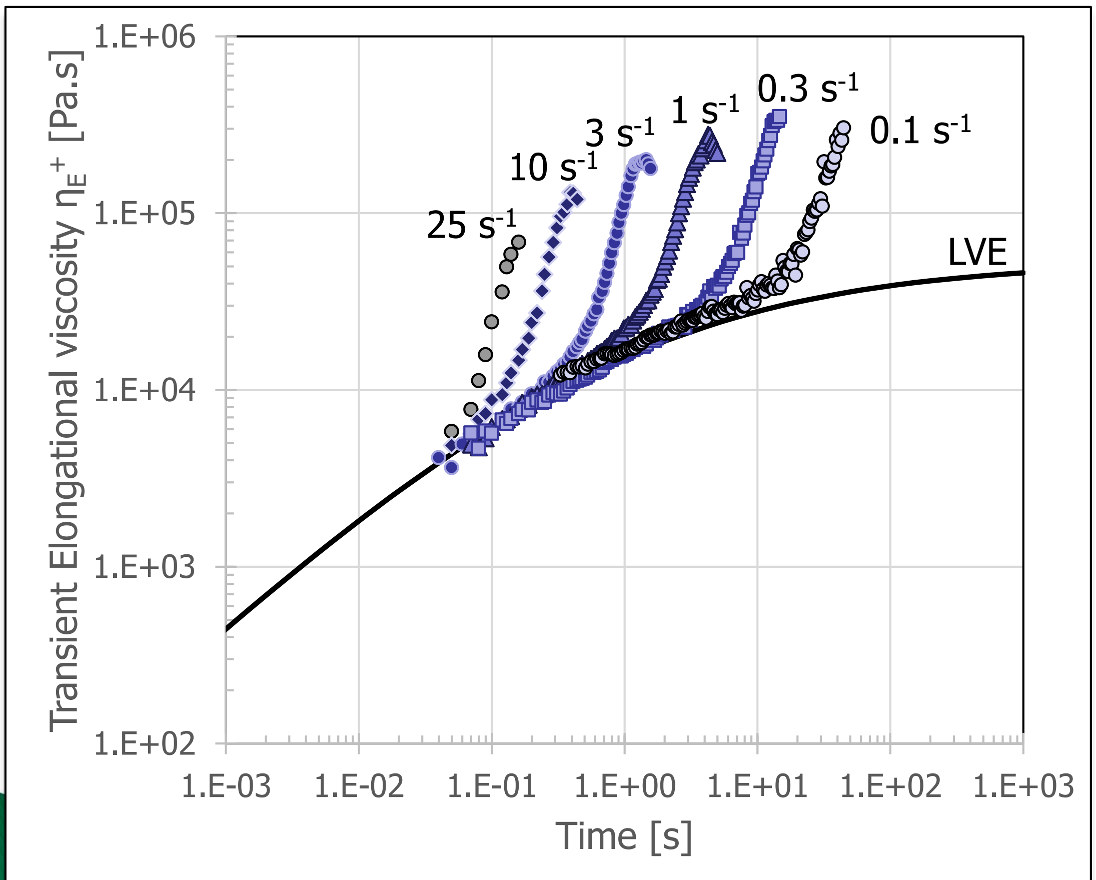
Relaxation time distribution:

- melt rheology equivalent of the molecular weight distribution.
- Calculated from the G′ and G″ master curves with the so-called Regularization method

- very broad distribution with asymmetrical shape biased towards longer relaxation times.
- The calculation does not directly show the high molecular weight shoulder seen with GPC

Results

- Reference: **LD1**
  - Autoclave LDPE - density= 0.917 g/cm^3 , MFI = 7 g/10 min



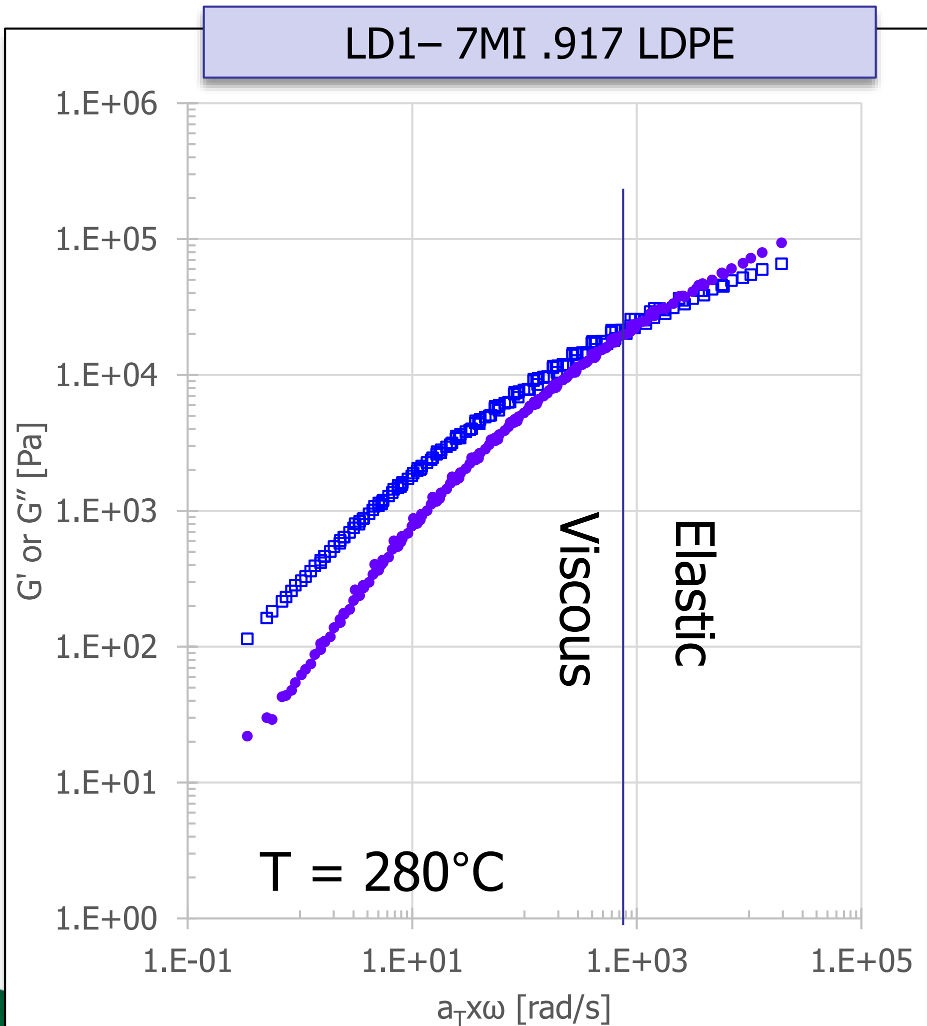
Transient elongational viscosity measurements at 140°C with the SER-3

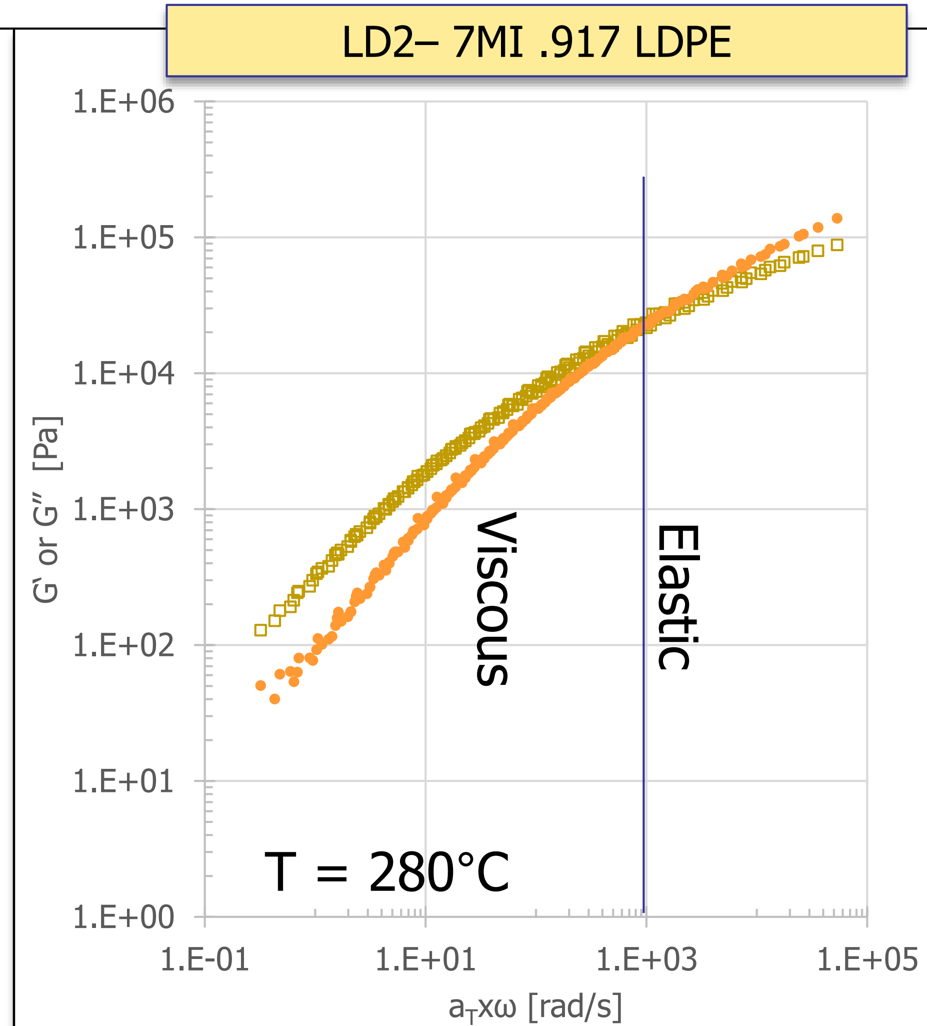
- LVE = 3 x η^* (Carreau-Yasuda model)
- Strong strain hardening (deviation from LVE) characteristic of high density of long chain branching LCB

Comparisons

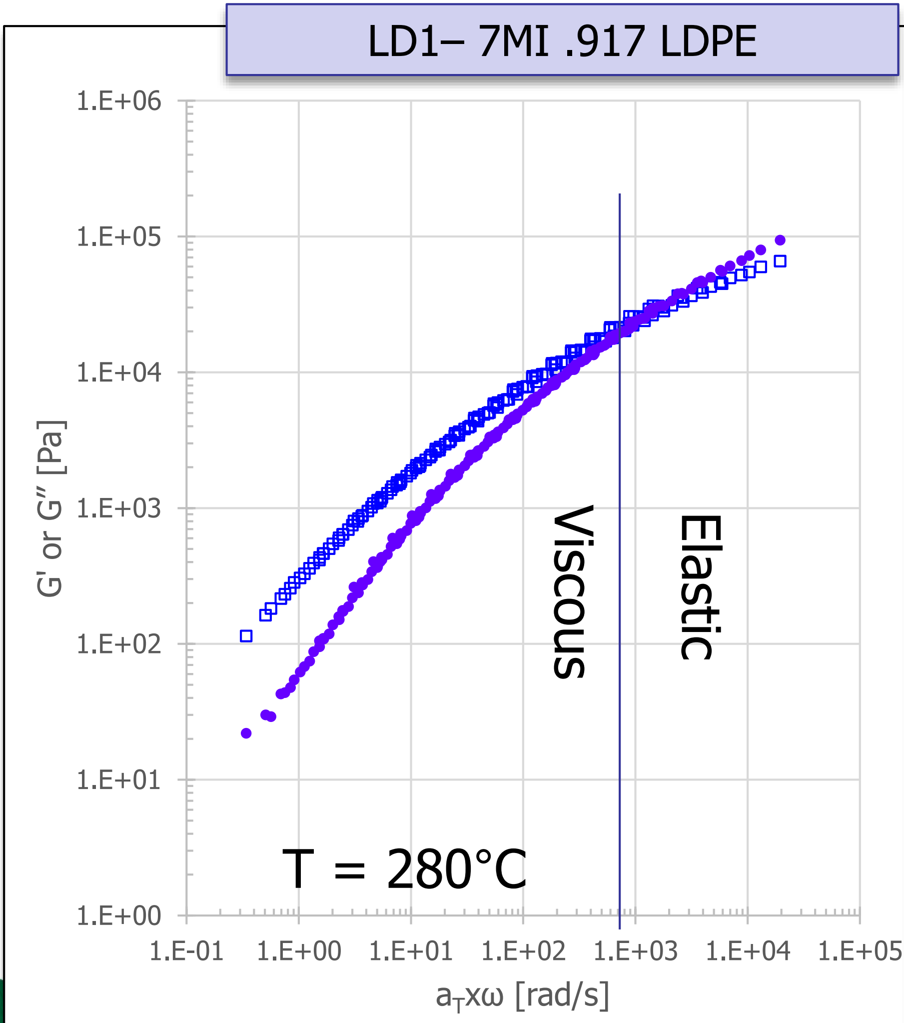
- Comparison of G'/G"
- Comparison of complex viscosity master curves
- Comparison of relaxation time distributions
- Comparison of transient extensional viscosity

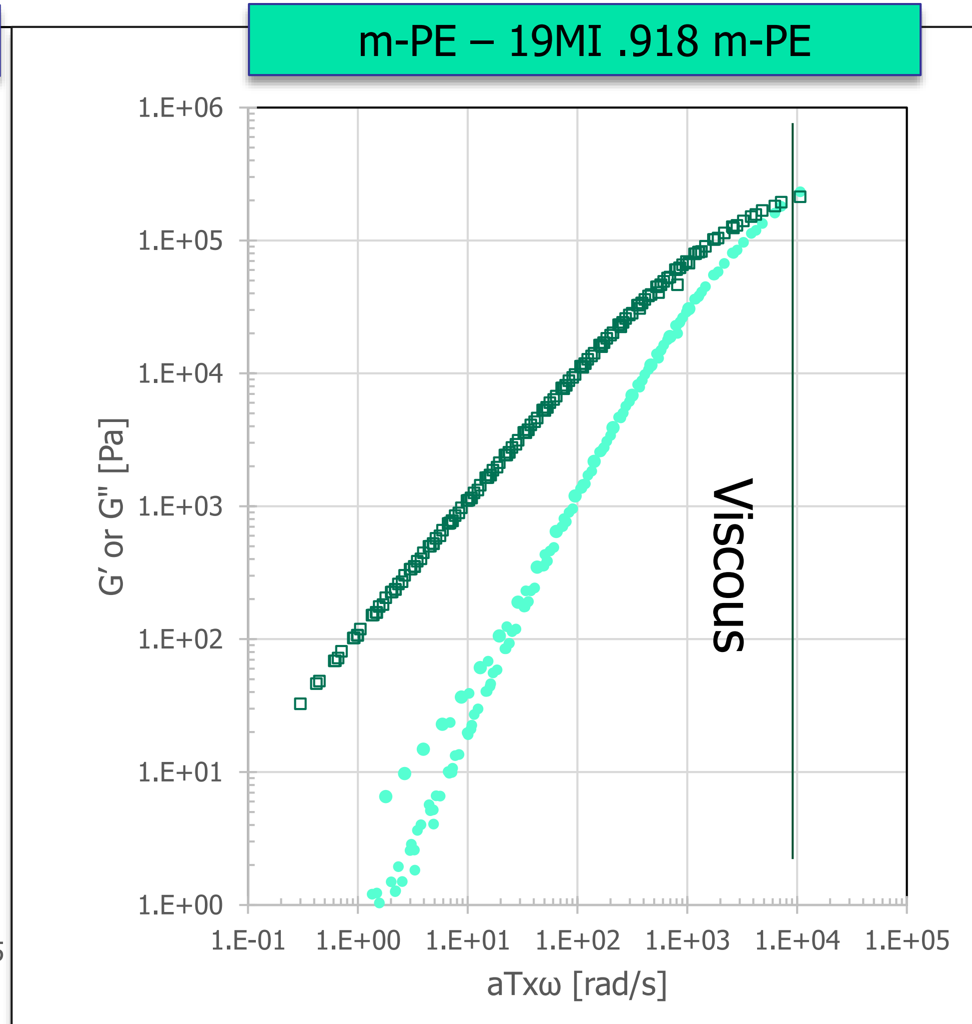
Comparison – G' and G"



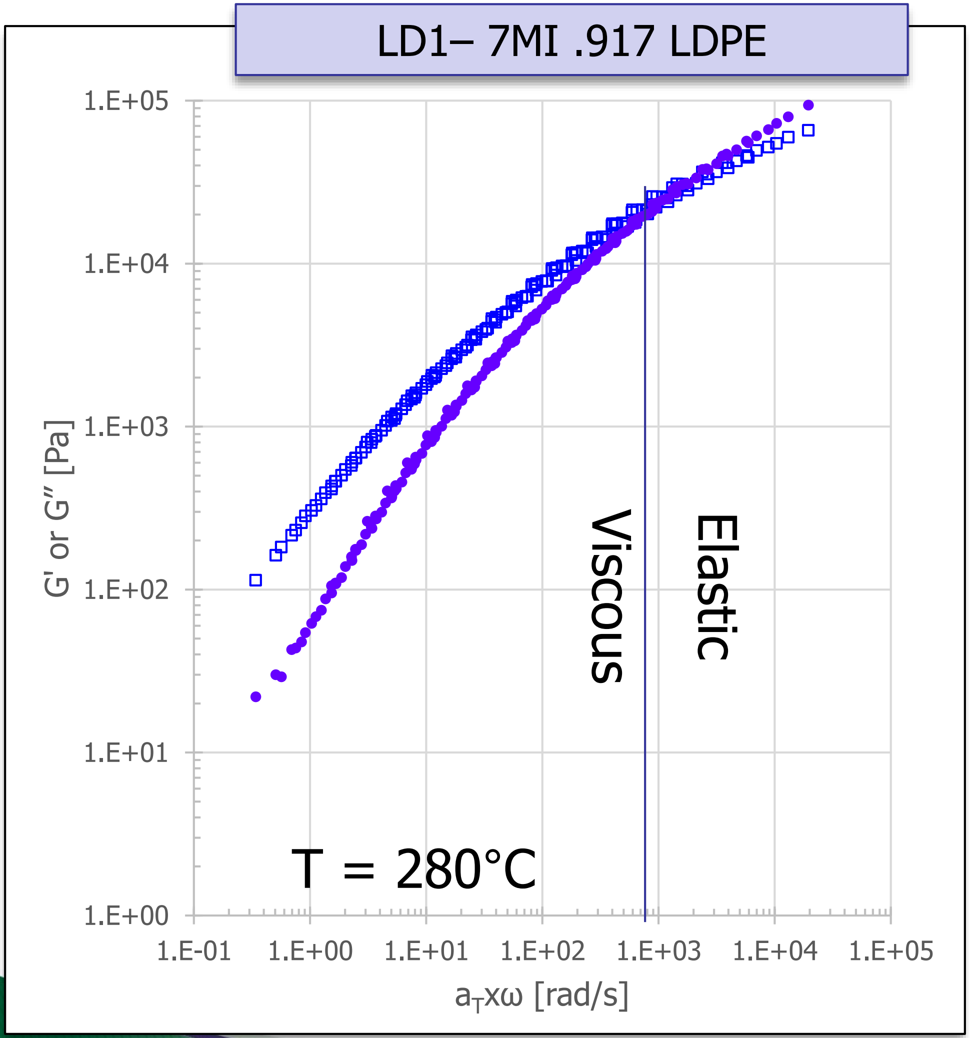


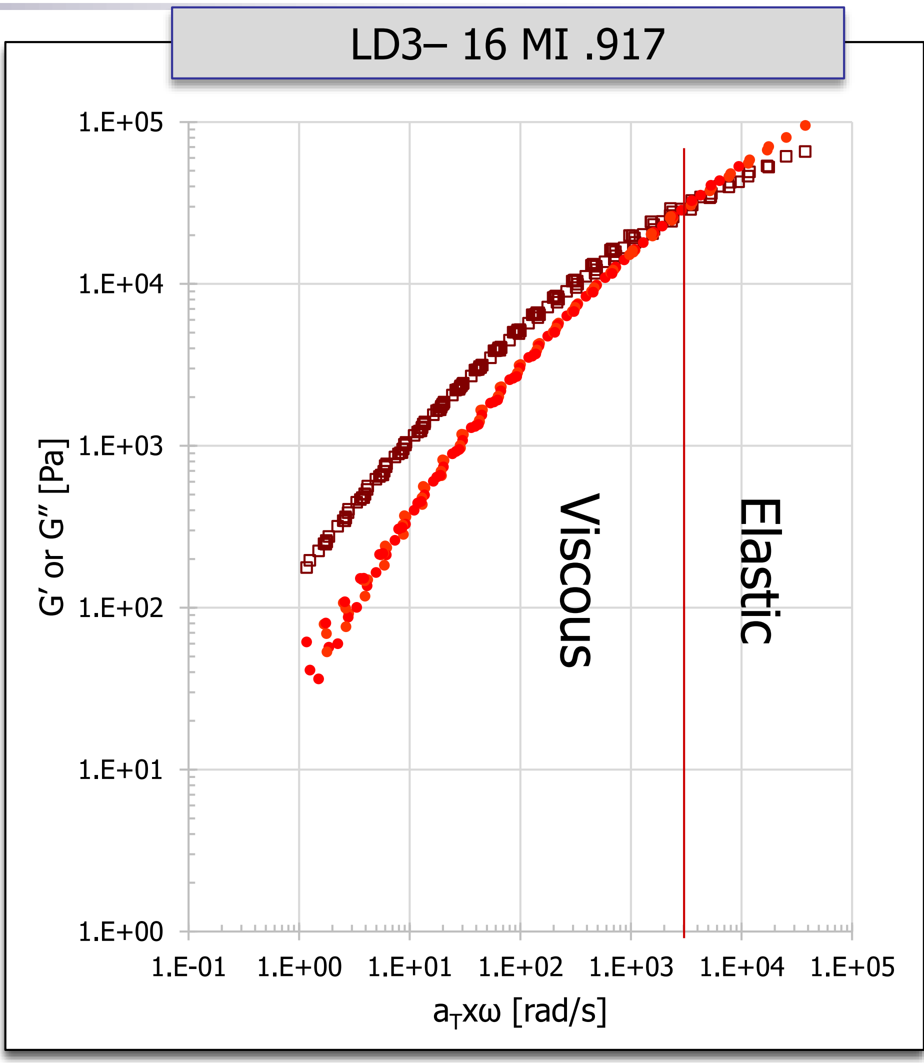
Comparison – G’ and G”



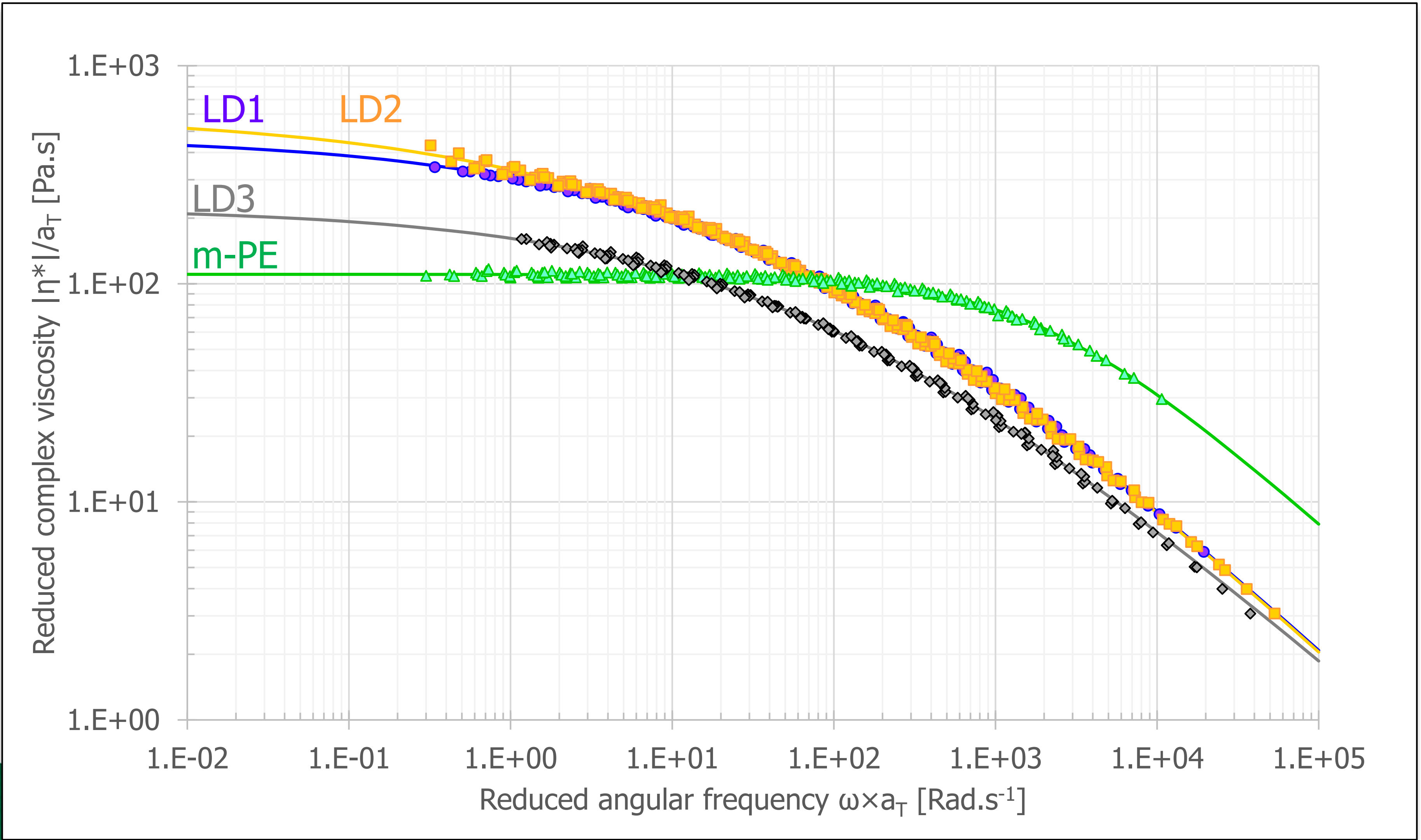


Comparison – G' and G"

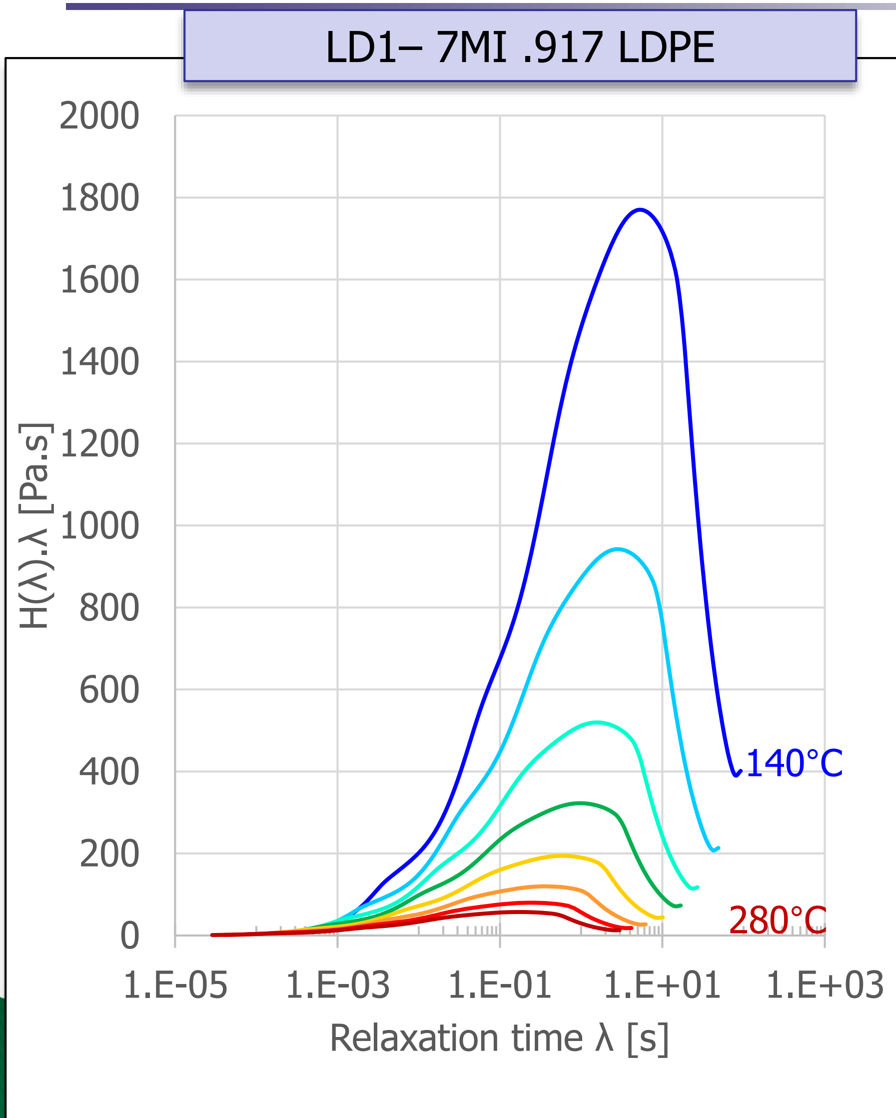


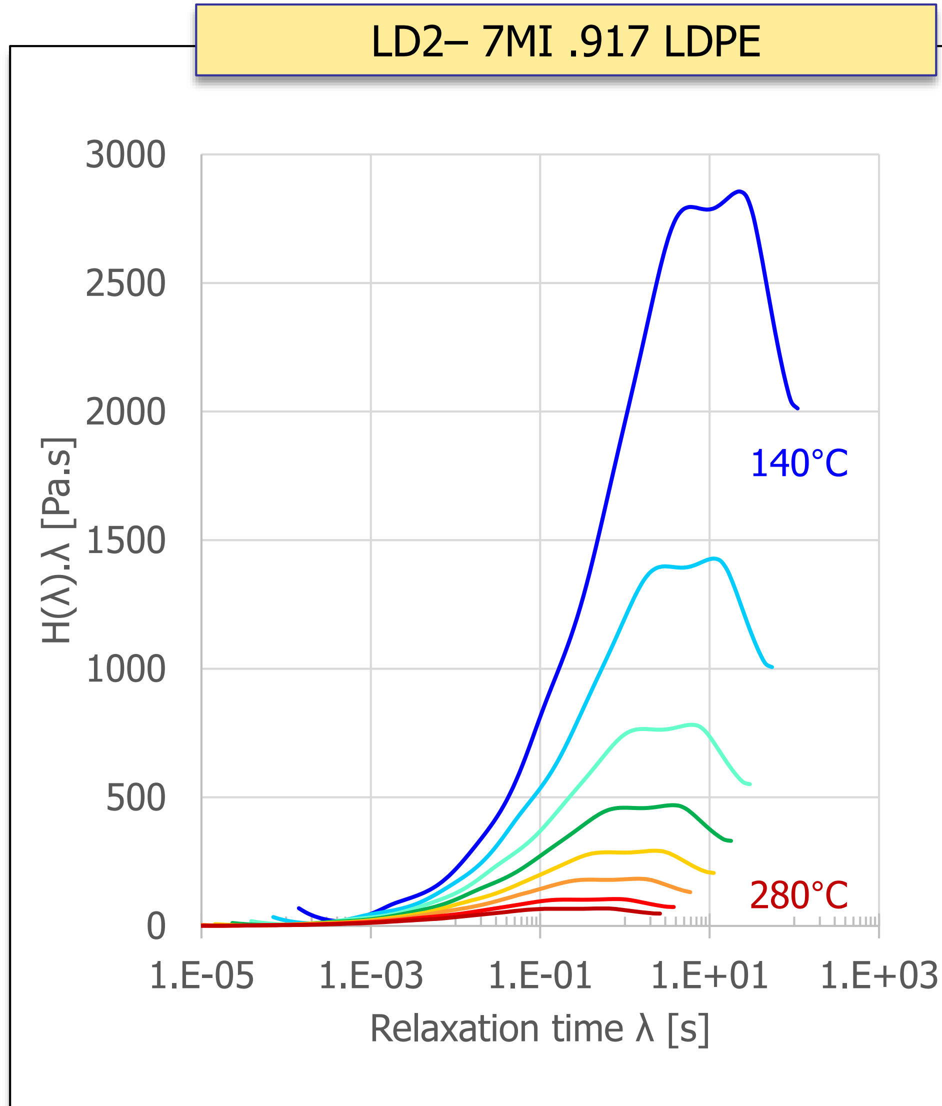


Comparison – Complex viscosity

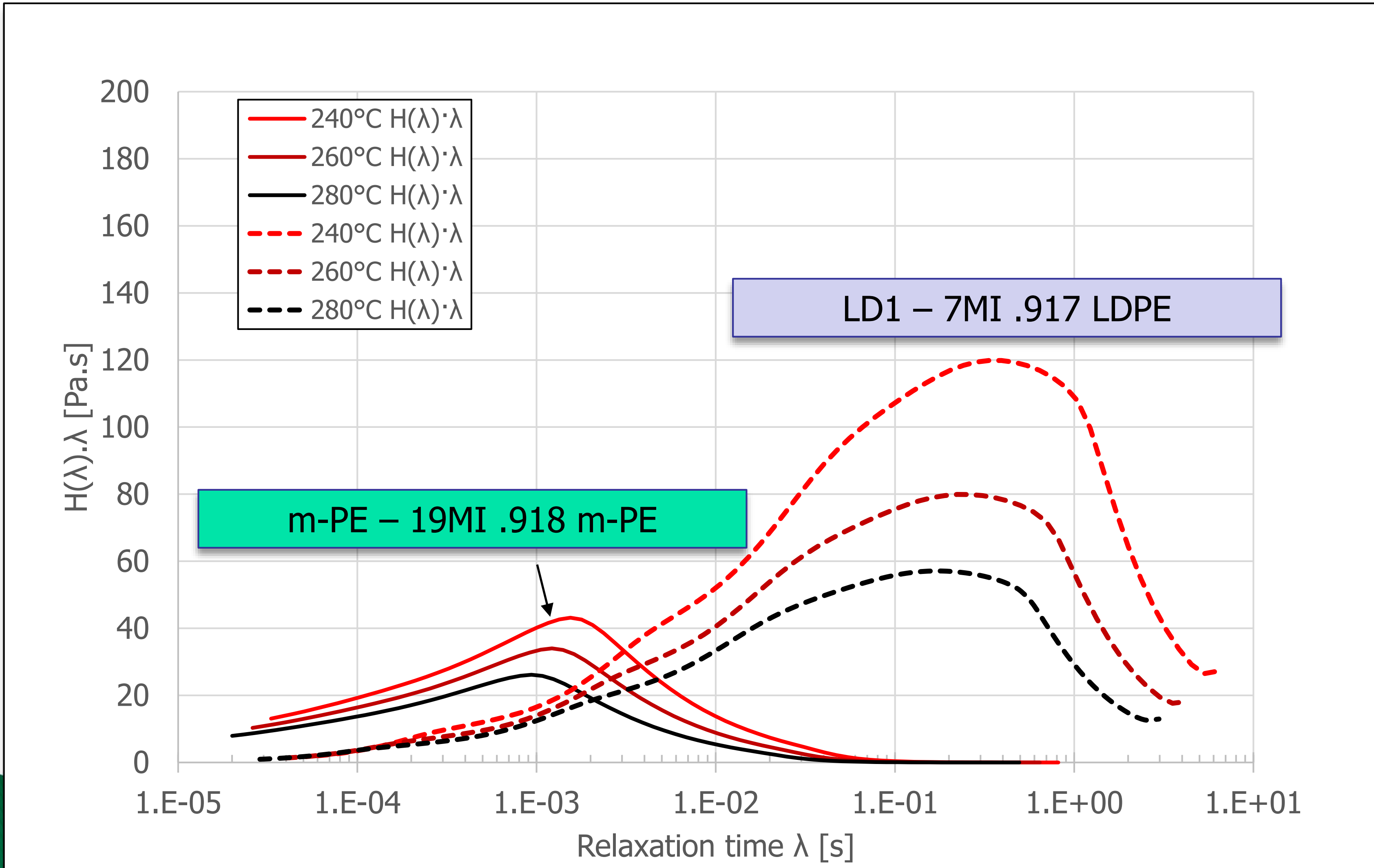


Comparison relaxation time

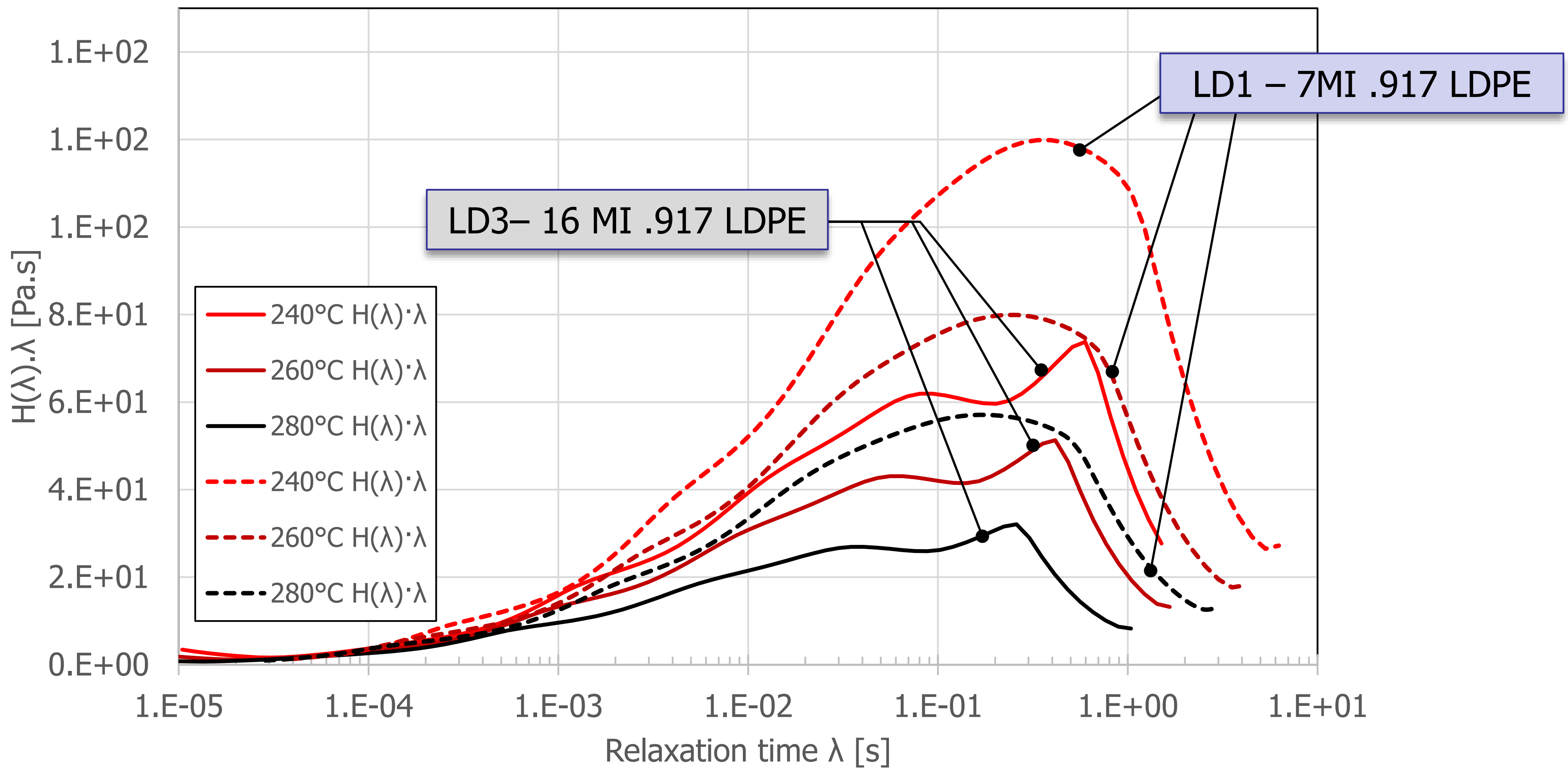




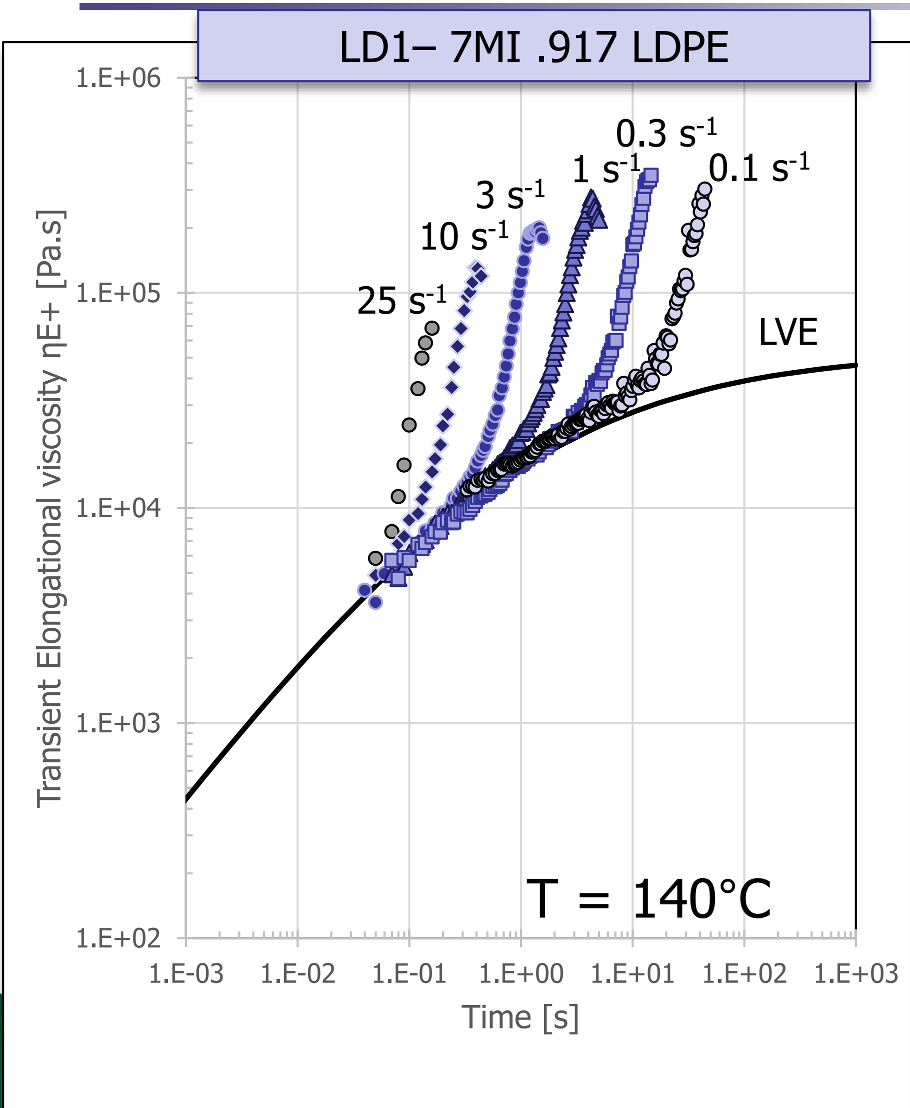
Comparison relaxation time

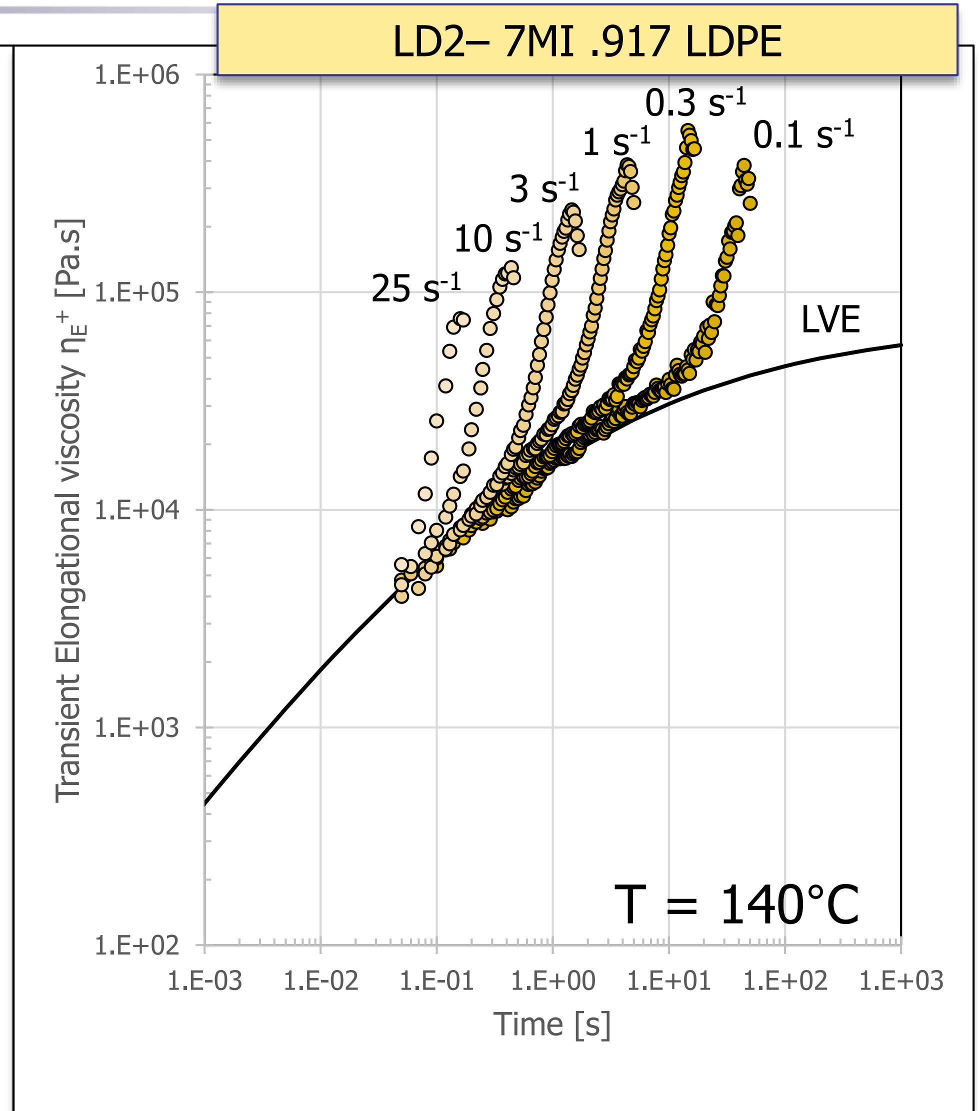


Comparison relaxation time

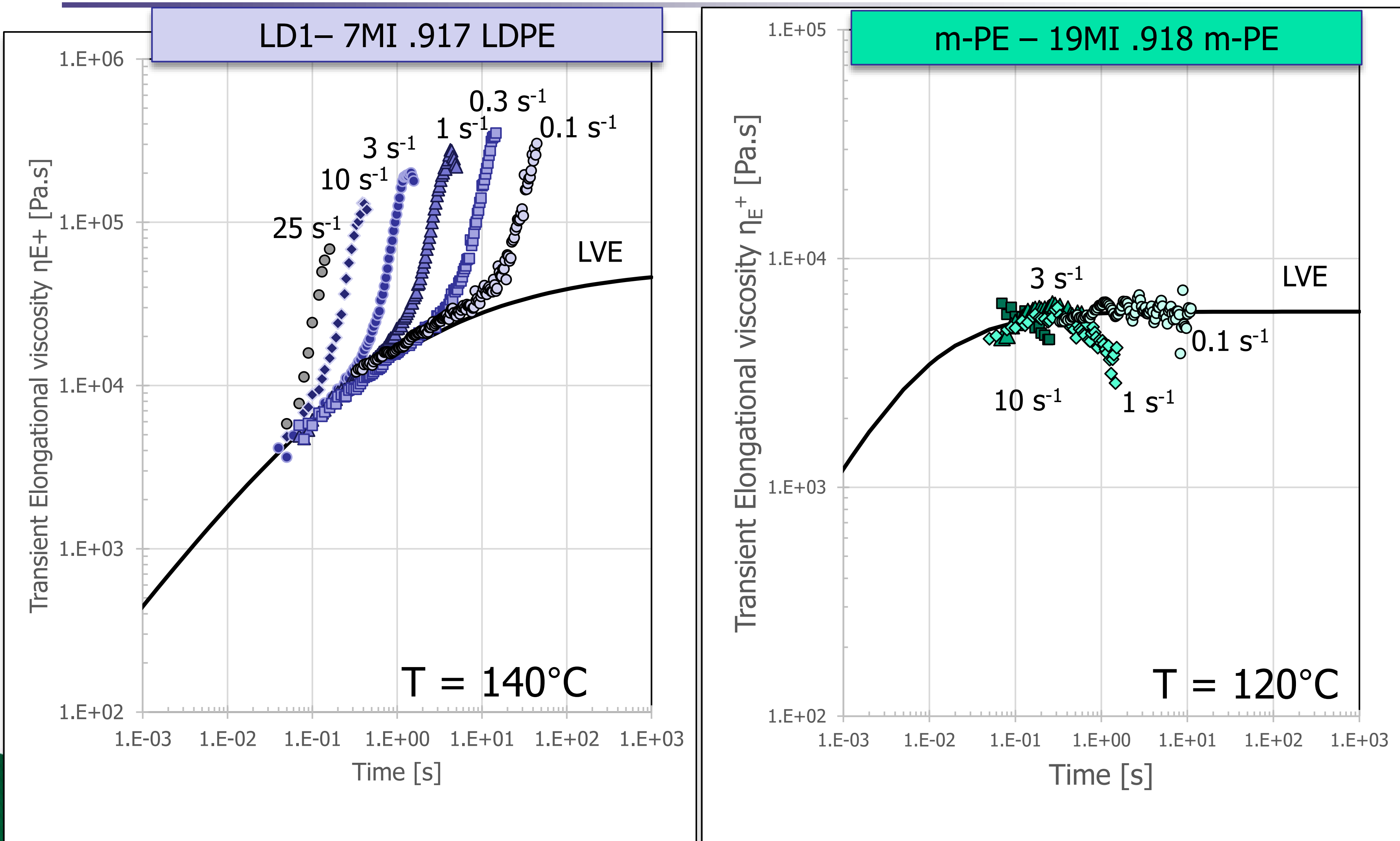


Comparison – Elongational Viscosity



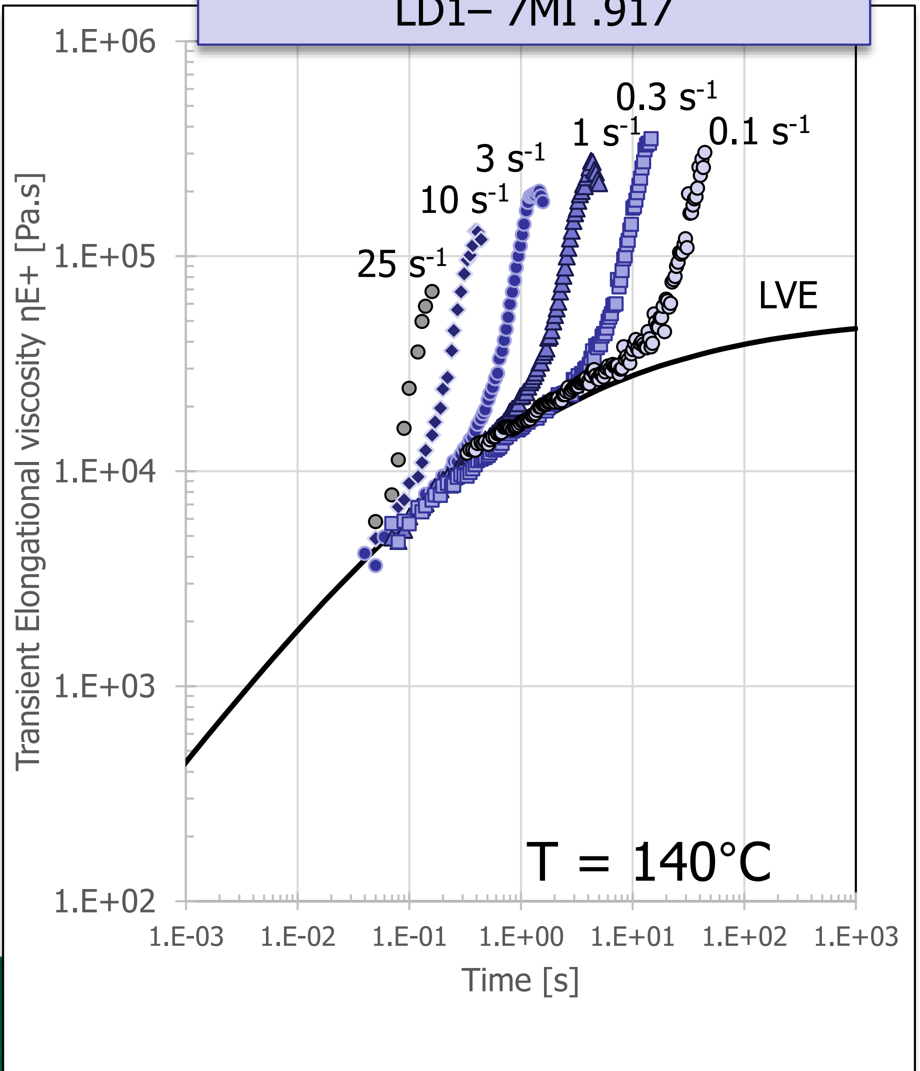


Comparison – Elongational Viscosity

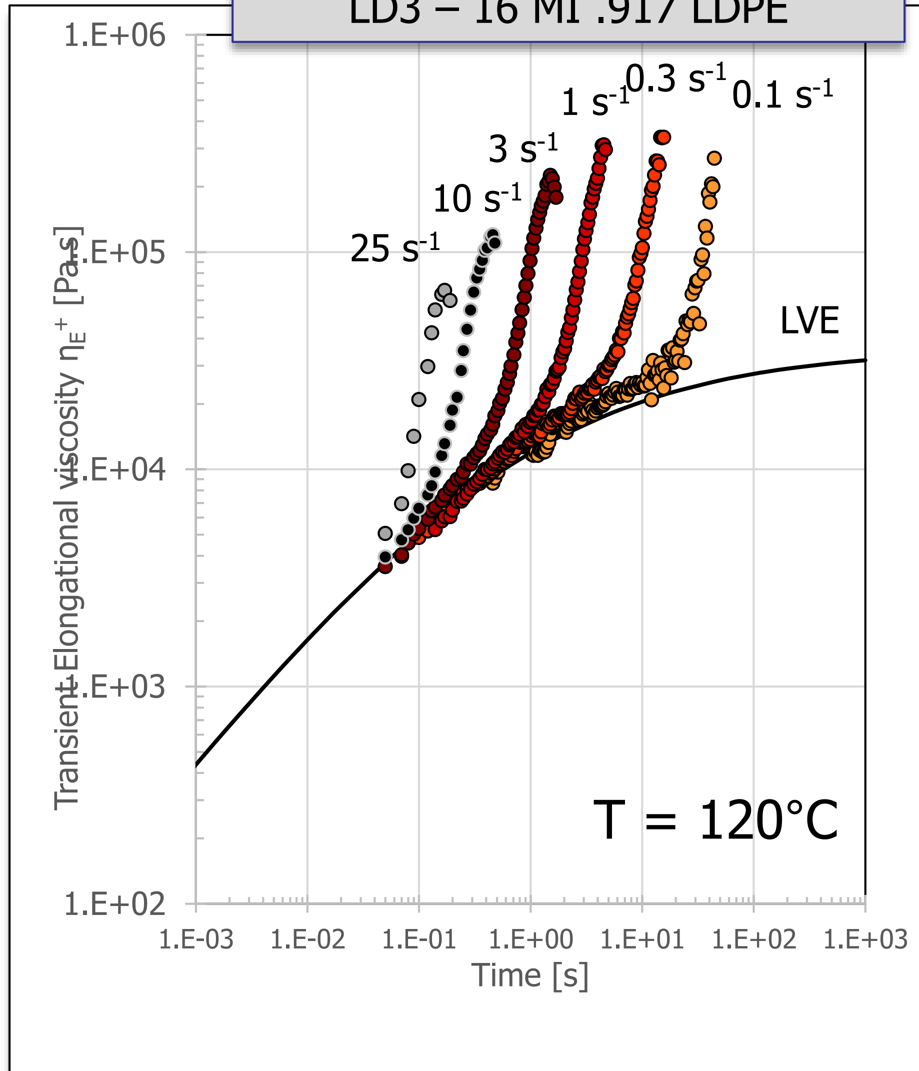


Comparison – Elongational Viscosity

LD1– 7MI .917



LD3 – 16 MI .917 LDPE



Key Rheological parameters

Material	Zero shear viscosity η_0 at 280°C† [Pa.s]	Pseudoplastic (shear thinning) index† [-]	Storage modulus G′ at G″ = 500 Pa at 180°C‡ [Pa]	Peak relaxation time at 280°C [s]	Width half maximum of relaxation time [decades]
LD1	471.92	0.3389	129.4	0.159	≈ 2.19
LD2	602.06	0.2735	150.8	0.544	≈ 2.65
LD3	223.34	0.2948	130.3	0.259	≈ 2.14
m-PE	110.50	0.3404	4.8	$9.37\ 10^{-4}$	≈ 1.55
Physical meaning	Molecular weight	De-entanglement rate to recoil rate	Melt elasticity	Melt elasticity	Polydispersity

† Carreau-Yasuda curve fit
‡P.A. Clevenhag, C. Oveby – TAPPI PLACE 2004

Key Rheological parameters

Material	Ultimate Trouton Ratio at 25 s-1	Ultimate Trouton Ratio at 1 s-1
LD1	**27.2**	**36.1**
LD2	**29.4**	**45.9**
LD3	**31.3**	**53.2**
m-PE	**1.3** for $\dot{\varepsilon} = 10\ s^{-1}$	**1.8**
Physical meaning	Melt strength at high stretch rate	Melt strength at medium stretch rate

Conclusions

- Melt rheology is a powerful tool for the investigation of the molecular structure and the polydispersity of a given polymer

- Looking at shear rheology only is too limited when comparing the behavior of different polymer families related to extrusion coating process

- Elongational viscosity provides valuable information regarding melt strength

- Future work will be carried on:
  - With more polymers to be investigated within the LDPE (Autoclave and Tubular), m-PE, PP, EVA, PLA, biopolymers, PET etc…
  - Processing evaluation work will be carried out (measurement of edge bead profile, neck-in, determination of stable process window etc)
  - A correlation between processing characteristics and shear and elongational viscosity will be evaluated
  - Possibly, a process model will be built using a viscoelastic constitutive equation which takes into account the elongational and shear viscosity data

Thank you

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