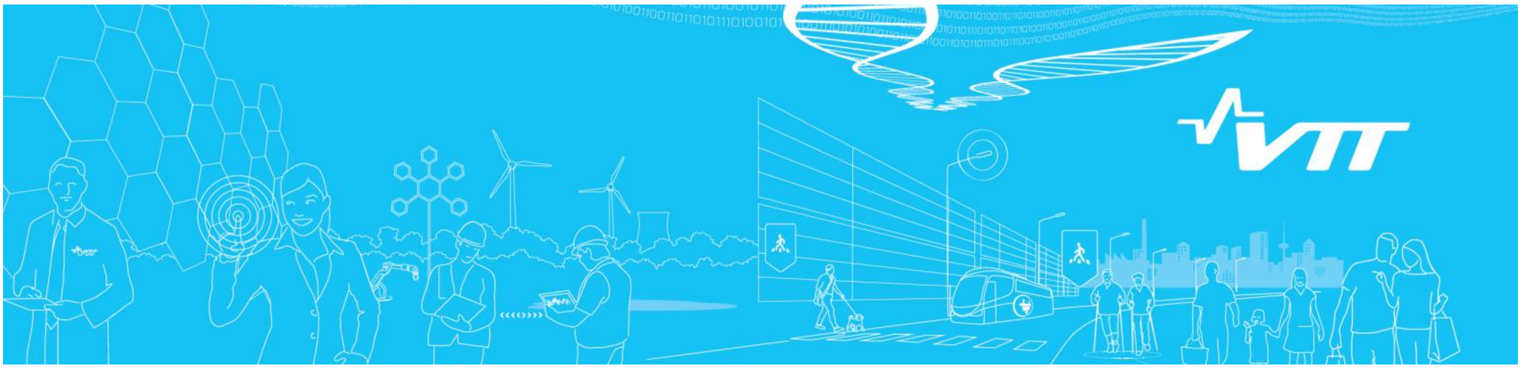

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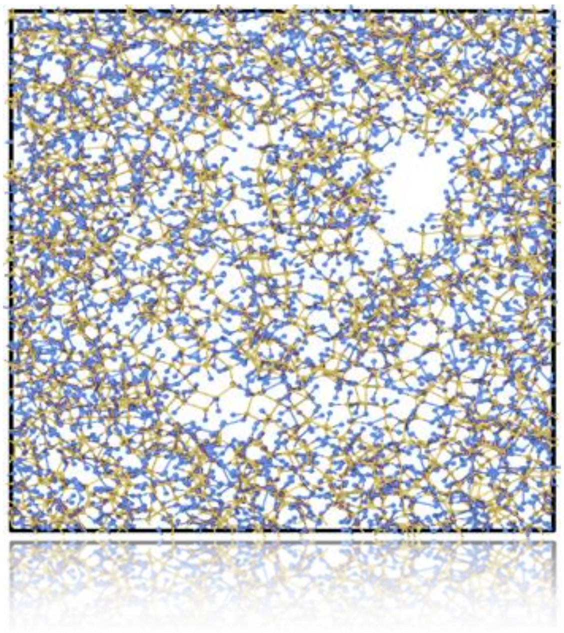

# Modelling tools for the combined effects of thermal and radiation ageing in polymeric materials

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**Report's title**

Modelling tools for the combined effects of thermal and radiation ageing in polymeric materials

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**Summary**

We carried out a literature survey on the combined thermal and radiation ageing of polymer formulations, and on possible ways of considering their synergistic effects in the lifetime prediction of nuclear power plant components. We looked for proposed ageing mechanisms, identified materials modelling methods feasible for studying them, and compiled an overview of previous works related to the topic.

We found that the mechanisms underlying combined thermal and radiation ageing can be exceedingly complex, involving various chemical and physical processes across multiple structural and time scales. Probably due to this, practical lifetime prediction methods are semi-empirical and based on accelerated ageing experiments. Methods applicable to combined thermal and radiation ageing include the superposition of time-dependent data method, and the superposition of dose-to-equivalent-damage data method. The semi-empirical methods are limited in their predictive capability, as they cannot address possible changes in the dominant ageing mechanisms. For this reason, anomalous ageing phenomena such as the reverse temperature effect can render their predictions useless.

Mechanistic details of both thermal and radiation ageing can be addressed with the theoretical tools of computational materials science. For example, electronic structure calculations can be used to assess the feasibility of proposed reaction paths, and to predict the associated kinetics. At the other end of the spectrum, finite element analysis can be used to study how ageing-induced microstructural changes translate into the degradation of mechanical properties. Nevertheless, there remains a formidable gap between the present multi-scale materials modelling capabilities and practical lifetime prediction.

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# Preface

This study was carried out during the year 2016 as part of the "Condition Monitoring, Thermal and Radiation Degradation of Polymers Inside NPP Containments" project (COMRADE), which is one of the projects in the Finnish Research Programme on Nuclear Power Plant Safety 2015–2018 (SAFIR2018). The study was financed by the State Nuclear Waste Management Fund (VYR) and VTT Technical Research Centre of Finland Ltd.

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The Authors

# Contents

# 1. Introduction

Materials based on organic polymers have many applications in nuclear power plants (NPP). They are found in cable sheathing, mechanical gaskets, joint sealants and linings, among others. In some applications, the functionality of a polymeric component can be vital for the safe operation of the plant. For example, cables provide the electronic safety systems with the necessary link to power, control and instrumentation, without which they cannot function.

NPP components can be exposed to serious environmental stressors. For a polymeric component, the primary stressors are elevated temperatures, ionising electromagnetic radiation and the presence of molecular oxygen. Long-term exposure to such conditions induces changes to the composition of the material, which, in turn, translates into changes in its physical properties. When properties relevant to the functionality of the component degrade, the process is referred to as ageing. In some components, ageing can ultimately result in failure or malfunction. Understanding the ageing behaviour is thus important for both material selection and lifetime management.

The most reliable way to assess the ageing behaviour of a polymeric component is to monitor it for its full service life in the actual operating environment. For most purposes, this is utterly impractical. A more pragmatic approach is to use accelerated ageing experiments to predict the long-term ageing behaviour. In such experiments, the component is subjected to exaggerated temperatures and dose rates for a time that is considerably shorter than its intended service life. The environmental conditions and the progress of ageing are monitored throughout the experiment. Certain assumptions about the underlying mechanisms make it possible to extrapolate the ageing behaviour to lower temperatures, lower dose rates, and longer exposure times. One of the key assumptions is that the same mechanisms are at work in the accelerated experiments and in the actual operating conditions.

Predictive modelling of thermal and radiation ageing has a valuable role in the lifetime management of polymeric NPP components. Lifetime prediction methods can be used to estimate the residual service life of a component in service, or the expected service life of one to be installed. Residual service life predictions can lead to the investigation of components that are at risk of significant ageing. Lifetime prediction methods can also be used to identify conditions in which supplementary ageing management might be necessary.

At their best, lifetime prediction methods based on accelerated ageing can provide an accurate simulation of the real ageing behaviour. There are, however, situations in which the simulation is not representative of what happens in the actual operating conditions. Such situations arise, for example, when there is complex synergism (or antagonism) between the processes induced by thermal motion and ionising electromagnetic radiation. This means that the combined effects of the two stressors are more severe (or less severe) than the sum of their contributions considered separately. Other confounding factors include the onset of diffusion-limited oxidation and other dose rate effects.

In the present work, we report a literature survey on the combined thermal and radiation ageing of polymer formulations, and on possible ways of considering their synergistic effects in the lifetime prediction of polymeric NPP components. We report proposed mechanisms behind the ageing, as well as possible synergistic (and antagonistic) effects, identify materials modelling methods feasible for studying them, and cite previous works related to the topic.

# 2. Thermal and radiation ageing

The ageing of a polymeric component is dictated by three basic factors: (i) the polymer system itself, (ii) the environmental conditions, and (iii) the duration of the exposure.

Typical polymer formulations involve a base polymer and various different additives. The macroscopic properties of the formulation are largely determined by the long chain structure of the base polymer. The additives can include fillers, plasticisers, stabilisers, antioxidants, fire retardants and pigments, among others. Several properties of the material can be adjusted by changing the loadings of these additives. The ageing behaviour is strongly dependent on the polymer formulation.

The environmental stressors induce physical and chemical processes that lead to changes in the molecular level composition of the material. These changes are behind the observed degradation of material properties. As an example, the degradation of mechanical properties due to thermal and radiation ageing typically involves: (i) a decrease in elongation at break, (ii) an increase in hardness, and (iii) an increase in density.

In the following, we present a summary of the primary physical and chemical processes underlying combined thermal and radiation ageing of polymeric materials. Our treatment is based on, and follows closely, the works of (Schnabel, 2014) and (IAEA, 2000a). The discussion on synergistic and antagonistic effects is partly based on material from the COMRADE project seminar “Degradation of polymers in NPPs”, which was held in Borås, Sweden, on the 21st of September 2016.

## 2.1 Interaction of high-energy photons with matter

Ionising electromagnetic radiation is attenuated in matter via elementary absorption and scattering processes. These include the photoelectric effect, Compton scattering, electron-positron pair production and photonuclear absorption.

- In the photoelectric effect, the incident photon is absorbed by an atom or a molecule, with part of the photon energy going into the release of an electron, and the remainder into its kinetic energy.
- Compton scattering involves the inelastic collision of an incident photon with an electron of the absorbing matter. In the process, part of the photon energy and momentum are transferred to the electron, leading to its release.
- Electron-positron pair production can occur when photons interact with the Coulomb field of an atomic nucleus. The process becomes possible when photon energies exceed twice the electron rest mass.
- Photonuclear absorption refers to the absorption of a high-energy photon by an atomic nucleus. This interaction can lead to the emission of one or more neutrons, or a charged particle.

In short, the elementary absorption and scattering processes lead to electronic excitations and the formation of radical cations and free electrons. The free electrons lose their kinetic energy in inelastic collisions with nearby atoms, which leads to further excitation and ionisation events.

## 2.2 Primary reactions induced by ionising electromagnetic radiation

The elementary absorption and scattering processes lead to the formation of electronically excited molecules, radical cations, and free electrons. These primarily generated species either decompose or react with the nearby molecules.

- The electronically excited molecules are likely to relax via bond scission, which also leads to the formation of free radicals.
- The radical cations can decay via various routes. Firstly, they can be neutralised by thermalised (i.e. free and slowed down) electrons. Secondly, they can interact with neighbouring molecules and undergo, for example, addition and charge-transfer reactions. Finally, they can decompose to form cations and free radicals.
- The free electrons lose their kinetic energy in inelastic collisions with nearby molecules. In the process, they generate further radical cations, free electrons, and electronically excited molecules. Majority of the thermalised electrons are captured by parent radical ions, which results in electronic excitations.
- Radical anions can be formed when the thermalised electrons collide with molecules of sufficiently high electron affinity. The radical anions decompose rapidly to form stable anions and free radicals in a process known as dissociative electron capture.

Table 1 summarises the primary chemical processes induced by ionising electromagnetic radiation. In brief, the absorption and scattering of high-energy photons leads to free radical and ionic reactions. As the absorption and scattering processes are temperature-independent, reactions can be induced at all temperatures. Apart from the primary radiolytic act, the same processes occur during the absorption of fast electrons. High-energy photons and electrons thus induce similar chemical alterations in organic matter.

*Table 1. Primary processes during the absorption of high-energy photons by organic matter. Adopted from (Schnabel, 2014).*

| Process | Chemical equation |
|---|---|
| Primary radiolytic act | $\mathrm{M} \rightarrow \mathrm{M}^{+}_{\bullet} + \mathrm{e}^{-}_{\mathrm{fast}}$ |
| Inelastic collision of fast electron | $\mathrm{e}^{-}_{\mathrm{fast}} + \mathrm{M} \rightarrow \mathrm{M}^{+}_{\bullet} + \mathrm{e}^{-}_{\mathrm{kin}} + \mathrm{e}^{-}_{\mathrm{kin}}$ |
| Capture of thermalised electron by positive ion | $\mathrm{e}^{-}_{\mathrm{th}} + \mathrm{M}^{+}_{\bullet} \rightarrow \mathrm{M}^{*}$ |
| Capture of thermalised electron by neutral molecule | $\mathrm{e}^{-}_{\mathrm{th}} + \mathrm{M} \rightarrow \mathrm{M}^{-}_{\bullet}$ |
| Decomposition of excited molecule | $\mathrm{M}^{*} \rightarrow \mathrm{R}^{\bullet}_{1} + \mathrm{R}^{\bullet}_{2}$ |
| Decomposition of excited molecule | $\mathrm{M}^{*} \rightarrow \mathrm{A} + \mathrm{B}$ |
| Decomposition of radical cation | $\mathrm{M}^{+}_{\bullet} \rightarrow \mathrm{R}^{\bullet} + \mathrm{X}^{+}$ |
| Decomposition of radical anion | $\mathrm{M}^{-}_{\bullet} \rightarrow \mathrm{R}^{\bullet} + \mathrm{X}^{-}$ |
| Charge transfer | $\mathrm{M}^{+}_{\bullet} + \mathrm{Y} \rightarrow \mathrm{M} + \mathrm{Y}^{+}_{\bullet}$ |
| Energy transfer | $\mathrm{M}^{*} \rightarrow \mathrm{M} + \mathrm{Y}^{*}$ |

The absorption and scattering of high-energy photons is non-specific with respect to the involved species, that is, except for their electron densities. In other words, every chemical bond is susceptible to cleavage, and all parts of the molecules may be affected. Despite the randomness in the absorption of radiant energy, the consequent chemical alterations may be quite non-random. For example, in linear polymers, transfer, migration and trapping processes may support the dominance of specific reactions. Such processes include, among others, excitation energy transfer via a donor-acceptor mechanism, charge transfer via electrons and electron holes, and radical migration via hydrogen transfer.

## 2.3 Degradative effects

In the following, we summarise the main degradation mechanisms that lead to the observed macroscopic changes in polymer formulations. In all cases, the underlying elementary mechanisms include thermal motion and the interaction of high-energy photons with matter, as well as the consequent primary chemical reactions.

### 2.3.1 Chemical ageing mechanisms

Thermal and radiation ageing of organic polymers is primarily due to chain scission, crosslinking and oxidation reactions. Each type of reaction can be initiated by both thermal motion and radiation. Other relevant reactions include the formation and disappearance of double bonds, depolymerisation, and the elimination of side groups. All of the reactions, except the last one, can affect the polymer backbone.

- **Chain scission** refers to a chemical reaction in which a skeletal bond of the polymer chain is cleaved. Successive chain scission reactions thus lead to a decrease in the polymer's average molecular weight. Chain scission reactions can be classified according to the mechanism of scission or its location.

- **Crosslinking** refers to a chemical reaction in which a covalent bond is formed between adjacent polymer chains. Successive crosslinking reactions lead to the formation of a three-dimensional polymer network. This is observed as an increase in the polymer's average molecular weight.

Molecular oxygen has a significant effect on the thermal and radiation ageing of organic polymers due to its reactivity towards free radicals. The presence of oxygen enhances thermal and radiation ageing in most polymers. Moreover, most of the failures observed in practical conditions are due to thermo-oxidative ageing.

- **Oxidation reactions** involve a free radical chain mechanism with: (i) an initiation step that leads to the formation of free radicals, (ii) a propagation step that leads to the formation of peroxy radicals and hydroperoxide, as well as intermediary radicals, (iii) a branching step that leads to the decomposition of hydroperoxide, and (iv) a termination step that leads to the recombination of radicals to form inert species.

Oxidation reactions can be initiated by both thermal motion and radiation. They lead to multistage reactions that can end in either chain scission or crosslinking, the yields of which are dependent on the polymer formulation. Oxidation reactions typically dominate polymer ageing in practical conditions. For example, linear polymers that crosslink when exposed to ionising radiation in the absence of oxygen, undergo predominantly chain scission in its presence. Such polymers include, among others, polyethylene, polypropylene and poly(vinyl chloride). There are also polymers in which the presence of oxygen decreases the chain scission yield. In other words, it exerts a protective effect. Poly(methyl methacrylate) is an example of such polymer.

With sufficiently high radiation dose rates, oxidation reactions consume the oxygen dissolved in the polymer faster than diffusion processes can replenish. This condition is referred to as diffusion-limited oxidation (DLO). The process depends on the diffusion and dissolution rate of oxygen, the radiation dose rate, and the sample geometry. DLO can, for example, lead to pronounced ageing near the surface of a sample where the oxygen concentration is the highest. DLO is the primary dose rate effect in the radiation ageing of polymers. The same phenomenon is also encountered in purely thermal ageing.

### 2.3.2 Physical ageing mechanisms

Primary physical ageing mechanisms include the evaporation and migration of plasticisers. Plasticisers evaporate at the surface of the material, while their concentration at the surface is replenished by diffusion from the bulk. The role of plasticisers is to increase the plasticity of the polymer formulation. Decrease in their concentration thus has consequences for the material's mechanical behaviour. These ageing mechanisms are particularly important in materials with a high plasticiser content. In some applications, different polymer formulations come into direct contact with each other. This can lead to the diffusion of plasticisers (or other additives) from one material to the other, constituting a physical ageing mechanism. Material compatibility issues can also emerge at other interfaces. There can also be interactions between the degradation products of the different materials, which can potentially affect the ageing behaviour.

### 2.3.3 Ageing through a physical transition

Some polymers are semi-crystalline, with a crystalline melting region near the temperatures in which they are used. The crystalline phase is significant for the polymer's physical properties. The same is true for its ageing behaviour, as chemical reactions are hindered in the rigid crystalline regions, and the formed free radicals may be trapped within them. Most polymers behave similarly with respect to thermal and radiation ageing: generally, an increase in temperature results in an increase in the degradation rate. However, for semi-crystalline polymers, ageing can be faster at lower temperatures. This so-called "reverse temperature effect" stems from self-healing mechanisms (including recrystallization and radical recombination) that take effect at elevated temperatures (Burnay and Dawson 2001). For this reason, care must be taken when extrapolating the results of accelerated ageing experiments on semi-crystalline polymers. If the extrapolation is done over the crystalline melting region, the accelerated ageing will not be representative of ageing at practical operating conditions.

### 2.3.4 Protective agents

Measures exist for protecting organic polymers from ionising electromagnetic radiation. For example, certain protective agents, known as antirads, are added to polymer formulations. They typically function as antioxidants or free radical scavengers, thus preventing oxidative chain reactions. Additives can also act as energy sinks by absorbing electronic excitation energy from the base polymer. For instance, aromatic compounds operate in this manner. Energy transported to (or directly absorbed by) the aromatic groups is converted into thermal motion by collisions with nearby molecules. Due to this, aromatic polymers are fairly resistant to ionising electromagnetic radiation.

### 2.3.5 Synergistic and antagonistic effects

The various mechanisms underlying thermal and radiation ageing may exhibit synergistic and antagonistic (as well as cumulative and competitive) effects.

- Synergism refers to the situation where the combined effects of the environmental stressors are more severe than the sum of their contributions considered separately.

- Antagonism refers to the situation where the combined effects of the environmental stressors are less severe than the sum of their contributions considered separately.

In practice, both effects are observed in the combined thermal and radiation ageing of polymeric materials. Based on the earlier summary of the primary degradation mechanisms, we identified some conditions where the effects of the two stressors might interfere with each other.

- The elementary absorption and scattering processes of high-energy photons are temperature independent. Thus, the primary reactions induced by ionising electromagnetic radiation can occur at all temperatures. In contrast, the probability of thermally-induced reactions increases with temperature.

- A large part of the radiation-induced bond scission reactions are counterbalanced by recombination reactions. In this context, the influence of thermal motion is significant. This is primarily due to the increased mobility of the molecules and molecular segments, that affects the ensuing radical reactions. For example, in amorphous linear polymers, the increased segment mobility decreases the probability of recombination reactions.

- Diffusion of oxygen (as well as other species) is driven by both concentration gradients and thermal motion. While both radiation and thermal motion initiate oxidation reactions, only thermal motion contributes to the processes that replenish the oxygen concentration within the polymer. This is seen, for example, in diffusion-limited oxidation.

- Increase in temperature can lead to phase transformations, for example, the melting of crystalline regions in semicrystalline polymers. As chemical reactions are hindered in the rigid crystalline regions, and free radicals may be trapped within them, their melting would change the overall ageing behaviour of the polymer. Similar effects could be expected, if other physical transitions take place.

- Increased temperatures can also initiate different self-healing mechanisms, such as recrystallisation and radical recombination reactions in the reverse temperature effect.

# 3. Lifetime prediction methods

Lifetime prediction methods have a valuable role in in the lifetime management of polymeric NPP components. They can be used to estimate the residual service life of a component in service, or the expected service life of one to be installed. The predictions can lead, for example, to the investigation of components that are at risk of significant ageing. Lifetime prediction methods can also be used to identify conditions in which supplementary ageing management might be necessary. In both cases, there has to be sufficient confidence in the applicability of the method and the environmental monitoring history.

Practical lifetime prediction methods are all semi-empirical and based on accelerated ageing experiments (IAEA 2000a, IAEA 2000b). In such experiments, the component is subjected to exaggerated temperatures and dose rates for a time that is considerably shorter than its intended service life. Certain assumptions about the ageing mechanisms make it possible to extrapolate the ageing behaviour to lower temperatures, lower dose rates, and longer exposure times. One of the key assumptions is that the same ageing mechanisms are at work in the accelerated experiments and in the actual operating conditions. Possible confounding factors, such as dose rate effects, diffusion limited oxidation, and synergistic effects have to be taken into account when designing the ageing experiments.

In the following, we introduce the most important practical lifetime prediction methods. The methods do not consider environmental stressors other than temperature and ionising electromagnetic radiation. It is remarkable, that majority of the polymer formulations used in NPPs can be addressed with this toolbox.

## 3.1 Arrhenius relation

The Arrhenius relation can be used for lifetime prediction when only thermal ageing is considered. The approach is based on the following assumptions: (i) that the molecular collision probability increases at a constant rate with increasing temperature, and (ii) that the dominant ageing mechanism stays unchanged throughout the considered temperature range (Fuse et al. 2014). The equation for lifetime prediction is:

$$\Delta t_1 = \Delta t_2 \mathrm{e}^{E_\mathrm{a}/(\mathrm{R}T_1 - \mathrm{R}T_2)} \tag{1}$$

where $\Delta t_1$ is the ageing time required at temperature $T_1$ to simulate a service life of $\Delta t_2$ at the temperature $T_2$, and $R$ is the universal gas constant. The activation energy $E_\mathrm{a}$ can be determined from the slope of time to equivalent damage versus 1/T plots that are obtained from ageing experiments at different temperatures. The feasibility of the approach for specific conditions (material, temperature range) can be assessed by comparing the shapes of the experimental time-degradation curves at various temperatures. The Arrhenius approach requires relatively small amounts of data, which is an obvious advantage. As the method is not applicable to radiation ageing, any synergistic or dose rate effects are also ignored. Further details of the method and examples of its use are given in (IAEA 2000a, IAEA 2000b).

## 3.2 Power-law extrapolation

The power-law extrapolation method can be used for lifetime prediction when only radiation ageing is considered. The method is based on isothermal radiation ageing experiments carried out at several different dose rates. The dose required to reach a specific end point criterion, i.e., dose to equivalent damage (DED), is assumed to follow a simple power law:

$$\mathrm{DED} = kD^n \tag{2}$$

where $D$ is the dose rate, and $k$ and $n$ are material-specific parameters. When there is no dose rate effect, the parameter $n$ equals zero, and the damage depends only on the total absorbed dose. The method is especially useful for materials with a dose rate effect. The extrapolation is, however, limited to the temperature used in the accelerated ageing experiments. Moreover, the extrapolation range is generally limited at higher temperatures. The power-law extrapolation method is the only feasible method for polymers with a reverse temperature effect. Further details of the method and examples of its use are given in (IAEA 2000a, IAEA 2000b, IEC 2014).

## 3.3 Superposition of time dependent data

The superposition of time dependent data method can be used for lifetime prediction when combined thermal and radiation ageing is considered. The method relies on accelerated ageing experiments carried out at various different dose rates and temperatures. The time evolution curves of an ageing indicator (e.g. elongation at break) are superposed into a so-called master curve. This is achieved by using a temperature and dose rate dependent shift factor function, which is parameterised in the process. The semi-empirical shift factor function is of the form:

$$\mathrm{a}(T, D) = e^{-E_\mathrm{a}/\mathrm{R}(1/T - 1/T_\mathrm{ref})}\left(1 + kD^n e^{E_\mathrm{a}/\mathrm{R}(1/T - 1/T_\mathrm{ref})}\right) \tag{3}$$

where $E_\mathrm{a}$ is the activation energy of thermal ageing, $T_\mathrm{ref}$ is the reference temperature of the master curve, $k$ and $n$ are material-specific parameters related to radiation ageing. When the dose rate is set to zero, the shift factor simplifies to the Arrhenius relation:

$$\mathrm{a}(T,0) = e^{-E_\mathrm{a}/\mathrm{R}(1/T-1/T_\mathrm{ref})} \quad (4)$$

At the reference temperature, the shift factor simplifies to the power-law form:

$$\mathrm{a}(T_\mathrm{ref}, D) = 1 + kD^n \quad (5)$$

The superposition of time dependent data method can account for both dose rate effects and synergistic effects in thermal and radiation ageing. However, like the other methods, it has its limitations. Firstly, setting up the shift factor requires a large matrix of experimental data. Secondly, the superposition is only possible if a single dominant ageing mechanism is at work under the considered conditions. The method has been demonstrated on a range of polymeric materials. It works best for amorphous polymers, and is not usually good for polyolefins or semicrystalline polymers. Further details of the method and examples of its use are given in (IAEA 2000a, IAEA 2000b, IEC 2014).

## 3.4 Superposition of dose to equivalent damage data

The superposition of DED data method can be used for lifetime prediction when combined thermal and radiation ageing is considered. Like the superposition of time dependent data method, it relies on accelerated ageing experiments carried out at various different dose rates and temperatures. The method involves generating a series of curves of end point doses as a function of dose rate for different temperatures. The shift factor function required to superpose the curves is only dependent on temperature, and is often of the Arrhenius form. The superposition of DED data method is applicable to materials that exhibit more than a single dominant ageing mechanism under the considered conditions. The method has been demonstrated on a range of polymers, particularly cable materials. It is particularly useful for materials that exhibit a strong dose rate effect. Like the other methods, it has its limitations. Firstly, setting up the shift factor requires a large matrix of experimental data. Secondly, the method is not applicable to materials that exhibit the reverse temperature effect in the temperature range of interest. Further details of the method and examples of its use are given in (IAEA 2000a, IAEA 2000b, IEC 2014).

## 3.5 Other methods

Specific lifetime prediction methods have been developed for natural rubber, poly(vinyl chloride) and polyethylene based materials. Their details are given in (IAEA 2000b).

# 4. Numerical modelling of ageing phenomena

The lifetime prediction methods introduced in the previous chapter are all semi-empirical. In other words, they do not have real predictive power with respect to the mechanisms of ageing. If the dominant mechanisms change over the considered environmental conditions, the methods lose their applicability. In a worst case scenario, this could happen without the user realising it.

In an ideal world, the ageing behaviour of a polymer formulation could be predicted starting from the basic laws of physics. As for most real-life systems, the complexity of the problem is prohibitive. However, many mechanistic details of thermal and radiation ageing can be addressed with the currently available tools of computational materials science. In the following, we propose ways in which numerical modelling could provide insight into the details of the ageing process. The list is, by no means, comprehensive, and several other possibilities exist as well. A visual summary is given in Figure 1.

Starting from the lowest level models and moving up with respect to both structural and time scales:

- Electronic structure calculations based on density-functional theory (DFT), or some other approach, such as the Hartree-Fock (HF) or tight-binding (TB) methods, can yield accurate information on the energetics and thermodynamics of chemical reactions.
    - Such calculations could be used to assess the feasibility of proposed reactions paths behind the chemical ageing mechanisms, and to determine their associated kinetics.
    - As an example, Mayes and Broadbelt (2012) used DFT-based electronic structure calculations to discover a concerted reaction behind the thermally-induced depolymerisation of cellulose.
    - Due to their computational cost, electronic structure calculations are currently limited to systems consisting of (roughly) hundreds of atoms.
    - Ab initio molecular dynamics methods, such as Car-Parrinello molecular dynamics (CPMD), can be used to study dynamic phenomena. Again, the system size and time scales are rather limited.
    - For further information on electronic structure calculations, see e.g. (Martin 2004).
- Reactive molecular dynamics (RMD) simulations, which are based on reactive interatomic potentials and Newtonian dynamics, can yield rough predictions of chemical reaction paths, as well as estimates of the associated kinetics.
    - As an example, Polvi et al. (2012; 2013; 2014) used RMD simulations to study the primary radiation defect production in polyethylene and cellulose.
    - Electrons are not explicitly present in an RMD simulation. For this reason, reactions involving electron transfer are problematic. Also, the interaction of high-energy photons with the atoms has to be modelled indirectly.
    - Due to their computational cost, practical RMD simulations are currently limited to systems consisting of (roughly) thousands of atoms, and to times in the nanosecond to picosecond range.
    - For further information on RMD simulations, see e.g. (Liang et al. 2013).
- Classical molecular dynamics (MD) simulations, which are based on non-reactive interatomic potentials and Newtonian dynamics, can yield predictions on how molecular structure translates into various thermodynamic and mechanical properties. In the context of polymer ageing, MD simulations could be used, for example, to study the diffusion of molecular oxygen, as well as other relevant species. Phase transformations, and their effect on the local electrostatic environment (which can affect chemical reactions paths), could also be considered.
    - Due to their computational cost, practical MD simulations are currently limited to systems consisting of (roughly) tens or hundreds of thousands of atoms, and to times in the picosecond range.
    - Simulation size and time scales can be extended by so-called coarse-graining methods. For example, instead of atoms, the particles can be used to represent individual molecules or monomer units. This requires a specialised

structural representation and a corresponding interaction model. This kind of particle simulations are called coarse-grained molecular dynamics (CGMD) simulations.

  - For further information on MD simulations, see e.g. (Frenkel and Smit, 2002).

- Finite element analysis (FEA) (or finite element method, FEM), which is a numerical technique for solving boundary value problems for partial differential equations, can be applied to a wide range of continuum mechanics problems. In the context of polymer ageing, FEA could be used, for example, to study how ageing-induced microstructural changes translate into the degradation of macroscopic mechanical properties. Realistic microstructural descriptions could be derived from imaging experiments, such X-ray nanotomography and electron microscopy. The modelling of DLO and its effect on the mechanical properties of a polymeric component could also be feasible.
  - As an example, Laiarinandrasana et al. (2012) used FEA to model the effect of filler content on elastomer relaxation rate.
  - For further information on FEA, see e.g. (Zienkiewicz et al. 2013)

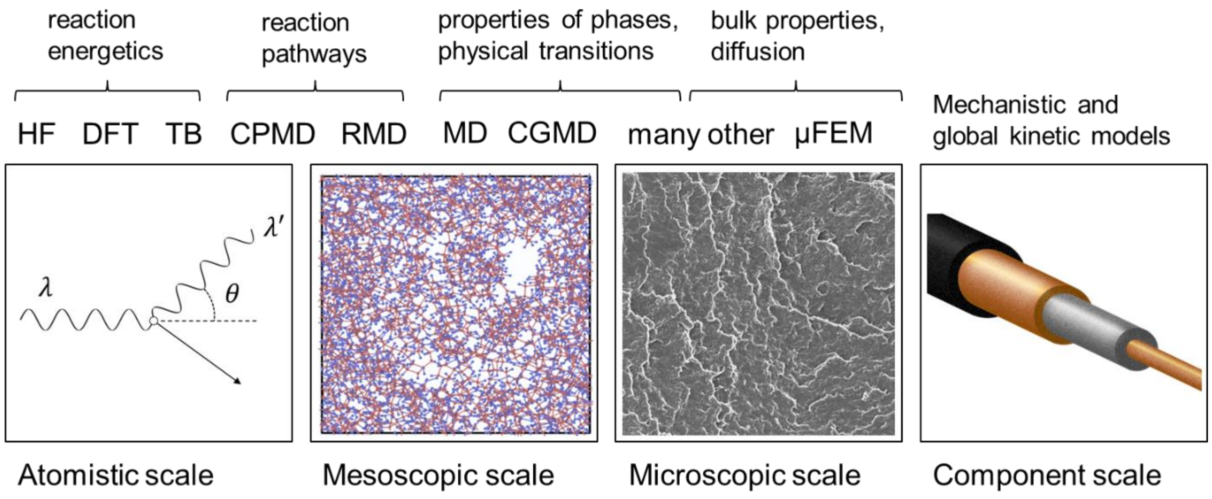

*Figure 1. Scales and processes of thermal and radiation ageing coupled with numerical modelling methods.*

## 5. Conclusions

We carried out a literature survey on the synergistic effects of temperature and radiation in polymer ageing, and on possible ways of considering them in the lifetime prediction of nuclear power plant components. We looked for proposed mechanisms behind the synergistic effects, identified materials modelling methods feasible for studying them, and compiled an overview of previous research related to the topic.

We found that the mechanisms underlying combined thermal and radiation ageing can be exceedingly complex, involving various chemical and physical processes across multiple structural and time scales. Probably due to this, practical lifetime prediction methods are semi-empirical and based on accelerated ageing experiments. Methods applicable to combined thermal and radiation ageing include the superposition of time-dependent data method, and the superposition of dose-to-equivalent-damage data method. The semi-empirical methods are limited in their predictive capability, as they cannot address possible changes in the dominant ageing mechanisms. For this reason, anomalous ageing phenomena such as the reverse temperature effect can render their predictions useless.

Mechanistic details of both thermal and radiation ageing can be addressed with the theoretical tools of computational materials science. For example, electronic structure calculations can be used to assess the feasibility of proposed reaction paths, and to predict the associated kinetics. At the other end of the spectrum, finite element analysis can be used to study how ageing-induced microstructural changes translate into the degradation of mechanical properties. Nevertheless, there remains a formidable gap between the present multi-scale materials modelling capabilities and practical lifetime prediction. Bridging the gap is clearly beyond the resources available in the context of the SAFIR2018 programme. However, modelling focused on a particular synergistic mechanism or some other relevant detail of the ageing process is feasible.

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