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*

*Equilibrium melt generation*

*Building cross-links*

*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
Effect of chain scission in XLPE

<table>
<thead>
<tr>
<th>Bonds broken (%)</th>
<th>Avg MW (repeat units)</th>
<th>Gel fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>84110</td>
<td>98</td>
</tr>
<tr>
<td>0.6</td>
<td>44873</td>
<td>70</td>
</tr>
<tr>
<td>1.2</td>
<td>5923</td>
<td>25</td>
</tr>
<tr>
<td>2.3</td>
<td>361</td>
<td>0</td>
</tr>
<tr>
<td>3.2</td>
<td>130</td>
<td>0</td>
</tr>
<tr>
<td>6.3</td>
<td>40</td>
<td>0</td>
</tr>
</tbody>
</table>
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
Chemicroystallisation

![Graph 1: Crystallinity (%) vs. Time (ns)]

- 1.1% of bonds deleted

![Graph 2: True stress (GPa) vs. True strain]

- Fresh
- Aged
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)