Computational methods in polymer ageing studies – case studies

Polymers in nuclear applications 2023
16th March 2023

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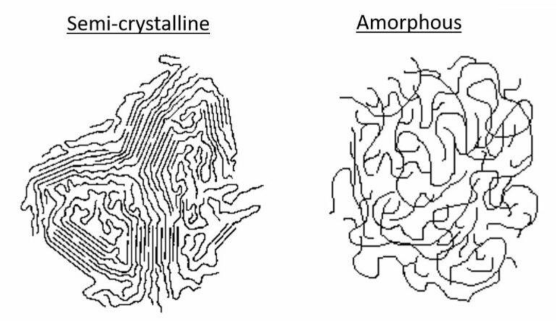
Starting point

- Pristine polymeric component:
  - amorphous or semicrystalline base polymer
  - fillers, plasticisers, stabilisers, antioxidants, pigments etc.
- Observed mechanical properties
  - molecular structure → properties of component phases
  - microstructure + interfaces → macroscopic properties
- Primary stressors in an NPP environment:
  - thermal motion
  - ionising radiation
  - molecular oxygen
- Long-time exposure results in changes in the molecular structure, which translates into degradation of mechanical properties
  - degradation behaviour depends strongly on the formulation



The Importance of Crystallinity in Plastics Performance (madisongroup.com)

The conventional way

- Semi-empirical methods that are based on simulating in-containment conditions by accelerated ageing tests

- Practical methods include:
  - Arrhenius relation
  - Power law extrapolation model
  - Superposition of time dependent data
  - Superposition of dose to equivalent damage data

thermal aging
radiation aging
coupled effects of both

IEC TS 61244-2

- Remarkably, most types of polymers can be addressed with this toolbox

- Underlying assumptions:
  - the degradation mechanism/pathway stays the same throughout the considered range of conditions
  - molecular collision probability increases at a constant rate with increasing temperature

The computational methods

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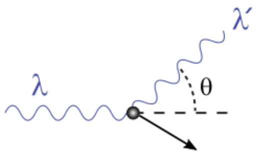
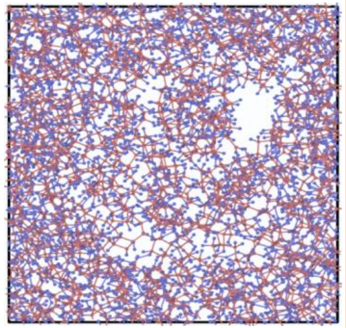
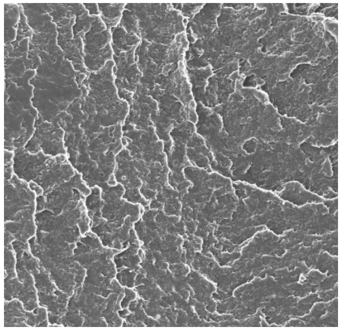
reaction energetics | reaction pathways | properties of phases, physical transitions | bulk properties, diffusion

HF DFT TB CPMD RMD MD CGMD many other μFEM

Mechanistic and global kinetic models







Atomistic scale

Absorption and scattering processes that generate
- radical cations,
- free electrons,
- electronically excited molecules

Temperature-independent

Mesoscopic scale

Subsequent reactions of intermediates… oxidative chain reactions.
Leads to:
- main-chain scission
- crosslinking

Segment mobility increases towards higher temperatures

Microscopic scale

Solvation and diffusion of molecular oxygen.
- usually enhances radiation-degradation
- might change the dominant mechanism

Same thing for O_2 diffusion

Component scale

Reactions hindered in crystalline regions.
- electrostatic environment can significantly affect the reactions

Temperature effects here as well

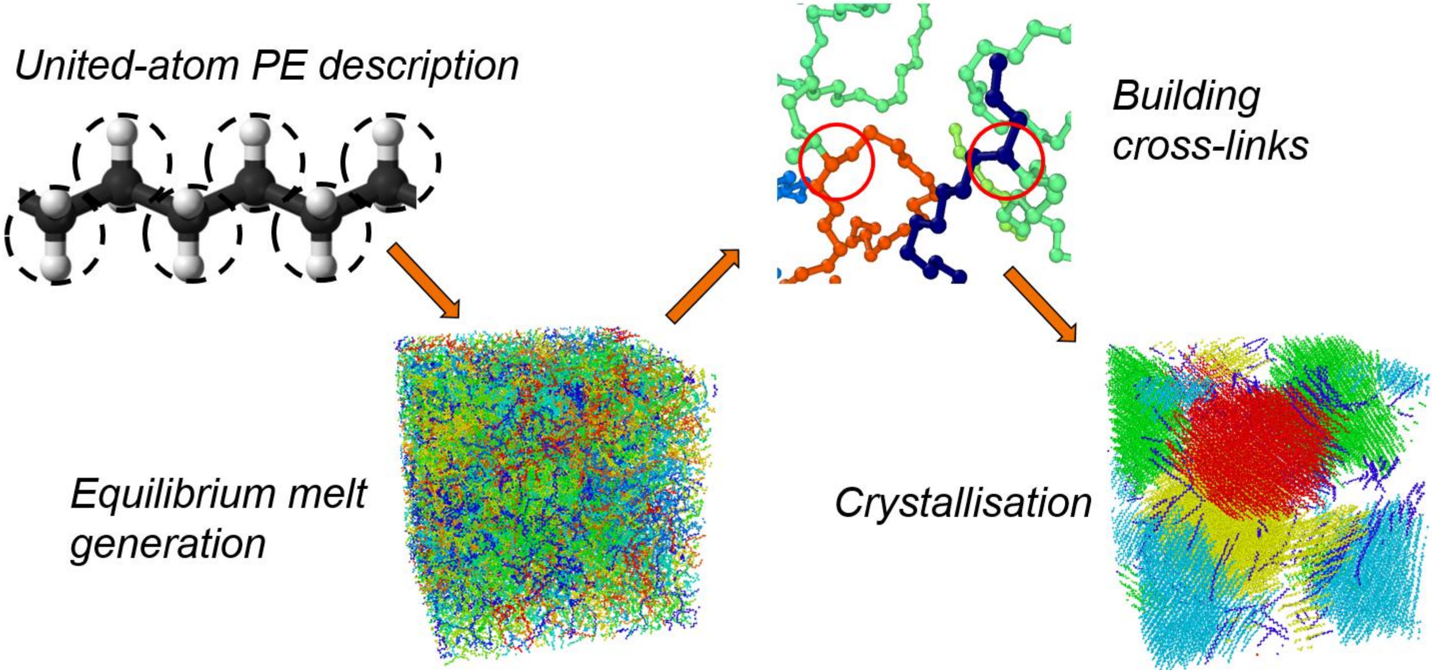
Case 1 – Application of MD in simulating mechanical properties of XLPE

1. Create the material virtually
2. Artificially age it
3. Stretch it
4. Compare to experimental data
5. Find weaknesses in the model
6. Repeat

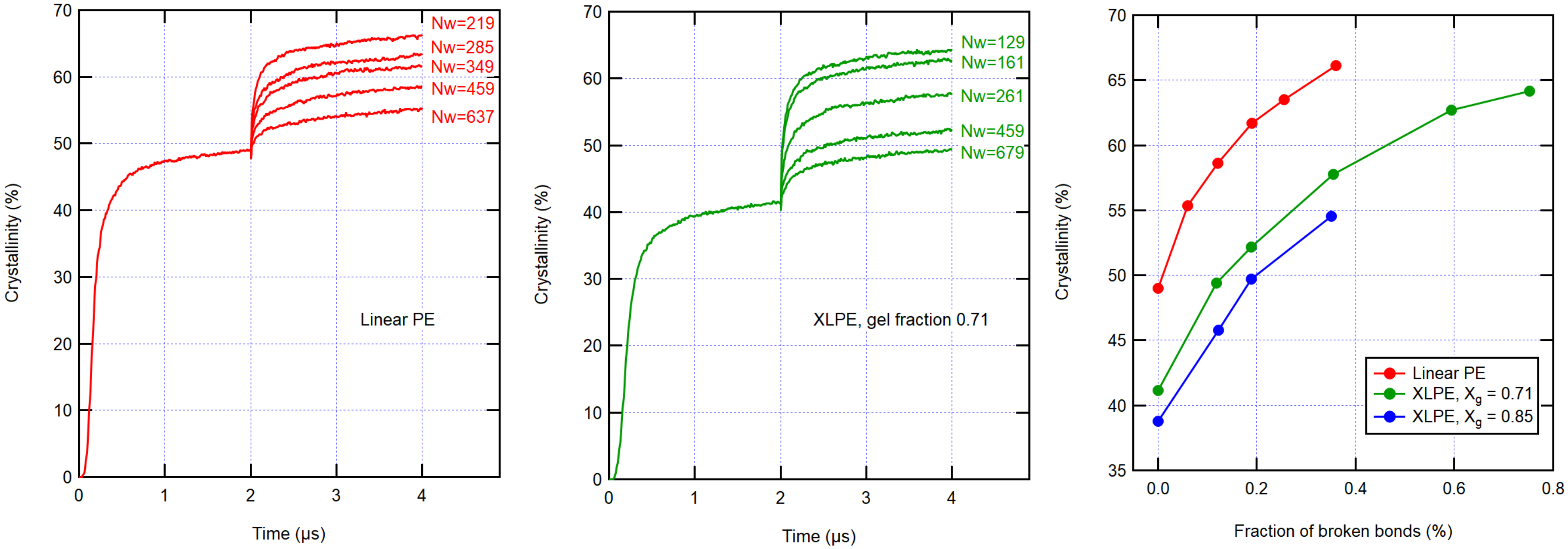
X. Can we use this in something useful?

Structure generation

- The standard story as in *Paajanen et al Polymer 171 (2019) 80–86*

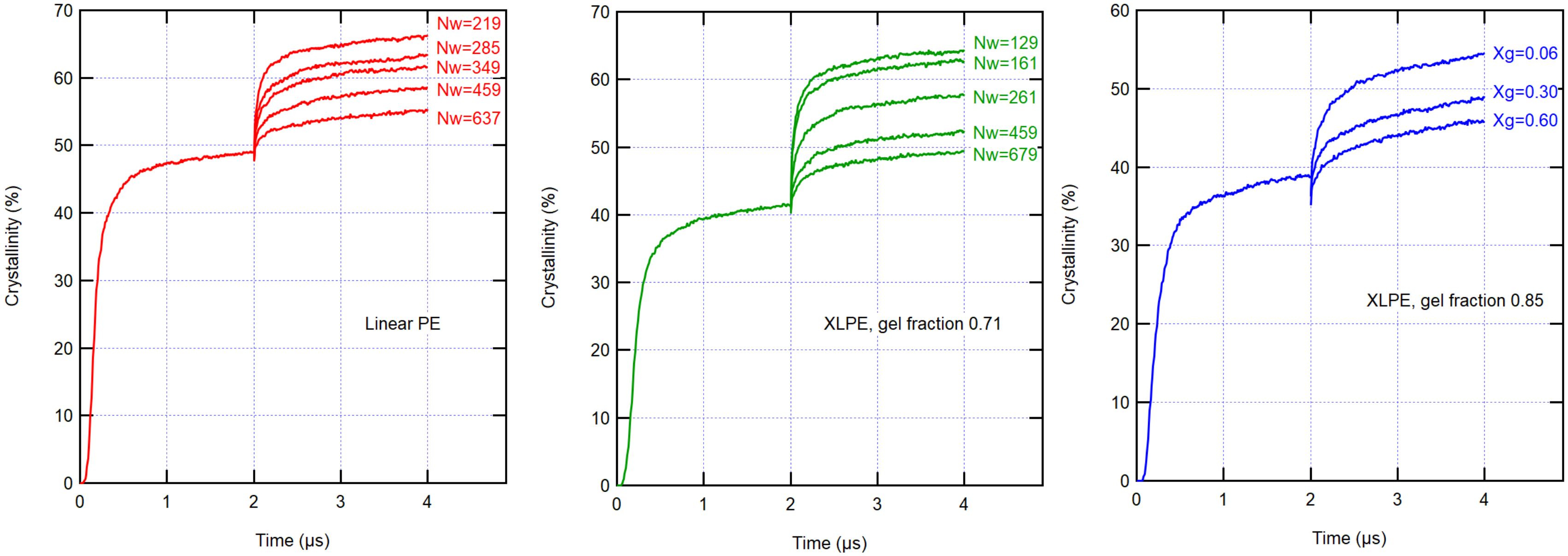


Ageing and mechanical properties



- Breaking C-C bonds (chain scission) is measured by using averaged molecular weight Nw
- Effects to crystallinity

Ageing and mechanical properties



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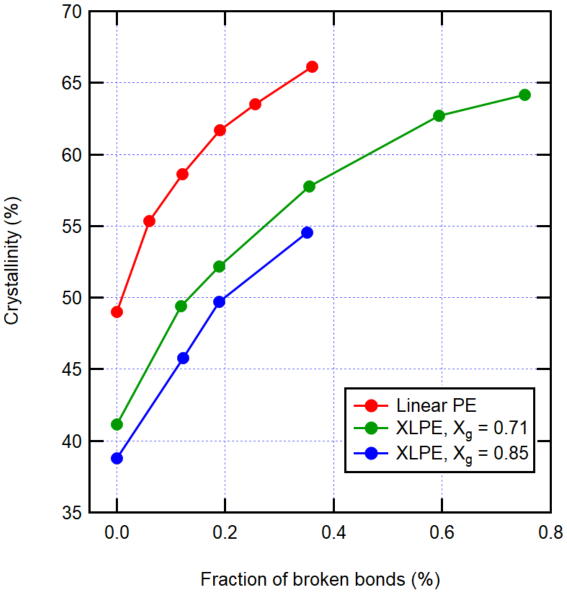


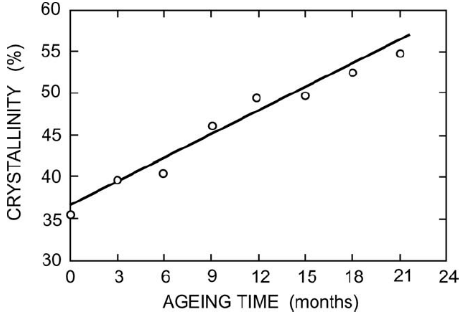


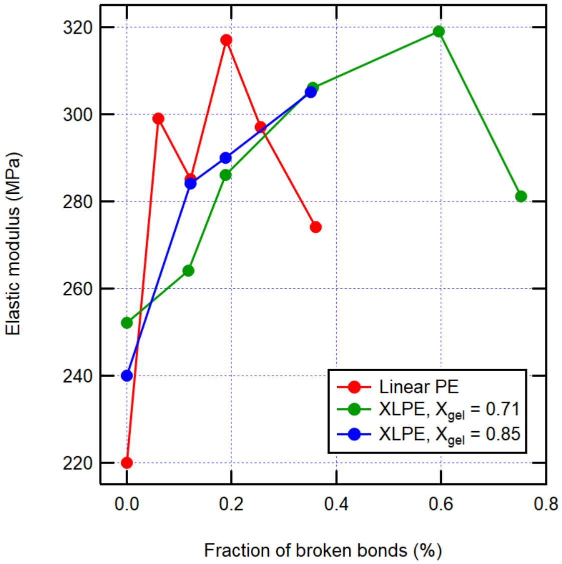
Figure 6 Mass-based crystallinity versus aging time.

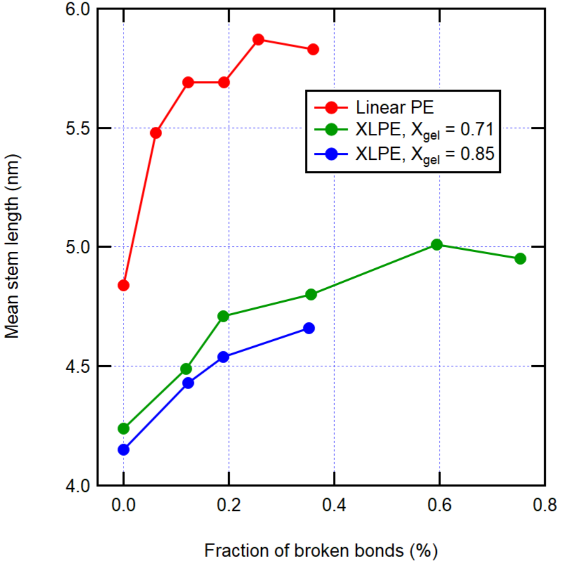
Salem F. Chabira,[1] Mohamed Sebaa,[1] Christian G'sell[2]

Journal of Applied Polymer Science, Vol. 124, 5200–5208 (2012)

- Small amount of chain scission has already a significant effect to crystallinity
- Comparison to literature data → Similar trend

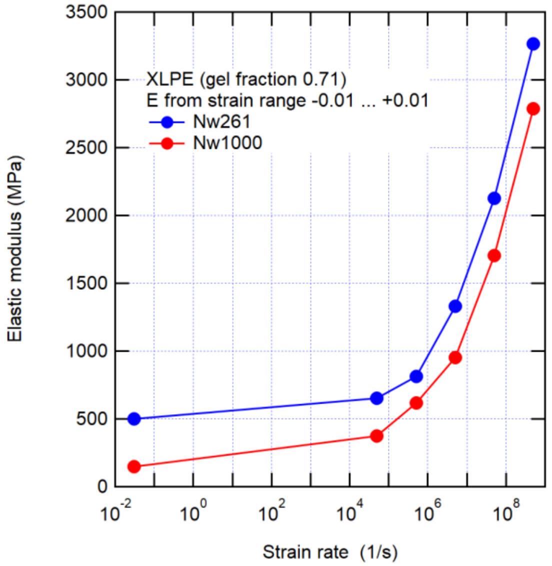
Ageing and mechanical properties

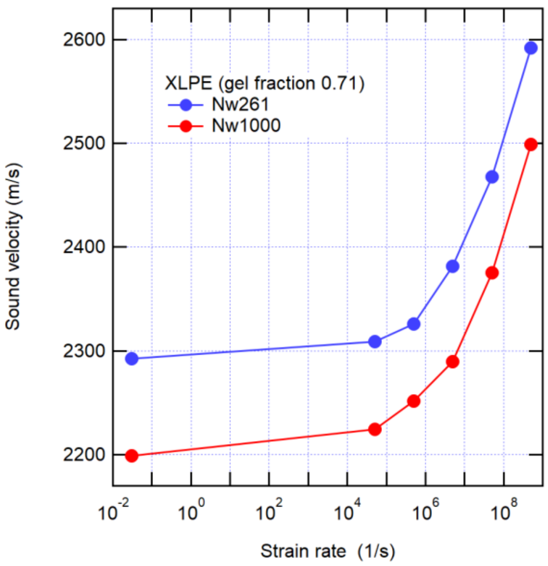


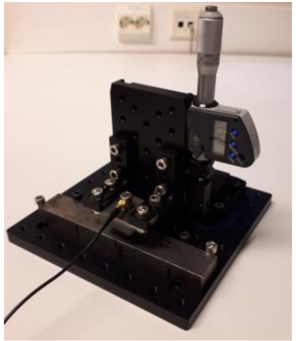


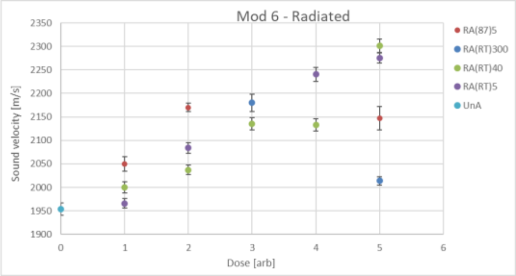
- Tensile test with small displacement (10^7 1/s) → E increases
- Mean stem length = mean length of the straight sections of the chains (no branches) – Could it explain the increase in E?

Ageing and mechanical properties









- The applied strain rate was high and displacement small – How does the E change in more realistic test setup?
- Furthermore, sound velocity can be predicted too!
- Future application: measure sound velocity non-destructively from cable and use computational calculations to predict the remaining lifetime

Case 2 – Antioxidant study

- How does the antioxidants affect to the ageing of the polymer?
- Can we somehow simulate their role in the ageing by using COMSOL finite element analysis, solver, and simulation software package?

Antioxidant kinetics

Initiation:

- $RH \rightarrow R\cdot + H\cdot$
- $\delta ROOH \rightarrow \alpha R\cdot + \beta ROO\cdot$

Propagation:

- $R\cdot + O_2 \rightarrow ROO\cdot$
- $ROO\cdot + RH \rightarrow ROOH + R\cdot$

Termination:

- $R_1\cdot + R_2\cdot \rightarrow R_1\text{-}R_2 + X$
- $R_1\cdot + R_2OO\cdot \rightarrow R_1\text{-O-O-}R_2 + X$
- $R_1OO\cdot + R_2OO\cdot \rightarrow R_1\text{-O-O-}R_2 + O_2 + X$

$$\frac{d[R\cdot]}{dt} = G\cdot 10^{-7}\cdot I + 2k_{1u}[ROOH] + k_{1b}[ROOH]^2 - k_2[O_2][R\cdot] + k_3[ROO\cdot][RH] - 2k_4[R\cdot]^2 - k_5[R\cdot][ROO\cdot] + 2k_{63}[ROOR]_{cage}$$

$$\frac{d[ROO\cdot]}{dt} = k_{1b}[ROOH]^2 + k_2[O_2][R\cdot] - k_3[ROO\cdot][RH] - 2k_4[R\cdot]^2 - k_5[R\cdot][ROO\cdot] + 2k_{60}[ROO\cdot]^2 - k_{S1}[ROO\cdot][AH] - k_{S2}[ROO\cdot][R\cdot]$$

$$\frac{d[ROOH]}{dt} = -k_{1u}[ROOH] - 2k_{1b}[ROOH]^2 + k_3[ROO\cdot][RH] - 2k_4[R\cdot]^2 - k_5[R\cdot][ROO\cdot] + k_{S1}[ROO\cdot][AH]$$

$$\frac{d[ROOR]_{cage}}{dt} = k_{60}[ROO\cdot]^2 - (k_{61} + k_{62} + k_{63})[ROOR]_{cage}$$

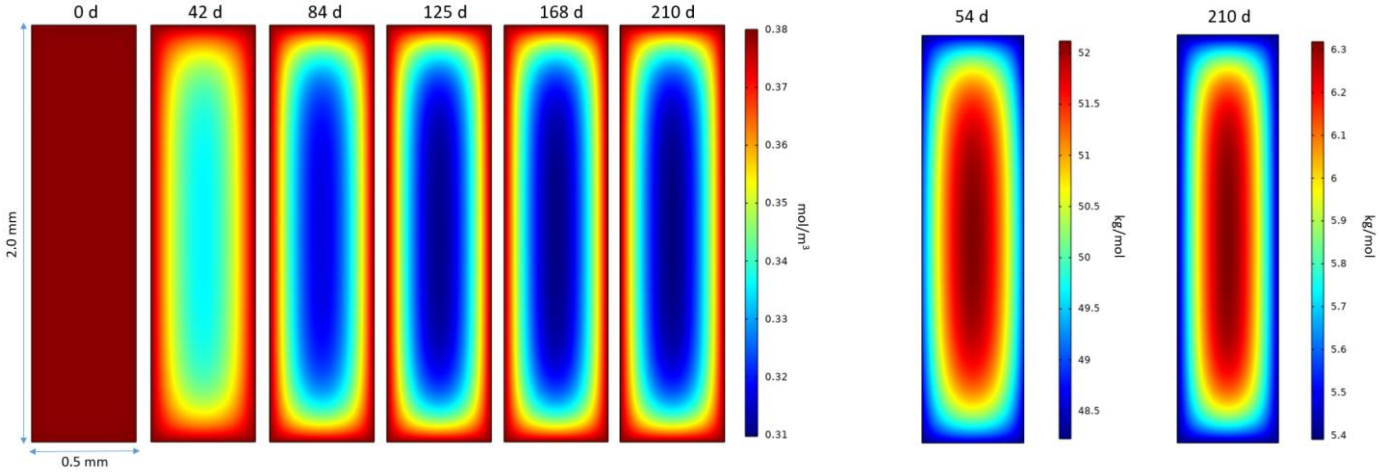
$$\frac{d[O_2]}{dt} = -k_2[O_2][R\cdot] + 2k_{60}[ROO\cdot]^2 + D_{O2}\nabla^2[O_2]$$

$$\frac{d[AH]}{dt} = -k_{S1}[ROO\cdot][AH] + D_{AH}\nabla^2[AH]$$

$$\frac{d[A\cdot]}{dt} = k_{S1}[ROO\cdot][AH] - k_{S2}[ROO\cdot][A\cdot]$$

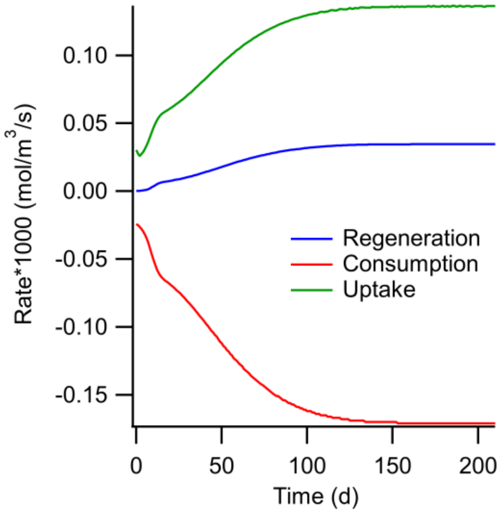
- The model is based on:
  - The Basic Autoxidation Scheme (BAS) and
  - Derived differential equations which describes the time evolution of the relevant chemical species
- The polymer degradation mechanism, oxygen diffusion, and antioxidant depletion were implemented in both 2D and 3D finite-element models to obtain realistic component-scale predictions on thermal degradation

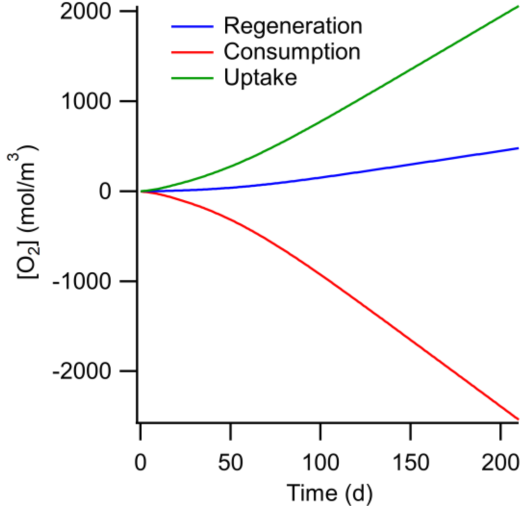
COMSOL model predictions



- 2.0 x 0.5 mm 2D XLPE sample aged
  - Distribution of oxygen concentration and molecular weight
- Rather homogenous distributions in both cases (confirmed experimentally, indentation)

COMSOL model predictions



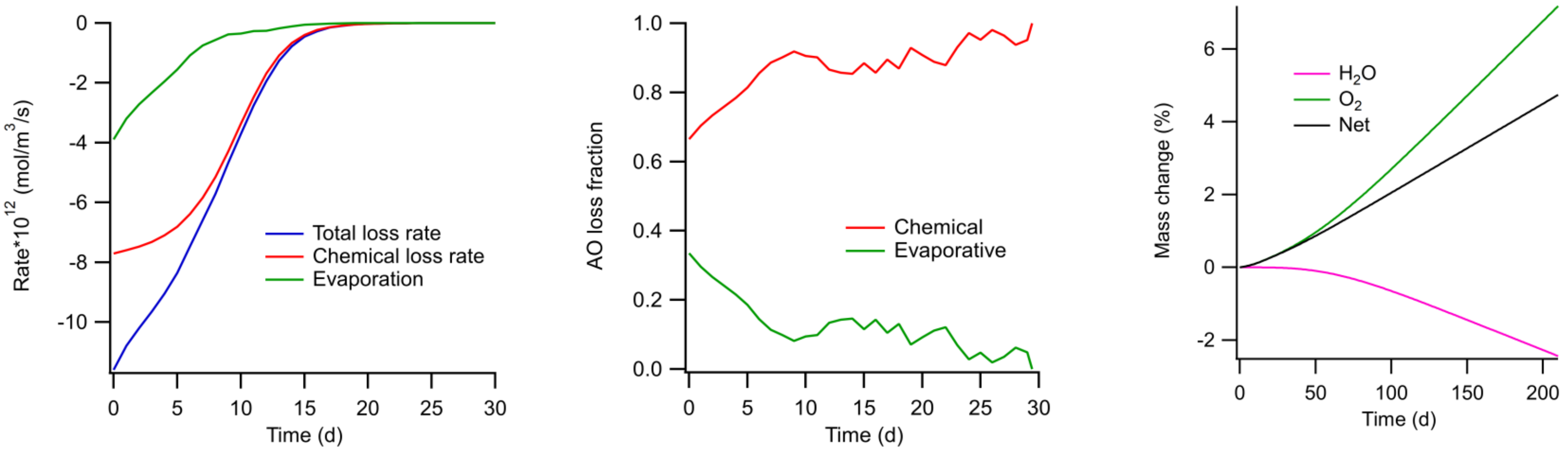


- Overall oxygen consumption and uptake can be calculated

$$\frac{d\langle x_5\rangle}{dt} = -k_2\langle x_1 x_5\rangle + k_{60}\langle x_2^2\rangle + \langle\nabla\cdot(c_{55}\nabla x_5)\rangle$$

- Regeneration – Oxygen is actually produced in some of the ageing reactions

COMSOL model predictions



- Similarly, the antioxidant evaporation and chemical consumption can be calculated
- Evaporation significantly contributes to antioxidant loss, but does not dominate in this case
- Mass losses can be calculated in principle for any desired component, here water as an example

Summarizing modelling perspectives

- Several computational modelling methods exists for different size and time scales
- MD approach can be applied on molecular scale simulations to obtain predictions on mechanical properties of XLPE – the obtained sound velocity values seemed to be similar magnitude as experimentally was measured
- COMSOL approach was applied to predict antioxidant behaviour in artificially aged XLPE sample and seem to give reasonable predictions
- It would be good if both methods could be further benchmarked against experimental data

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beyond
the obvious

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