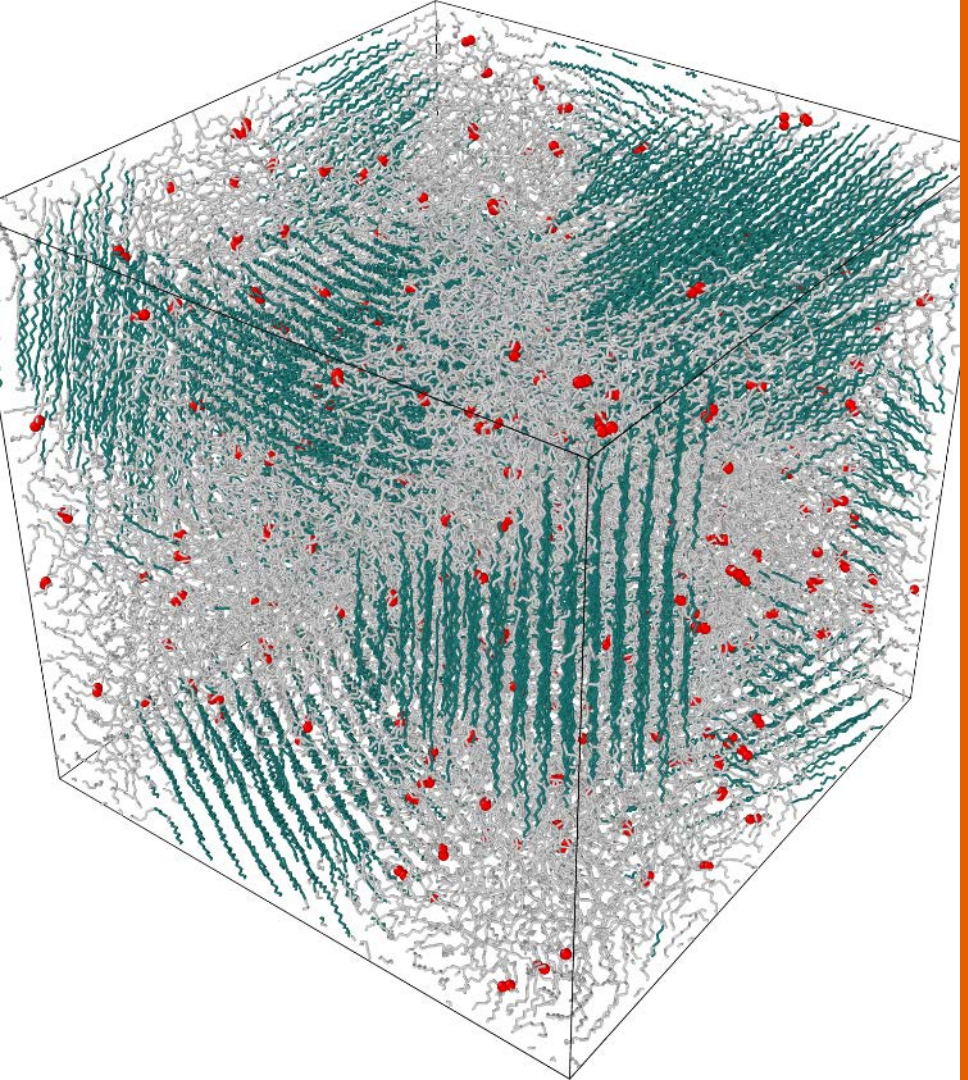


COMRADE Task 3.1

Jukka Vaari

Objective

- To explain the anomalous ageing phenomenon (”reverse temperature effect”), observed in certain semicrystalline polymeric materials, based on molecular-level structure of the materials
- The specific material studied is polyethylene
- Aging of the material is simulated by creating cross-links between chains and by dissociating chemical bonds within chains
- Mechanical properties are determined by simulating the tensile test

Reverse temperature effect

- Celina *et al.*, Rad. Phys. Chem. 48 (1996) 613

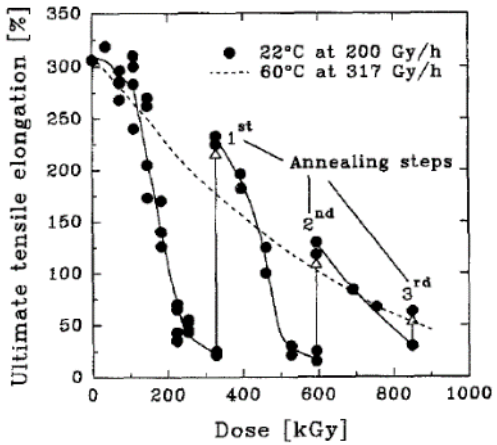


Fig. 5. Decrease in ultimate elongation during degradation at 22°C and 200 Gy/h and the recovery of mechanical properties upon annealing at 140°C for 24 h after 328, 594 and 849 kGy.

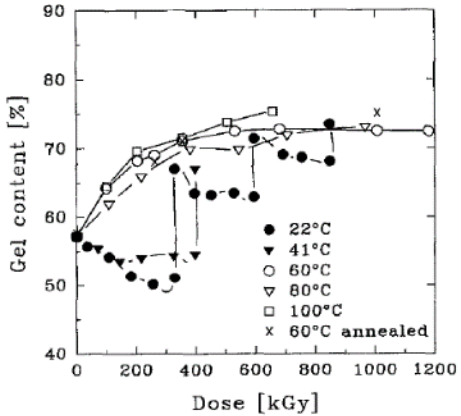
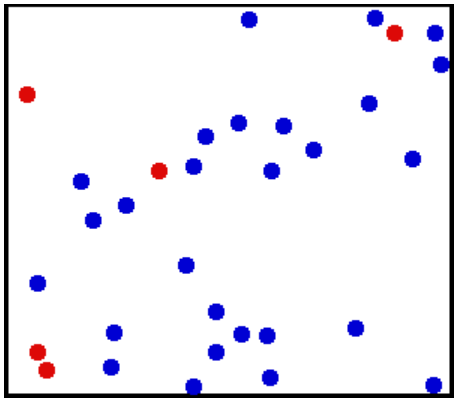


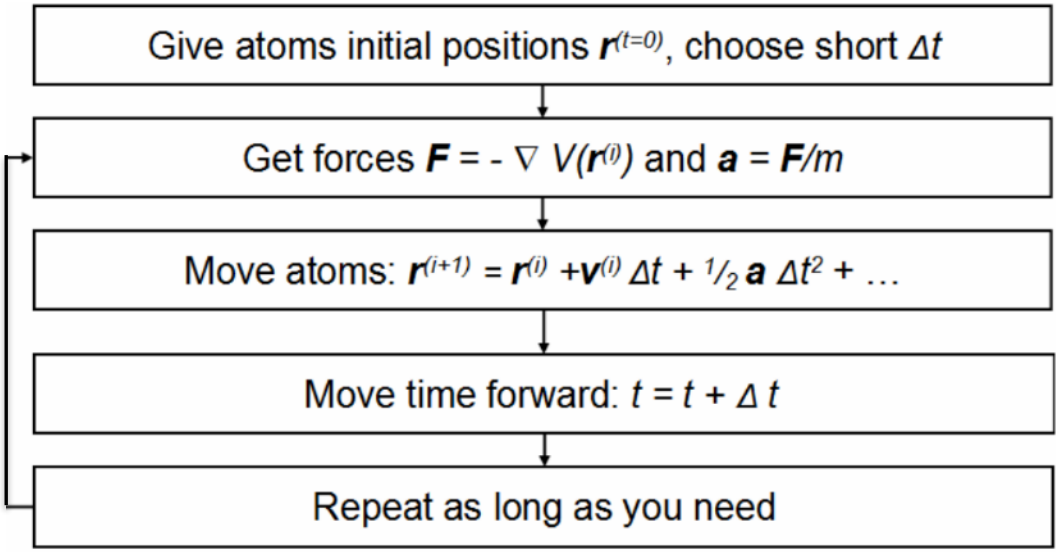
Fig. 6. Changes in the gel content during combined radiation-temperature exposures as a function of temperature showing predominantly scission at lower temperatures and crosslinking at higher temperatures as well as a marked increase in the gel content during annealing of the samples aged at 22 and 41°C.

Since oxygen must be present during the radiation aging for these anomalous effects to occur, oxidized species *must* be involved in both the rapid loss of mechanical properties at low temperatures and in the subsequent crosslinking during annealing.

Molecular Dynamics

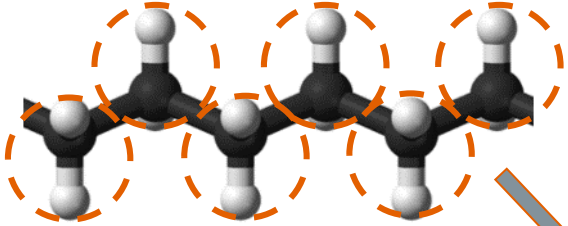
- Molecular dynamics (MD): a technique for computing the movement of atoms or molecules using classical equations of motion
- Classical: F=ma



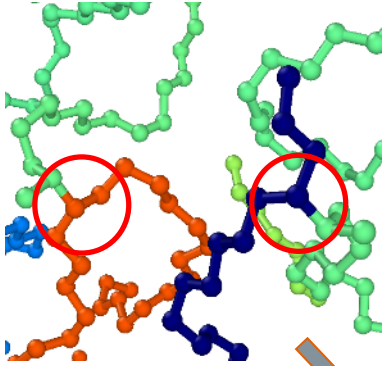


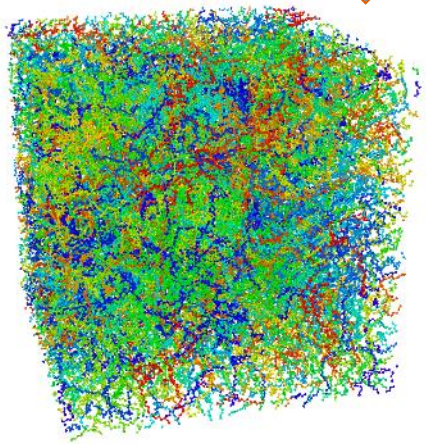
Structure generation

United-atom PE description



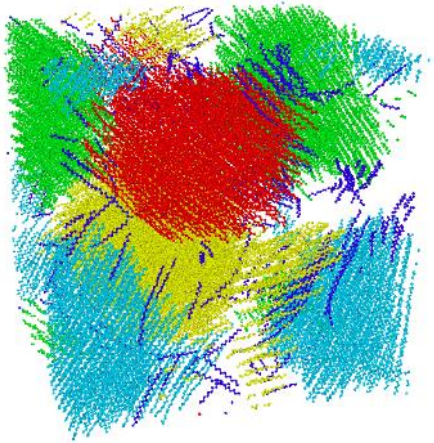
Building cross-links





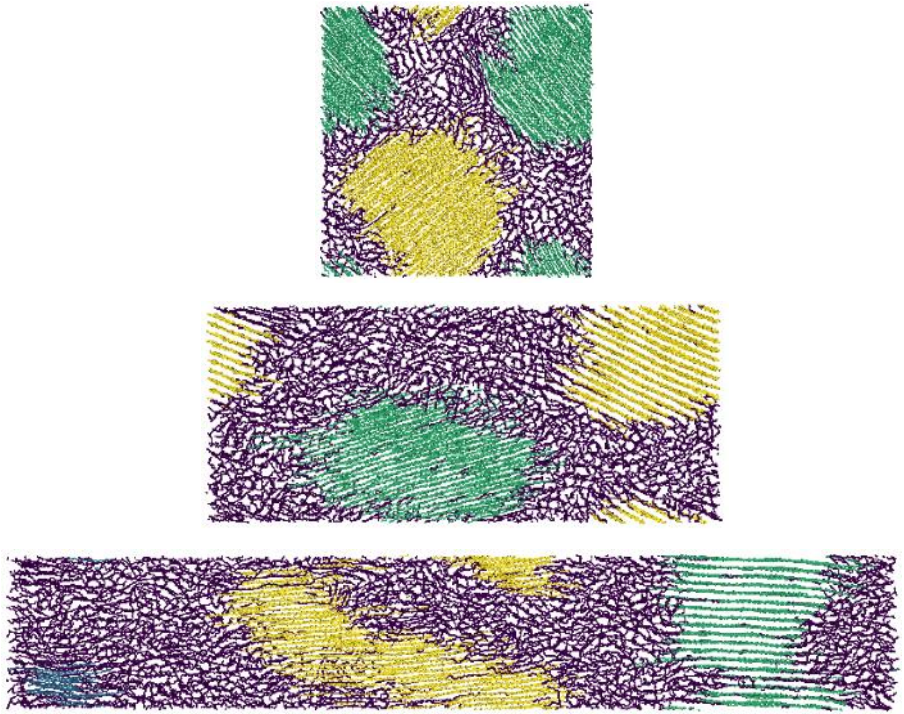
Equilibrium melt generation

Crystallisation



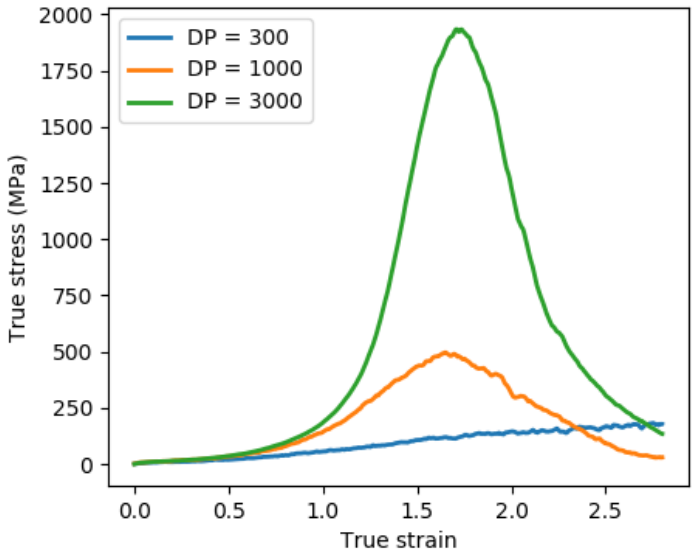
Tensile test

- Uniaxial deformation of the initial structure
- Stress-strain curve readily computed
- Stretch-induced bond breaking effects can be included



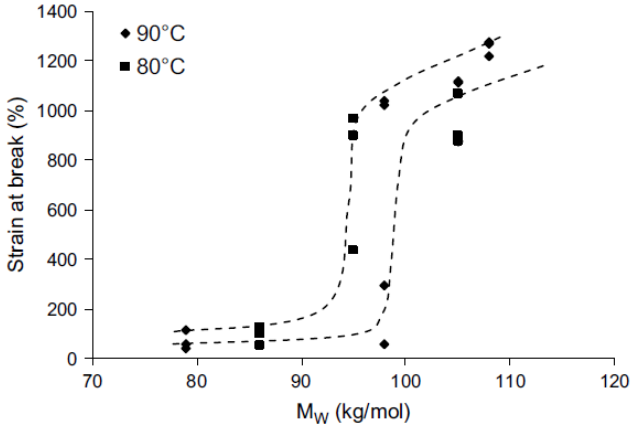
Effect of chain length

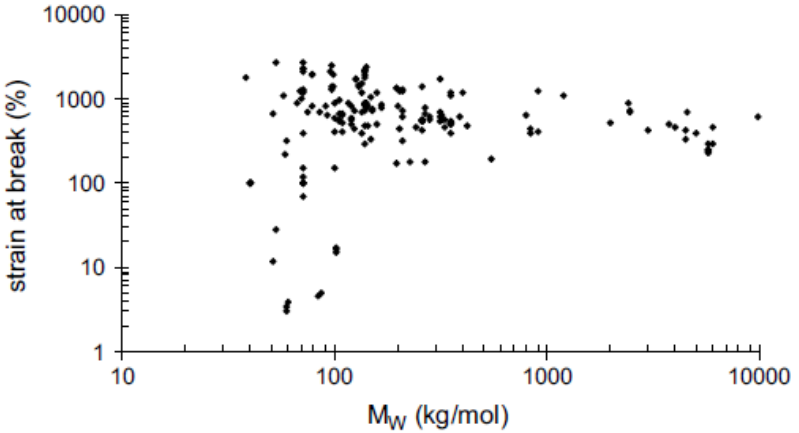
- When chain length is increased, the chains become more entangled
- Such entanglement leads to significant strain hardening, which is required for the material to be ductile
- The result implies loss of mechanical properties when chain scission dominates the aging process



Effect of chain length

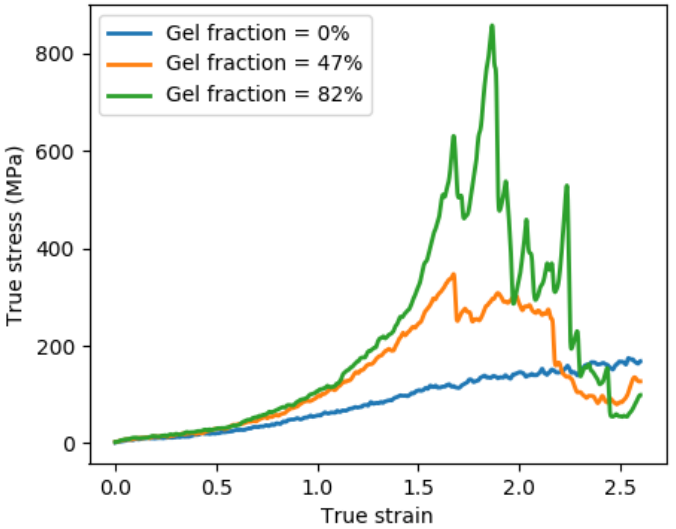
- Fayolle *et al.* Polymer Degradation and Stability 92 (2007) 231
  - Thermal oxidation of PE at 80 °C and 90 °C





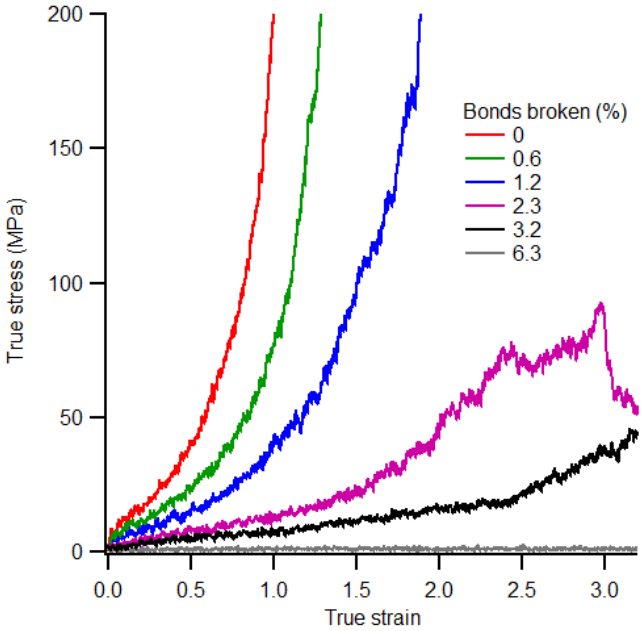
Effect of cross-linking

- Cross-linking effectively increases the chain length
- Accordingly, cross-linking improves mechanical properties, as cross-links can be viewed as rigid entanglements
- However, tensions in the cross-linked chain network are unevenly distributed, which results in stress-induced chain scissions



Initial structure: amorphous 300 x 300

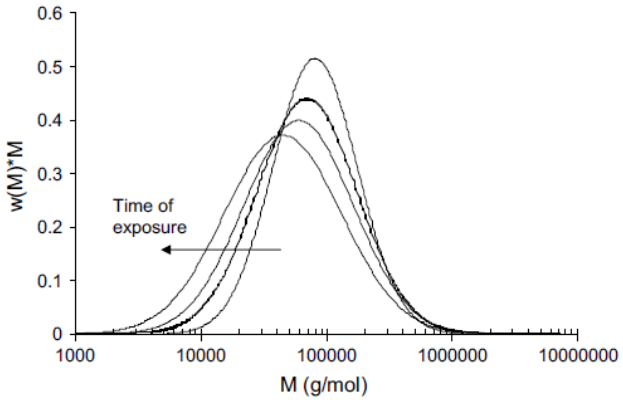
Effect of chain scission in XLPE

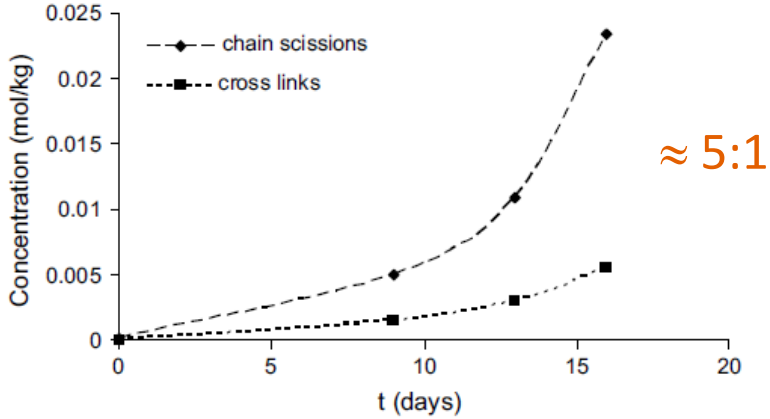


Bonds broken (%)	Avg MW (repeat units)	Gel fraction (%)
0	84110	98
0.6	44873	70
1.2	5923	25
2.3	361	0
3.2	130	0
6.3	40	0

Thermal aging: chain scission dominates

- Fayolle *et al.* Polymer Degradation and Stability 92 (2007) 231
  - Thermal oxidation of PE at 80 °C and 90 °C



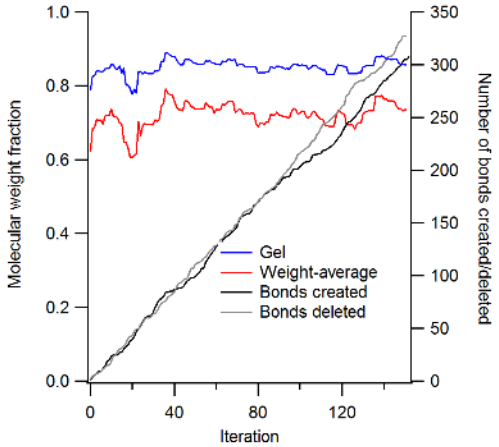


≈ 5:1

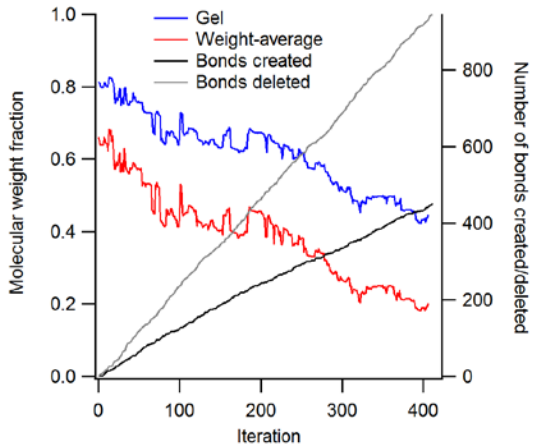
Competing chain scission and cross-linking

Ratio of bond scissions / cross-links

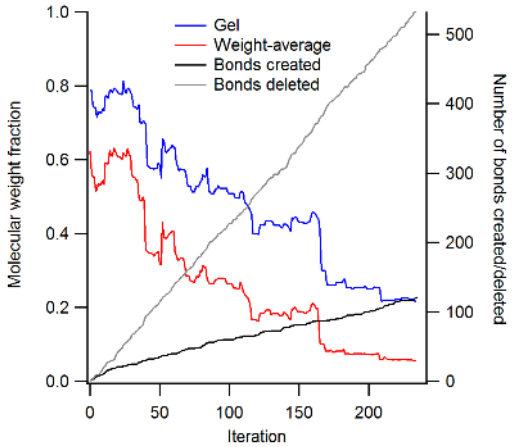
1:1



2:1



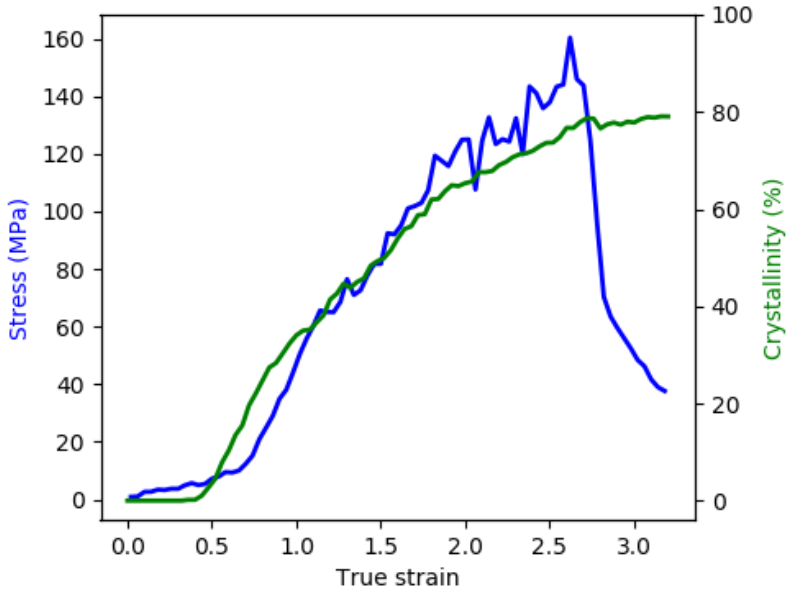
4:1



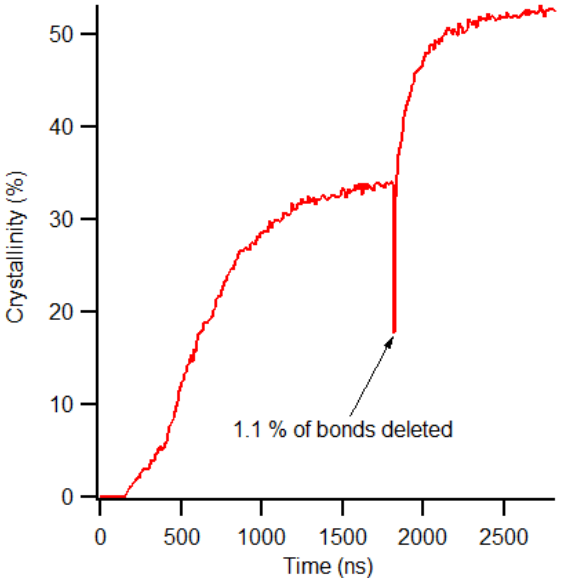
Equal rate of chain scissions and cross-link formation leads to a gel fraction of 0.8

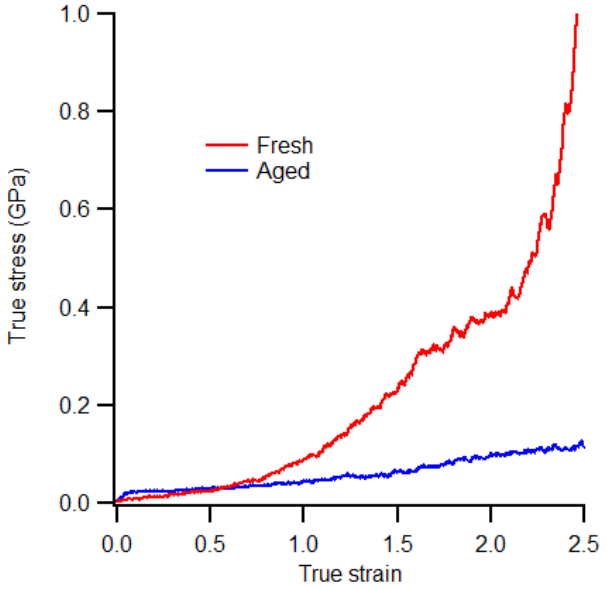
Role of crystallinity

- Uniaxial deformation induces crystallization due to chain alignment
- Initial configurations mainly affect properties at small deformations



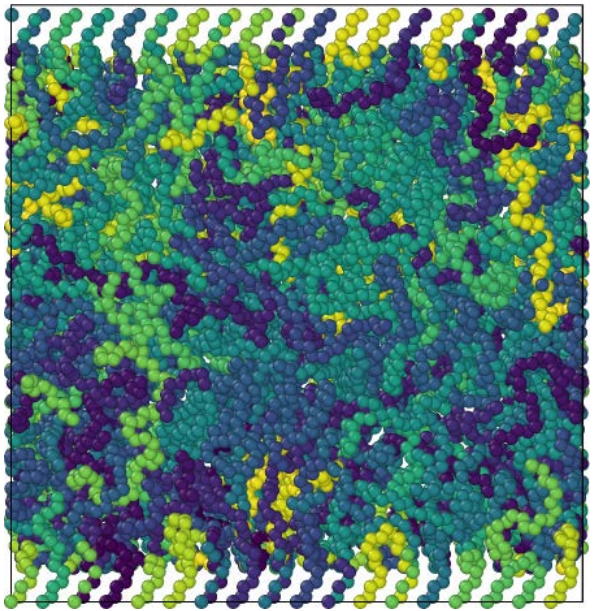
Chemicrystallisation





Future work: small deformations

- The lamellar crystal morphology is crucial if small deformation properties need to be modeled
- Elastic modulus, poisson's ratio and density required for calculating the velocity of sound
- Goal: interpretation of ultrasonic NDT data



Summay

- Molecular dynamics was used to study the reverse temperature effect in polyethylene
- Effect of two main aging mechanisms (chain scission and cross-linking) on mechanical properties has been analysed
- Chain scission leads to loss of mechanical properties in both linear and cross-linked polyethylene
- Cross-linking improves mechanical properties
- Results are in qualitative agreement with the explanations given for the reverse temperature effect by Celina *et al.* (1996)