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Working at DSM Material Science Center, Geleen – The Netherlands – From May 1st on *“Influence of Temperature and Composition on Mechanical Properties of Thermoplastic Elastomers (TPEs)”*

Outlines

- Background

  Thermoplastic Elastomers (TPEs):

  Morphology and Structure

  Failure behavior at different temperatures

- Experimental tests to further understand the failure mechanism

  Influence of SB/HB ratio and plasticizers

  Influence of Mw

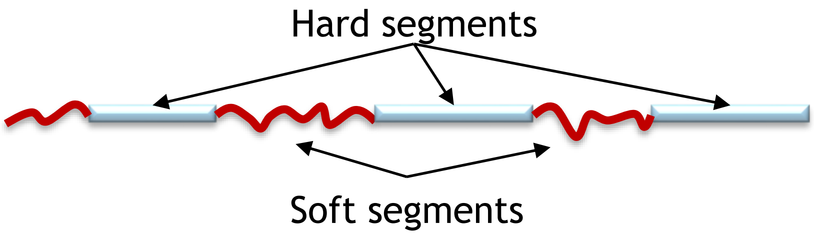
- Follow-up

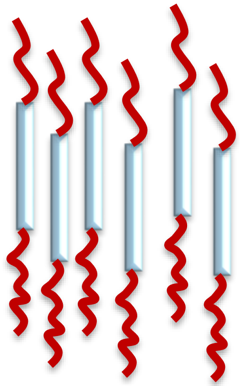
  Fracture tests

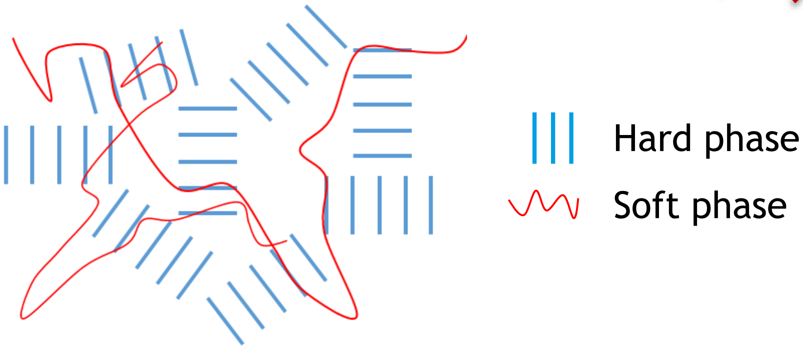
  Tests on samples with different initial morphology

Thermoplastic Elastomers (TPEs)

Segmented block copolymer

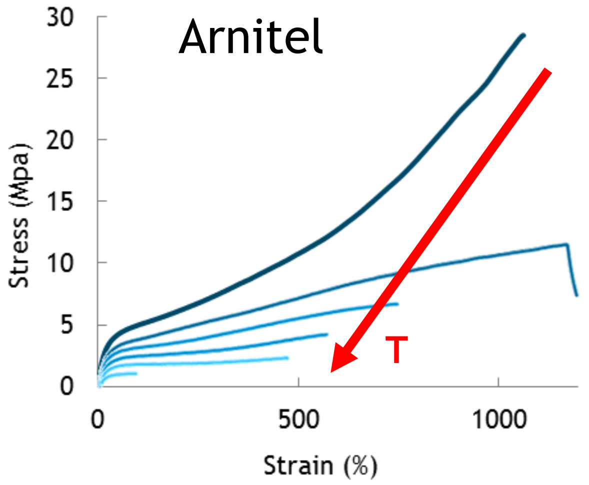




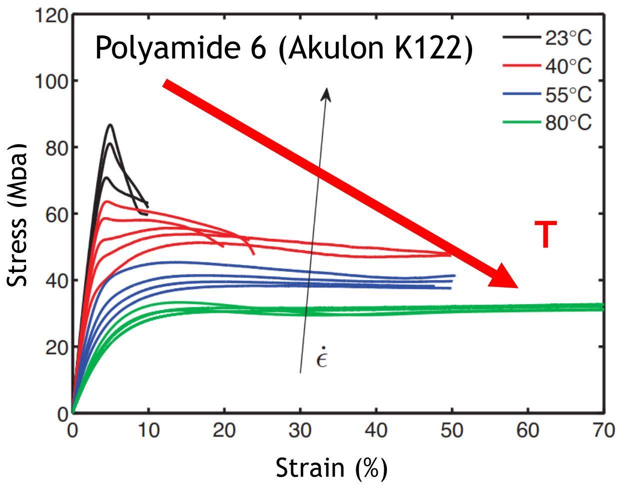


TPEs behave very differently from typical semi-crystalline polymer

Strain at Break dramatically decreases with temperature



Increase of Strain at Break with temperature



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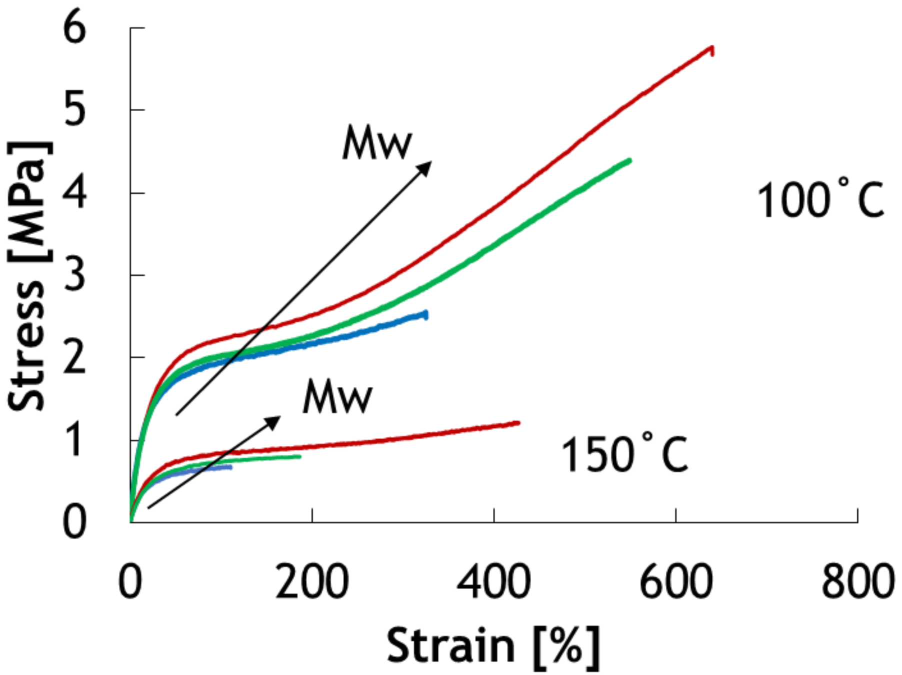
What parameters characterize the failure behavior of these materials?

- Molecular weight
- Strain rate
- Fracture mechanism
- Structural transitions during stretching

Effect of Molecular Weight

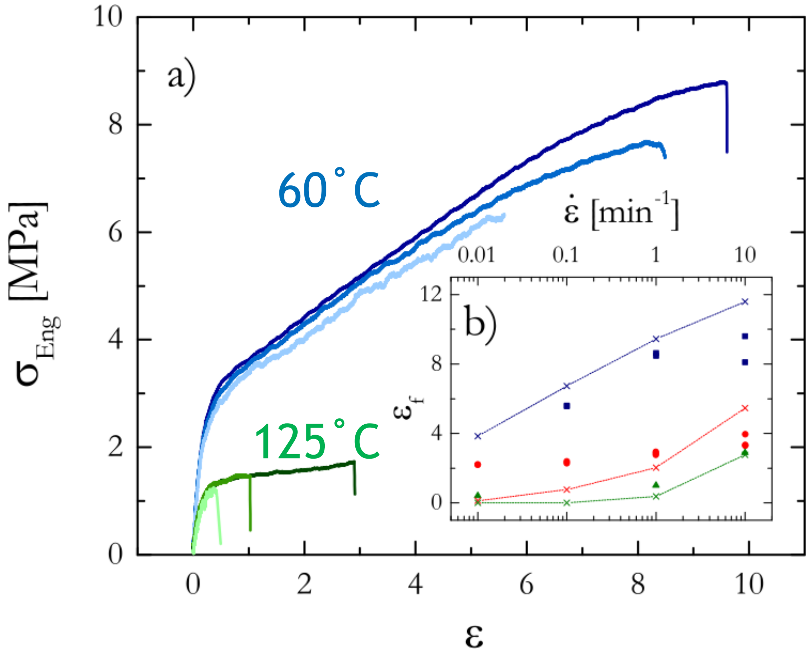


Mw delays the effect of high temperature on Strain at Break:

Higher stresses and strains at failure

Effect of Strain Rate

Lower strain rates lead to lower strain at break



This effect seems to be less severe than the one of the temperature.

Strain rate ranging from 10min^{-1} to 0.001min^{-1}

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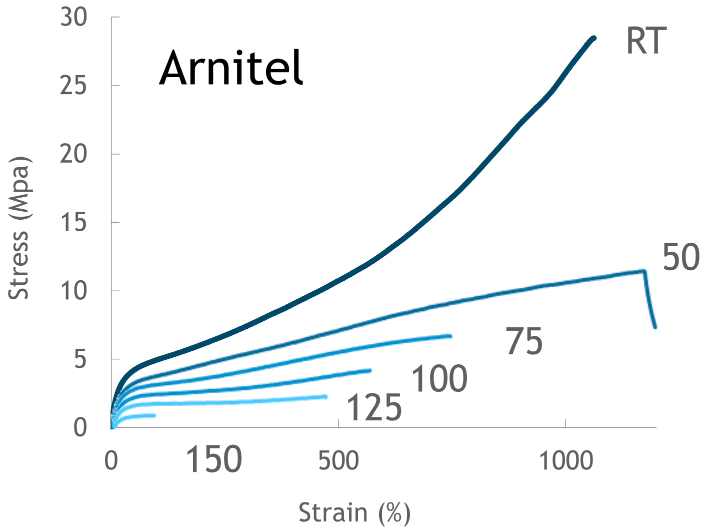
Different fracture shapes

Embrittlement at higher T

Different fracture mechanisms at different Temperatures



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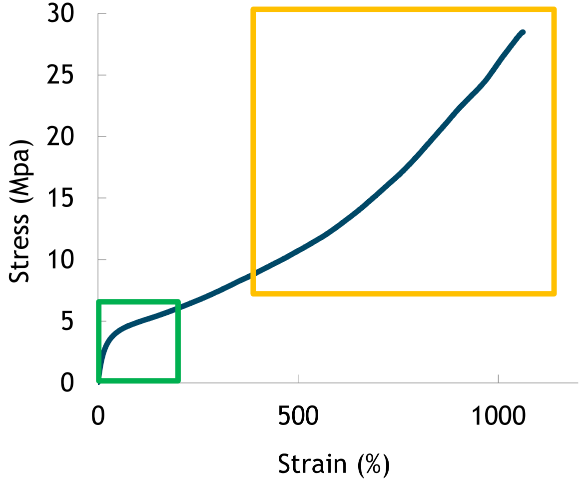
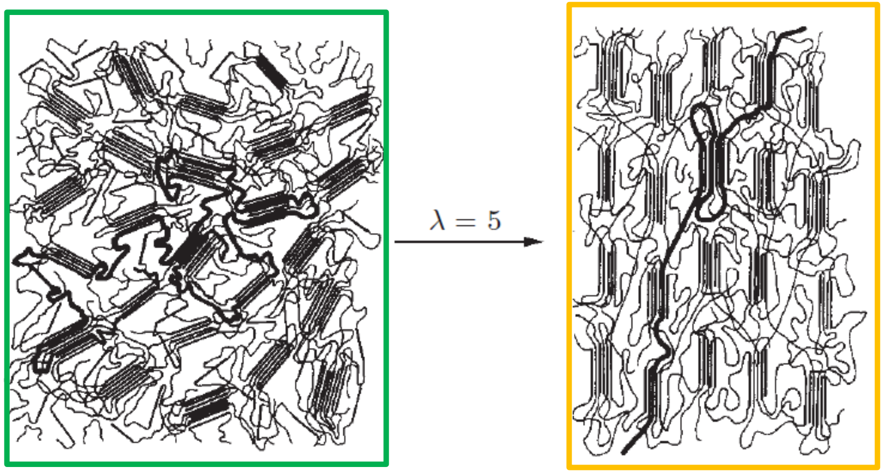
Change of chain conformation during stretching

From isotropic to oriented state



At Room Temperature!



Fischer et al.

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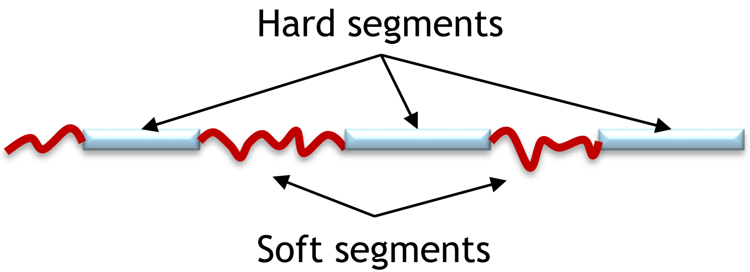
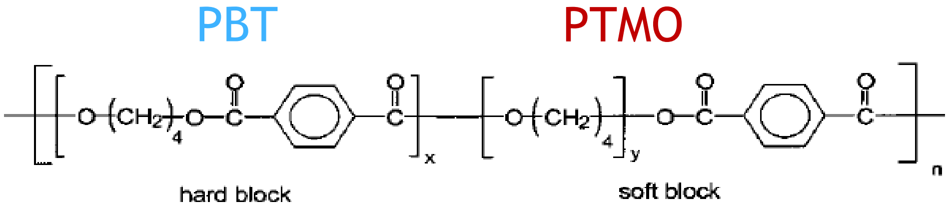
Experiments

Model Experimental System

Structure: molecular level





Polycondensation-based, semi-crystalline block copolymer, TPEs composed of poly(butylene terephthalate) (PBT) blocks to make up the solid phase (HBs) and polyether-based blocks (PTMO) to make up the soft phase (SBs)

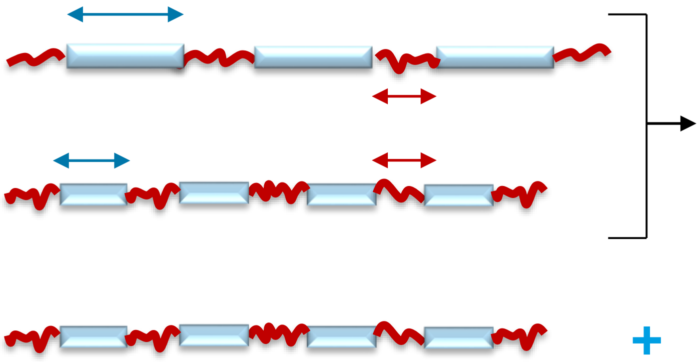
1st System: different SB/HB ratio - same SB length

Decreasing amount of PBT

60_PTMO2k_29

70_PTMO2k_33

70_PTMO2k_33+P



$HB_{wt\%}$ = 40%

$HB_{wt\%}$ = 30%

SB length= 2 kg/mol

+ 15% Plasticizers

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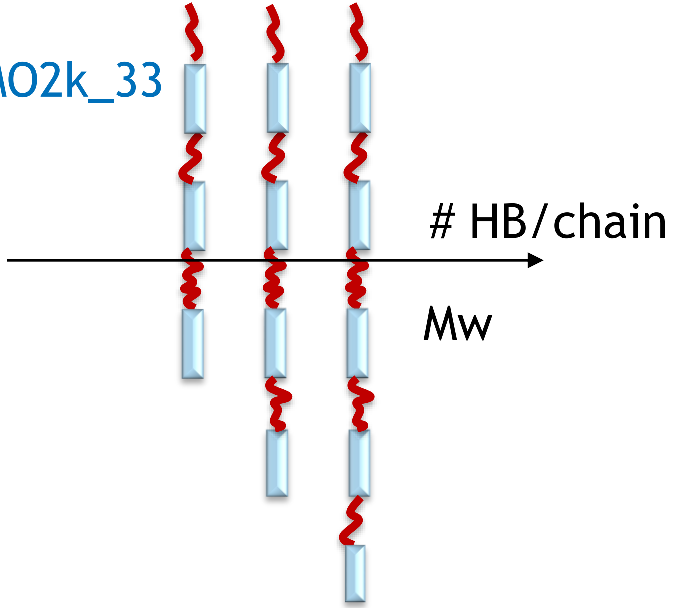
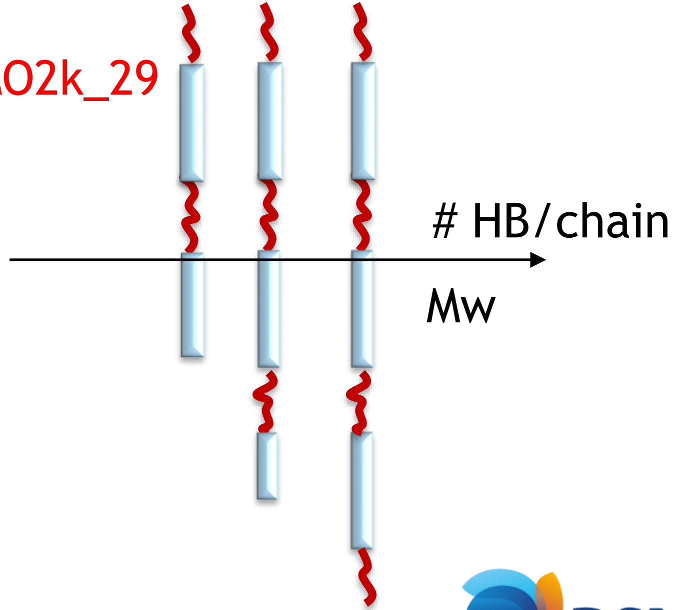
2nd System: Different Molecular Weights

Mw varies, all the other parameters are fixed

70_PTMO2k_33



60_PTMO2k_29



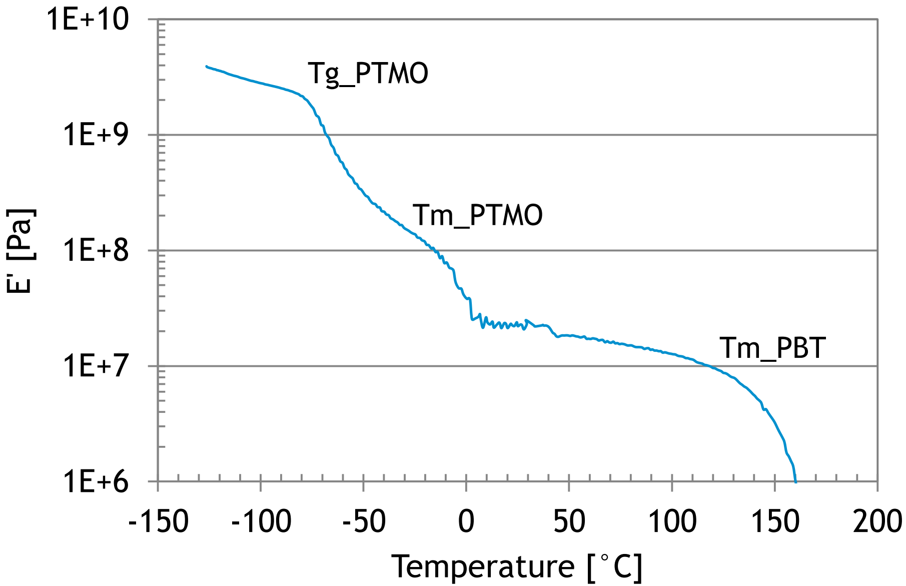
Experiments

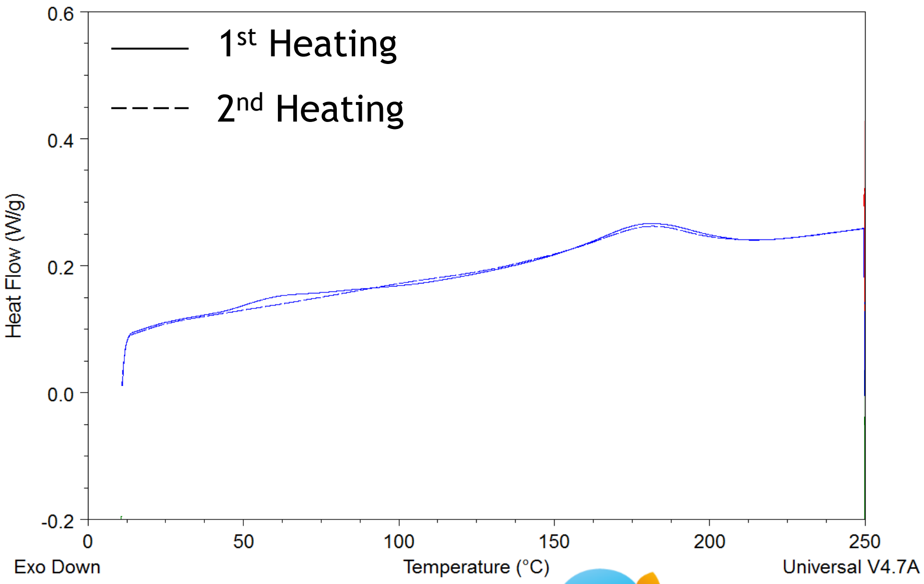
1st system: grades with different HB/SB ratio

Slow decrease in elastic modulus with temperature

Linear properties - DMTA and DSC

$Tm_{70\_PTMO2k\_33} = 180^{\circ}C$





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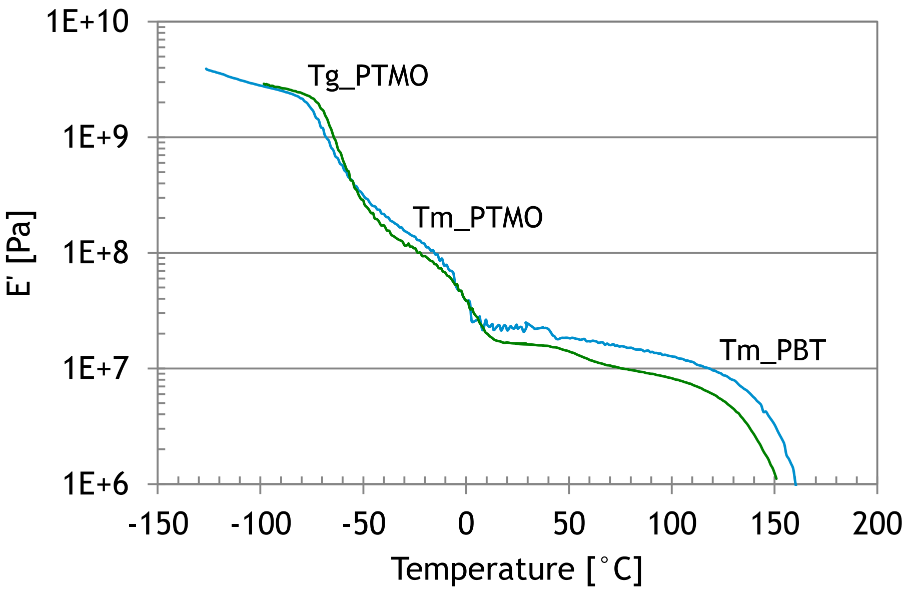
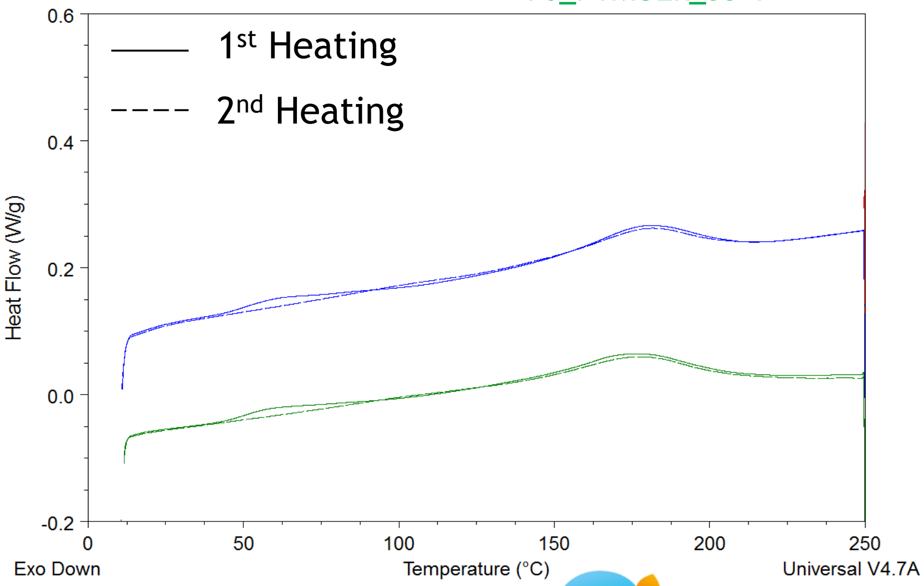
Lower modulus for the diluted system

Plasticizers reduce modulus with a very small shift in Tm

$Tm_{70\_PTMO2k\_33}$ = 180˚C
$Tm_{70\_PTMO2k\_33+P}$ = 173˚C





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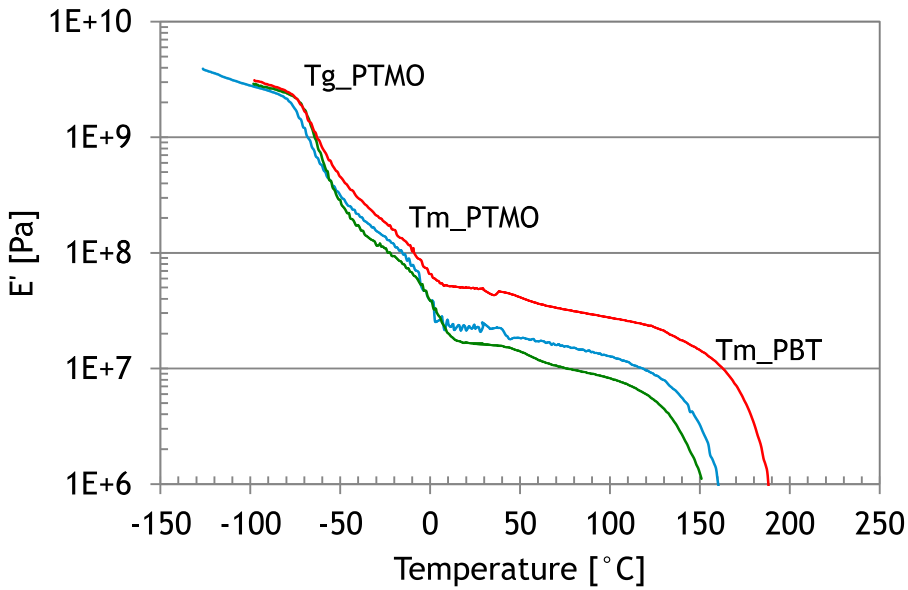
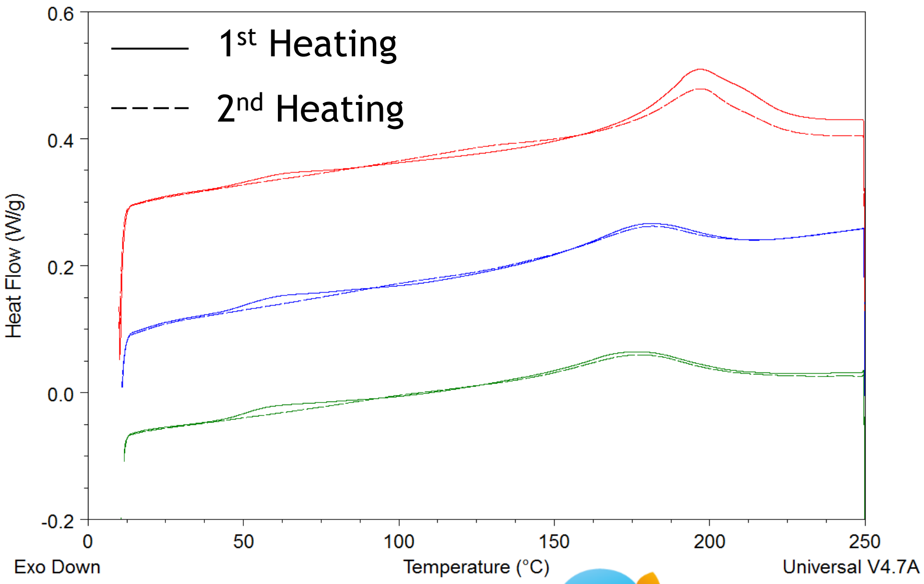
Higher modulus and Tm with higher HB wt%

Linear properties - DMTA and DSC

$Tm_{60\_PTMO2k\_29}$ = 196˚C
$Tm_{70\_PTMO2k\_33}$ = 180˚C
$Tm_{70\_PTMO2k\_33+P}$ = 173˚C





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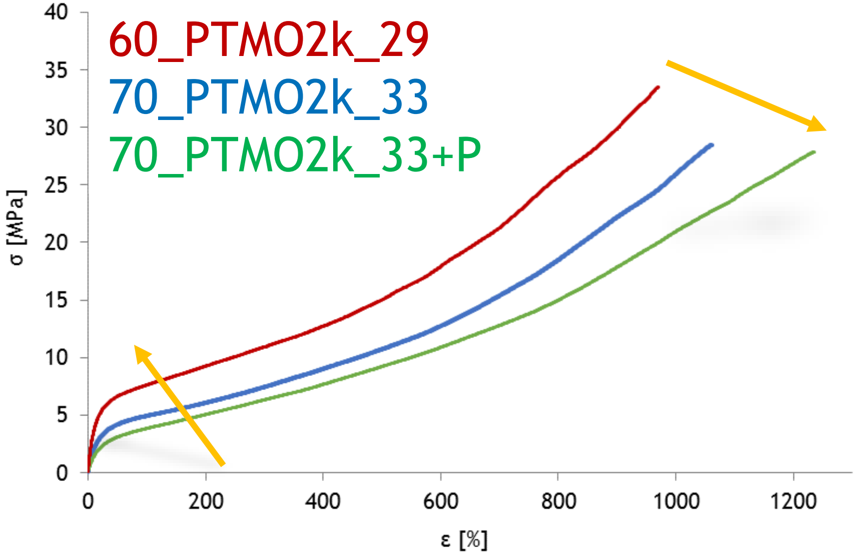
Modulus and stresses increase with HB wt%

Non linear properties - Tensile test at T=RT



- High stresses and less ductility for the samples with a higher HB content.
- The Diluted 70_PTMO2k_33 system is softer and more ductile

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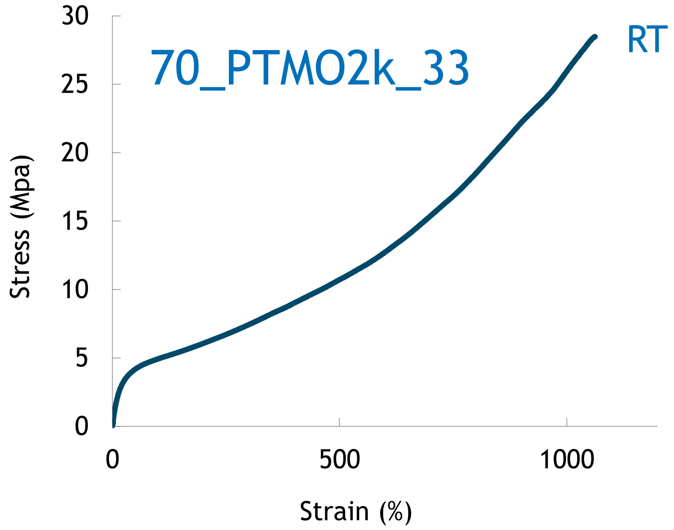
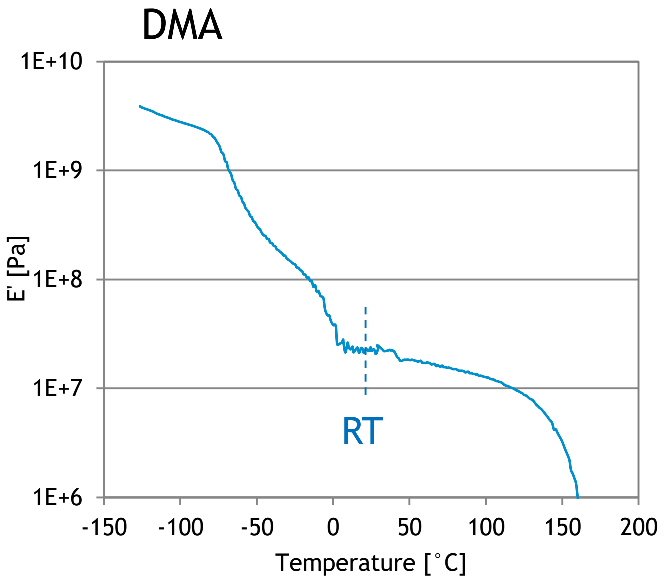
Different SB/HB ratio model system

Non linear properties - Tensile test at T>RT





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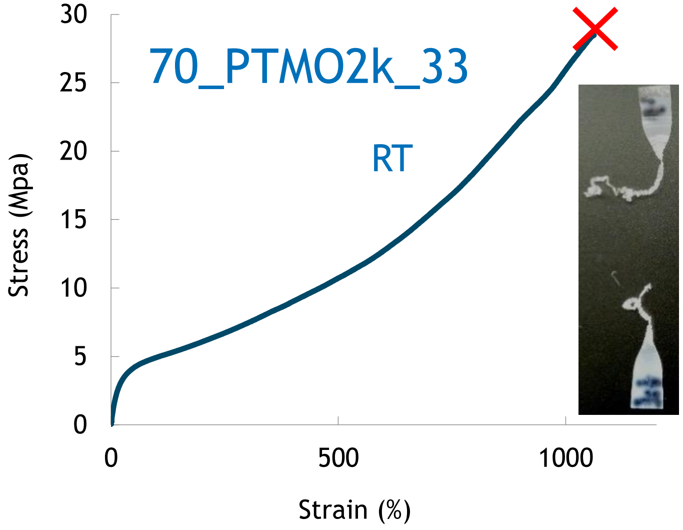
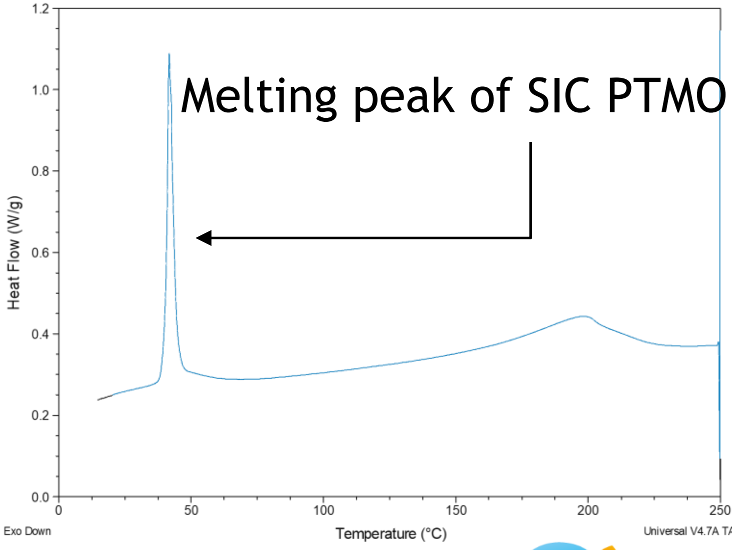
Clear Strain Induced Crystallization (SIC) of the Soft Block (PTMO)



DSC on Broken sample



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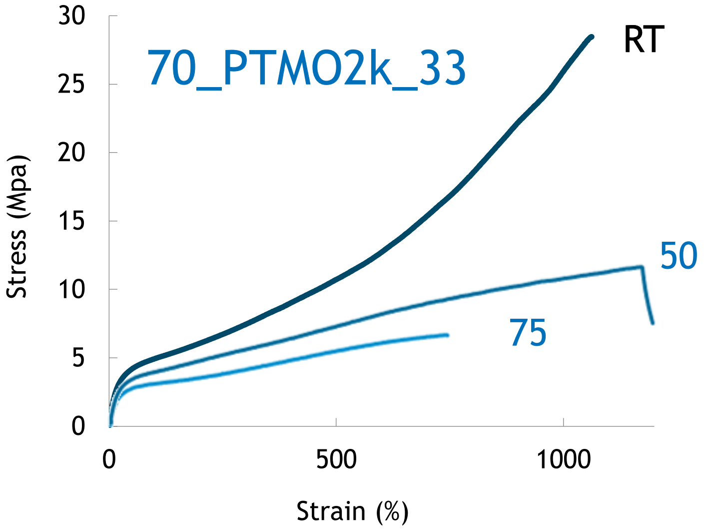
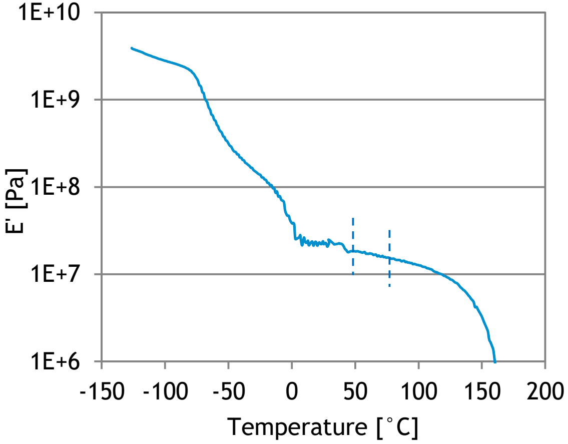
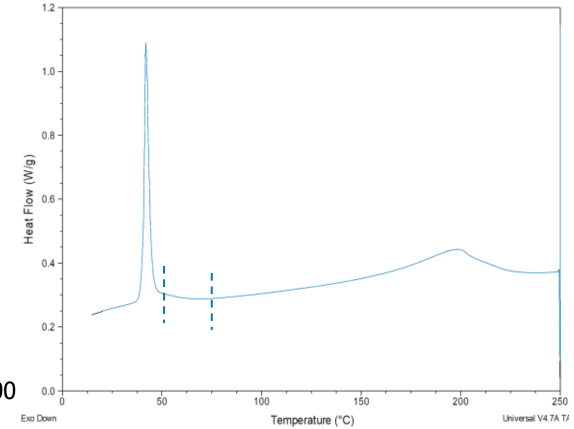
At T>50˚C SIC of Soft Blocks is not present anymore



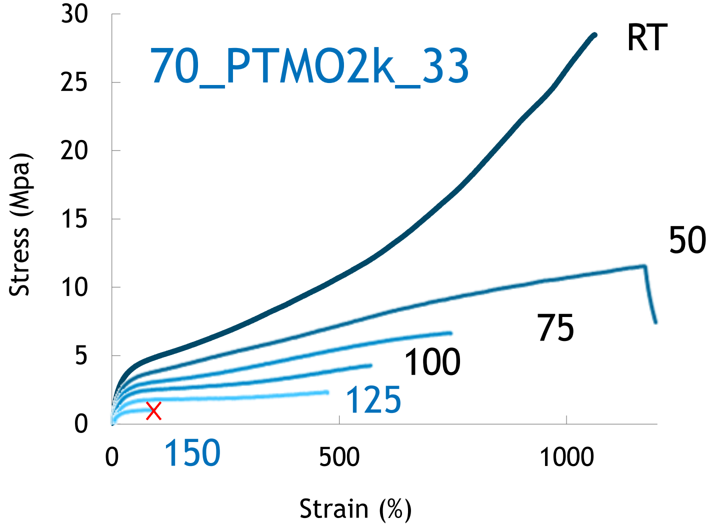
DMA

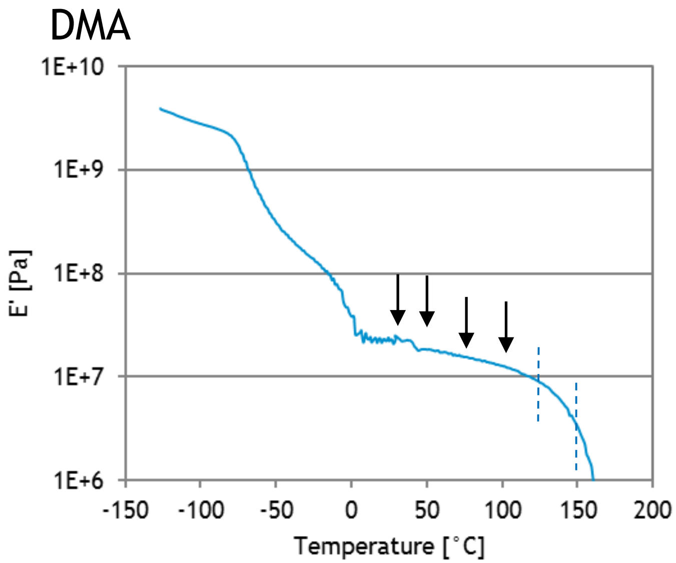


DSC on sample broken at RT



Progressive decrease of Strain at Break, drastic drop at 150˚C





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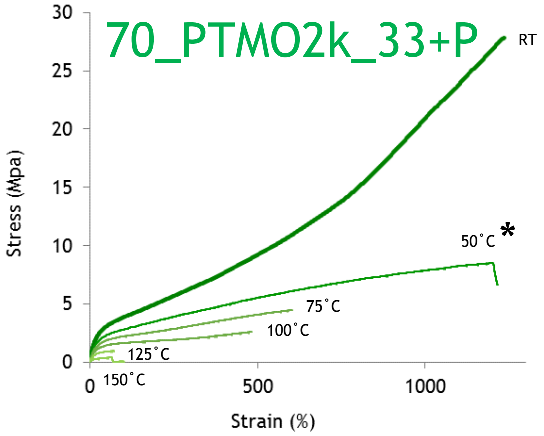
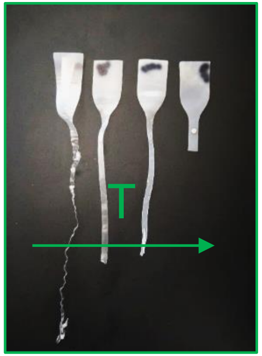
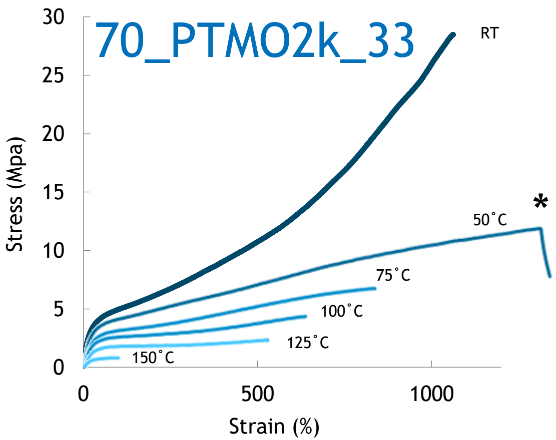
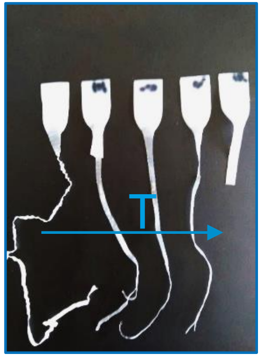
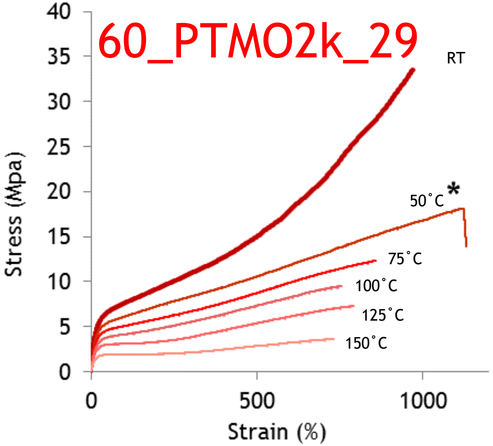
Similar trend for all the samples



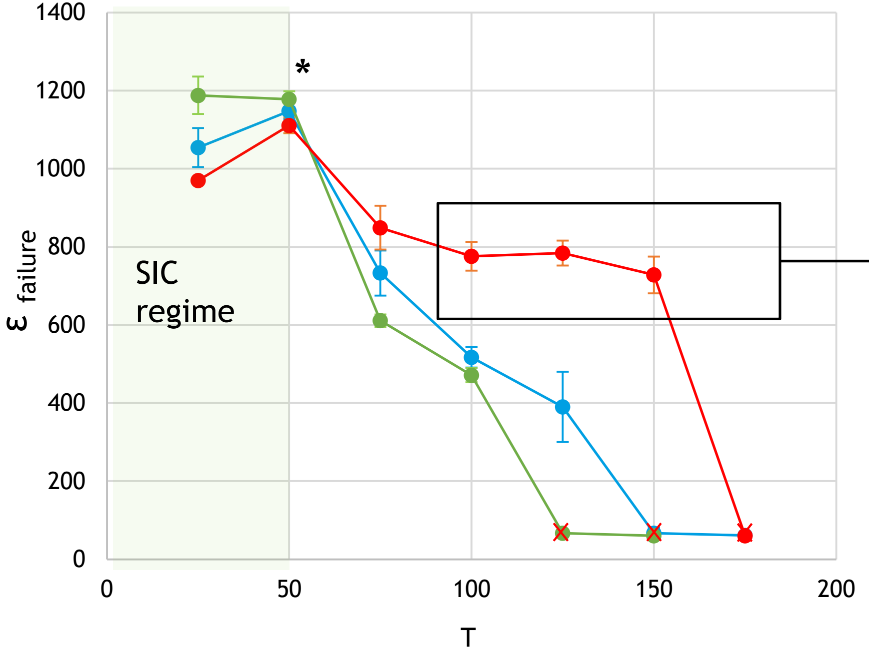








Higher Temperature resistance for the higher HB content system

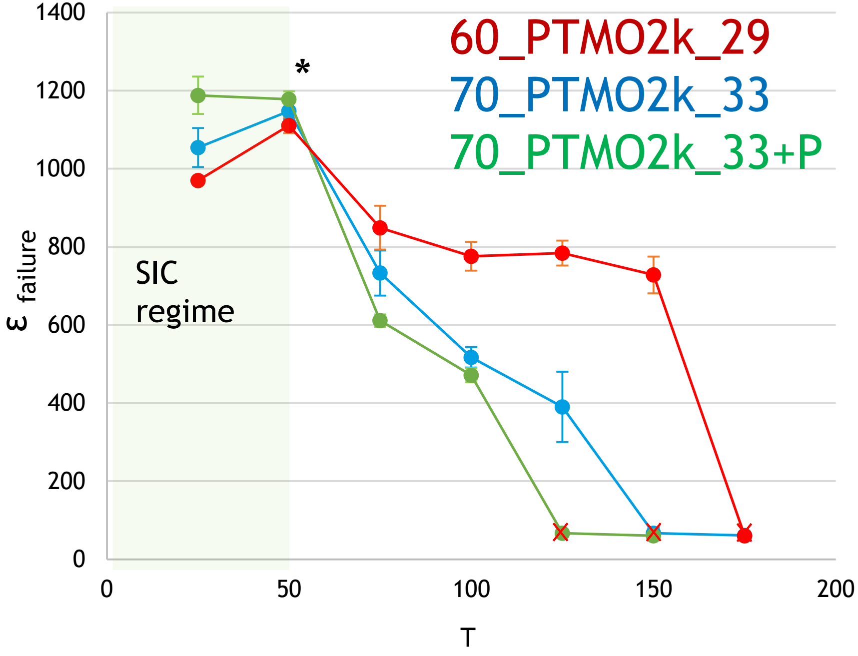


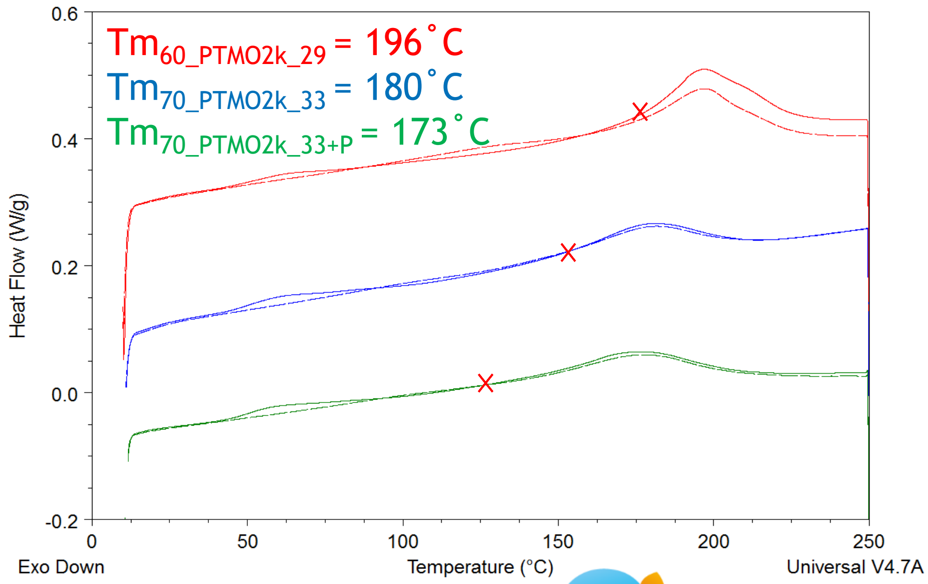
Less temperature dependent

60_PTMO2k_29
70_PTMO2k_33
70_PTMO2k_33+P

Strain at break decreases prior to reach the melting peak

Drastic drop of $\varepsilon_{failure}$ when the melting peak is reached





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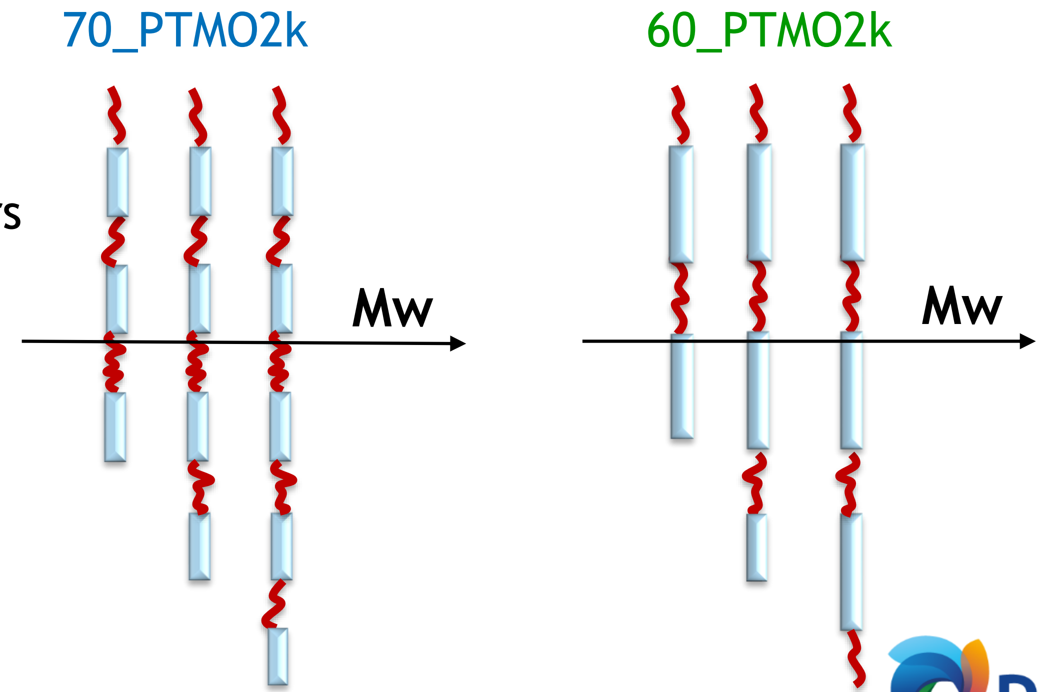
Experiments

2^{nd} system: influence of Mw

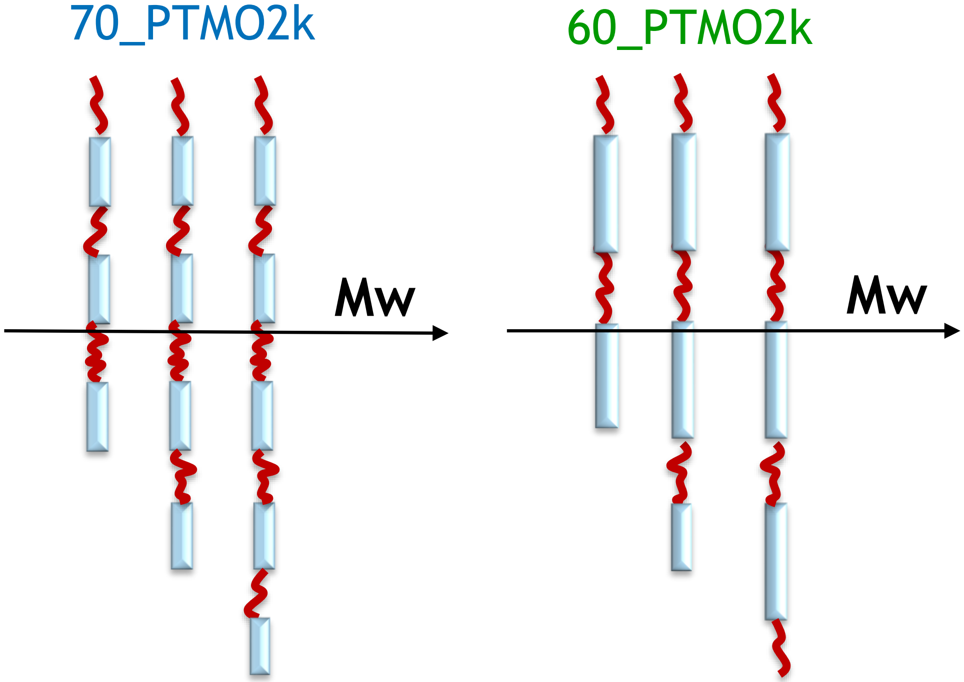
Different Mw for two SB/HB ratios

- SSPC at 0/6/12 hours
- Fixed Block length, only Mw changes



Different Mw for two SB/HB ratios

SSPC time (hours)	Mn (kDa)	Mw/Mn (-)
0	24.6	2.0
4	31.9	2.0
6	34.2	2.0
9	43.9	2.0
12	50.2	2.0
0	27.2	2.0
4	37.6	2.0
6	38.5	2.0
9	50.6	2.0
12	67.0	1.9



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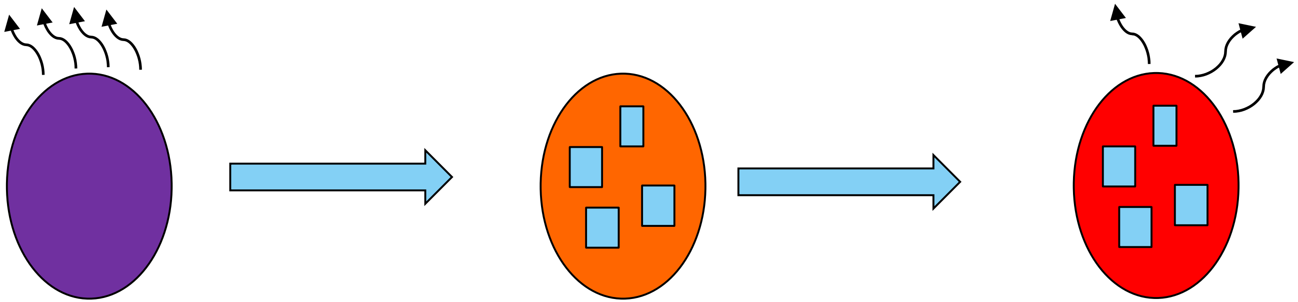
Solid State Post Condensation (SSPC)

High Temperature
Low Pressure

T < Tc
P=Atm.

Tg < T < Tmelt
Low pressure



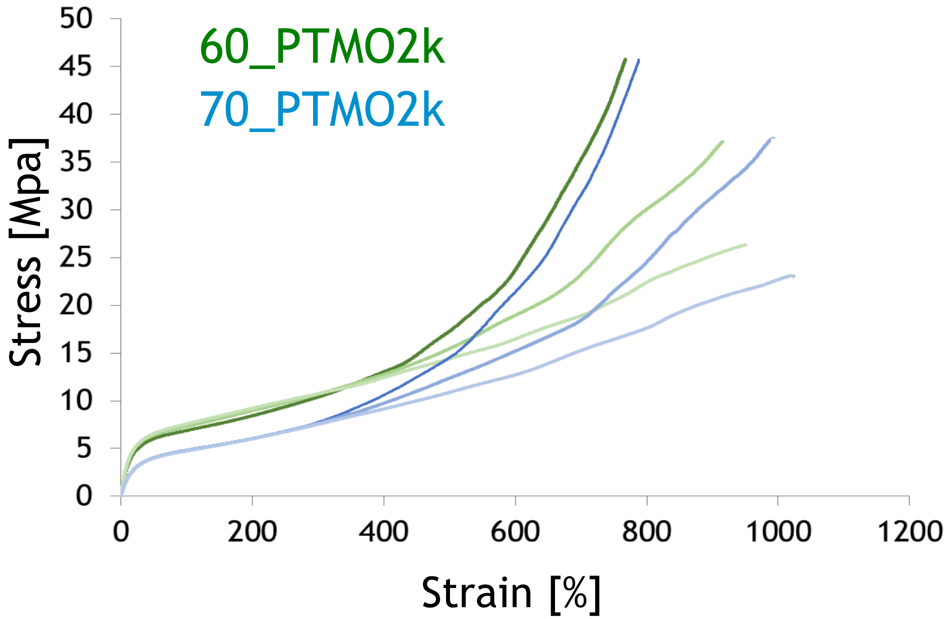
Melt polymerization:
Transesterification +
Polycondensation

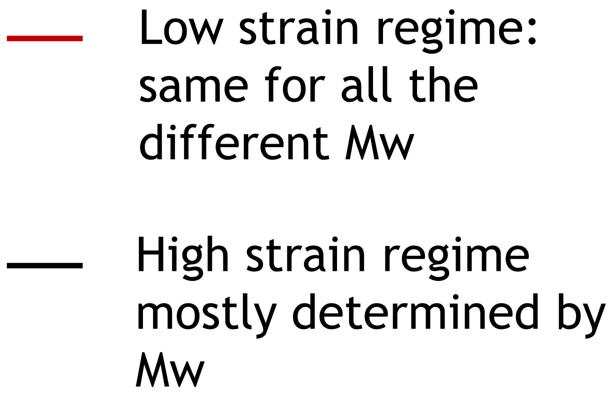
Cool down:
crystallize
fraction of hard
phase

Hold below Tmelt
at low Pressure ->
Condensation occurs, MW
increases in solid state

Increase of Hardening with Molecular Weight

Tensile test at T=RT

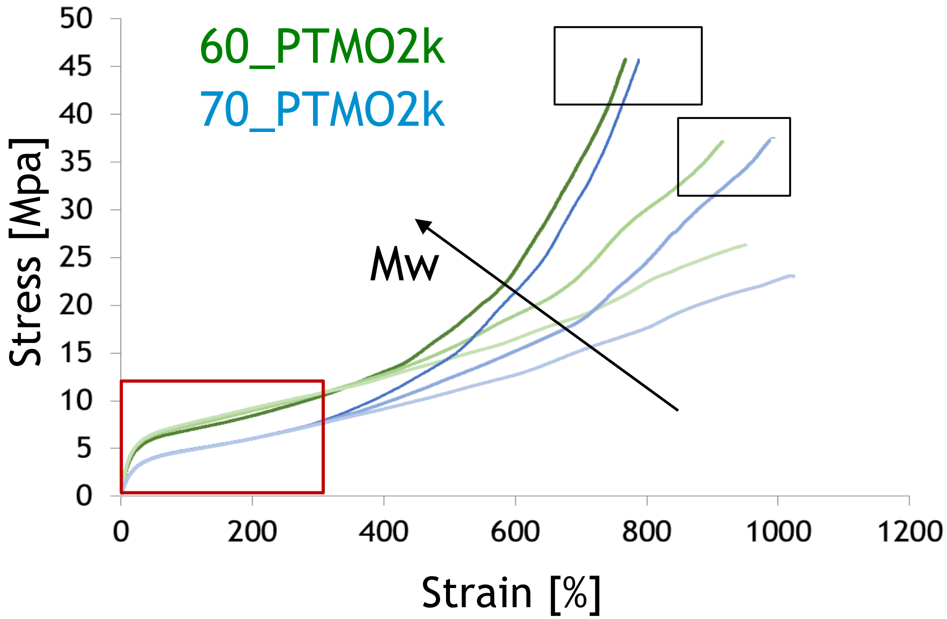




Mw increases from light to dark

Increase of Hardening with Molecular Weight

Tensile test at T=RT

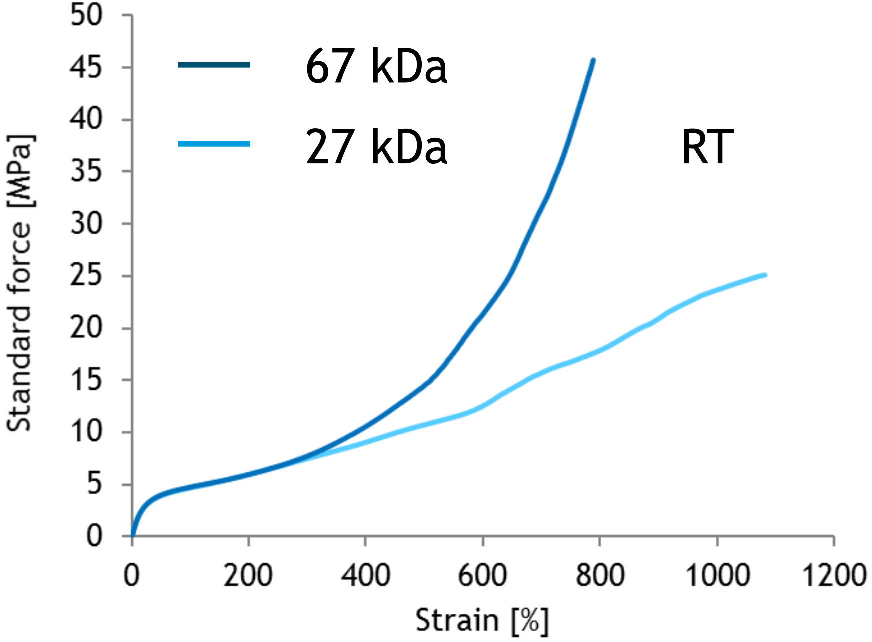


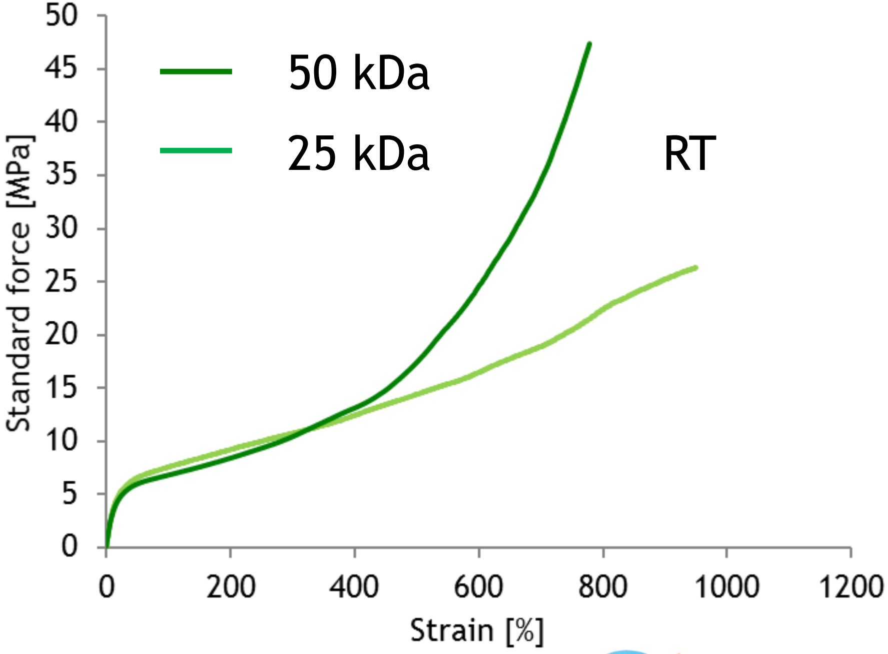
Low strain regime: same for all the different Mw

High strain regime mostly determined by Mw

Mw increases from light to dark

Increase of Hardening and Strain at break with Mn





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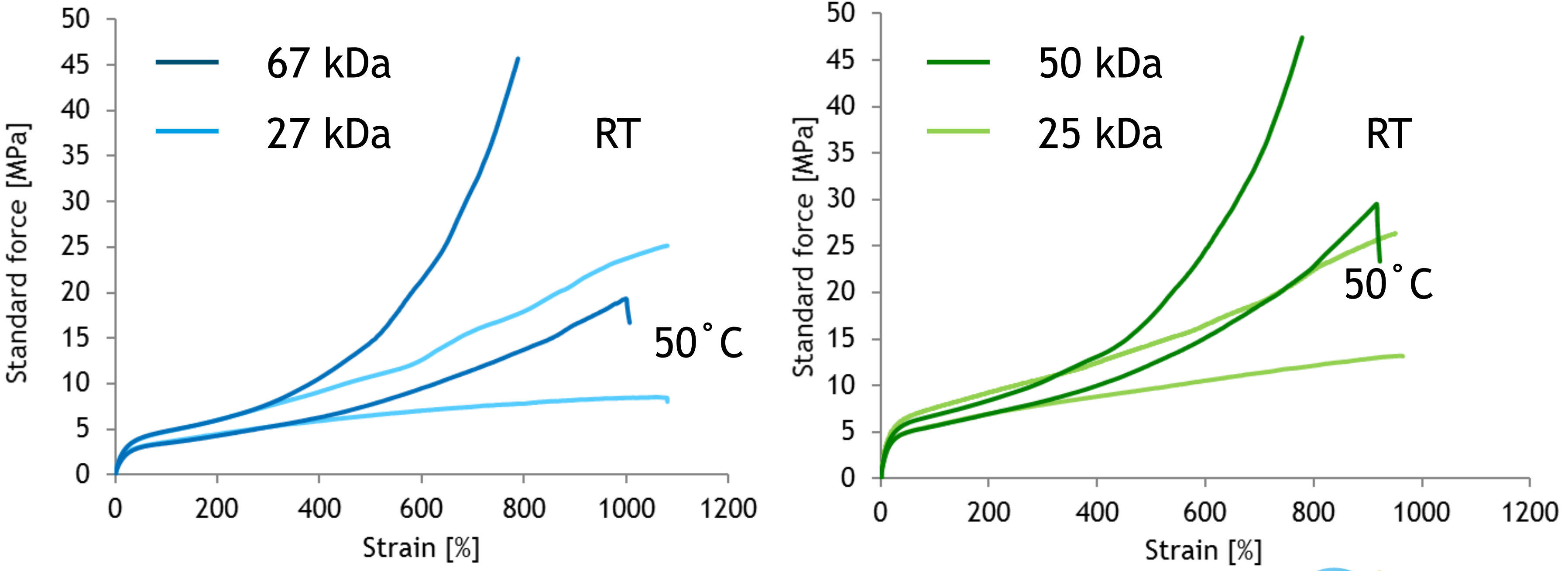
Increase of Hardening and Strain at break with Mn



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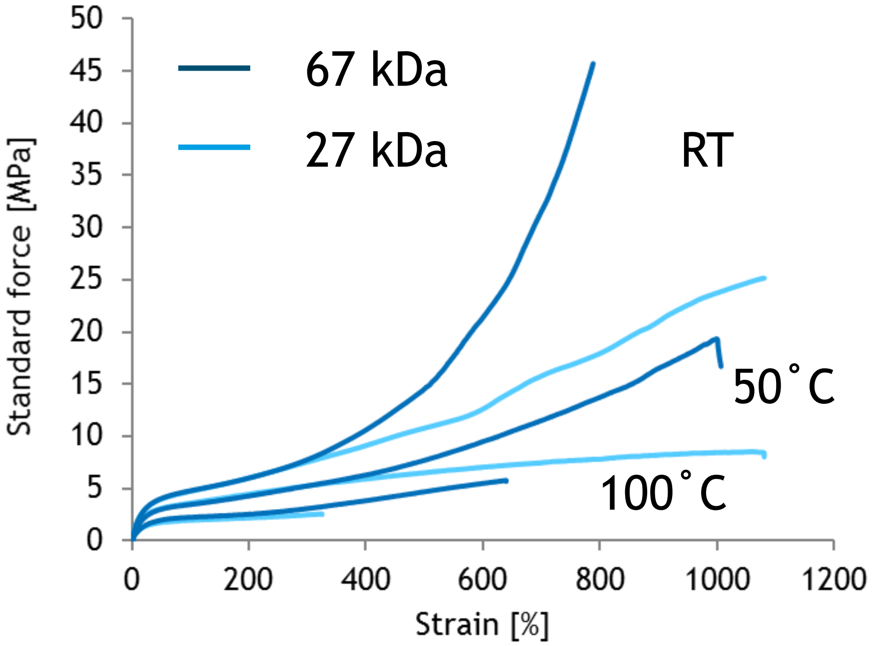
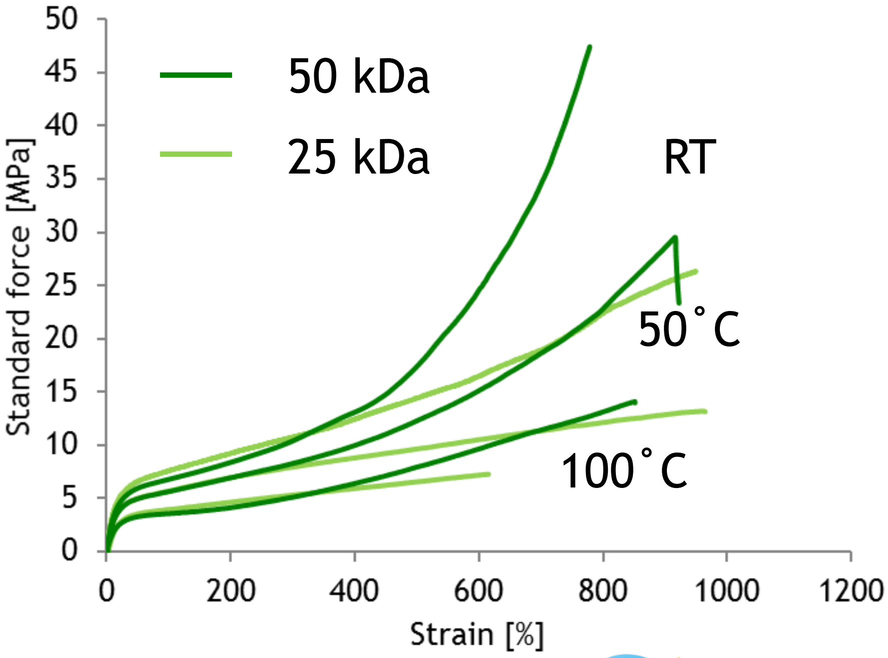
Increase of Hardening and S@b with Mn

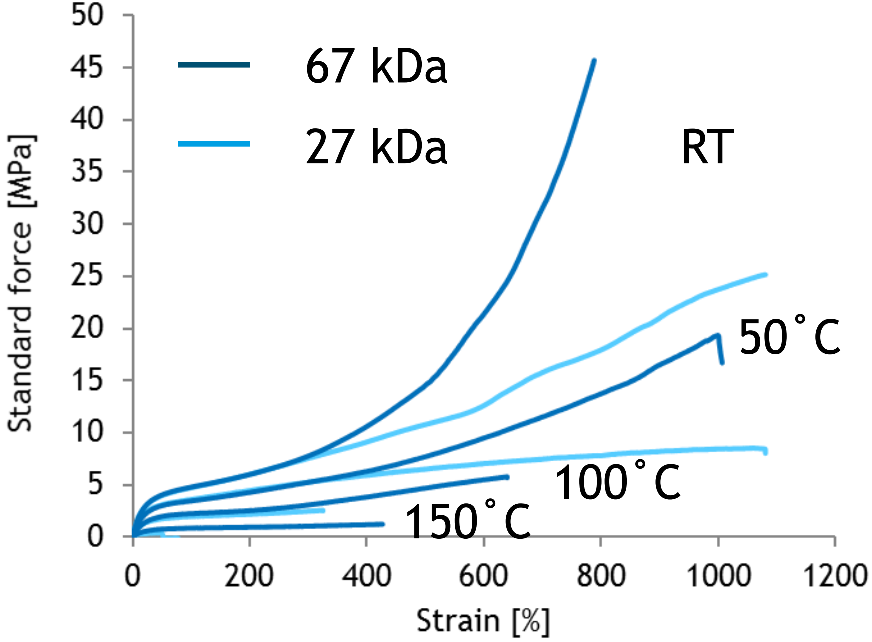
Hardening at $T>T_{SIC\_SB}$

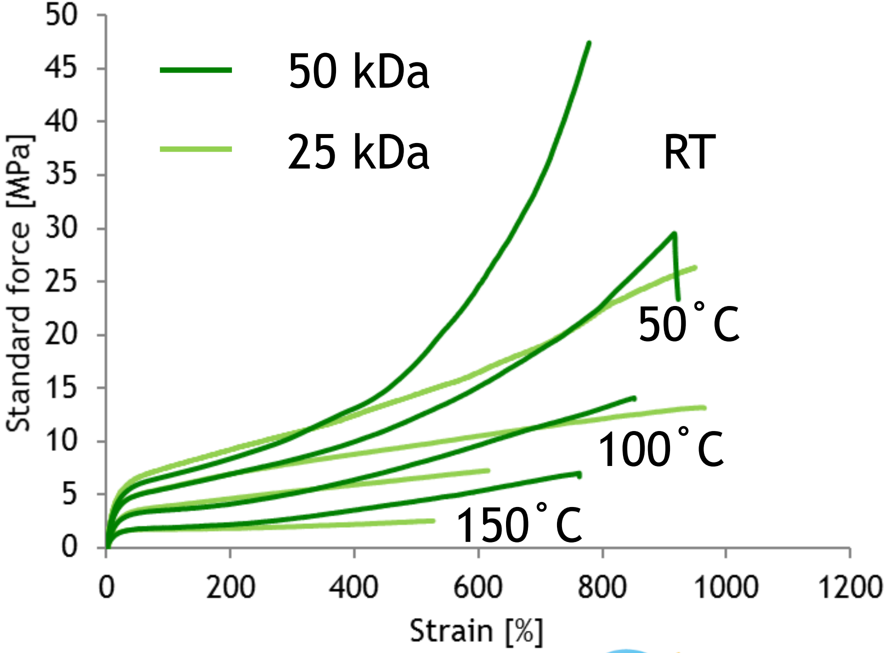




Increase of Hardening and S@b with Mn

Hardening at $T > T_{SIC\_SB}$





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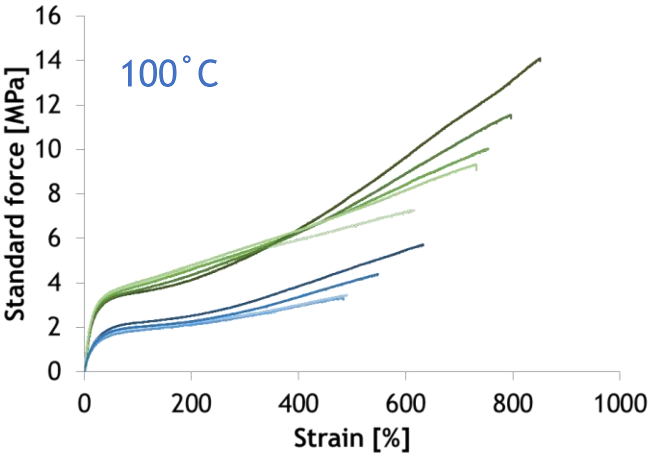
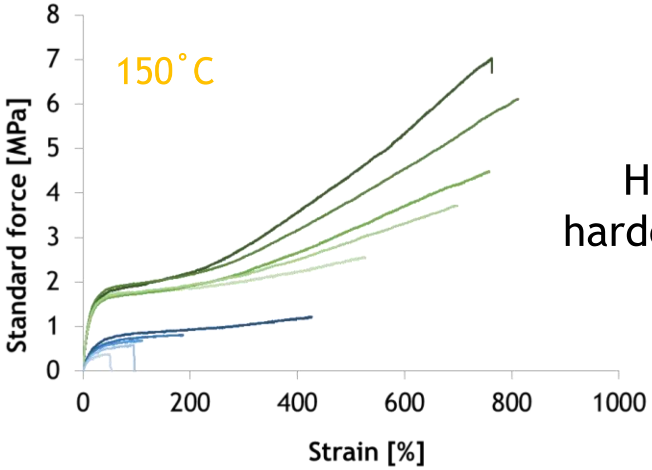
Hardening at higher temperatures

Tensile test at T>RT

60_PTMO2k
70_PTMO2k





Higher Mw samples show hardening even at T>> Tm_SIC

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Experimental results - Summary

- Increasing HB wt% (HB block length and Tm):

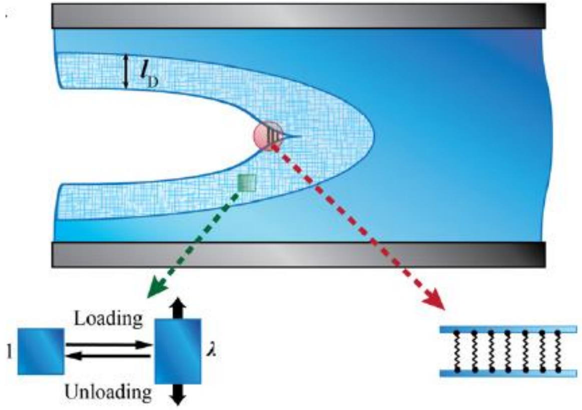
  - Higher stresses at all T
  - Higher Strain at Break at high T and delayed effect of T on Strain at Break

- Increasing Mw (Chain length/Entanglements/# HB per chain):

  - Same stresses in the small strain regime (ε~<200%)
  - Boosted hardening in the high strain regime and even at $T>T_{m,SIC\_SB}$
  - Higher Strain at Break and Stresses at higher Temperatures

Future directions

Fracture tests



Why?

- Look at where the failure starts, how the crack propagates at different T
- Quantify the energy needed to propagate the crack
- Tensile tests assume a homogeneous stress distribution
- Characterize the switch from ductile to brittle

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Fracture tests: Temperature dependence

RT

Blunting and residual plasticity in the fracture shape

100˚C

Almost no blunting and sharp fracture shape

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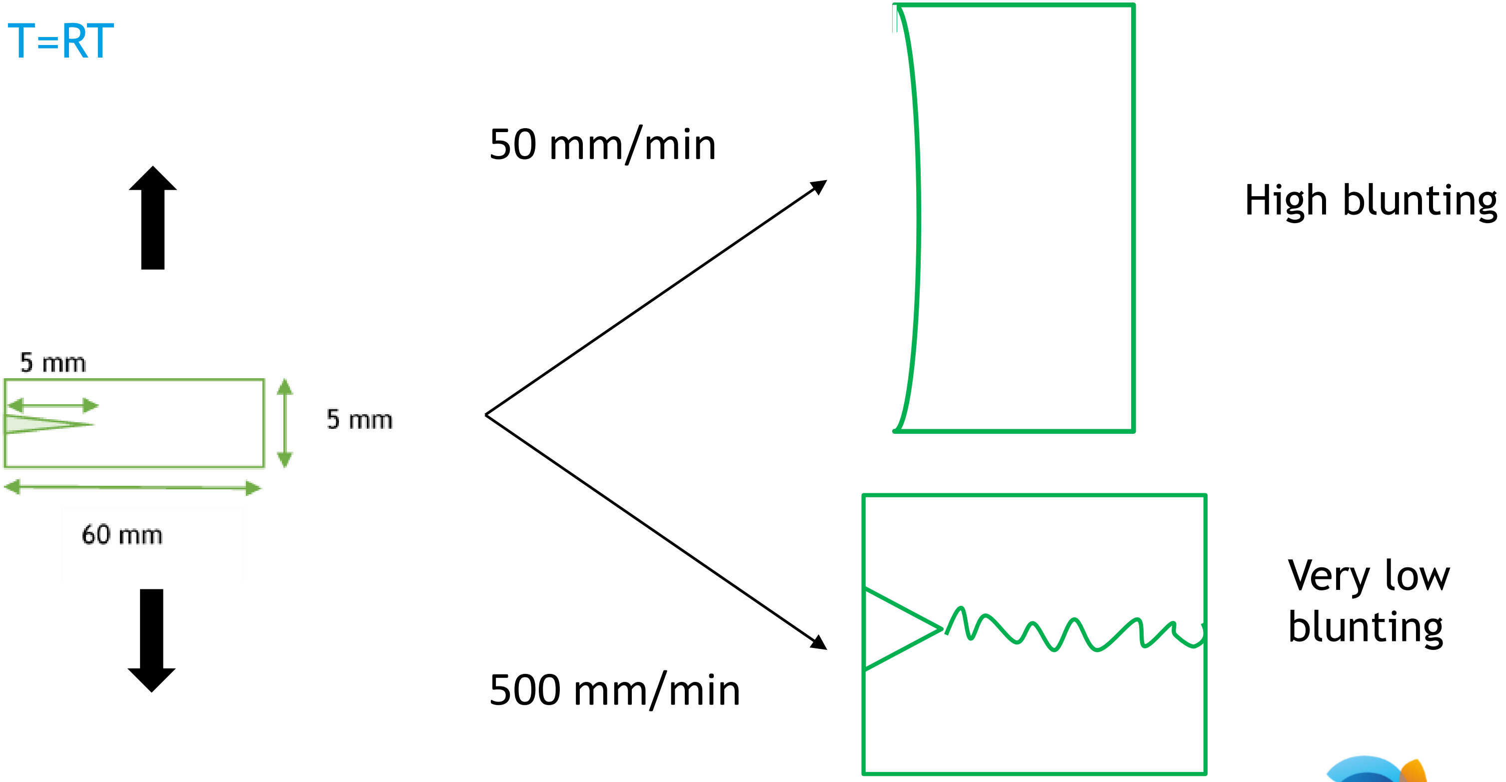
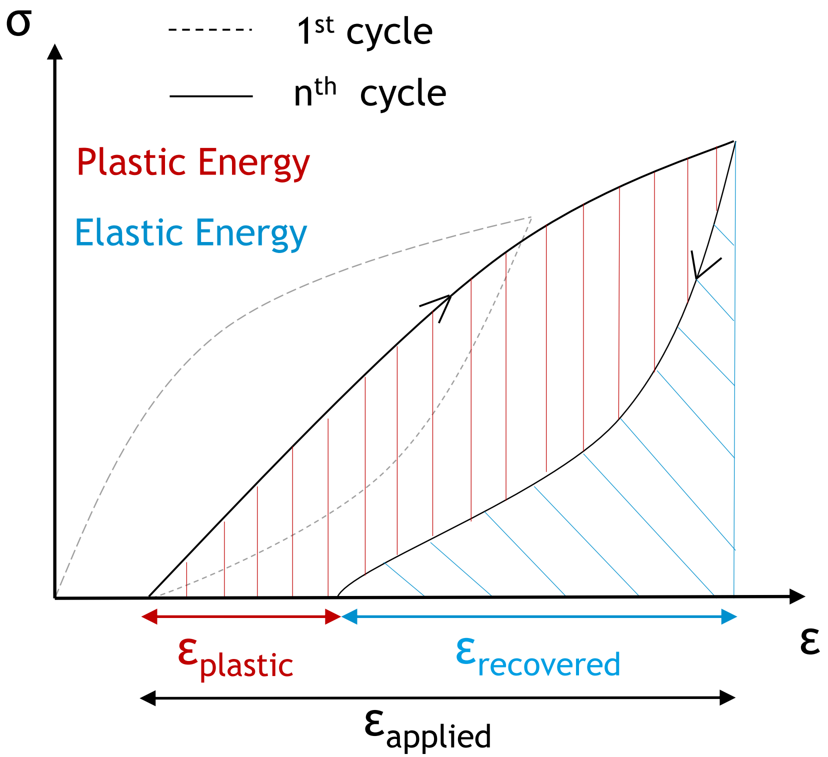
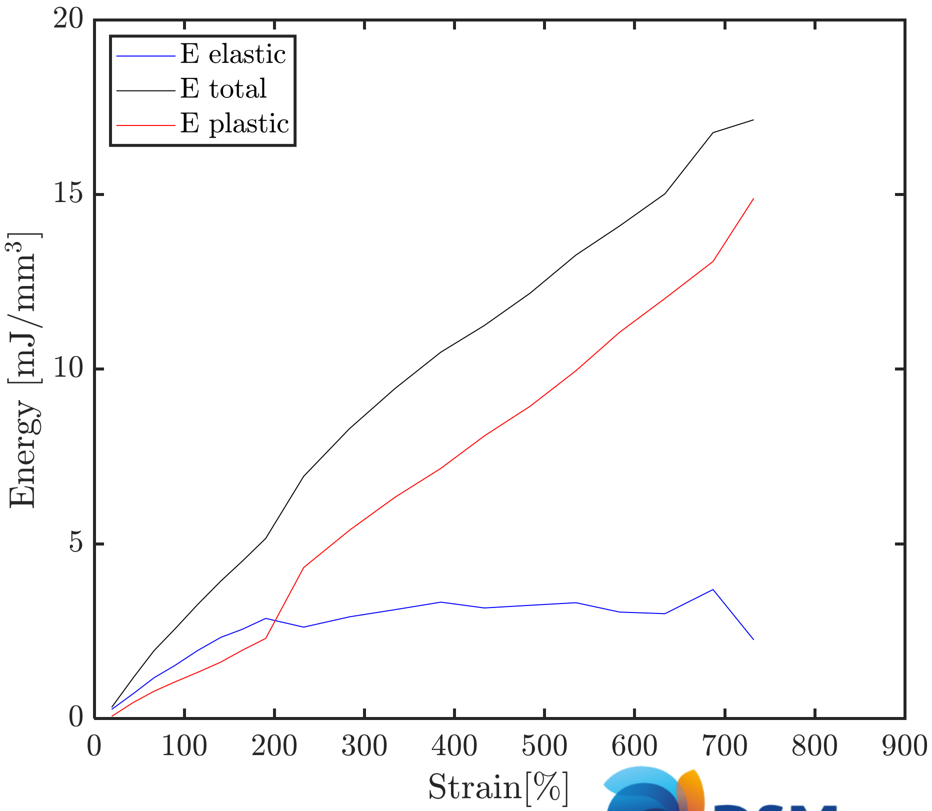
Fracture tests: strain rate dependence

At T=RT



Elastic energy available for the crack to run





DSM
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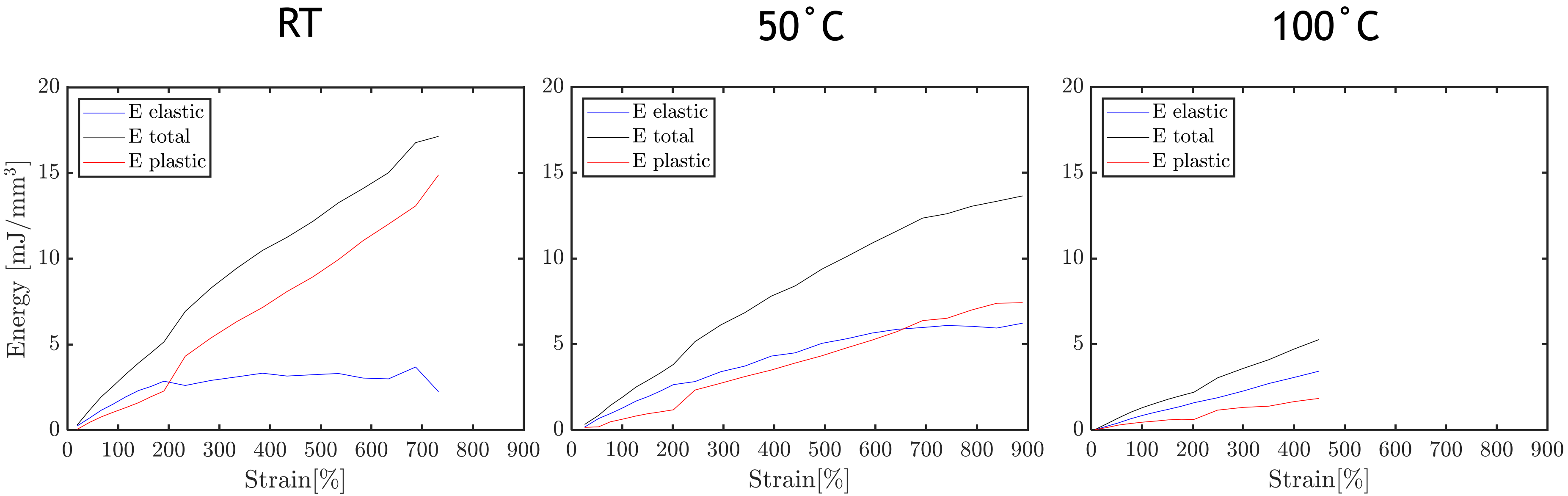
Elastic and plastic behavior: effect of Temperature

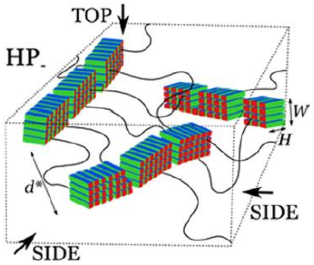
Calculation done on Cyclic tests run on 70_PTMO2k_33



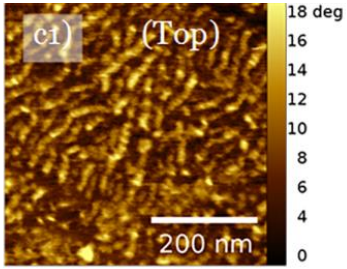
Influence of the initial morphology

Hot-press (HP) and Solvent casting (SC)

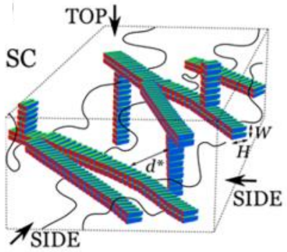
<u>HP samples</u>



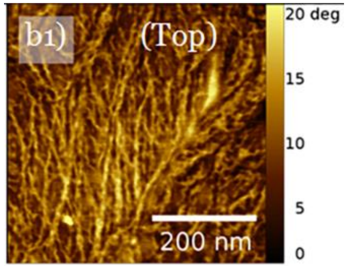
Top view →



SC samples



Top view →

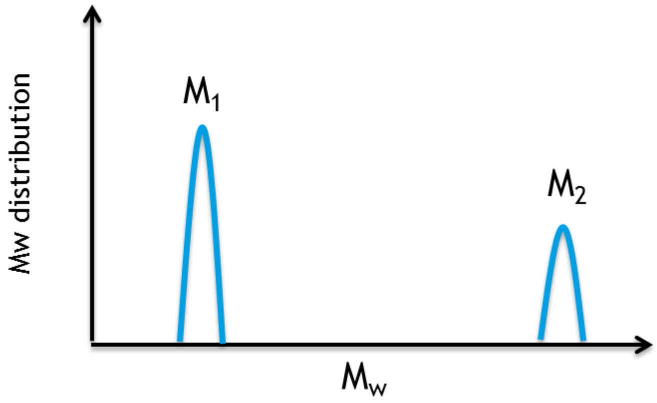


"Process-Oriented Structure Tuning of PBT/PTHF Thermoplastic Elastomers"
[Matthias Nébouy, André de Almeida, Solène Brottet, and Guilhem P. Baeza]

Effect of Molecular Weight - Blends

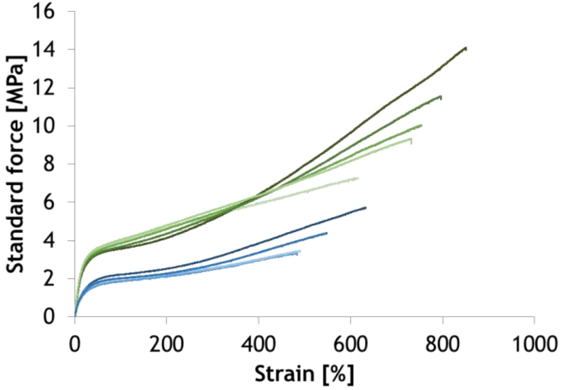
- Is the average molecular weight that counts? Or a fraction of longer chains is enough?

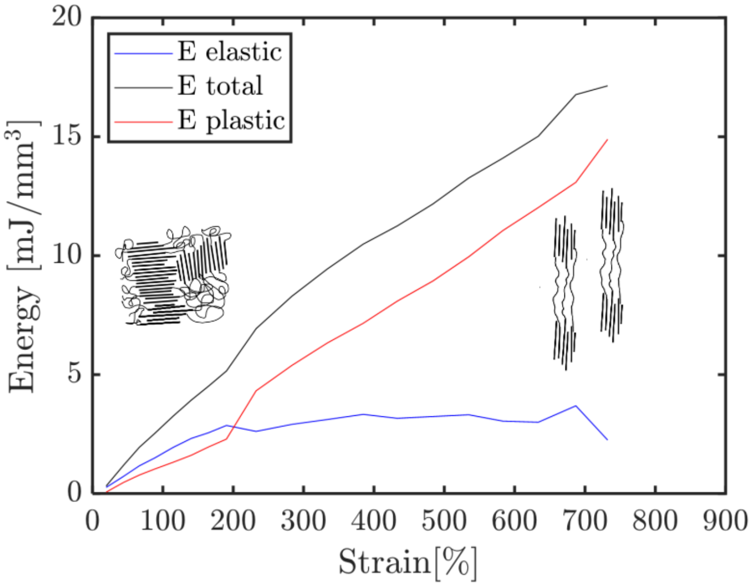
- Where does the hardening come from at higher T for the higher Mw samples?



- Is the increase of strain at break due to more entanglement between chains or because of more Hard Block per chain?

Wrap-up





Investigation of the effects of SB/HB, Mw and Temperature → Trying to quantify what happens locally, where the failure starts → Structural transitions: change in how the energy is stored in the sample

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