Task 3.1: Literature review on synergistic effects in polymer ageing & modelling possibilities

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COMRADE Task 3.1

Combined effects higher than the individual effects applied separately…

- Goals:

1. to carry out a literature review on the synergistic effects of thermal and radiation ageing in polymeric materials

2. to identify modelling methods that could be applied to study these phenomena

- …with the lifetime prediction of NPP components in mind.

A brief recap

- 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

  } + (potentially) complicated couplings
- Long-time exposure results in changes in the molecular structure, which translates into degradation of mechanical properties
  - degradation behaviour depends strongly on the formulation

Lifetime prediction methods

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

- Practical methods include:
  - Arrhenius relation — thermal aging
  - Power law extrapolation model — radiation aging
  - Superposition of time dependent data — coupled effects of both
  - Superposition of dose to equivalent damage data — coupled effects of both

- 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

Scales and processes of radiation ageing

reaction energetics

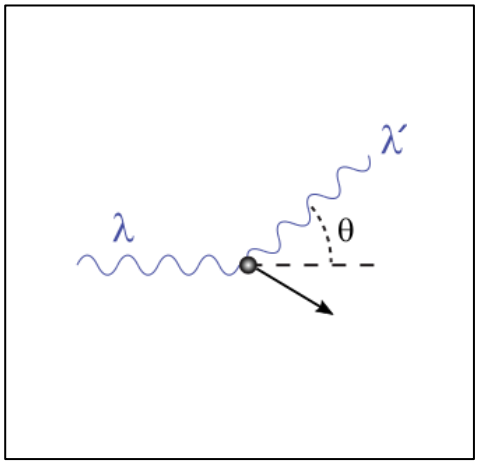
reaction pathways

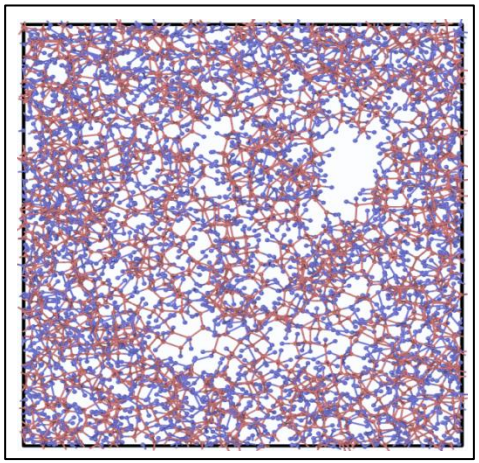
properties of phases, physical transitions

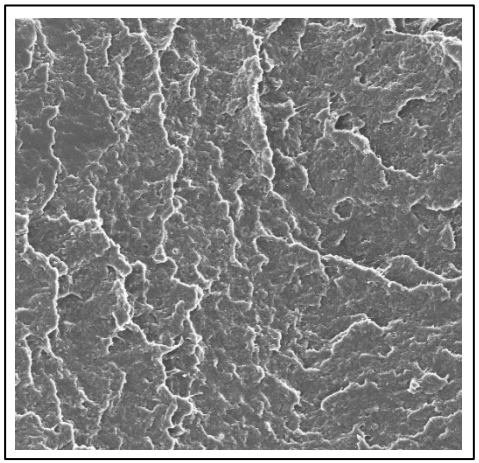
bulk properties, diffusion

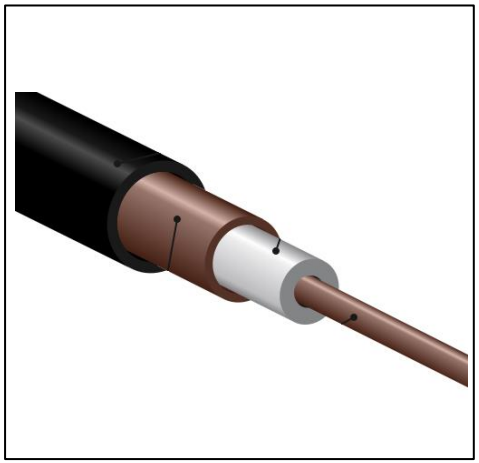
HF DFT TB | CPMD RMD | MD CGMD | many other μFEM

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