ESR 9 – Simone Sbrescia

Enrolled at the UCLouvain – Supervisor: Evelyne Van Ruymbeke

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)"*

Background

Graduated in Materials Engineering at the University of Naples Federico II 2015-2017

Internship at the Italian Institute of Technology, Naples – 2017

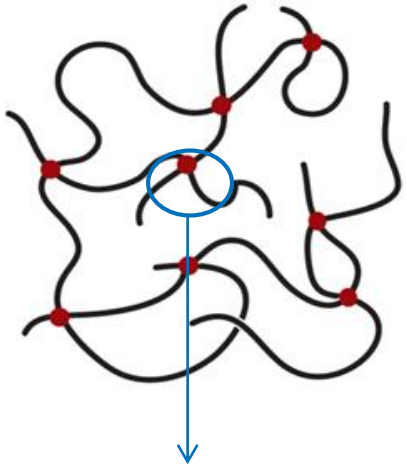
"A novel platform for 3D Tissue culture: full differentiation in microfluidic device and continuous monitoring of barrier functions"

Outlines

- Thermoplastic Elastomers (TPEs)
  Overview
- Research project starting point
  Tests done and planned- exploring the failure mechanism
- Actual developed model
  Predicting the failure mechanism: achievements and limitations
- Improvement of materials properties
  Proposals – Questions – Expectations

Thermoplastic Elastomers (TPEs)

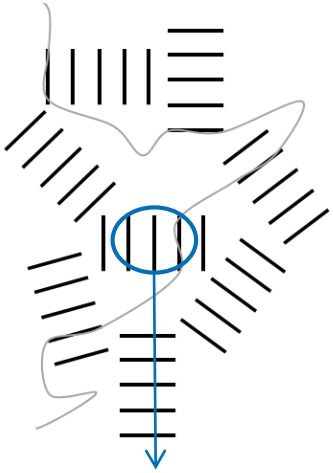
Elastomer



Chemical crosslinks

✓	High elongation at break at room temperature	✓✓
✓	Easy tunable mechanical properties	✓✓
✓✓	High creep resistance	✓
✓	Resistant to high temperatures	✗
✗	Melt processable: injection molding, blow molding, …	✓
✗	Recyclable	✓

TPE



Physical crosslinks

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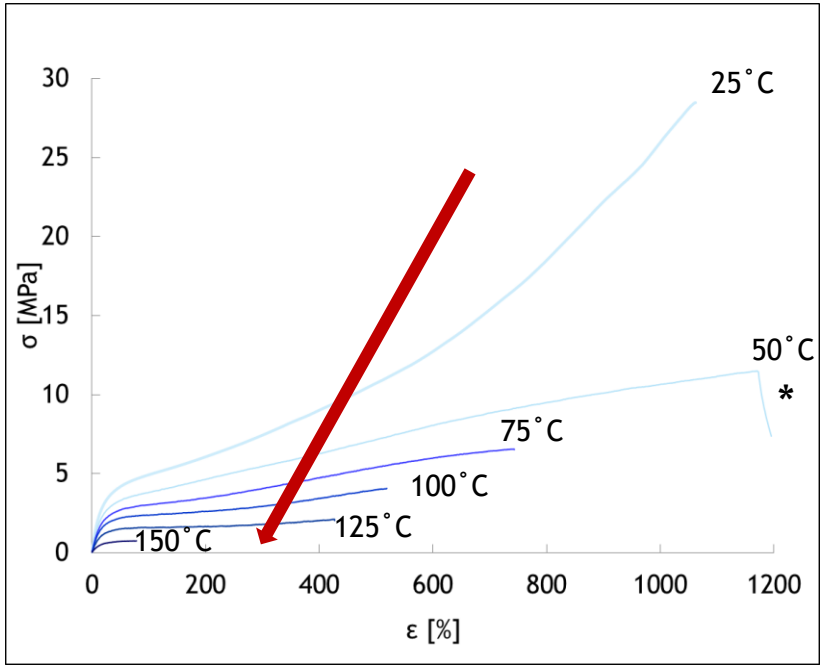
Thermoplastic Elastomers (TPEs)



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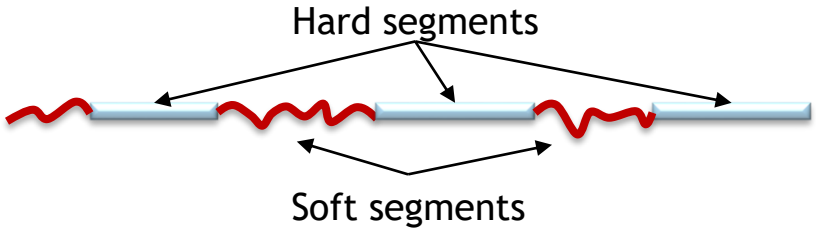
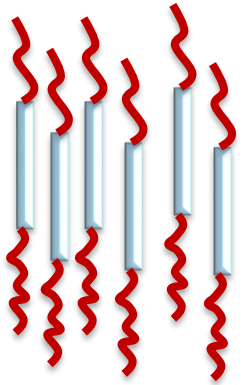
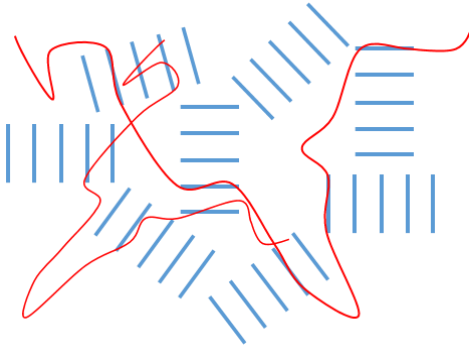
Thermoplastic Elastomers (TPEs)

Segmented block copolymer







Hard phase

Soft phase

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Thermoplastic Elastomers (TPEs)

Examples of different systems broadly

Well definite hydrogen bonding systems
monodisperse HBs, ribbon like crystals

Copolyesters
polydisperse blocks, well defined melting points

TPUs (Thermoplastic PolyUrethanes)
less well defined melting point -> mixture hardblock crystals and H-bonded domains

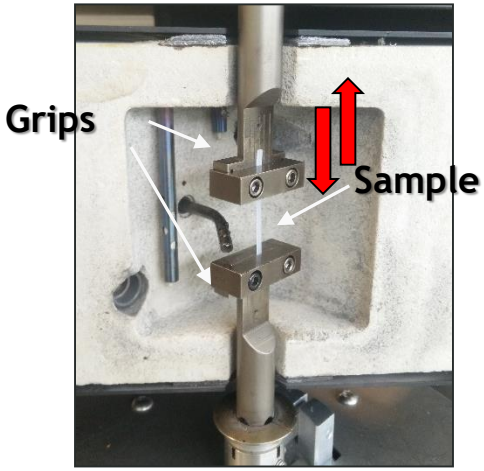
Investigate TPEs'properties

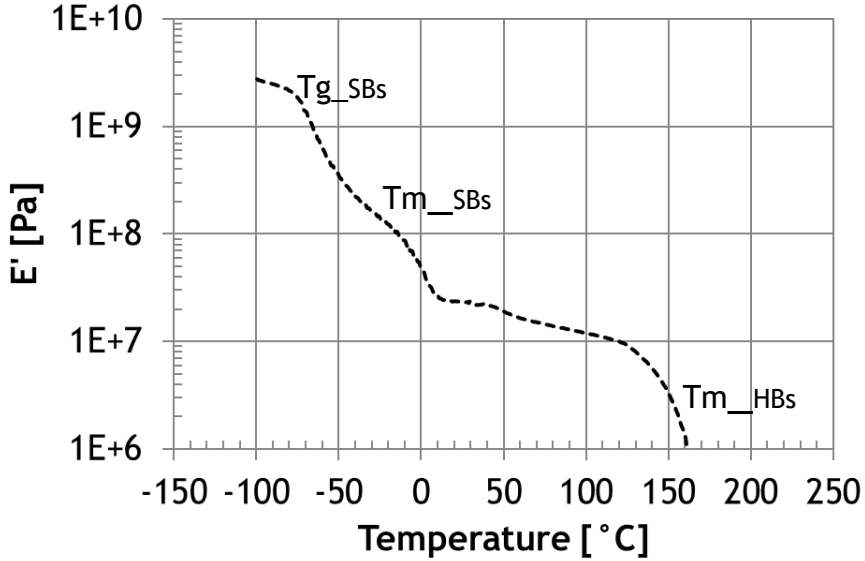
Adopted techniques to investigate the behavior at room and higher temperatures

- Dynamic Mechanical Analysis (DMA)
- Tensile test
- Fracture test
- Cyclic test

Running tests: Dynamic Mechanical Analysis

A sinusoidal stress is applied and the strain in the material is measured





- E' Vs T
- SBs Tg
- SBs Tm
- HBs Tg

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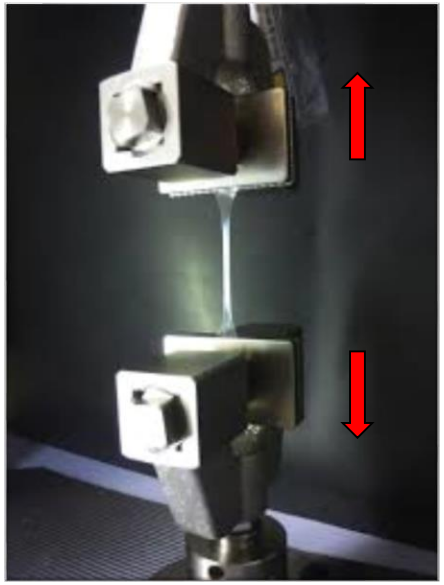
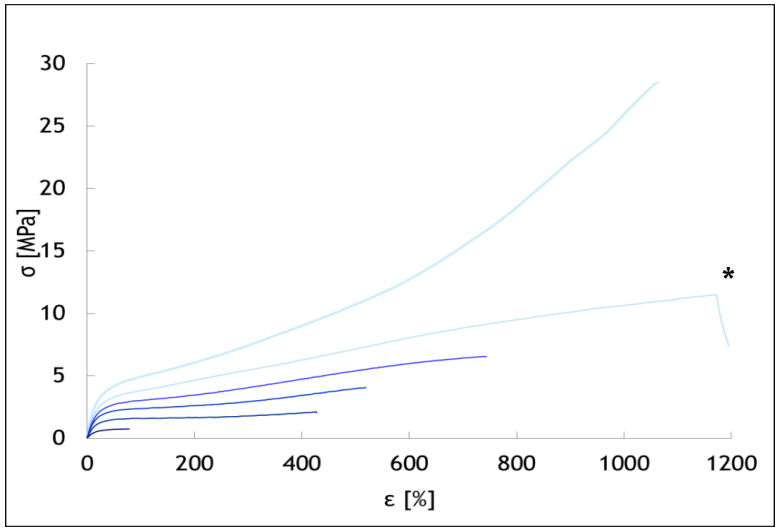
Running tests: Tensile test

Adopted techniques to investigate the behavior at high temperatures





- σ Vs ε
- ε_f , σ_s

- No failure initiation
- No failure propagation

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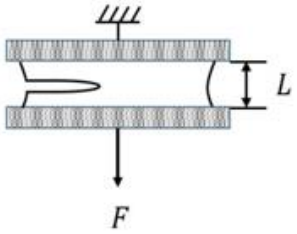
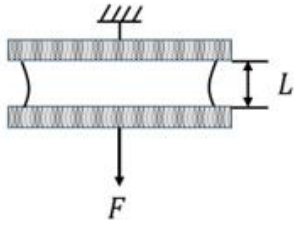
Further tests: Fracture test

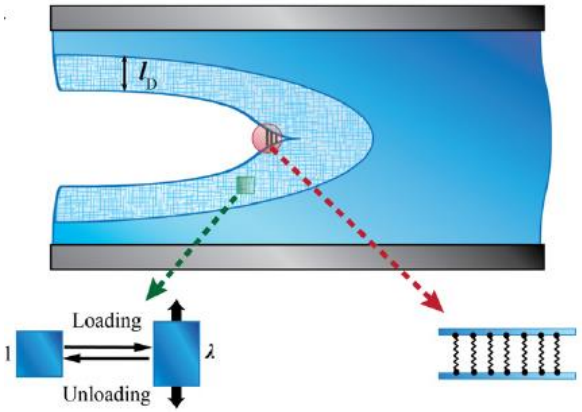
Looking closer at where the failure starts

Notched sample



Unnotched sample





- Energy for crack initiation
- Energy for crack propagation
- Crack shape

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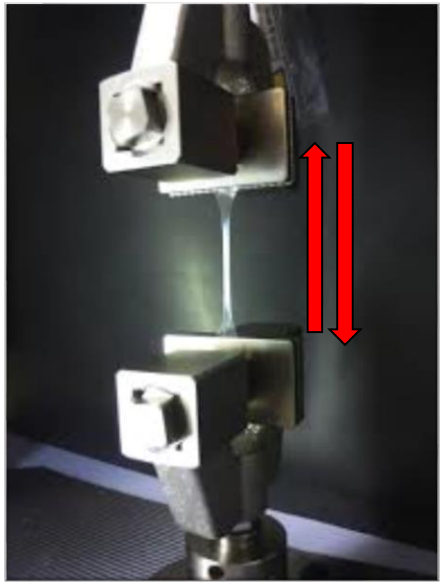
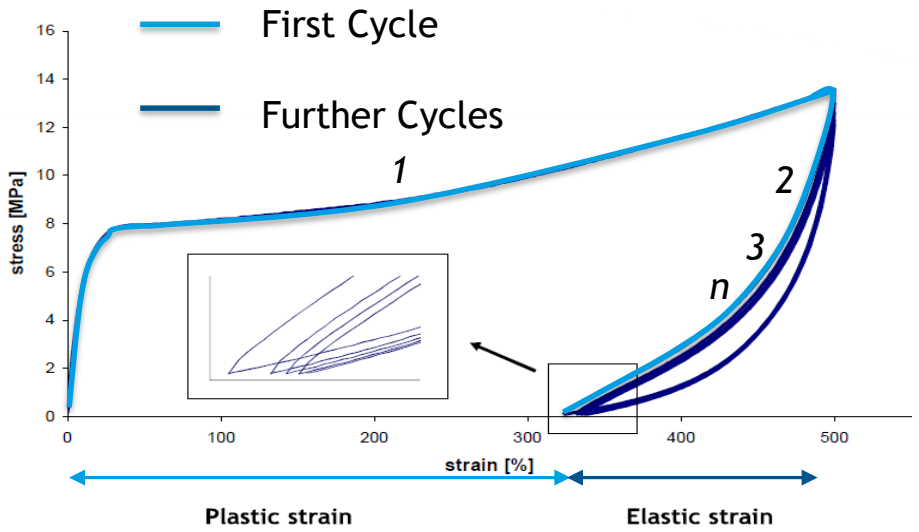
Further tests: Cyclic test

Structural transitions during stretching





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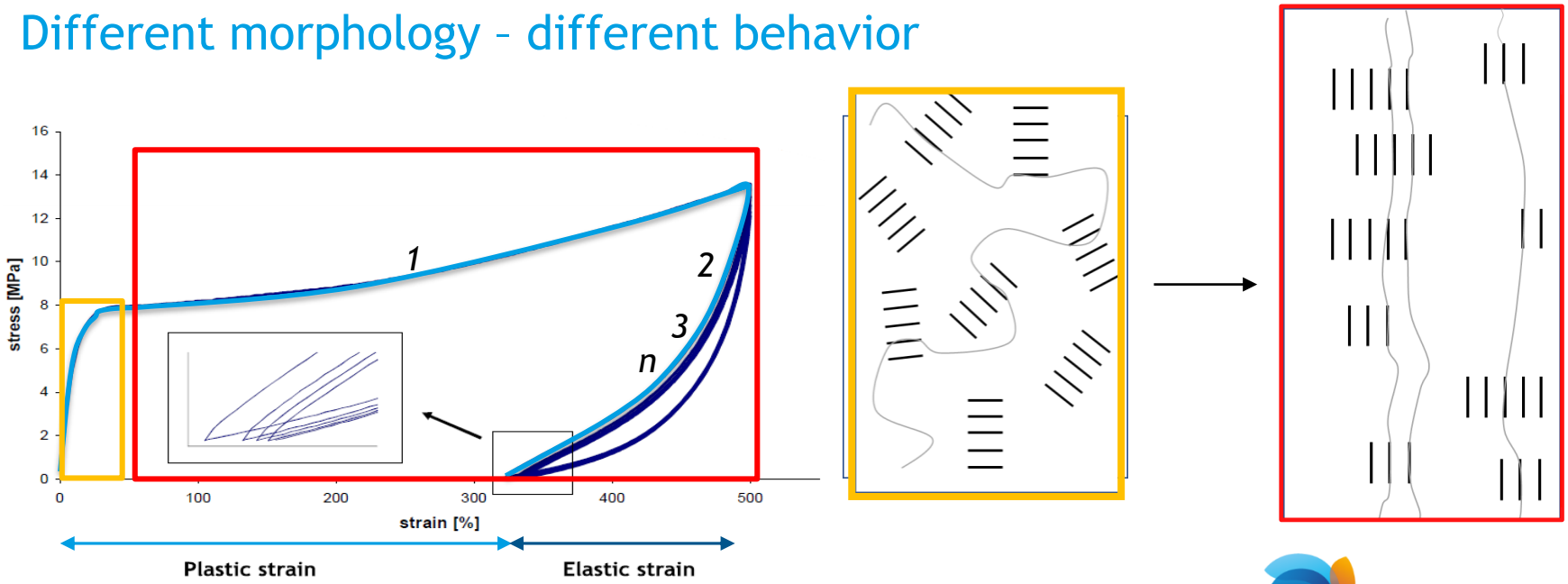
Further tests: Cyclic test

Structural transitions during stretching

Different morphology – different behavior



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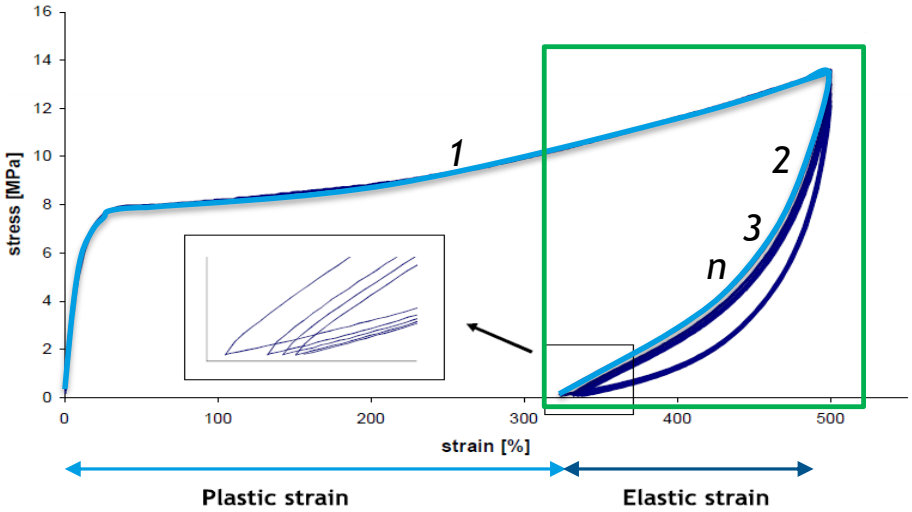
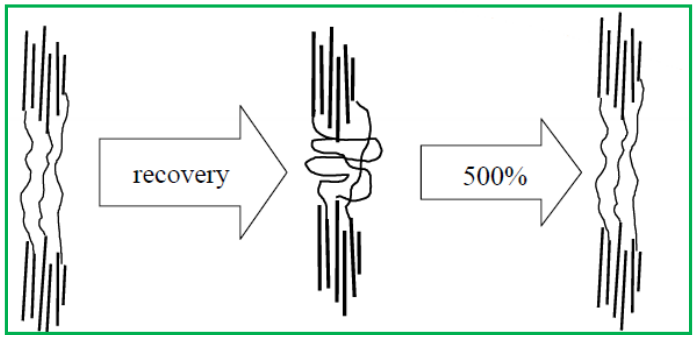
Further tests: Cyclic test

Structural transitions during stretching

Different morphology – different behavior





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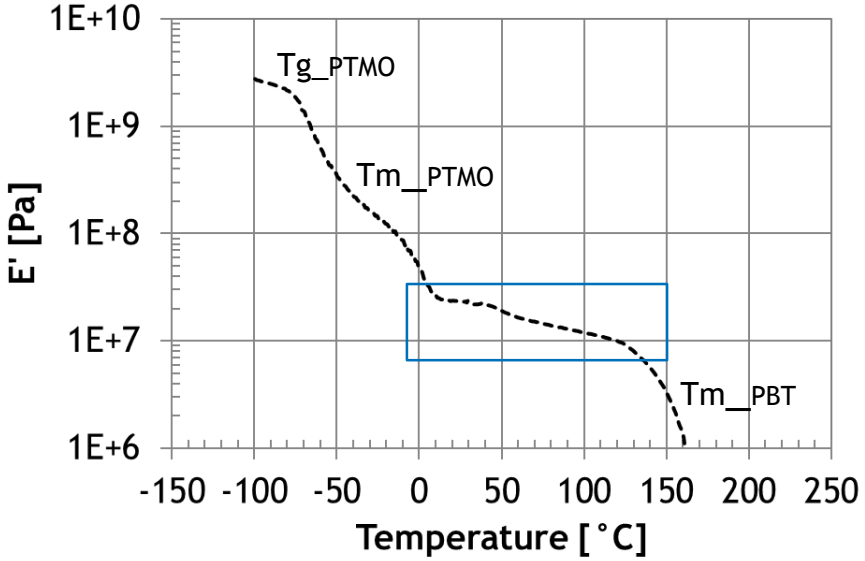
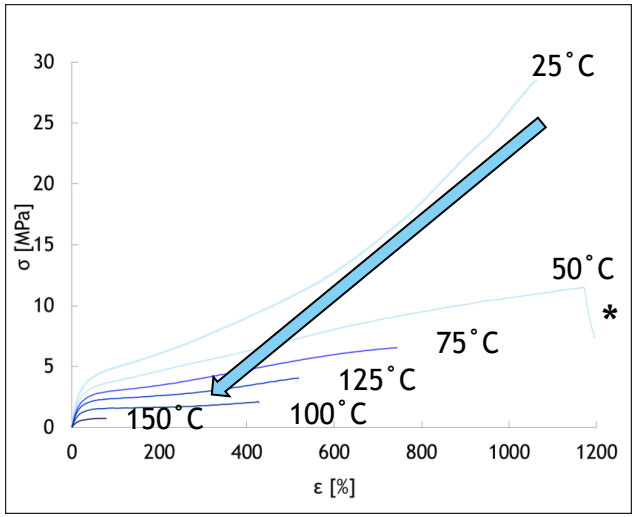
Experimental observations

Common undesired behavior of TPEs

Strain at Failure (ε_b) dramatically decreases with Temperature increase





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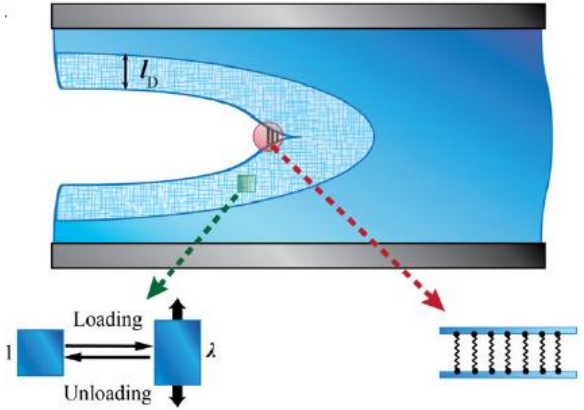
Experimental observations

Common undesired behavior of TPEs

Different fracture mechanisms at different temperature?



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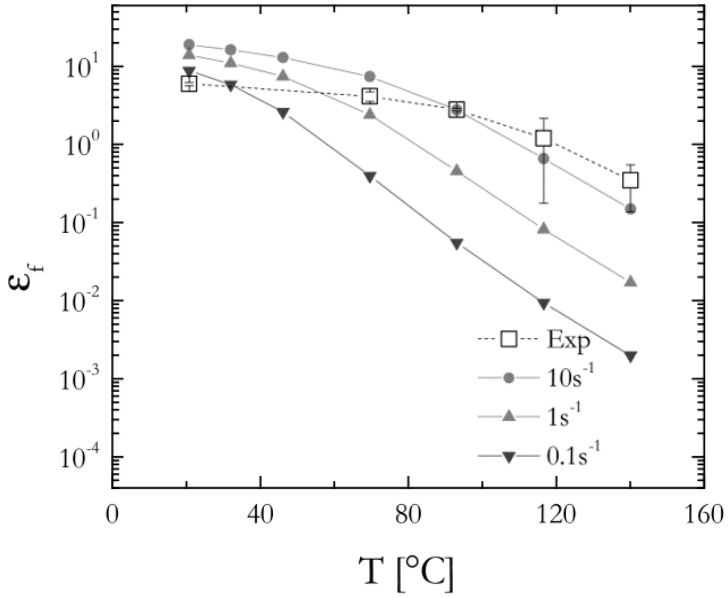
Model for TPE Failure

Able to describe:

- Drop of strain at break by increasing Temperature
- Increase of strain at break by increasing Molecular weight (M_w)
- Increase of strain at break by increasing Strain rate

$$\varepsilon_f = \frac{k_B T}{v^* a} \ln\left[1 - \frac{\dot{\varepsilon}}{k_0}\frac{v^* a}{k_B T} e^{\frac{\Delta G - b v^*}{k_B T}} \ln A_{th}(M_w)\right]$$



"A model for failure in thermoplastic elastomers based on Eyring kinetics and network Connectivity", [S. Aime, N. D. Eisenmenger, and T. A. P. Engels]

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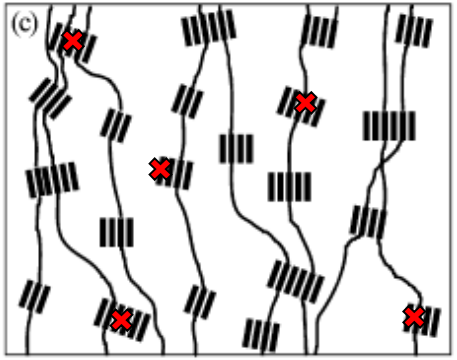
Failure Mechanism

Current model to explain reduction in strain-at-break with T

Loss of connectivity

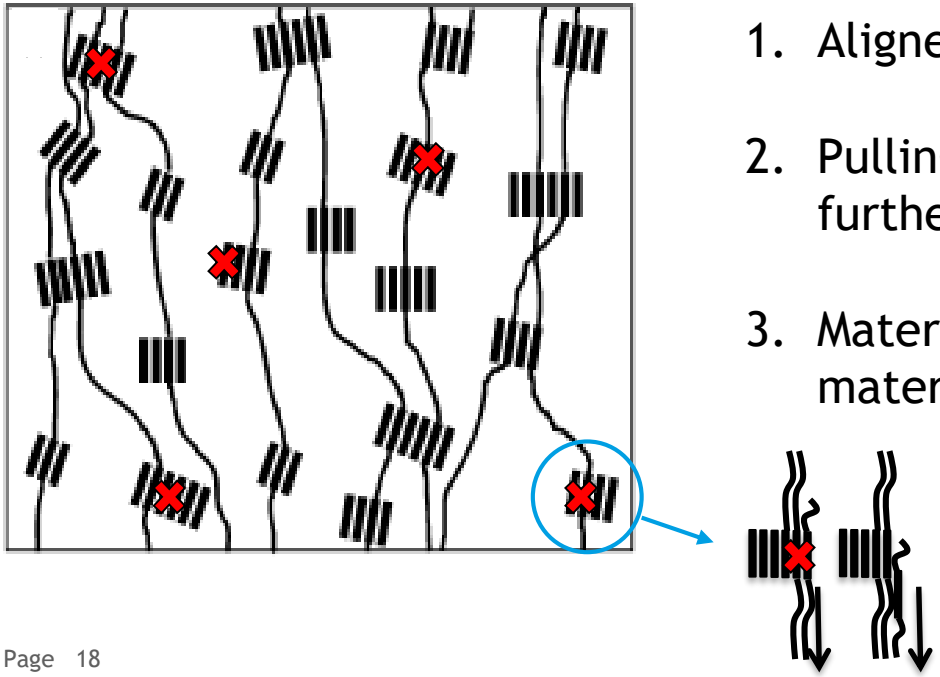


Kinetics of bond breaking/reformation

$$AB \leftrightharpoons A + B$$

Failure Mechanism: Connectivity

Loss of connectivity



1. Aligned chains connected via HBs
2. Pulling out of chains by applying further strain
3. Material fails when two parts of the material are not connected anymore

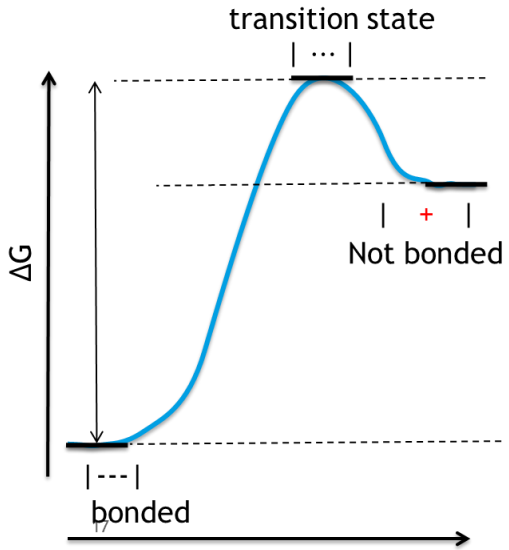
Failure Mechanism: Kinetics

HBs activation energy to break apart

Sensitive to *temperature* and *stress* (Eyring-like behavior)

- No stress applied

$$AB \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} A + B$$



"A model for failure in thermoplastic elastomers based on Eyring kinetics and network Connectivity",
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Failure Mechanism: Kinetics

HBs activation energy to break apart

Sensitive to *temperature* and *stress* (Eyring-like behavior)

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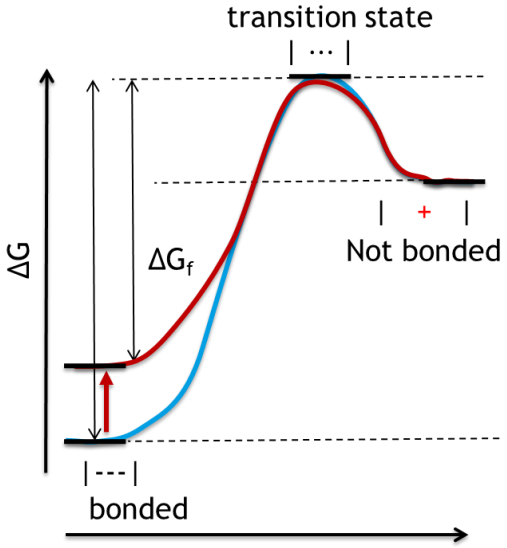
$$AB \underset{k_{21}}{\overset{k_{12}^{stress}}{\rightleftharpoons}} A + B$$



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Model's limitations

Doesn't take into account:

- Orientation of the HBs - How quickly the morphology reaches the fibrillar state could help improve properties. ⟹ Cyclic tests

- Entanglements – the dependence on molecular weight suggests that entanglements could contribute to strength in addition to HB above a critical Mw. ⟹ Model system ready to be tested

- Stress intensification/different mechanisms at different temperature - The model assumes a single failure mechanism. This may be false. ⟹ Fracture tests

Improving elongation-at-break

How can we increase the elongation at break at higher temperatures?

Connectivity

Modifying SB/HB ratio

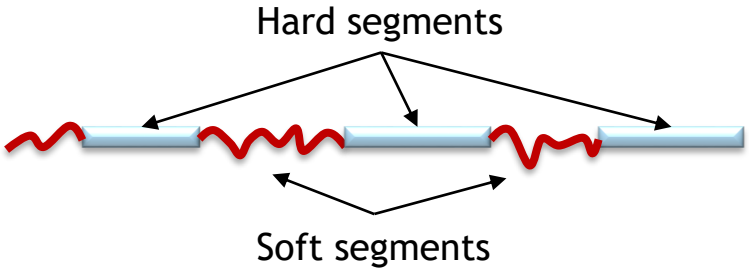
Increasing Molecular Weight

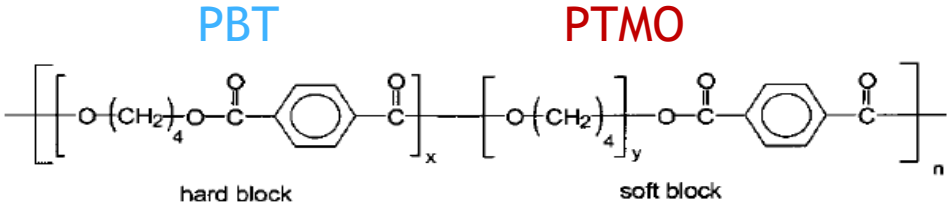
Kinetics

Adding additional dynamics to the system

Model Experimental System

Structure: molecular level

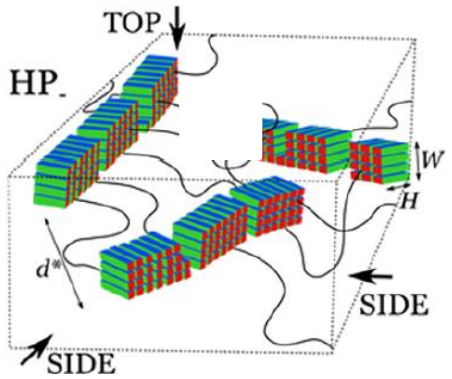




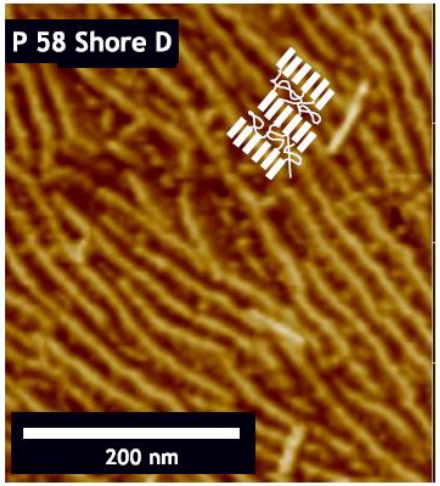
Polycondensation-based, semi-crystalline block copolymer, TPEs composed of poly(butylene terephthalate) (PBT) blocks to make up the solid phase (HBs) and polyether-based blocks (PTMO) to make up the soft phase (SBs)

Model Experimental System

Structure: molecular level



Top view →



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

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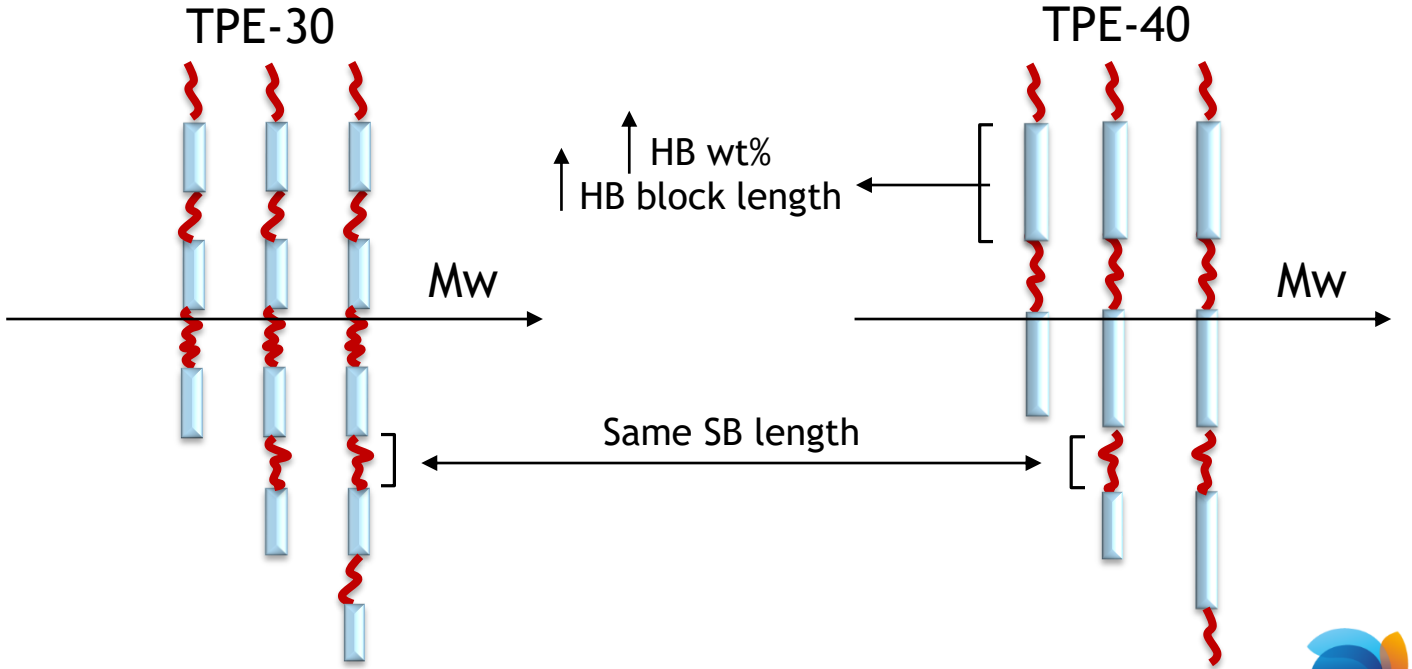
Model Experimental System

Different SB/HB ratio and different Mw



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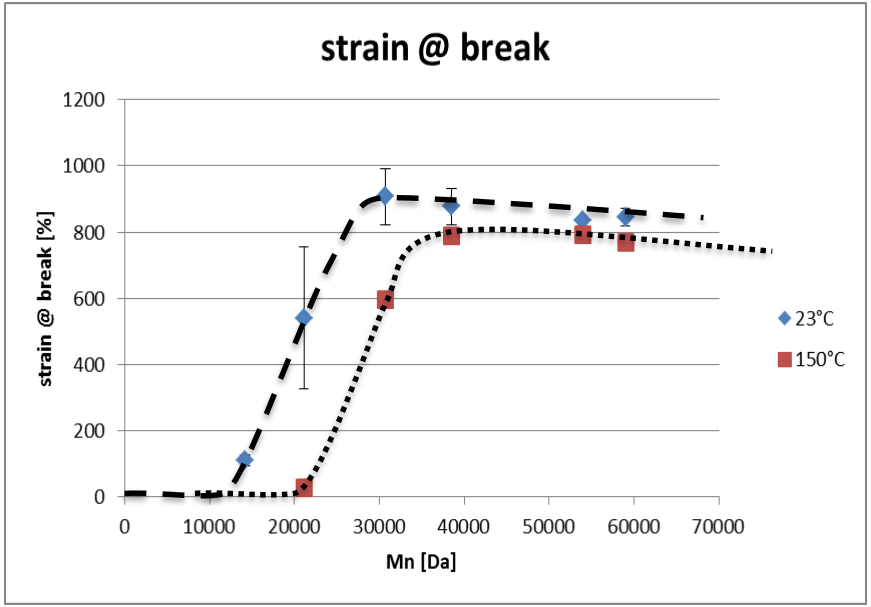
Questions

Molecular weight

Mw increases elongation at break at room temperature and delays the effect of high temperature on strain at break

More entanglements between chains?

More HBs per chain?



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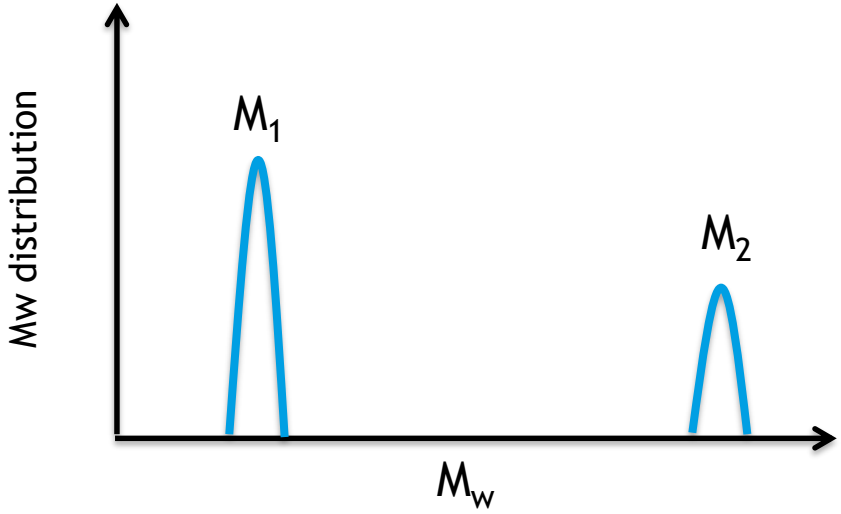
Questions

Molecular weight

- Is it the average molecular weight that counts?
- Same results with just a fraction of longer chains?



Additional dynamics

Looking for a model system

- Increase the number of connections within the network
- Dissipate the energy near where the failure begins
- “Self-healing/ Self-reinforcing” by creating new connections during stretching

Additional dynamics

Looking for a model system

- What kind of Dynamic?
  Fast or Slow
- What's the needed amount?
  We're diluting the main system

- Increase the number of connections within the network
- Dissipate energy near where the failure begins
- Self healing by creating new connections during stretching

Conclusions

- TPEs show an undesired and unexpected common feature
  The understanding of this failure mechanism is of key importance

- The actual model can describe qualitatively ε_f Vs T
  Validate and improve the model with further tests

- Understand how to improve TPEs' properties
  SB/HB ratio – Molecular weight – Additional dynamics and/or chemistry

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