

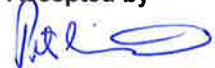


Methods used in evaluating the severity of dose rate effect

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Summary	
<p>The polymer degradation induced by ionizing radiation is mostly governed by radicalization of single atoms or molecules in polymer chain or matrix and the following chemical reactions that ultimately lead to polymer chain scission. Current view is that the dose rate effect exists both at low dose rates and high dose rates. The mechanism governing dose rate effect at high dose rates is based on diffusion of oxygen in the polymer matrix. At low dose rates the mechanisms is different and based on polymer related complex chemical reactions initially induced by the ionizing radiation. Total of three semi-empirical methods were found that could be used to evaluate the severity of dose rate effect on polymers: power law method, superposition of time depended data and superposition of dose to equivalent damage data. Methods seem to work for wide range of polymers when evaluating the dose rate effect on both low and high dose rates but they have some limiting factors related to them. The methods cannot be used for semi-crystalline materials that are known to be prone to reverse temperature effect. These methods require also experimental data from thermal, γ-radiation or combined environments in order to draw reliable function for dose rate effect evaluation. This would yield significant extra costs compared to conventional qualification process. In case of chlorosulphonated polyethylene (CSPE) it has been observed that there is very small variation on degradation rates of CSPE grades coming from different manufacturers. This would indicate that already existing data from CSPE could be used in estimation of the severity of dose rate effect without causing significant error to the dose rate effect analysis or increase in qualification cost.</p>	
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Preface

This study was made as part of the project “Condition Monitoring, Thermal and Radiation Degradation of Polymers inside NPP Containments (COMRADE)” executed within the SAFIR 2018 research program. The purpose was to gather and analyze methods that could be used in estimation of severity of dose rate effect on polymeric materials. Finnish State Nuclear Waste Management Fund (VYR) and VTT Technical Research Centre of Finland Ltd are acknowledged for funding this work.

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1. Introduction

Different polymer components are used in inside nuclear power plant (NPP) containments in various applications e.g. due to their tightness or insulating properties. During a normal service of a NPP, they are exposed to ionizing radiation which is along with elevated temperatures a key aging factor for these kinds of materials. Depending on the use of the polymer component, they are qualified according to proper standards, such as IEEE (Institute of Electrical and Electronics Engineers) 383 or STUK-YTO-TR 210. The acceptance criteria in qualification is usually defined as some value of mechanical property, 50 % absolute or relative elongation value being one of the most commonly used on cable insulator or jacketing materials, that the tested component must fulfil. The used standards provide the accelerated ageing treatment parameters, and in irradiation ageing a certain limit for dose rate and absorbed dose are usually defined. Usually the used dose rate during accelerated ageing is very high e.g. STUK-YTO-TR 210 defines the used dose rate to be > 10 kGy/h. However, the actual dose rate during normal use of NPP is typically several magnitudes lower (< 1 Gy/h) according to [Penttilä et al. 2016]. Thus a question concerning the ability of accelerated ageing by using higher dose rates to produce same degradation mechanisms and an equal amount of degradation in polymers compared to the typical service environment with lower dose rates in NPP containments arises.

It is shown by many references in literature [Gillen et al. 1981, 1989, 1993, Reynolds et al. 1995] that at very low dose rates oxygen molecules have time to diffuse homogeneously throughout the polymer and thus oxidation induced degradation is distributed evenly within the polymer which can further cause additional damage to the polymer structure. As a result the use of low dose rate during irradiation causes greater amount of degradation to polymer compared to higher dose rates when the absorbed dose is kept constant. However, dose rate effect can be detected also at high dose rates. During accelerated irradiation ageing diffusion limited oxidation (DLO) can become a significant factor affecting to the degradation of the irradiated polymer. Any DLO effects will give inaccurate simulation on the ageing in both cases where the designed service life is simulated or even in DBA (Design Basis Accident) simulations if the oxidation is homogenous. During DBA dose rates are typically some hundreds of grays which might allow homogenous oxidation on some polymer grades while the use of dose rate in range of kilograys would most likely cause DLO based dose rate effect and thus yield in inaccurate degradation for the tested material. It is apparent that accelerated irradiation (and thermal) ageing data needs to be carefully interpreted in order to avoid their faulty application to real conditions.

This report concentrates on the irradiation based degradation of polymers and more precisely on methods that can be used in evaluation of dose rate effect as function of dose rate i.e. predicting from experimental data whether equivalent absorbed dose at lower dose rates causes more degradation in polymer than the corresponding equivalent absorbed dose at higher dose rates. These kinds of models could provide cheaper and more practical way to approach the existence of dose rate effect on certain polymer grade than time consuming low dose rate irradiation experiments. Applicable method would ease the recognition of the existence and severity of the dose rate effect so it could be taken into account when polymer component lifetime is predicted during qualification.

2. Goal

The goal of this literature study was to summarize the mechanisms of polymer degradation under ionizing radiation and governing dose rate effect for polymers. Different methods that can be used in evaluation of dose rate effect and predict long-term ionizing radiation damage are gathered and their applicability to estimate the severity of dose rate effect is evaluated.

3. Radiation induced degradation of polymers

In order to understand polymer ageing due to ionizing radiation some aspects of molecule scale chemistry or degradation mechanisms needs to be mastered. Radiation induced degradation is very similar to thermal induced degradation which is also important to understand when accelerated ageing is conducted [Celina, 2013]. In this chapter the interaction between ionizing radiation and polymer structure is discussed briefly and followed by description of polymer degradation mechanisms induced by ionizing radiation and ending with a description of the dose rate effect.

3.1 Interaction with ionizing radiation

The chemical reactions governing irradiation based ageing on polymer materials inside NPP containments are launched by interacting β -particles, γ -quantum and neutrons produced during nuclear fission and radioactive decay of fissile material. α -radiation is not relevant in this context since its contribution to ageing of polymeric materials during designed service life, postulated accidents (scenario does not include core damage) or severe accidents (scenario includes core damage) is negligible in this context [Penttilä et. al. 2016]. Also β -radiation is only relevant during postulated accidents and severe accidents due to its considerably greater attenuation in medium. Neutron radiation (or more precisely the ratio of thermal and fast neutrons) governs the criticality of the running reactor and it is thus a major source of ionizing radiation during power operation. During accidental scenarios (i.e. postulated accident or severe accident) neutron radiation is present due to ongoing fission and radioactive decay but the magnitude is depending on the nature or severity (e.g. amount of core damage) of the accident. The difference which distinguishes γ -radiation from β - and neutron radiation is the dualistic nature of γ -radiation. This dualism is typical for electromagnetic radiation and the energy of γ -quantum is related to frequency of the the photon as

$$E = h\nu \quad (1)$$

where h is the Planck's constant and ν is the frequency, being typically $>10^{20}$ Hz. In the case of γ -radiation term particle can be misleading since the actual radiation is emitted as high frequency photons resulting from radioactive decay. β - and neutron radiation do not obey same equation as γ -radiation since they consist of charged on non-charged particles having certain kinetic energy. The amount of energy that particle possess depends on radiation characteristics e.g. on the charge, mass and velocity of the particle. The common factor is however that each type of radiation carries enough energy to free electrons from atoms or molecules, causing ionization and further chemical reactions with the polymer backbone. Thus all previously discussed forms of radiation can be stated as ionizing radiation.

The mechanism governing the interaction of β -particles with polymers is the charge of the particle reacting with the outer electrons of atoms in polymer material. The atoms located in the polymer structure are excited as the kinetic energy of the particle is transferred to the atom. This excitation includes exciting the electrons to higher states and ionization of atoms and molecules. Due to the charge and mass of β -particle they are more prone to interact with other atoms compared to neutron and γ -radiation. Attenuation of β -radiation is thus more pronounced, e.g. with relatively large particle energy 10 MeV, β -radiation can penetrate up to ca. 5 cm thick polyethylene sheet.

γ -radiation can interact with polymers either by the photoelectric effect, Compton effect, pair production or photonuclear absorption[Schnabel, 2014]. The first of the three mentioned types of interaction are presented in Figure 1. The dominant interaction mode is governed by the energy of the photon. Photoelectric effect is the most common interaction when the energy of the photon is relatively low ($<0,05$ MeV [Kulshreshtha et al. 2002], <1 keV [Schnabel, 2014]). In this interaction photon will react most likely with electrons located on

the outer shell of the atom and the probability to react with electrons on the inner shells increase with increasing photon energy. The interacting photon is completely consumed in the ejection of electron (point A in Figure 1). In Compton scattering energy of the photon is somewhat greater than in photoelectric effect (0,1-10 MeV) and the collision of photon and electron is somewhat elastic in nature. The incident photon transfers a part of its energy to the electron causing ejection of the electrode and after the interaction scatters away with changed wavelength (point B in Figure 1). At high photon energies (equal or greater than 1,022 MeV, which is twice the rest mass energy of an electron) and when interaction takes place in the vicinity of a nucleus, pair production can occur where in addition to ejected electron an additional positron is created (point C in Figure 1). Photonuclear absorption occurs when photon with high energy (MeV range) absorbs to a nucleus causing emission of a neutron or neutrons.

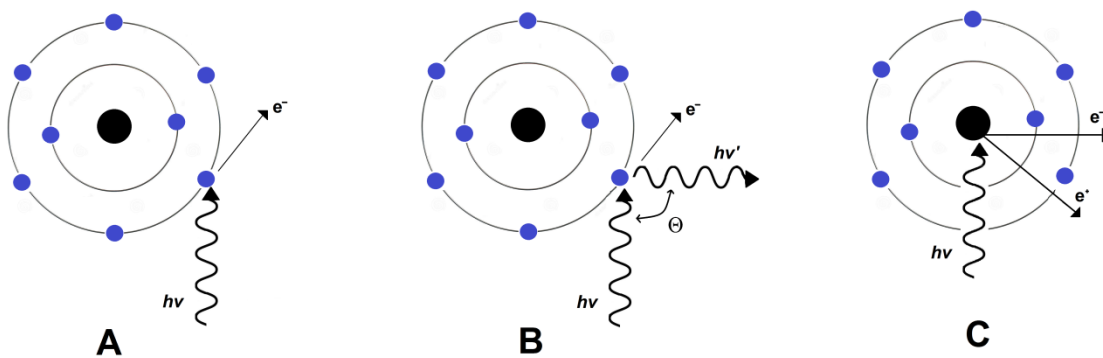


Figure 1: Principle of gamma rays interacting with an atom: A) Photoelectric effect B) Compton effect C) Pair production. The atom nucleus is centred (black circle) and surrounded by electrons (blue circles).

Neutrons do not possess a charge but are able to interact with matter if they possess enough kinetic energy. The interaction mechanism between matter and neutron radiation is somewhat indirect. Neutrons collide with atoms in elastic and inelastic manner causing recoil to the electrons and protons. Fast and thermal neutrons can also collide with atom nucleus causing transmutations to radioactive isotopes [Kulshreshtha et al. 2002]. However, in the case of polymers where atoms such as carbon, oxygen and hydrogen comprise the vast majority of the bulk material structure, it is rare. The likelihood that a neutron interacts with another atom is described with neutron cross section, where larger neutron cross section means more likely reaction between nucleus and the target atom. Typical atoms included in polymer backbone tend to have low neutron cross sections. Only in cases where some polymer additives possessing larger neutron cross section, such as Sb, polymers may become active due to neutron radiation.

3.2 Radiation induced degradation mechanisms

Ionizing radiation induces excited states on molecules in bulk polymer transferring them from a neutral charge state to a charged state simultaneously creating additional electrons. These charged particles and electrons continue to interact with surrounding molecules causing different reaction paths resulting in radical formation or other reaction products. These primary reaction paths have been listed by [Schnabel, 2014]. The reaction paths that end up in radical formation include decomposition of excited molecules, radical anions and radical cations. There are few fundamental degradation mechanisms that are caused by these radicals.

3.2.1 Crosslinking vs. chain scission

Crosslinking and chain scission are processes that are always present at the same time when polymer is degraded due to ionizing radiation. The tendency to crosslink or chain scission is described with a parameter called *G value*. It is defined as the chemical yield of radiation in number of molecules reacted per 100 eV of absorbed energy. For crosslinking $G(X)$ values and for chain scission $G(S)$ values can be defined. When relation $G(S)/G(X)$ is below 1, crosslinking dominates and when above 1 chain scission is the dominant degradation mode. Very low $G(S)$ and $G(X)$ values are characteristic to irradiation resistant materials.

Chain scission can be described as cutting a covalent bond between two atoms located in polymer structure due to excitation of an atom structure induced by ionizing radiation, which yields in two unstable structures that are prone to react with their surrounding molecules. In crosslinking, linear polymers are joined together thus forming a three dimensional network structure. Crosslinks are spots in polymer structures where radicals are recombined. Crosslinking can be divided in two types as shown in Figure 2: H- and T-types, where H-type is induced by secondary radicals formed from the break of side chain link or radical reacting with double bond between two carbon atoms. T-type crosslinking appears when primary radicals from main chain scission react with secondary radicals. H-type crosslinking tends to dominate in flexible polymers and T-type is more likely to occur on rigid polymers.

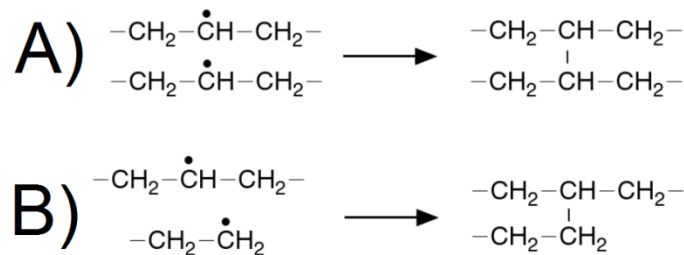


Figure 2: Two general types of crosslinks between two separate polymer chains after radicals in each polymer chain react. A) represents H-type and B) T-type crosslinking.

Factors affecting to the amount of radiation induced crosslinking include physical and chemical properties of polymer, molecular weight and configuration. The most important physical properties are crystallinity and mobility of polymer chains. Polymer microstructure can be seen as mixture of crystalline and amorphous regions and the relative sizes of these regions are determined during the manufacturing of the polymer. Radiation induced crosslinking concentrates on amorphous parts of polymer structure. Secondary radicals and mobile polymer chains are required in amorphous regions in order to complete crosslinking. The degree of crystallinity has thus an effect to the crosslinking susceptibility. Mobile polymers, in this context meaning the ability of carbon atoms rotate within the main chain, are more susceptible to crosslinking. The glass-transition temperature, T_g , is a measure for this property.

Chemical properties that have effect on crosslinking ratio include bond strength, unsaturation, attachment of certain atom/molecule group to the main polymer chain and branching. The concept of bond strength is somewhat straight forward. The bond between two atoms has certain strength and in order to break such a bond, higher energy than the bond strength needs to be absorbed in it. Unsaturation means the presence of unsaturated double bonds between the carbon atoms. Even small radicals are capable to break the double bond creating a polymer radical which is susceptible to form crosslinks. Different polymers contain groups that give to the polymer their characteristic properties e.g. PVC has an additional Cl atom attached to the systematic polymer backbone structure. These groups

can cause polymer structure to be more prone to either towards to crosslinking or chain scission under ionizing radiation. These additional groups can increase bond strength between carbon atoms and stiffen the structure (e.g. methyl group) or dissipate the absorbed energy preventing any structural changes from happening (e.g. phenyl group) [Makuuchi et al. 2011]. Also the location of additional atoms can effect to the radiation caused degradation e.g. randomly distributed halogen atoms can enhance crosslinking while uniform distribution increases chain scission. The amount of branching has effect on crosslinking capability while increasing branching decreases crosslinking.

3.2.2 Radiation induced oxidation

Irradiation conducted in air tends to be more detrimental to polymers than irradiation conducted in a vacuum. This is due to presence of oxygen which is known to accelerate radiation induced degradation. The free radicals formed within the polymer during the irradiation react with oxygen molecules diffused within the polymer matrix which yields in formation of peroxide radicals. These radicals will cause oxidation and oxidative chain scission (or crosslinking in case where it is predominant degradation form). Depending on the polymer nature oxidation can either increase chain scission (e.g. polyethylene) or decrease it (e.g. PMMA). In Figure 3 the initial step in oxidation reaction between radical and oxygen molecule (No. 1 in Figure 3) and the following reaction mechanisms induced by it, is presented. Excess heat and/or moisture can further complicate oxidation process and yield in products containing carbonyl groups such as carboxylic acid.

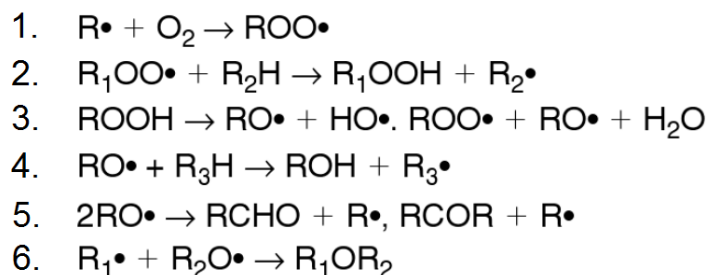


Figure 3: Auto-oxidation reaction mechanism in polymer.

The rate of oxidation is comparable to oxygen consumption or the formation of oxidized products. Many factors, such as diffusion, atmosphere, temperature, dose rate, morphology and dimension of polymer, have an effect to the oxidation rate but the most important one is the effect of diffusion. In the case of polymers irradiated in air, diffusion is affected by the thickness and structure of irradiated polymer as well as the used dose rate. The effect of thickness is simply related to the fact that in the case of thinner polymer samples homogenous distribution of oxygen takes less time via diffusion than in the case of thick samples. Also the amount of crystallinity has effect since in amorphous phases diffusion is faster than in the crystals. Dose rate has a direct influence to oxidation. Since the radicals formed during irradiation react with oxygen molecules forming peroxide radicals, diffusion of oxygen is the limiting factor for oxidation. When very high dose is applied, all oxygen reacts very fast and oxygen transferred via diffusion to the polymer reacts on the very surface of the polymer and thus the degradation based on oxygen radicalization is limited to the near surface areas i.e. polymer is degraded heterogeneously. On the other hand, at very low dose rates when oxygen is consumed less by the forming radicals, oxygen molecules have time to diffuse homogeneously throughout the polymer and thus oxidation induced degradation is distributed evenly within the polymer. Homogenous oxidation pronounces organic peroxide formation which can cause additional damage to the polymer structure [Reynolds et al. 1995]. As a result the use of low dose rate during irradiation causes greater amount of degradation to polymer compared to higher dose rates when the absorbed dose is kept constant. This kind of behaviour is governed by oxygen diffusion as well as dose rate and it

is generally stated to be DLO. It can be considered to be as one of the three types of mechanisms causing dose rate effect. The other two mechanisms are based on radiation-induced chemical pathways and mixing the relation between thermally-induced and radiation-induced chemistry by changing dose rate in the middle of the ageing procedure. Several studies have recognized dose rate effect to exist [Clavreul 1999, Gillen et al. 1981, Pinel et al. 1991, Placek et al. 2003, Reynolds et al. 1995].

3.3 Radiation-induced ageing during accelerated ageing treatments

During accelerated irradiation ageing treatments considerably larger dose rates are used in order to minimize treatment times and cost. The dose rate is kept constant during the accelerated ageing as stated in many instructions e.g. in [STUK, 2004]. Due to the constant dose rate during the accelerated ageing, dose rate effect coming from interference of the balance between thermally-induced and radiation-induced chemical reactions can be neglected. Radiation-induced accelerated ageing and related dose rate effect can be thus illustrated with relation of dose-to-equivalent-damage (DED) parameter and dose rate as plotted schematically in Figure 4 which is reproduced based on the studies conducted by Gillen et al. on thermal and radiation ageing of different polymer types [Gillen et al. 1989, Gillen et al. 1993]. Decrease in DED-value, when dose rate is shifted, is an indication on dose rate effect.

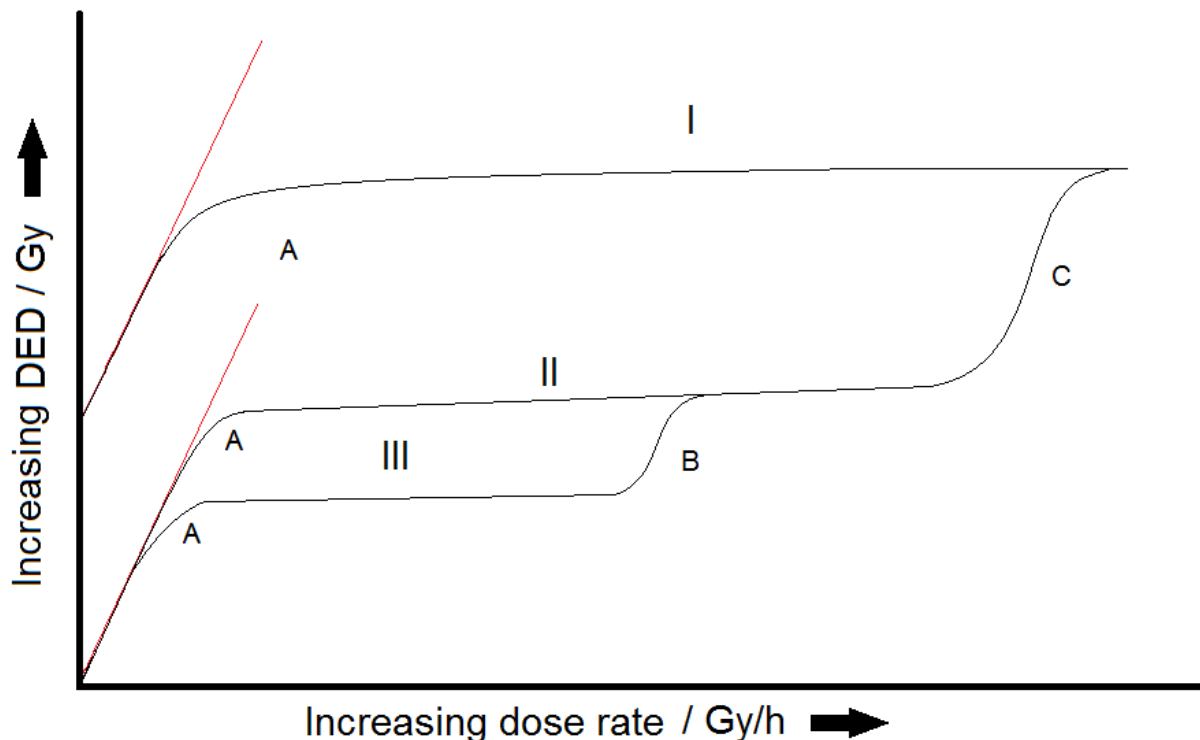


Figure 4: Schematic illustration on different ageing effects on polymers as function of dose rate. Curves I to III plot DED values as function of dose rate. Curve I describes behaviour when irradiation is done in vacuum, curve II when in air and curve III when in air on a polymer that shows complex dose rate effect.

DED parameter represents the dose that is required to cause a certain amount of degradation in a chosen material property (usually 50% of elongation-at-break) at certain dose rate. It can be defined for a polymer when irradiation data is obtained at different absorbed doses. DED values can be plotted as function of dose rate as more data at several

dose rates is obtained. Curve I in Figure 4 represents situation where polymer is aged in inert atmosphere (no oxygen present). At intermediate dose rates (where extreme values are excluded), curve has slope of almost 0 which indicates that very minor or no dose rate effect exists i.e. the amount of degradation induced by ionizing radiation in the polymer is not depending on the dose rate. As the behaviour of curve I is examined further to the relatively low dose rates, curvature exists followed by ending to a straight line. During this curvature a small dose rate effect may take place, depending on the governing thermal and radiation degradation pathways [Gillen et al. 1993]. As the dose rate approaches zero value, the effect of irradiation induced ageing diminishes and the ageing is only governed by thermal energy. At the linear region the amount of degradation is thus directly linked and solely determined by the time of exposure at the constant temperature. The slope of the curve at this region would be one. The existence of this linear region is not depending on the nature of the atmosphere.

When curve II in Figure 4 is examined, one can distinct an additional curvature (marked as C) at very high dose rates which resembles the DLO. As the dose rate increases above a certain limit, homogenous oxidation will decrease causing a decrease in degradation (DED-value increasing). The decrease in degradation will reach the same level as in the case of curve I due to the fact that oxidation will occur in thinner and thinner parts in the vicinity of the surface as the dose rate increases. Contribution of DLO to the degradation will diminish as the dose rate achieves a rate of sufficient magnitude (some very large dose rate). At intermediate dose rate one can observe a very small dose rate effect as dose rate is decreasing. The slope of the curve at this region is typically between 0 and 0,4, depending on the polymer type.

Dose rate effect can be observed also at intermediate dose rates as distinguished by curve III in Figure 4. At high and very low dose rates the curve is congruent with curve II but a change in DED can be observed at intermediate dose rates. This is thought to be related to the rate-limiting steps of the oxidation chemistry. Radicals having a long lifetime can be trapped inside of crystalline areas or breakdown of intermediate hydroperoxide species is sluggish enough that their effect to the degradation is not observed during the relatively short ageing treatment and following material testing period.

According to DED vs. dose rate plots, dose rate effects can be evaluated at relatively high and low dose rates if proper irradiation testing data is available. However, one should be capable to evaluate the homogeneity of ageing since at high dose rates the effects of DLO can be emerged. DLO is known of its complicating effects to temperature or radiation induced ageing in cases where highly accelerated ageing and large/thick samples are used. DLO can be thus considered to be one mechanism explaining dose rate effect at very high dose rates. In the next section methods that use empirical data in plotting single DED measurements vs. dose rate are introduced.

4. Methods used in dose rate effect evaluation as function of dose rate

Long-term low dose rate ionizing radiation is typical exposure for NPP polymer components located inside containments. Review for research related to extrapolating methods on long-term radiation effects has been conducted by Gillen and others [Gillen et al. 1981, 1989, 1993]. Research work has concentrated mostly on methods based on superposition and power law method which are evaluated in IAEA document [IAEA, 2000] and later approved as standardized methods for lifetime prediction [IEC, 2014]. These methods require experimental data and homogenous oxidation on samples used in accelerated ageing tests.

4.1 Power law method

The power law method requires experimental data on samples at constant temperature and irradiated with different dose rates. Minimum of three dose rates should be chosen and the dose rates should be chosen at different magnitudes i.e. values at one order of magnitude lower than the previous value. From each dose rate sets, samples are tested at different absorbed doses. Typically tensile testing and relative elongation at break (EAB) values are applied. The experimental data from constant dose rate experiments are then plotted as function of dose as schematically shown in Figure 5. The DED-values (usually 50% EAB) are defined from each constant dose rate data sets, meaning that at least three different data sets described in Figure 5 are required by the method. The obtained DED values are then plotted in logarithmic form against dose rate, forming a linear plot as seen in Figure 6. DED values at lower dose rates can be extrapolated by using logarithmic form function:

$$DED = K * D^n, \quad (1)$$

where K and n are constants and n has value of <1 . D is the dose rate.

The power law method is relatively simple to use and it has been shown to work for polyolefins at the vicinity of room temperature. The method can be well used for DED value extrapolation on two decades lower dose rates than the experimental data acquired when the experimental data is obtained at near room temperature values. In the case of higher temperatures the extrapolation is more limited due to the increasing effects of thermal ageing. For the regions where thermal ageing is dominant, power law method would overestimate the DED values. It is also important that the experimental data shows linear behaviour and no complex dose rate effects exist on the polymer. Currently power law method is the best method available for extrapolating dose rate effect on materials that have tendencies towards reverse temperature effect i.e. in the presence of radiation degradation is faster at lower than at higher temperatures.

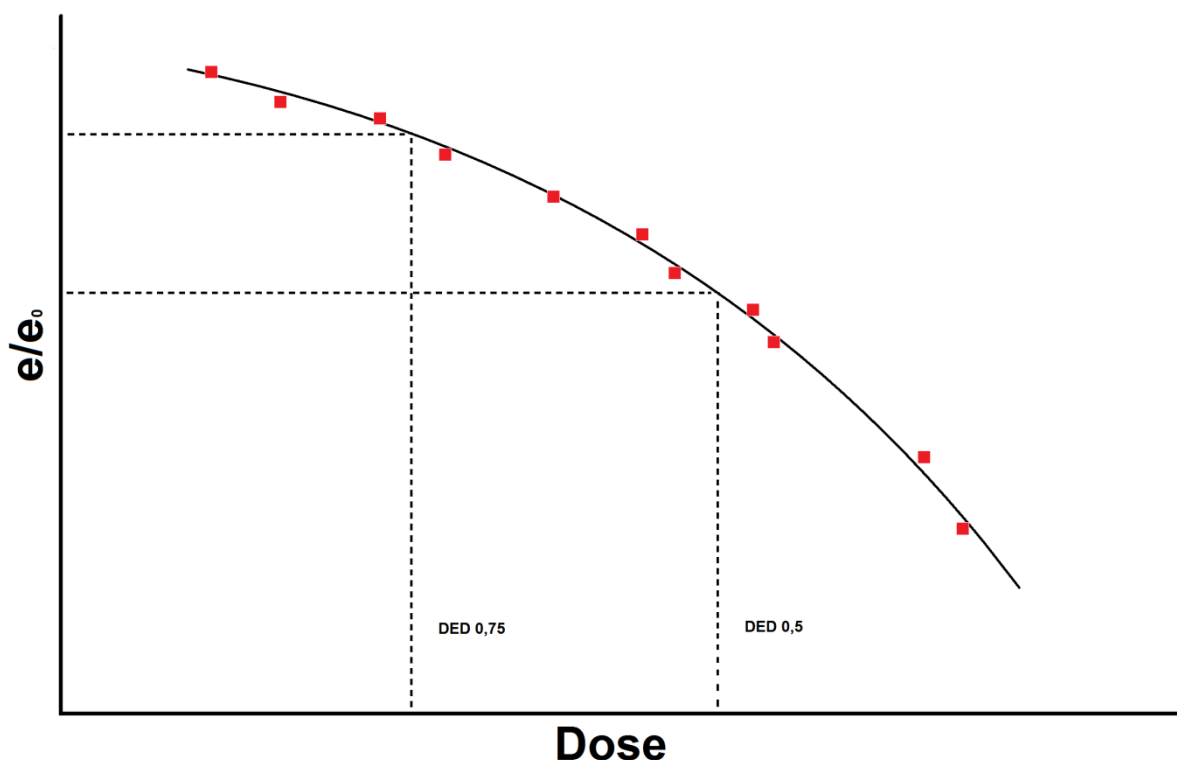


Figure 5: Schematic illustration on defining DED value from constant dose rate ageing data.

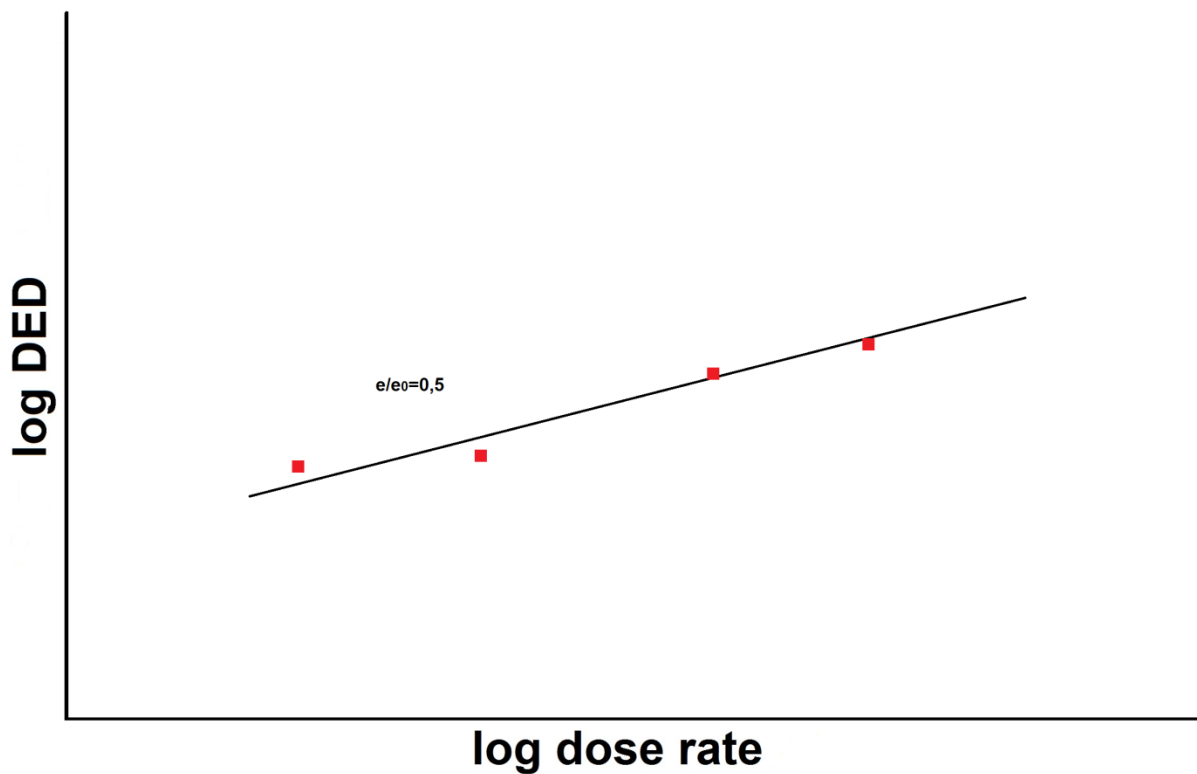


Figure 6: Schematic illustration on power law extrapolation method. The logarithmic DED values defined in Figure 5 are plotted vs. the logarithmic dose rate. The formed straight can be extrapolated to lower dose rate values.

4.2 Use of superposition principle in the description of dose rate effect

Superposition principle is standard procedure used during extraction of activation energy out of thermal ageing data and it can be applied also in combined thermal and radiation ageing predictions. The use of superposition requires experimental data and the quality of the data defines in which way the superposition principle is applied. There are two different ways that one can apply superposition principle when extrapolation of dose rate effect is considered: superposition of time-dependent data and superposition of DED data. These two methods are described next.

4.2.1 Superposition of time dependent data

This method uses also experimental data in dose rate extrapolation. The data should comprise from irradiation treatments done at three different dose rates and preferably at three different temperatures. In addition to irradiation data obtained at different dose rate-temperature combinations, data on thermal ageing at three temperatures is required. More thermal ageing and combined dose rate-temperature data can be used in order to provide more accurate evaluate of the model parameters.

The actual model predicts the DED parameter as function of dose rate:

$$DED = D * t_m/a(T, D) \quad (2)$$

Where D is dose rate, t_m is the time required to achieve the desired damage level at the reference conditions and $a(T, D)$ is the shift factor for combined thermal-irradiation ageing data. The shift factor can be related to the temperature and dose according to following equation:

$$a(T, D) = e^{\left\{ -\frac{E}{R\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)} * \left(1 + Dx \exp\left(\frac{Ex}{R\left(\frac{1}{T} - 1T_{ref}\right)}\right) \right) \right\}} \quad (3)$$

where E is apparent activation energy, k and x are model parameters. The apparent activation energy E can be calculated from the shift factors of the experimental data sets that are plotted as damage parameter (e.g. EAB) vs. logarithmic time axis as shown in Figure 7. The shift factors of thermal ageing data represent the “gaps” between the data sets obtained at different temperatures. They can be thought to represent the functions that are used to superpose the time dependent data to one master curve. In the case of thermal ageing data, master curve is formed on damage parameter vs. $\log(a(T, 0) * t)$ plot, where $a(T, 0)$ is the shift factor and t is time. The formed master curve is shown schematically in Figure 8.

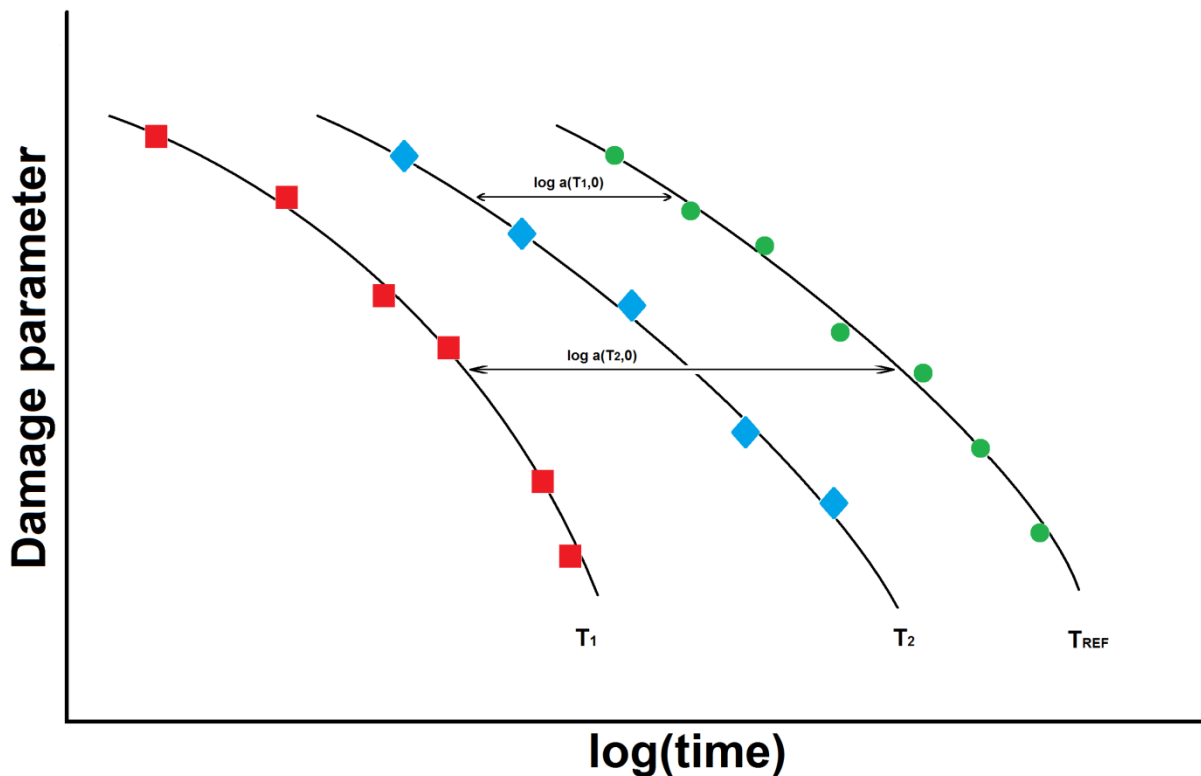


Figure 7: Determination of shift factors $a(T, 0)$ from thermal ageing data. Red squares, blue diamonds and green circles represent obtained experimental data at temperatures of T_1 , T_2 and T_{REF} , respectively.

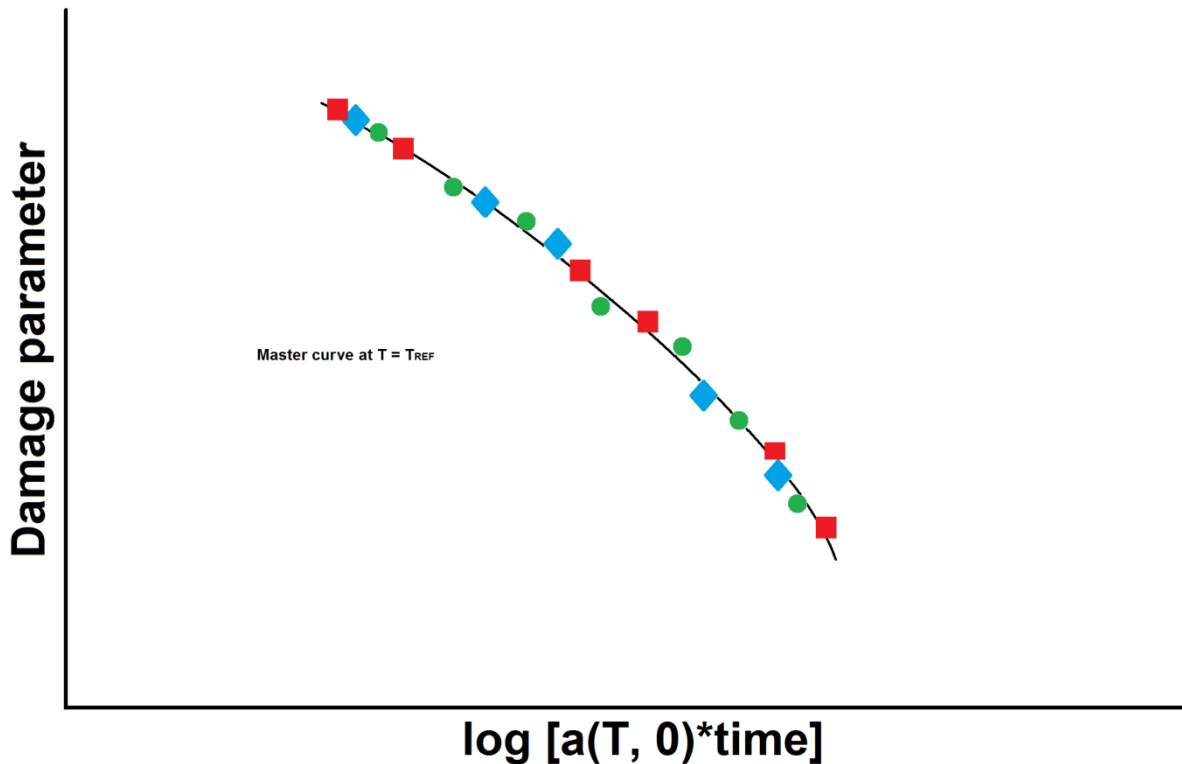


Figure 8: Master curve formed from the superposed experimental data by using the shift factors. Red squares, blue diamonds and green circles represent obtained experimental data at temperatures of T_1 , T_2 and T_{REF} , respectively.

As the master curve is formed, the shift factors are simultaneously determined. The shift factors from each temperature can be plotted against $1/T$ which will provide a straight line. The slope of this line is the apparent activation energy E .

In order to yield in a fully functional model, the model parameters k and x needs to be determined. This is done by using the combined thermal-irradiation data. Here again the data obtained at each temperature-dose rate combinations is superposed to one master curve (identical to Figure 7, expect the shift factors are $a(T, D_n)$). As the shift factors for each temperature-dose rate combinations are determined, the shift factors are plotted against the dose rate on a logarithmic scale as shown in Figure 9. From these plots the model parameters k and x are obtained by fitting.

After defining the apparent activation energy E and the model parameters k and x , DED values can be calculated based on equation 2. Based on this calculation, dose rate effect can be extrapolated to lower dose rates. This is shown schematically in Figure 10. The method has been confirmed to work on quite a few polymer materials (e.g. ethyl vinyl acetate (EVA)) and elastomeric materials (e.g. ethylene propylene diene monomer (EPDM) and nitrile). However, it should be noted that this method presumes that the ageing mechanism during accelerated ageing stays as the same through the whole temperature scale that is used during the ageing treatments of experimental samples. Any signs in the change of ageing mechanism can be seen in the shape of the formed curves at each ageing temperature (i.e. changes in the curve shapes in Figure 7). If there are changes in the curve shapes, superposition of the curves cannot be done sufficiently.

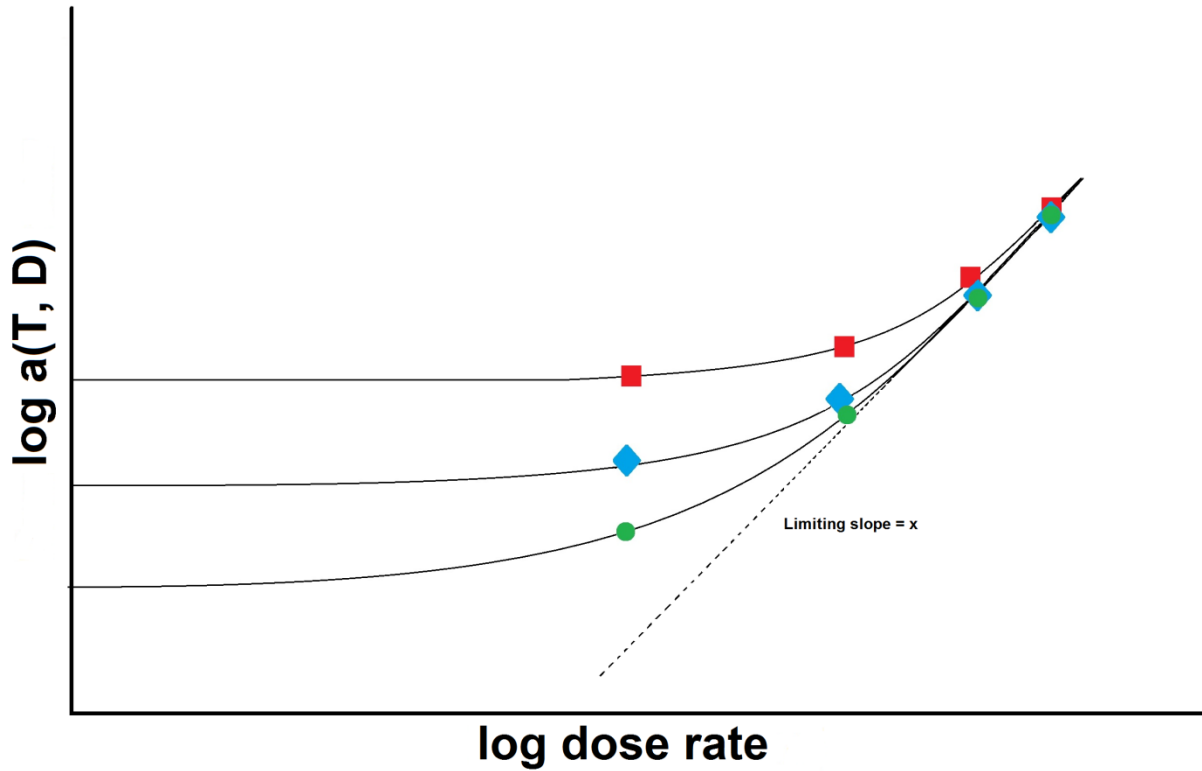


Figure 9: Fitting results of equation 3 to experimental values of $a(T, D_n)$. Limiting slope i.e. parameter x is plotted as dashed line. Red squares, blue diamonds and green circles represent obtained experimental data at temperatures of T_1 , T_2 and T_{REF} , respectively.

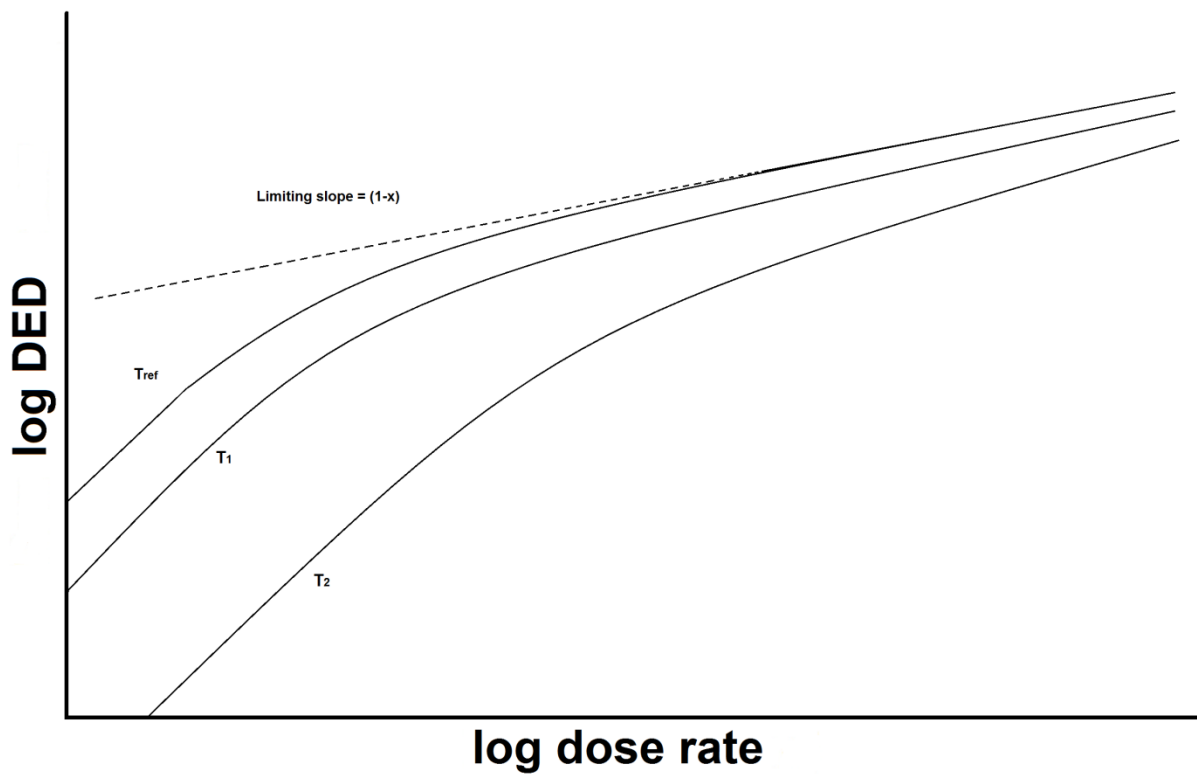


Figure 10: Calculated DED values as function of dose rates for same temperatures as applied in experimental data.

4.2.2 Superposition of DED data

This method is very similar to the superposition of time dependent data. It uses experimental data on combined thermal-irradiation ageing, but the actual superposition is conducted on logarithmic DED vs. dose rate data plots. Experimental data at least on three dose rates and two temperatures is required. The DED values are first determined in similar way that shown in Figure 5. The application of superposition principle on DED data is shown in Figure 11. At this stage any DLO effects should be excluded from the data. The shift factors used to form the master curve are calculated by the Arrhenius form equation:

$$a(T) = \exp\left(-\frac{E}{R\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)}\right) \quad (4)$$

The activation energy E is calculated only from the thermal ageing data. The master curve can be shifted in the desired temperature with the shift factors and the DED value can be read as the function of dose rate. This method enables extrapolation of dose rate effect both in thermal and radiation dominated regions, but in the temperature regions which are in the vicinity of thermal transitions (i.e. thermal transition of the polymer where crystalline regions of the polymers tend to melt), care should be taken when interpreting the results. Also in this case, predicting behaviour of semi-crystalline polymers that have tendencies towards the reverse temperature effect, the method is applicable only above crystalline melting point.

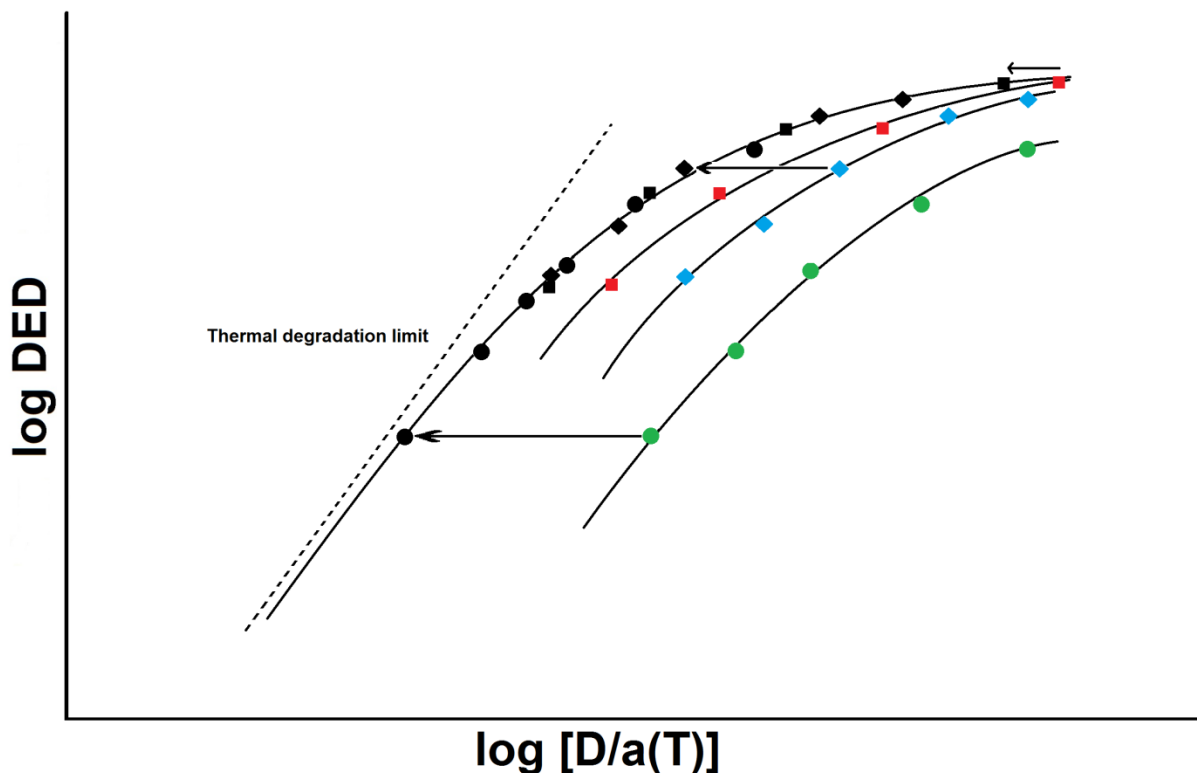


Figure 11: Schematic presentation of superposition of DED data. Coloured markers represent DED values obtained at certain temperature and dose rate. DED values are superposed to master curve with shift factors that take Arrhenius form.

4.3 Application of the identified methods

Qualification is the process in which the ability of the material to fulfil the pre-defined requirements is determined. The defined requirements usually involve exposure to conditions that are equivalent to the ageing that take place during designed service life of NPP followed by DBA and an acceptance criteria based on some mechanical property of the tested polymer. From the qualification obtained objective evidence ensures that the pre-determined requirements are fulfilled and the tested polymer will survive in its designed use. This can be defined as validation. To improve qualification and validation of polymeric materials, the accelerated irradiation ageing procedures used during qualification should be considered. During the accelerated irradiation ageing large dose rates (e.g. >10 kGy/h) are typically used in order to minimize the irradiation time and cost which will yield in excluding the effects rising from the dose rate effect. Application of these predicting methods during qualification would provide possibility to evaluate the magnitude of dose rate effect and include it in the irradiation procedure by increasing the total absorbed dose, making the validation data more accurate. However, these predicting methods have their own limitations which have an effect on their robust use.

The identified methods cover a wide range of different polymer materials and have been shown to give accurate results in case of many polymer grades [IEC, 2014] if the methods are used properly on good quality experimental data. Good quality experimental data would mean that the ageing mechanism during accelerated ageing is constant and the used dose rates during irradiation would be low enough to achieve homogenous oxidation in the studied samples. An example on the use of superposition on data sets where shifts in curve shapes can be observed referring change in ageing mechanism can be seen in JNES study [Yamamoto and Minakawa, 2009]. In addition to good quality data, the methods would require data at different temperatures and dose rates. Quite often this would mean dose rates that are only couple decades higher than the intended extrapolated dose rate. The use of relatively low dose rates and temperatures during irradiation or thermal ageing of tested samples would yield in long treatment times. In addition the size of the test matrix would grow significantly compared to conventional qualification test since several samples are aged at different environments. In conventional qualification a single set of samples are first irradiated with constant dose rate until the absorbed dose is equal to the dose that would accumulate during the designed service life and the following DBA. After this, proper DBA testing is conducted. Material specific analysis on dose rate effects would require additional ageing data at different dose rates and/or at different temperatures. This would increase the cost of qualification significantly.

Application of superposition techniques has been reported in [Gillen et. al, 2010]. For chlorosulphonated polyethylene (CSPE) superposition of DED data was done for six different cable qualities consisting of CSPE coming from different manufacturers. It was noted that the differences between the CSPE qualities were relatively small when the combined data was superposed by using DED data. This would provide possibility to use existing data to evaluate the dose rate effect in the case of CSPE. According to the data, with dose rate of 3 kGy/h total dose of 2000 kGy is required to decrease the EAB to 50% while with dose rate of 0,3 Gy/h only total dose of 100 kGy is required to cause EAB to reduce to 50% in service temperature of 50°C. To achieve equivalent amount of damage at high dose rates, the accumulated dose needs to be taken into account. Based on this it is apparent that using high dose rates during accelerated ageing combined to absorbed dose calculated from the designed service conditions (e.g. 60 kGy after 60 years of use) will underestimate the degradation that CSPE will undergo in the real conditions. Thus based on the existing experimental data, dose to equivalent damage values obtained for CSPE could be used in scaling the total absorbed doses used during accelerated ageing to correspond the damage levels yielding from the real service environment.

Also it should be noted that these methods do not predict correctly the dose rate effect on lower dose rate than the obtained experimental data on semi-crystalline materials that have tendencies towards the reverse temperature effect. Polymers such as ethylene propylene rubber (EPR), EPDM, crosslinked polyethylene (XLPE) and crosslinked polyolefin (XLPO) have been reported to show reverse temperature effects [Gillen et. Al 2010] making the superposition methods unreliable to use. On these kinds of polymers the power law method is the best available method but it seems that no satisfactorily functioning predictive method exists leaving the extrapolation of dose rate effect for these material more challenging.

5. Conclusions

Ionizing radiation induces excited states in atoms that form the polymer structure and these unstable radicals will react with the surrounding material. This will ultimately lead to changes in polymer chain structure (e.g. chain scission) and degradation of macroscopic material properties will be observed. Dose rate effect is apparent phenomenon on many polymer grades that has effect on the amount of degradation that the polymer is experiencing in ionizing radiation environments. The phenomenon yields either from physical or chemical aspects. At high dose rates DLO effects become evident cause for dose rate effect and at low dose rates more complex chemical reactions determine the magnitude of dose rate effect. Very large dose rates are used during the accelerated ageing in many of the current qualification processes due to the high cost of the irradiation treatments. This would yield in neglecting the additional degradation rising from the dose rate effect in cases when the irradiation treatment should simulate the ageing during the designed service life or even DBA.

There are few semi-empirical methods that can be used in predicting the magnitude of degradation caused by the dose rate effect. Power law method and the two methods based on superposition are shown to function in the dose rate effect modelling on many polymer grades excluding those which have tendencies towards complex dose rate effects. For these materials sufficiently working method to predict dose rate effect behaviour in the vicinity of thermal transient temperatures is currently lacking. However, the use of these methods requires additional experimental data obtained in ionizing radiation and thermal environments which is costly. Thus using already existing experimental data could be used in estimation of dose rate effects. This would be possible in case of CSPE where differences in degradation data between different material manufacturers are remarkably low when the data is superposed and dose rate effects evaluated.

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