THRESHOLDS FOR RADIATION SENSITIVITY OF POLYMERS IN COMBINED RADIATION-THERMAL ENVIRONMENTS

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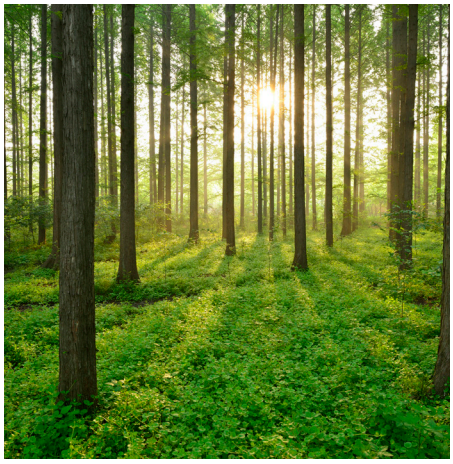
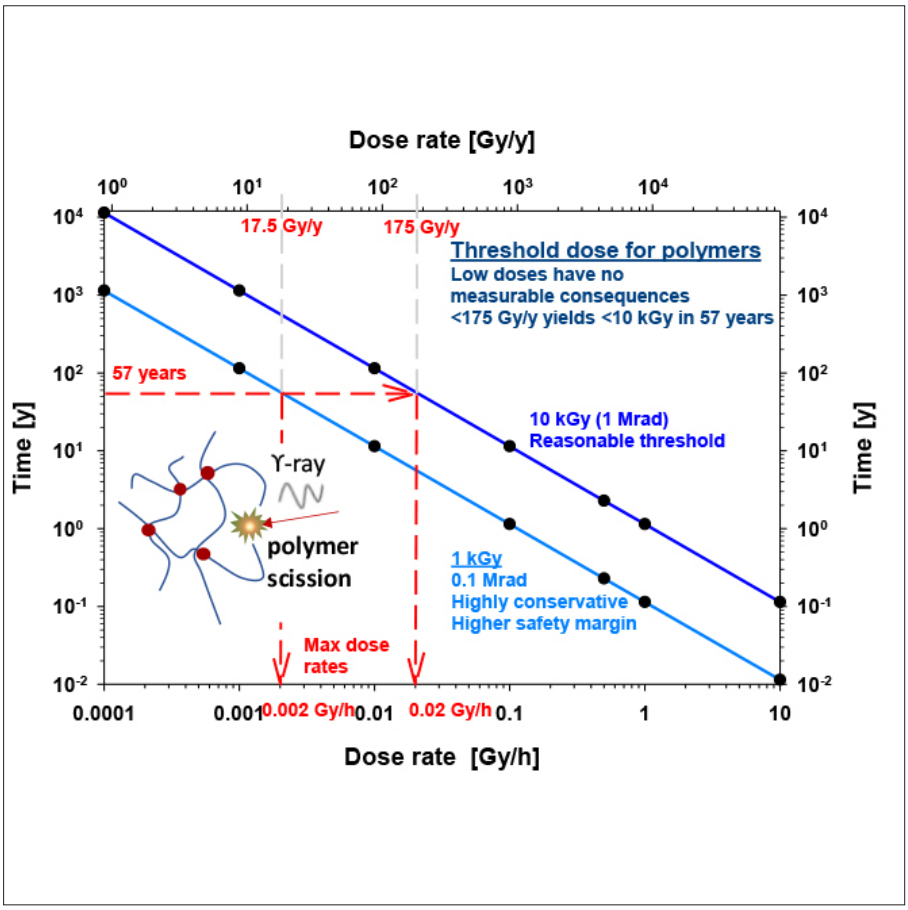


POLYMERIC MATERIALS IN NUCLEAR APPLICATIONS



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Thresholds for radiation sensitivity of polymers in combined radiation-thermal environments

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Foreword

This report forms the results of a project performed withing the Energiforsk Polymers in Nuclear Applications Program. The Energiforsk Polymers Program aims to increase the knowledge of aspects affecting safety, maintenance and development of components containing polymers in the Nordic nuclear power plants. An important part of this is to study ageing and degradation of different polymeric materials that are used in nuclear applications.

The aim of this study is to define radiation dose thresholds for polymers in combined radiation-thermal environments, below which the radiation impact on polymer degradation is minimal in comparison with other factors. The purpose of this is to better adapt qualification and monitoring to the factors that have the most impact on degradation in the conditions where the polymeric material will be applied. The results show that it would be realistic and beneficial to use such radiation dose thresholds, and that they would simplify material qualification and condition monitoring for extended use.

The study was carried out by Mathias C. Celina. The study was performed within the Energiforsk Polymers Program, which is financed by Vattenfall, Uniper, Fortum, TVO, Skellefteå Kraft and Karlstads Energi.

These are the results and conclusions of a project, which is part of a research Program run by Energiforsk. The author/authors are responsible for the content.

Summary

The safe, reliable and extended operation of nuclear power plants depends on many materials of polymeric (plastics) nature, such as cables, seals, elastomers, coatings, assemblies and components in electronic systems. Operational conditions may include high temperature and steam, but also radiation in some locations. Generally, elevated temperature coupled with radiation is detrimental for all polymers and results in material degradation over time. Plant applications of polymers therefore rely on established design standards, material qualification testing, predictive ageing studies and often ongoing performance monitoring. Through decades of research in polymer degradation, it is also now established that polymers can withstand low radiation doses very well. This means thresholds doses below which radiation ageing is of little concern should be considered, as defined thresholds can assist qualification, performance assessment, material condition monitoring and extended plant operation.

Published data for radiation dose sensitivities of a broad range of elastomers/polymers often used in plant environments have been reviewed and summarized. It is confirmed that material degradation from radiation alone is just noticeable for exposure doses beyond 20 kGy (2 Mrad), meaning a radiation dose threshold of 20 kGy can be defined as likely not compromising material performance properties. With perhaps some synergism (convoluted and more pronounced material aging under combined temperature and radiation) and accommodating perhaps some elusive slow ageing phenomena currently not understood, a highly conservative radiation threshold will be 1 kGy (0.1 Mrad), where with certainty the common properties of the usual polymers/elastomers will not change.

There are some plant operational conditions where cumulative radiation dose exposure over 50 years will remain below 1kGy, and accident scenarios involving high radiation will not be of concern. For such environments, radiation will not be a determining degradation factor and materials will instead age thermally or through others means (perhaps plasticizer or stabilizer loss, or hydrolysis). The use of justifiable radiation thresholds could simplify material qualification, identification of material vulnerabilities and condition monitoring for extended use considerations. Disregarding low radiation doses could be compensated by improved ageing studies, a better understanding of long-term thermal degradation processes and material performance for extended use applications.

Keywords

Polymers, Radiation, Thermal, Degradation, Sensitivity, Combined Environments, Thresholds

Polymerer, Strålning, Termisk, Nedbrytning, Känslighet, Kombinerade Förhållanden, Tröskelvärden.

Sammanfattning

Polymera material, såsom kablar, tätningar, elastomerer, ytbeläggningar och komponenter i elektriska system, är kritiska för säker och pålitlig drift av kärnkraftverk, men driftförhållandena kan innefatta höga temperaturer, ånga och även strålning på vissa platser. Generellt sett är förhöjda temperaturer och strålning skadliga för polymerer och leder till nedbrytning av materialet över tid. Användningen av polymerer i kärnkraftverk förlitar sig därför på etablerade designstandarder, materialkvalificering och åldringsstudier, ofta tillsammans med kontinuerlig tillståndsövervakning av komponenter. Decennier av forskning inom nedbrytning av polymerer har visat att polymerer tål låga stråldoser mycket bra. Detta innebär att tröskelvärden för stråldoser, under vilka materialåldring är av ringa betydelse, bör etableras, då dessa skulle kunna vara hjälpsamma vid kvalificering, prestandabedömning och tillståndsövervakning för förlängd anläggningsdrift.

Litteraturdata för stråldoskänslighet för ett flertal olika elastomerer/polymerer som ofta används i kärnkraftverksmiljöer har granskats och sammanfattats. Från dessa kan det bekräftas att materialåldring från enbart strålning är knappt märkbar för stråldoser under 20 kGy (2 MRad). Detta betyder att ett tröskelvärde för maximal stråldos som sannolikt inte äventyrar materialegenskaper kan definieras som 20 kGy. Med synergism (snabbare åldring under kombinerad termisk och strålningsåldring än var och en för sig sekventiellt) och med eventuella fenomen från långsamt åldrande i åtanke, kommer 1 kGy (0,1 Mrad) att vara ett mycket konservativt tröskelvärde där de vanliga polymerer/elastomerer med säkerhet inte kommer att förändras.

Det finns vissa driftsförhållanden i kärnkraftverk där den kumulativa stråldosen är under 1 kGy under 50 års drift, och där olycksscenarier med högra stråldoser inte är av betydelse. I sådana miljöer kommer strålning inte att vara en avgörande faktor för nedbrytning, och polymererna kommer istället att åldras termiskt eller genom andra mekanismer (exempelvis hydrolys eller förlust av mjukgörare eller antioxidanter). Befogade tröskelvärden för strålning skulle kunna förenkla materialkvalificering, identifiering av svagheter hos materialen och tillståndsövervakning för förlängd kärnkraftsverksdrift. Åsidosättandet av effekten av låga stråldoser kan kompenseras för genom förbättrade åldringsstudier, djupare förståelse för långsiktiga termiska åldringsprocesser och materialprestanda för förlängd drift.

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1 Introduction

1.1 OPENING STATEMENT

The construction and continuing use of nuclear power plants (NPP) relies on our ability to design and manage complex engineering systems that balance significant benefits (meaning CO_2 neutral electricity generation) with operational challenges of large scale nuclear technology and demands on best engineering practices. Our utilization of nuclear power requires ongoing cutting-edge expertise for the selection of best available functional materials, optimized design principles, and safe operation strategies that link long-term materials behavior with controls, sensors, redundancy design, and ongoing risk mitigation through knowledge of how engineering materials/systems may change over time. Existing nuclear infrastructure ages under complex combined environments and a single driver may not always be dominant. Natural ageing of materials and system components is a multi-factorial behavior as the convoluted sum of multiple processes, such as intrinsic oxidation, hydrolysis or diffusive changes, as well as degradation effects that are cumulatively incurred during ongoing material utilization. Aging processes in NPPs occur similarly, in a sense of multi-factorial long-term environmental conditions, as encountered in other complex systems where materials may have known aging sensitivities such as other power generation, aircraft, satellite, communication, and high value infrastructure in transportation and defense. Polymers and elastomers tend to age in many applications, due to heat, oxidation, ultraviolet exposure, hydrolysis or when in contact with aggressive media. One key difference here, however, is the presence of ionizing radiation in some NPP environments that other systems do not have to accommodate to the same degree.

Aside from metals, concrete and perhaps specialized ceramics, polymer materials are an integral part of nuclear power generation systems and are used in cables as insulation and jacketing, seals, and coatings. They are also found in many electronic subcomponents as encapsulation or functional materials in sensors, controls, circuit boards, micro-chips and similar. When it comes to the processes of their long-term ageing behavior and our understanding through applied material science, one area of ongoing interest for the continued safe operation and lifetime extension of NPPs are polymers used in cables and seals. Hence, the use of polymers and development of suitable materials with specific properties was always part of the utilization of nuclear power, going back all the way to the Manhattan Project in the 1940s. In parallel with the development of modern polymer material science, the science and engineering fields of polymer radiation chemistry and physics evolved. A reputable science/engineering journal on this topic is itself called “Radiation Physics and Chemistry” and was started in 1977 when this research area deserved its own journal and publication emphasis. Material science progress was driven by our need to understand radiation effects in materials and how properties change during extended exposure, and hence how materials may change over time in NPP application environments. Concerns about sensitivities of polymers to radiation doses and also to elevated temperatures became an integral part of material qualification (see for example standard testing requirements in 1974 [1]).

Over the last decades much has been learned about the behavior of polymers under what we call combined radiation-thermal environments. However, our understanding needs additional refinement and clarity under extended low dose rate conditions. We also recognize that at some radiation dose level, radiation damage to polymers will be less important and in essence inconsequential. Therefore, radiation doses will have some threshold before they constitute a concern for polymer property changes or have negative impact on a material application. This is not any different than manageable exposure doses for human beings before radiation exposure becomes a concern, although on a very different level. For example, the annual limit for radiation exposure of a normal citizen should be limited to 1 mSv per annum (where 1 mSv is the dose produced by exposure to 1 milligray (mG) of radiation), but a radiation worker may receive up to twenty times this dose (or 100 mSv averaged over five years). Humans may develop radiation sickness with acute exposure to 0.5 Gy and a 50% chance of death after exposure to 5 Gy over 30 days. Note that the human acceptable dose rate is 1e-3 Gy/y or 1.14e-7 Gy/h, which is very low and much lower than the usual dose rates involved in experimental work on polymer radiation chemistry. Importantly, polymers are many times more robust than humans (on the order of 10^5 or 10^6 better), as they can often handle radiation doses in the kGy regime without significant consequences in terms of functional property changes. The concept of a radiation threshold is analogous to the human acceptable dose rate, meaning a certain dose level is regarded as inconsequential.

1.2 POLYMER RADIATION CHEMISTRY

Exposure of organic materials or also humans to high energy radiation (here gamma, x-ray or indirectly also high energy particles that deposit local energy into a material) involves the fundamental principle of free radical generation. This is due to the sensitivity of carbon-carbon and similar chemical bonds to scission and follow-up reactions during radiation exposure. This means molecules are being fragmented and new slightly different molecules may form. This is all part of radiation chemistry of organic materials and the reader is referred to many summaries on this topic readily available in the existing literature [2-7]. Point is, the physics of radiation exposure and its energy deposition into materials results in radiation chemistry, which has become a separate subtopic in the field of chemistry due to the involvement and consequences of radiation-induced free radical reactions.

Studies on the radiation chemistry of polymers was historically linked to high dose rate exposure and elevated temperatures and this happened for two reasons. Firstly, the diagnostics of free radical generation in polymers as a consequence of radiation exposure was not possible with trace analytical methods (as sufficiently high sensitivity did not exist), meaning considerable exposure and chemistry had to usually occur to study the reactions of free radicals. And secondly, the initial needs in the nuclear industry were related to high dose rate exposure to better understand material behaviour under potential ‘accident conditions’ where materials may suddenly be exposed to high radiation doses and temperatures. It is also fair to state that material screening/testing was therefore often conducted under high dose rate conditions to quickly compare material properties and gain knowledge on

maximum acceptable doses before materials may no longer adequately perform. Early reports showed originally high dose data for material behaviour [8]. Radiation chemistry and polymer materials degradation under low dose rates was traditionally less of an interest due to a) experimental challenges in gamma exposure facilities requiring significant attenuation, and b) the extended length and hence cost of such studies.

Over time, with the evolving needs of extended NPP operation, likely beyond initial operational qualification targets, the aspects of low dose rate conditions over many years became more important. Additional understanding of polymer material behaviour over decades of 'use conditions' and the issue of cumulative low doses for requalification purposes has become a more important research direction. But it is also important to briefly reflect on a few other essential aspects in relation to polymer radiation chemistry and material property changes. Besides radiation exposure, temperature and oxygen also play key roles. Elevated temperature also means materials are exposed to 'thermal energy' and scission or limited 'decomposition' reactions may occur. Oxygen is a reagent that oxidizes hydrocarbon based polymers and oxidative degradation is hence a key additional ageing concern for polymers [9]. Collectively, all three degradation modes involve free radical chemistry, where oxygen containing species contribute via hydroperoxy, peroxy and hydroxyl radicals and its associated reaction mechanisms. Importantly, radiation chemistry due to the indiscriminate energy of gamma rays will proceed under both inert or oxidative conditions, although the resulting intermediate free radicals are of different nature, and hence slightly different dominant processes may occur. For example, scission versus crosslinking reactions depend on the presence of oxygen. And these different types of radiation chemistry pathways may also be material specific. Generally, inert radiation chemistry is less detrimental to polymers than are oxidative processes.

Most importantly, since temperature, oxidation and radiation exposure all involve free radical chemistry, we can combine their degradation processes within the terms of thermo-oxidation and radiation-induced oxidation. Further, the description of polymer degradation under combined radiation-thermal environments is widely pursued [10]. Another aspect that deserves mentioning is the access of oxygen into a material which is usually controlled via diffusion and solubility [11,12]. Under high degradation rates, oxygen supply into a material may not be sufficient and hence there could be oxidatively driven processes at a material surface, but more inert (meaning no oxygen is present) dominated processes within a material. This heterogeneous aging behaviour is described as diffusion-controlled oxidation (DLO), with many articles published on this topic in polymer degradation [13-16].

It is also important to mention that radiation-thermal degradation is included in the many studies that have focused on condition assessments of existing hardware and material lifetime extension for continued operation of NPP facilities. This means slow ageing processes have been recognized. The engineering community is actively focused on understanding ageing processes that may not be immediately apparent or do not strongly show up in short term accelerated ageing studies, including individual efforts in many countries (including the Nordic countries) [17-21]. For example, slow diffusion processes cannot be easily accelerated, but may become

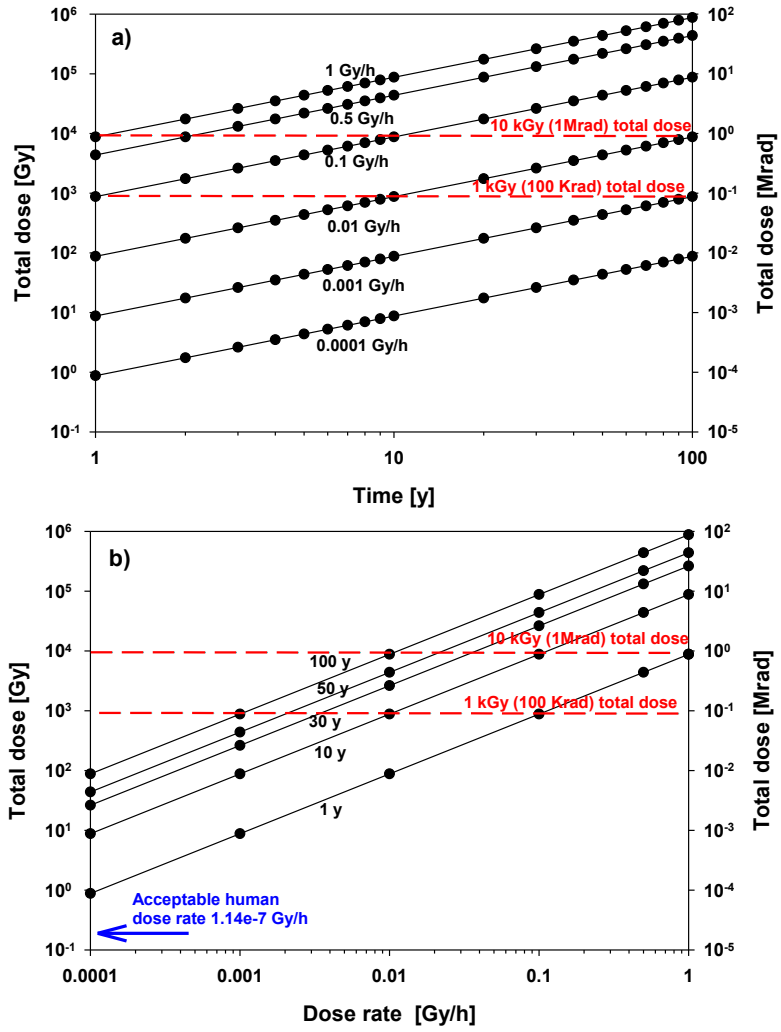
more detrimental over decades; one example is plasticizer loss from PVC insulation that is not necessarily a degradation chemistry process, but a physics behaviour of a filled material with a 'mobile' compound and concentration gradient [22-24]. There is a global effort towards gaining a better understanding of the state of 'aged' hardware, residual margins and justifiable approaches towards extending safe and reliable operations [20,21,25,26]. In support, radiation stability of polymers is a broad research topic, also for radiation treatments and medical device sterilization as supported by IAEA activities [27,28].

1.3 AGEING UNDER CONDITIONS WITH WEAK RADIATION LEVELS

Most previous R&D on oxidative polymer degradation under combined radiation-thermal conditions has focused on higher dose rate conditions from experiments usually not lasting longer than a few years, with extrapolation to lower dose rate conditions. It has also been accepted that DLO conditions at exposure rates beyond ~ 0.5 kGy/h will need to be taken into account and should be interpreted as DLO rather than dose rate effects, if non-proportional ageing effects with dose are observed [10,29-33]. The goal is to avoid DLO conditions during experiments or at least take this issue into account [33,34]. True physical dose rate effects usually occur only at much higher dose rates (on the order of 10^10 G/h) when 'spur overlapping' in high energy deposition participates [35,36]. In radiation chemistry, 'gamma spur overlapping' refers to the phenomenon where reactive species, created by gamma irradiation, are produced in close proximity and their tracks (or 'spurs') then overlap, leading to interactions between these species instead of reactions with the surrounding material. Absent such effects meaningful non DLO affected aging studies of cable insulation materials exist and extrapolation to low dose rates has been a key research focus [10,33,37,38]. Some limited studies towards much lower dose rates have been conducted, but the key problem is that measurable material property changes require time to achieve deposited dose. The usual studies of no more than a few years of exposure will simply not be sufficiently informative, other than showing low doses have not yet changed the polymer [10,38]. One solution recently was to apply sensitive oxidation rate measurements as one avenue to probe the oxidation of polymers over three orders of magnitude in dose rate (from 0.3 to 300 Gy/h) with the goal of refining models for degradation behaviour under combined radiation-thermal conditions [10]. At lower temperatures (below 50°C) and low dose rate conditions (below 1 Gy/h), we are still dealing with combined radiation-thermal degradation conditions, yet the challenge is that both temperature and radiation induced degradation rates decrease substantially. For the purpose of this analysis and report, it makes sense to define very slow ageing as the aging regime for temperatures below 50°C and dose rates below 0.01 Gy/h. Fig. 1 below shows that even the low dose rate (at least considering the usual accelerated exposure conditions) of 0.01 Gy/h will generate close to 10 kGy (1 Mrad) over a 100-year timeframe. A ten times higher dose rate of 0.1 Gy/h over 100 years will certainly deposit doses on a magnitude that is known to be problematic for some polymers. This means at dose rates of 0.01 to 0.1 Gy/h, it may indeed take decades for slow radiation-initiated polymer ageing processes to result in measurable property changes. And it is intrinsically difficult to separate either thermally or radiation driven dominant processes over such extended durations. Fig. 1c shows clearly how

anticipated use time when projected towards dose thresholds (as discussed in detail later) determines maximum permissible dose rates. Due to the very long times involved, even minor dose rates will nevertheless generate total doses of potential concern for materials.

The key limit in our existing data is that the usual accelerated aging studies of polymer materials need significant dose to induce material changes, and we therefore require extrapolations to lower dose rates and extended times. This intrinsically involves uncertainty related to extrapolation and the issue becomes a 'catch 22', with more readily available data meaning more extrapolations and uncertainty, or perhaps more meaningful data but significantly longer experimental times.



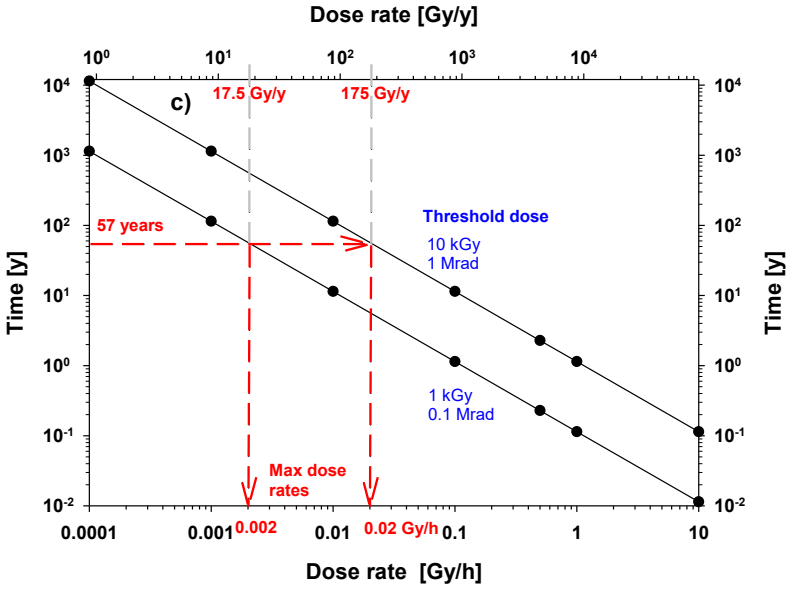


Fig.1: Total doses as a function of extended time and 'low' dose rate conditions. As shown in c) expected time with dose thresholds determine maximum dose rates.

1.4 OVERARCHING SCOPE AND GOALS

There are a few options to more meaningfully predict the aging of polymers over decades when slow degradation rates occur in the application (lower dose rates below 0.1 Gy/h at temperatures below 50°C). One option is to better predict the performance and property changes of materials at slow ageing conditions through extended experiments and with better models [10,38]. Another option is dedicated condition monitoring and feedback on the material property changes of interest from within the application space, meaning systematic and repetitive characterization of retrieved aged specimens from NPP environments. However, their ageing conditions may not be static, not particularly well defined, or specimens may simply not be retrievable (which is an ongoing challenge as well).

Another pathway that the polymer aging community may have mostly 'overlooked' is the aspect of minimum doses required for radiation-driven property changes to evolve. Even if the degradation becomes radiation dominated at slow conditions at ambient temperatures (decades of use), we also know that at some threshold level cumulative radiation exposure (total dose) will not be sufficient to substantially change a material and cause a noticeable reduction in their use properties. This means that existing ageing data on radiation sensitivities of polymers could and should be re-examined for the minimum doses required to induce measurable property changes. Ultimately, minimum radiation threshold levels should exist, and with known dose rates in a given environment or application, exposure times of concern or 'failure' times could then be derived and used for predictions of minimum performance. Radiation threshold levels with conservative assumptions for potential convolution by radiation-thermal synergism, and also in comparison with the intrinsic thermal-only degradation pathways, could be derived with adequate margins for different polymer types.

The goal of this report and review is to open up a discussion and explore the advantages (pros) and disadvantages (cons) of an approach towards radiation thresholds in polymer materials performance. Is it possible to define radiation levels that are not substantial enough to induce measurable materials degradation? What would be the corresponding dose rates below which radiation-induced degradation could be treated as insignificant, given many decades of use in an NPP application environment? A number of factors are in favour of such an analysis and approach describing the extended aging of polymer under very low radiation-thermal rates within the context of radiation thresholds.

- Data on radiation sensitivities and material degradation at low temperatures exist.
- Polymer radiation damage is to the best of our knowledge only an issue of total dose (at least in the exposure environments we are considering here).
- There is no documented dose rate effect at low dose rate conditions when DLO and temperature effects are correctly interpreted, meaning polymer damage is cumulative with dose only and independent of dose rate.
- The activation energy of radiation degradation is either zero or very low meaning additional data at low temperatures aside from RT conditions can be considered as well.
- Supported by data, it is known that low radiation doses do not measurably degrade polymers, but that different materials may also have different sensitivities.

With well-founded arguments towards radiation threshold levels, it should then be possible to adjust our material acquisition/qualification procedures and also discuss long-term aging in a more informed manner, in parallel with condition monitoring and existing strategies for predictive models:

- Define radiation threshold margins for specific polymer types subject to known polymer behaviour and available data.
- Define material qualification performance when radiation is not important, then subject mostly to thermal demands.
- Conduct ageing experiments with perhaps more emphasis on thermal sensitivities, extended time and a broader range of thermal ageing, to accommodate some radiation damage contribution.

Lastly, our discussion of radiation threshold values will need to be data based. This means a review of available ‘ageing data’ under radiation conditions at low temperatures for many polymers of interest is necessary. In some cases, data may however not be available. There are many polymer variants in commercial use, and while related materials may or may not have been studied previously, grouping may not be possible in all cases. For example, end users dealing with material selection in NPPs may have an interest in ‘general’ polymers such as rubbery materials and elastomers, i.e. silicone, EPDM, XLPE. There will likely be existing data for the latter three polymer types, but ‘rubbers’ are generic and perhaps not an optimized

material for radiation exposure. Data are available for neoprene or polyolefin based elastomers, but are not readily available for specific nitrile, butyl, or styrene-butadiene rubbers (SBR). For such generic rubbery materials, a low conservative threshold dose value should be applied absent any other data. There will also be a complication given by the fact that not all physical properties in polymers will change simultaneously as ageing progresses. There could be different sensitivities in relation to changes in tensile elongation, hardness or sealing force even if one would assume them being strongly coupled. However, it is also fair to argue that as long as no changes in tensile properties occur and no obvious changes in density or hardness are apparent, then more applied properties such as sealing force or 'leakage' in seal applications may also not be affected. This would be dependent on very little noticeable degradation chemistry. In many cases, conservative performance estimations can be derived based on the combined feedback from multiple property changes which are broadly indicative of polymer ageing as a function of deposited radiation dose.

This report is not intended to resolve every angle of different polymers and use expectations for low doses rates, but rather introduce a foundational general concept. The key notion will be introduced that radiation thresholds can be justified based on large available data sets. A previous report on this topic provides guidance that many polymers can handle low levels of radiation just fine, although quantitative aspects with clear threshold definitions are not given [39]. Unusual ageing effects subject to low dose rate conditions are not expected, aside from any other anomalous behaviour when polymers are used for decades. Stabilizer loss, hydrolysis, morphology changes, creep, stress built-up etc. may develop, but they are usually not driven by weak radiation exposure. Polymer groups can be compared with relative radiation sensitivities based on traditional ageing data. And lastly, pragmatic and conservative threshold values may be established by also considering limited radiation-thermal synergism [10,40,41], and the lack of matched accelerated ageing conditions [33,34], i.e. non-optimized ageing conditions in existing data.

2 Polymer degradation under combined radiation-thermal environments

It is important to reflect on a few key aspects of polymer degradation under combined environments. As mentioned, their degradation behaviour/mechanisms and effects are usually coupled within a multi-factorial ageing environment. Oxidation processes can be initiated thermally or through irradiation, however the resulting degradation chemistry is similar. It involves free radical initiation, propagation of oxidation and termination reactions, which have been summarized in oxidation models often with mathematical descriptions [42,43], and are based on original work on hydrocarbon and elastomer thermo-oxidation that goes back to the 1950s [44,45]. The results of oxidation chemistry in most polymers are molecular weight changes, also in relation to tie molecules and underlying lamellar structures in semi-crystalline materials [46-48], which may result in scission/crosslinking, hardening and changes in intended use properties of polymers [9].

Most importantly, the consequences of thermal or radiation damage in polymers are often near identical, which means they cannot be easily decoupled, but also that a certain amount of thermal damage may equate to an equivalent total exposure dose and vice versa. This means that some low level radiation damage for material testing may be instead accommodated with longer time or higher temperature ageing, as long as strongly accelerated testing at too high temperatures with sensitivities to transitions in the polymer (T_g or T_m) are minimized. This means modified material qualification testing might be accomplished when low level radiation exposure should be excluded, and thermal only ageing should guide performance predictions.

We have a large database for materials performance and polymer degradation, and in approximate order of sensitivity the following is established knowledge [17,25]:

- Fluorinated semi-crystalline polymers are thermally very stable, but in contrast have known radiation sensitivity related to their tie molecules and morphology when semi-crystalline.
- Halogenated amorphous materials (fluoro-elastomers, PVC, hypalon, neoprene) are subject to dehydro-halogenation as well as thermo-oxidative sensitivities. This means parallel processes may occur in relation to release of corrosive gaseous by-products.
- Semi-crystalline polyolefins (XLPE, XLPOs) also display sensitivity related to morphology and tie molecule damage. Degradation of crosslinked materials below their melting point is usually more complicated.
- Crosslinked elastomers, which are mostly amorphous (in some cases with low crystallinity) (EPDM, EPR, polyolefin based) may have thermal exposure limits but usually age under radiation very-well.
- In addition, polymers may have different sensitivities for parallel changes in different physical properties. For example, minimum doses to noticeably change elongation, hardness, flexibility, sealing force or compression set for O-ring/seal materials may diverge and be material dependent. We may

expect perhaps one property to change first, whereas another one not until exposure to higher doses. Often not all such properties are measured in parallel. However, small noticeable changes in elongation, hardness, density, flexibility, compression set and similar properties are usually coupled. Oxidative radiation-thermal degradation usually affects multiple property jointly. Hence, broad ageing data sets offer a meaningful comparison to establish average threshold values.

A complicating factor is the fact that threshold values and observed behaviour will always contain a degree of extrapolation and hence uncertainty. We simply do not have 100-year material ageing data at low to moderate dose rates and RT. Our available data usually originate from accelerated aging studies with the key target often being the extrapolation of such data toward extended times at low temperature and dose rates, namely ambient aging conditions where materials may slowly age for decades. However, as discussed later, an initial threshold can be further considered for conservative margins in dose and temperature, uncertainties in material behaviour, and synergistic behaviour between radiation and temperature. This is all related to the discussion of disregarding a radiation component for the qualification of materials that will experience only minor exposure to radiation during service. This means we shall discuss available threshold values for reasonable extra safety margins to accommodate potentially unknown behaviour evolving over decades, such as radiation-thermal synergism or unexpected radiation sensitivity due to changes in morphology or slow thermal ageing. Similarly, some materials may show induction time behaviour where it may not be best to extract threshold values that go all the way before just noticeable changes occur. In this case, a reasonable reduction in a justifiable threshold value is also needed.

With the aim of establishing threshold values for numerous materials, we need to re-examine existing ageing data from whatever sources available under the following considerations:

- Select ageing data on polymer radiation effects at the lowest dose rate and temperatures available. This emphasizes the underlying material radiation sensitivity.
- Exposure dose/time needs to be selected from traditional ageing curves which means the usual data scatter and initial insensitivity in the low dose rate regime needs to be judged. A reasonable assessment is when tensile elongation or an equivalent property has not yet changed by more than 10% of the initial material property. This means the aging indicator or extent of fractional damage in the polymer is no less than 0.9 on a relative property scale.
- Complementary low temperatures and additional dose rates can be used for averaging of a threshold value when such data are available.
- Selection of threshold doses could be dependent on our expectations for different physical properties, for example the total dose for a noticeable change in tensile elongation, hardening, sealing force or similar needed properties may vary somewhat. However, usually such property changes develop more or less in parallel.

3 Behavior of cable insulation/jacketing materials under radiation and combined radiation-thermal environments

As emphasized above, it is best to group polymers based on established knowledge of their degradation sensitivities. Many previous studies on thermal and radiation ageing of polymers used for cable insulation/jacketing offer relevant data as an overview for their minimum radiation sensitivities.

There are published data sources detailing the insulation and cable jacketing material behaviour under radiation-thermal conditions. Many sources rely on data originally summarized in the early 2000s in an Excel file titled SCRAPS, which stands for Sandia's Cable Repository for Aged Polymer Samples, i.e. a summary compiled by the institution where these comprehensive data sets were generated. This file was published and is available as an Addendum to the Nuclear Energy Plant Optimization Final Report (SAND2005-7331 (Nov. 2005) and references therein) and has been referred to in a number of references [37,40]. Many publications have relied on this data summary for more in-depth discussions of material behaviour [17-19,33,37,40,49-53].

For the individual data summaries shown below, exposure conditions are usually under air, unless otherwise mentioned. This means radiation-thermo-oxidative conditions apply. However, the dose rate and temperature combinations are mostly low enough to avoid DLO complications [9,13-15,32]. Doses are shown, ideally at lower temperature and low dose rate conditions when subtle material changes just become noticeable. They represent reasonably homogeneous degradation and are not indirectly pushed to higher dose levels as when DLO conditions may apply and overall material degradation could be less. In some cases, data may only be available at moderate temperatures, yet sufficiently low such that the degradation is still dominated by radiation effects. Point is, we determine such data with the intent of representing mostly radiation driven material degradation which will facilitate our discussion of radiation thresholds.

Material property changes with increasing radiation dose are usually given by tensile elongation data, a common measurement with practical relevance. To assess radiation-thermal ageing the time/dose to a 50% loss in absolute elongation or residual 100% tensile elongation as a defined residual desired property are often documented. For example, a polymer insulation may initially stretch to 300%. A just measurable drop to 270 % elongation constitutes a 10% change in absolute elongation properties. Hence, there is no more than a 10% property change with 90% of the initial properties being maintained. In many ageing data compilations, subtle changes in density, hardness, gel content (crosslink state), and compression set or similar physical properties usually corroborate small changes in tensile elongation. These materials usually do not display changes in hardness, density or compression set greater than 10% without a beginning change in tensile elongation. Tensile elongation is therefore regarded as a sufficiently sensitive property and a good indicator for material ageing trends. It serves well for the purpose of determining

radiation threshold values in parallel with examining density, crosslinking or any other obvious material changes. In this context, the reader is referred to examples showing multiple primary experimental data in specific material irradiation studies which demonstrate how material property changes often develop in parallel and tensile elongation is a preferred property to offer guidance for quantitative ageing trends [17-19,33,37,40,49-53].

Fig. 2 shows an example from a published data set [54], how a dose below 100 kGy at RT for a particular XLPO material did not result in noticeable changes in tensile elongation and hence could be regarded as a threshold dose. It is important to highlight that a subtle change in properties is also a conservative assessment meaning the definition of thresholds are purposely meant to encompass only low dose levels, which increases confidence in their applicability and thereby justify remaining performance margins.

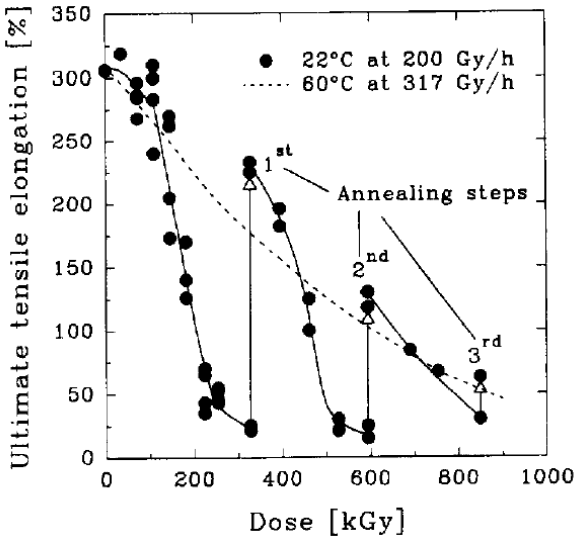


Fig. 2: Examples of reduction in tensile elongation with dose at RT or 60°C for a XLPO cable insulation material showing a threshold of ~ 100 kGy [54,55]. We note faster ageing at RT due to morphology/crystallinity effects and higher sensitivity of tie molecules. Upon high temperature exposure (re-melting), the initial loss of tensile elongation recovers. The determination of a threshold only concerns the early material change up to 100 kGy, with tensile elongation not measurably affected.

3.1 CROSSLINKED AMORPHOUS POLYOLEFINES

Amorphous rubbery polymers based on EPDM's, EPR's, and similar are often used as alternative materials to XLPE and perhaps halogenated materials. They are of crosslinked suitable rubbery nature with the term 'rubber' sometimes incorporated into their naming, for instance ethylene-propylene-rubber. They may have some small amounts of remaining crystallinity depending on their polymerization, manufacturing and copolymer composition, but their crystallinity is usually less than the level often seen for truly semi-crystalline polyolefins based on for example crosslinked polyethylene (XLPE).

Table 1: Threshold data for some crosslinked amorphous polymers

Materials: EPDM and PE/PP based copolymer elastomers with limited crystallinity	**Exposure condition T [°C]; γ [Gy/h]***	**Dose to approx. 10% property change [kGy][1]** ***(100 kGy = 10Mrad)***	**Comment**
EPR-01A-Anaconda Flameguard insulation	26; 980	< 97, perhaps 50?	Only elevated T data
EPR-01B-Anaconda Flameguard insulation	22; 15.7	124	
EPR-02-Anaconda Flameguard insulation	41; 58.6	~ 45	
EPR-03 Eaton Dekoron Elastoset	40; 60.4 40; 215	~ 50 ~ 70	~ 70 kGy for material C in [55]
Material- EPR-05- Okonite EPR	40; 430 80; 445	< 83 < 87	

3.2 CROSSLINKED POLYOLEFINS WITH SEMI-CRYSTALLINE MORPHOLOGY

Semi-crystalline XLPO materials are known to be complex in their behaviour under radiation-thermal environments. This is due to morphology and hence the presence of distinctly different phases which introduce a physics effect besides the usual radiation chemistry. Unexpected behaviour under low temperature and low dose rate conditions may exist due to aspects of polymer morphology, tie molecules and crystallization tendencies, with the partial melting and the melting behaviour of crystalline phase material being very important [54,55]. It means that the radiation-thermoxidative driven processes may in fact be more detrimental to the polymer when this degradation occurs more in the fully 'solid' state, i.e. below any partial melting of the crystallites.

Table 2: Threshold data for some crosslinked semi-crystalline polymers

Materials: Tough elastomers with known semi-crystallinity	**Exposure condition T [°C]; γ [Gy/h]***	**Dose to approx. 10% property change [kGy]** ***(100 kGy = 10Mrad)***	**Comment**
XLPE-01- GE Vulkene Supreme Insulation	43; 175	~ 100	~ 100 kGy D in [55]
XLPO-02A, BrandRex insulation	22; 16.8	~ 100	~ 100 kGy [54,55]
XLPO-03- Eaton Dekoron Polyset insulation	41; 64	~ 65	
XLPO-04- ITT Exane II Surprenant insulation	22, 15.7	~ 45	
XLPO-05- Rockbestos Firewall III Insulation	23; 210 40; 215	71 73	~ 75 kGy for B in [55]

[1] A 10% property change here and thereafter means primarily tensile elongation not changing by more than 10%. Other data (modulus, density, tensile strength, crosslink state…) when available in parallel have been confirmed to not change any faster. Importantly, tensile elongation is sensitive to aging.

3.3 HALOGENATED AND RELATED POLYMERS

Halogenated polymers such as chloroprene (neoprene), chlorosulfonated PE, PVC and fluorinated materials have been used in weak radiation environments, but their use may also depend on country specific preferences, and the use of fluorinated materials is also usually rather limited. For example, PVC is more widely used in the EU but no longer in NPP applications in the USA. These polymers usually have good properties against fuel/oil contaminants, moisture and are often regarded as chemically robust, unless they encounter strong alkaline conditions. They are widely used as cable jacketing materials. However, radiation-thermal conditions are also known to generate small amounts of HCl or HF which can lead to initiation of corrosion in the vicinity of such materials during extended use. Hence, while the polymer may in itself perform reasonably well, there can be concerns about cross-ageing issues and material degradation when traces of HCl are involved. HCl may also react with Cu to form soluble copper oxychlorides which as initiators could further enhance copper corrosion on the cable wires or may act as oxidation catalysts. Data for halogenated elastomers are summarized in Table 3. Fluorinated semi-crystalline polymers such as Teflon are known as perhaps more radiation-sensitive than other polymers, whereas fluorinated polymers with reduced crystallinity may perform to higher doses. Silicones are not halogenated, but they also show radiation sensitivities; they are included in the Table 4 below.

Table 3: Threshold data for some halogenated polymers

Materials: Chlorosulfonated and chlorinated elastomers	**Exposure condition T [°C]; γ [Gy/h]***	**Dose to approx. 10% property change [kGy]** ***(100 kGy = 10Mrad)***	**Comment**
Hypalon-01 CSPE Anaconda Flameguard jacket	22; 12	124	
Hypalon-02 CSPE Kerite outer FR jacket	22; 12; plus RH	140	
Hypalon-03 CSPE Samuel Moore Dekoron jacket	60; 131	< 92	Only elevated T data at lower dose rates
Hypalon-04 CSPE Anaconda Flameguard jacket	60; 165	115	Only elevated T data at lower dose rates
Hypalon-05 CSPE Rockbestos Firewall III	60; 184 80; 62	250 112	Only elevated T data at lower dose rates
Hypalon-06 CSPE Eaton Dekoron Elastoset jacket	60; 145 80; 56	174 ~ 50	Only elevated T data at lower dose rates
CPE-01-Anaconda Flameguard FR-EP	70; 128	> 85	Only elevated T data at lower dose rates
Neo-01- Neoprene Okonite jacket	22; 12 22; 11 + RH	> 50 > 50	
Neo-02- Neoprene Rockbestos Firewall III jacket	50; 138	~70	

PVC, which is used in its plasticized form is a more complicated material. Degradation involves radiation chemistry affecting its molecular structure, but 'ageing' also includes physical phenomena like loss of plasticizer over time [22,23].

There is general agreement that radiation initiates free radicals and that those in turn facilitate dehydrochlorination and other follow-up reactions; for detailed mechanistic aspects please see [56] . PVC can scission but also crosslink, which in some cases has been described as enhancing physical properties such as tensile elongation and thereby reducing plasticizer diffusion, although substantial doses were required to highlight this effect (> 2MGy) [57]. Most studies find agreement that the most sensitive parameter revealing chemical changes in PVC is discoloration (one study highlighted colour changes after only 5 kGy [58]) which is not surprising since dehydrochlorination results in conjugation, a foundation for colour. In line with chemical changes occurring, some physical property changes (tensile strength) were detected at 10 kGy [59]. In another study 25 kGy certainly resulted in measurable oxidation [60]. An early study of plasticized PVC cable jacketing exposed to ~ 20 kGy (~ 300 h at 73 Gy/h at 43°C) showed detectable changes in tensile strength and elongation [61]. As early as 1981 noticeable changes were reported for a plasticized PVC cable jacketing exposed to 0.25 Gy/h over 12 years at 42°C (~ 26 kGy (2.6 Mrad)) [62]. In one recent study, irradiated plasticized PVC with 200 kGy did not show significant changes in its properties related to solvent swelling (i.e. probing scission/crosslinking) meaning drastic structural changes do not develop with much higher doses [63]. Based on numerous studies, PVC is more sensitive than many halogenated elastomers; changes are detectable at the 15 to 25 kGy level.

Table 4: Threshold data for some other special polymers

Materials: Fluoro and silicone based cable insulation	**Exposure condition T [°C]; γ [Gy/h]***	**Dose to approx. 10% property change [kGy]** ***(100 kGy = 10Mrad)***	**Comment**
ETFE-01 Teledyne Thermatic white Tefzel insulation	70; 40	~ 50	
Sil-01- Silicone Rockbestos Firewall II insulation	41.5; 52.5	~ 27	
PVC with a focused on plasticized materials in cable jacketing	43; 73 Gy/h 42; 0.25 Gy/h RT; 5.87 kGy/h RT; 7.5 kGy/h RT; 5.9 kGy/h Higher dose rate	~ 20 kGy 26 kGy > 10 kGy ~ 15 ~ 15 (~ 20 kGy average)	Cable jacket testing [61] Cable jacket 12 y use [62] Very high dose rate [59] [64] [65] No plasticizer diffusion

3.4 OVERVIEW OF EXISTING DATA WITH EMPHASIS ON LOW DOSE CONDITIONS

Table 5 summarises a comparison of the lowest radiation doses for which materials changes have been noticed. Excluding a specific silicone insulation (~ 30 kGy) or a PVC (15 to 25 kGy), and with some rounding, it is reasonable to argue that 50 kGy (5 Mrad) is a dose level that these materials can handle. Considering some uncertainties in available data and that only the initial small changes are used, some rounding is justifiable. There should not be any concern when summarizing the 45 kGy for EPR and XLPO within a 50 kGy threshold. Including PVC, this threshold is lowered to 20 kGy, which is then conservative for the other polymers. However, let us keep in mind that many of these materials were qualified and likely designed for

radiation applications. This means these specific types of materials that had been examined in the past may also perform somewhat better than generic polymers of similar structure.

Table 5: Threshold data for some other specific polymers

Materials Comparison:	**Dose to approx. 10% property change [kGy]** ***(100 kGy = 10Mrad)***	**Comment**
EPR elastomers	45	
XLPOs	45	
Hypalon	> 100, ~ 50 at higher T	
Neoprene	50	
ETFE Tefzel	~ 50	More stable than expected, Teflon likely worse
Silicone insulation	~ 27	
PVC	~ 15 -25	Multiple studies

4 Justifiable radiation dose thresholds

Radiation dose thresholds may be used to justify not performing additional radiation testing for materials qualification purposes. Hence, quantitative threshold levels need to be conservative and should also accommodate any other ageing behaviours currently not well understood. Therefore, threshold data themselves need to embrace some safety margins to minimize risks and uncertainty margins in material reliability assessments. Any final threshold radiation dose levels hence should be based on a few key assumptions:

- Select lowest dose levels before material changes become noticeable. In the above data compilations, we defined 'noticeable changes on the 10% level'.
- Reduce the maximum permissible radiation threshold dose with additional safety margins for a number of reasons:
  a) Lower threshold to accommodate potentially slow additional ageing phenomena that may contribute to ageing behaviour over extended timeframes that can experimentally not be resolved. These could be slow creep, and/or the effects of more heterogeneous oxidation or slow diffusive morphology changes.
  b) Reduce threshold further to cover potential synergistic behaviour between radiation and thermally-driven long term ageing.
- The latter two aspects cover the possibility that so far unknown ageing effects may result in more pronounced material changes over extended low dose rate and low temperature conditions than observed for the documented threshold dose. While this is unlikely, a prudent approach requires considerations for safety margins when thresholds are embraced.

We also recognize that threshold data at least initially should be considered per material class and polymer type. While we anticipated some scatter in thresholds, the fact is that the range is not necessarily broad. **For many materials and polymer types a threshold range is observed in the 10 to 100 kGy (1 to 10 Mrad) range.** This is very consistent with anecdotal discussions in the field of polymer degradation for common polymers, that radiation doses lower than 1 Mrad are usually not of concern, and that doses above 10 Mrad should result in observable material changes. The exception to this 'experiential rule' would be the expected higher thresholds for highly crosslinked epoxies, other aromatic thermosets (cyanate esters, bismaleimides), or aromatic polymers like PEEK, PEK, PC etc. (see for example the technical note available on the web by Von White II et al. [39]). However, aside from epoxies such materials are not commonly found in the domestic NPP application environment.

With the data summarized in Table 5 it makes sense to define an **initial radiation threshold for a broad range of polymers as 20 kGy (2 Mrad)** and it is not necessary to distinguish between polymer types, even if some polymers may handle more radiation. Situations where the specifics truly matter could be resolved on a case by case basis.

In regard to synergism in the radiation-thermal degradation, there has been a concern that most ageing studies may not capture any situations where slow thermal ageing in subtle radiation environments is more detrimental than the sum of individual thermal and radiation degradation contributions. But to unequivocally demonstrate strong synergistic effects, the R&D community has only recently demonstrated some apparent synergism in the radiation thermal ageing of silicones [41] and some elastomers [40], and these were observed when reasonable dose rates were applied. There was also some evidence for synergism when examining a large dose rate range and the resulting oxidation rates for XLPO materials [10]. However, the factorial contribution from synergism has been low and material ageing has been observed to be no more than about three times more effective than the sum of the individual thermal and radiation terms when synergism applies. It is fair to state that synergism has not been an obvious behaviour that has immediately caught our attention in previous accelerated ageing studies. Plus, it is difficult to experimentally truly prove synergistic behaviour. For the purpose of thresholds here, we do not know if more pronounced ageing occurs over decades at low temperature and dose rates. These situations cannot be confidently predicted from the usual accelerated ageing studies.

Similarly, weak additional ageing behaviour that may occur over decades have also not been convincingly demonstrated, although we know that materials ageing can be more pronounced than predictions from fast accelerated ageing studies may suggest. The key words and context here are perhaps curved Arrhenius behaviour, mechanistic changes, additional slow ageing pathways evidenced by slow diffusion or molecular rearrangement processes. We also know that materials age and can fail more heterogeneously over long time spans as ageing induced stress may build up or materials harden (commonly observed for elastomers). Stress relaxation is more effective at high temperatures meaning ageing that results in stress due to oxidation, crosslinking, scission etc. may in itself be compensated for in some ageing studies, and in turn becomes more important in extended use environments. It is also known that in terms of reliability, materials usually suffer more from unexpected behaviours, have growing concerns and perhaps fail earlier, than performing much better than designed and expected. This is also due to perhaps growing or changing expectations during operation, applications outside of specs with additional factors in their use environment, and/or unexpected exposure and dynamic ageing processes perhaps outside of simulations by ageing studies. Surprises with materials perhaps performing much better than qualified are not often demonstrated. Consumer products mostly suffer from the opposite (early failure and something just happened, polymer embrittlement and cracks are real!). Noteworthy exceptions were the Mars Rovers which operated more than 20 times longer than designed, although minimum mission requirements were conservative taking into account major cyclic environmental changes.

In light of the above considerations for perhaps unknown ageing effect or additional demands that could occur, we should lower the justifiable radiation dose thresholds of ‘little concern’. A factor of 10 easily takes care of synergism and unknown aging behaviours that may occur over decades. This means the operational margin in terms of a total radiation dose is lowered. This reduces risk and is in line with our intent of a threshold where we may ultimately wish to argue that no radiation testing

or complex accelerated ageing efforts are needed. **A highly conservative threshold are hence radiation doses of less than 1 kGy (0.1 Mrad), with definitely no higher doses than 20 kGy (2 Mrad) as a broadly verified threshold for most polymers. A slightly conservative threshold which accommodates some risk mitigation (synergism, unknown ageing contribution) is generally 10 kGy (1 Mrad).** The 1 kGy highly conservative level (i.e. no consequences expected) will now have to be considered within the context of varying application demands.

4.1 MAXIMUM DOSE RATES IN APPLICATION ENVIRONMENTS

Any radiation dose threshold will have to be considered within the framework of performance expectations (meaning which environment applies) and anticipated operating times. This means the expected times in operation coupled with the projected dose rate condition in which the materials will be used. It is important to recall that we justify radiation dose thresholds based on operational environments with temperatures as close as possible to ambient conditions, which pushes the ageing process to be mostly radiation dominated. Of course, materials may fail only subject to ambient temperature ageing for other reasons - that's a separate issue - but such failure should then not be due to low radiation exposure (i.e. as it occurs below the threshold). The maximum dose rate which yields the threshold dose over any given time can then be calculated, with some examples for threshold values, dose rates and given operating times shown below:

Threshold 1 kGy (0.1 Mrad) (highly conservative threshold)					
Performance lifetime	**40 y**	**50 y**	**60 y**	**70 y**	**80 y**
Max dose rate to reach threshold	2.85 mGy/h	2.28 mGy/h	1.90 mGy/h	1.63 mGy/h	1.43 mGy/h
Dose accumulation rate	25 Gy/y	20 Gy/y	16.7 Gy/y	14.3 Gy/y	12.5 Gy/y
Threshold 10 kGy (1 Mrad) (justifiable less conservative threshold)					
Performance lifetime	**40 y**	**50 y**	**60 y**	**70 y**	**80 y**
Max dose rate to reach threshold	28.5 mGy/h	22.8 mGy/h	19.0 mGy/h	16.3 mGy/h	14.3 mGy/h
Dose accumulation rate	250 Gy/y	200 Gy/y	167 Gy/y	143 Gy/y	125 Gy/y

These thresholds will separate environmental conditions where radiation should not be of major concern versus applications where expected radiation doses are sufficiently high and will justify comprehensive material qualifications.

Environments covered by the lowest threshold (most conservative 1 kGy):

A low dose rate environment without any expectation for system-critical accident performance should justify the use or at least consideration of radiation dose thresholds to simplify expected ageing. An example is:

- Normal low radiation dose < 18 Gy/y yielding 0.72 kGy over 40 years (this is described as a normal low dose rate area)

An environment with an expected dose of no more than 18 Gy/y will easily accommodate the lowest and most conservative threshold of 1 kGy between 50 to 60 years, although it will become marginal beyond the 60-year level. However, with the multiple conservative approaches embedded in the definitions of the low 1 kGy threshold, we do not expect issues even towards the 80 year continued exposure situation which with 18 Gy/y would only yield 1.44 kGy, still a low and safe value from the material radiation sensitivity point of view. The point here is the notion that in some situations such thresholds will have some margin considering their derivation and meaning, where our intent is setting justifiable boundaries (some rounding and approximations fall within their definitions already). In contrast, if any material is expected to also handle large accident doses despite a normally very low dose rate environment, then the total dose to be covered will nevertheless be outside a justifiable radiation dose threshold.

Environments being marginal for highest threshold (least conservative 10 kGy):

Some operational environments and performance expectations might fall close to the least conservative but still safe and low threshold of 10 kGy (1Mrad). In such situations it would make sense to derive more informed decisions for the applicability of a threshold on a material case by case basis, rather than always relying on a fixed cut-off. Again the 10 kGy is meant to offer guidance with some margin in its vicinity. Depending on how much is known about specific material and polymer behaviour, a case could be made to regard total doses perhaps up to 50 kGy (< 5 Mrad) as a threshold. But it also means that then any safety margins for unknown behaviour, conservative engineering decision for ongoing operation, or cautious initial material selection principles would be at their limits. An example is:

- Normal radiation dose < 300 Gy/year yielding 12 kGy over 40 years
- Additional accident dose (H4) of 7.4 kGy
- This results in a total dose of ~ 20 kGy, which is beyond the least conservative radiation threshold (10 kGy), but not yet a significant concern as the lowest experimental threshold is 20 kGy (see Table 5). Additional material specifics should assist with a more informed rating.

Environments not covered by highest threshold value (least conservative 10 kGy):

Higher dose rate conditions, due to accident scenarios (likely demanded for qualification purposes) or in the vicinity of ongoing stronger radiation sources will fall outside any radiation dose threshold justifications. Dose levels beyond threshold justifications may originate in multiple ways:

- High anticipated accident doses that qualified materials will have to accommodate, for example 100 kGy (10 Mrad).
- Normal operational under high radiation dose rates in reactor coolant pump or heat exchange areas on the order of 4.38 kGy/year (~ 175 kGy over 40 years). Note that this matches anecdotal higher dose rate operational conditions in some USA NPPs on the order of 0.5 Gy/h (~ 4.4 kGy/y).

- Any combination of high dose levels expected under accident AND normal high dose rate operational conditions.

The above examples of applying radiation dose thresholds to different plant operational environments demonstrate that reasonably justifiable and highly conservative thresholds can be considered and allow for the distinction of plant conditions where radiation is not expected to be important for polymers. Further, the definitions derived are not absolute, but are rather meant to show how different environments could be discussed subject to some unknowns and hence uncertainty in the actual environment and derived threshold dose. Point is, boundaries and justifiable margins in either direction, coupled with material knowledge will always matter for informed and hence justifiable decisions.

4.2 THRESHOLDS COUPLED WITH SPECIFIC MATERIAL PERFORMANCE DEMANDS

Another aspect of general thresholds could be the questions whether physical property changes may depend differently on total degradation chemistry. It is important to remember that radiation damage in organic materials is initially chemistry, even if perhaps scission, and then enhanced mobility may affect crystallinity. Chemistry is the initiation and main degradation process, changes in physical properties will follow. For cables we care about elasticity, and of course also no changes in dielectric properties. For seals the primary concerns will be sealing force, hardness and compression set. For coatings the key property is often adhesion and a high quality continuous film (meaning micro-cracking opens up corrosion pathways).

All of such physical properties are however linked within a common, material degradation chemistry pathway. Radiation or thermal damage involving oxidation leads to scission, perhaps crosslinking, a changed molecular structure, different molecular mobility, subtle changes in polarity and H-bonding. A consequence of this 'degradation chemistry' are physical macroscopic changes exemplified by shrinkage, modulus changes, hardness (or softening), stress relaxation, tensile strength, adhesion, cracking, embrittlement and other changes. In the field of polymer degradation, it has long been recognized that a change in tensile elongation is a sensitive measurement. A few chain scissions, or some change in the effectiveness of tie molecules between the amorphous and crystalline phase are sufficient to gently affect stretching and macromolecular relaxation (viscoelastic) behaviour, meaning tensile elongation changes in principle respond to small levels of degradation chemistry. Similarly, a compression set or hardness change for a seal material does not require much chemistry. But the differences in the level of chemistry for either property change (tensile or hardness/compression) are negligible. Detailed studies of elastomer ageing have often shown that the underlying chemistry can be seen in multiple physical parallel property changes, meaning hardness/compression, brittle tendencies, even adhesion for that matter, is coupled with tensile properties that also depend on flexibility, hardness or elasticity.

These considerations matter, as we may be concerned that most radiation chemistry degradation has traditionally relied on tensile testing. But the point is that monitoring of related properties would not be more sensitive. This gives us confidence that general radiation thresholds of 1 to 10 kGy would equally apply to a coating for adhesion, a compression set or change in sealing force for a seal or gasket. A radiation threshold defines a very small amount of resulting degradation chemistry, and certain bare minimum chemistry is required to induce measurable physical property changes. One exception as an example, but not relevant for NPP purposes here, could be conductive polymers, where a few scission or single oxidation events could break conjugation and hence affect semi-conductivity. It is possible that in this case even less radiation dose could have a measurable physical effect.

In summary, to the best of our existing knowledge, polymer radiation sensitivities as quantified by tensile elongation are sufficiently sensitive and capture an average property change representative of many other useful properties in the application of polymers. Having other critical physical property changes without them showing up in tensile elongation is not expected. In addition, we have defined conservative radiation thresholds which embrace some unknown and perhaps minor variations in property sensitivities.

4.3 ADJUSTMENTS TO THERMAL AGEING TO ACCOMMODATE DOSE THRESHOLDS

If we were to embrace radiation dose thresholds we have to recognize that a small level of material ageing is effectively disregarded or at least judged to be inconsequential. The corollary to this is that the margin for 'thermal only' stability would have to slightly increase. This is first of all mostly a philosophical challenge, because no current lifetime prediction would have the fidelity to predict adequate performance for perhaps 50 but not 55 years. Such precision simply does not exist in the data available from current accelerated aging approaches. This means the small margin that a low radiation dose adds to overall expected ageing is already contained within the qualification of most materials. This was accomplished through excessive temperature-time and major radiation dose testing. In other words, if a polymer has the perceived ability to last for decades, it is unlikely that a small amount of radiation chemistry would push it over the edge, and a major error would occur if low radiation doses are not taken into account in qualification testing.

We are in agreement that any low radiation dose will represent a small amount of degradation chemistry. The question then arises, if this is not considered due to accelerated ageing being simplified by disregarding irradiation, how could thermal only testing be adjusted to add a small amount of extra ageing or indirectly accommodate slightly lower expected lifetimes. In a first approach, one may wish to consider higher temperature testing. However, this creates uncertainty with possible mechanistic changes, is further removed from the extrapolation regime (extended low temperature conditions), and aggressive short-term high temperatures exposure is often already contained in quick qualification testing. The point here is that increasing test temperatures will offer no additional meaningful guidance towards the need of better quantifying very long low temperature material

sensitivities. One possible strategy to accommodate the small loss of fractional ageing (meaning the threshold dose) will have to be through improved thermal ageing in the low temperature regime. The question is, does the material have recognizable thermal vulnerabilities predicted to occur over decades in the application space?

A better understanding of thermal margins and hence performance and reliability for the application could be obtained in two ways, by a) increasing thermal ageing times for traditional temperatures and b) additional thermal exposure temperatures that are so far not included in existing testing. We could accommodate the approach of disregarding the radiation component through improved predictive accelerated thermal ageing that will compensate for uncertainty from the radiation threshold. More meaningful thermal predictions mean increased confidence in margins, boundaries and hence more confident and reliable use of the material, whereby introducing some additional uncertainty through the elimination of the irradiation component is then indeed justifiable and already compensated for. These are suggestions, but essentially the removal of one fractional ageing component, even if justifiably small and not necessarily important, should be compensated for by improved ageing science, expanded testing and underlying understanding of material behaviour. This is also embracing the fact that long-term operation was less an issue in original qualification testing, and that condition-monitoring and extended operation is now a much more important aspect of current NPP operations. Material ageing science is a key contributor, where rational approaches and pragmatic decision making for what matters more or less should be part of our collective approach.

5 Summary opinion

Subject to specific conditions in a multi-factorial application environment all polymers usually degrade over time. It is well-established that radiation, elevated temperature and other environmental conditions (moisture, acids etc.) may induce noticeable material changes. However, it is also a fact that specific initial exposure levels, minimum doses, or fractional damage as integrated time-condition exposure, and hence some 'ageing history' are required before materials can be deemed 'aged'.

For polymers used in a broad range of nuclear power plant related application environments, such materials may not only age under extended thermal but also under radiation-thermal environments over time. Therefore, materials accepted for NPP applications usually undergo radiation and thermal testing for comprehensive material qualification purposes. This means that materials for NPP applications are usually of high quality, well-designed and represent niche market choices. They are often covered by standards from regulatory and oversight agencies that define qualification demands. However, qualification tests often require significant efforts, are costly and yet in some cases may not even be needed in every detail. Therefore, it is most important that necessary testing captures what is required and makes the most sense for qualification purposes.

A key question is, whether material qualification, selection and their extended use assessments could be simplified when only limited radiation dose exposure during their 'lifetime' occurs. If known radiation doses fall below certain thresholds, then such materials would not necessarily need to be qualified for use under elevated radiation conditions. Point is, low dose levels should then be regarded as neither contributing significantly to any material degradation processes nor to limits in the expected overall application demands.

This review has therefore focused on key aspects towards defining minimum dose exposure levels before radiation damage in polymers should be of concern. It has involved a broad scope involving multiple directions, from data gathering, identifying beginning material changes at low doses, dependence on material type, and operational environments towards dose threshold definitions that could assist in ongoing performance and NPP lifetime extension assessments:

- Examination of existing data on radiation dose sensitivities of polymers.
- Determination of threshold doses for which material changes are just noticeable, on the order of a 10% property change based on initial values.
- Definition of conservative and justifiable threshold radiation doses subject to known documented ageing sensitivities.
- Interpretation of threshold doses in the context of different types of NPP application environments (radiation levels).
- Cursory examination how threshold doses could be incorporated in material qualification testing if comprehensive radiation-thermal ageing studies are not pursued.

- Justification for extended material use when only limited radiation doses have accumulated in the past (material lifetime extension assessment).

Polymers in a broad range of components include semi-crystalline or amorphous, cross-linked and often elastomeric materials, with the addition of also halogenated materials as various types (chloroprene, chlorosulfonated, PVC, fluoro polymers). Perhaps in contrast with expectations from non-experts, the data summarized in this review demonstrate that despite a broad range of polymers, their initial radiation dose sensitivities fall within a variance of no more than one order of magnitude. Just noticeable material changes occur with dose deposition between 20 and 100 kGy (2 to 10 Mrad). This leads to the following threshold levels:

- Maximum justifiable dose thresholds on the order of 10 kGy, perhaps extended to 20 to 50 kGy if the polymers are well-understood and numerous aging studies exist.
- Highly conservative radiation dose threshold of 1 kGy which accommodates significant uncertainty in specific material behaviour (synergism, lack of ageing studies and particular sensitivities).
- For 50 year-use this means dose rates < 0.023 Gy/h (200 Gy/y), with the most conservative and highest confidence value ideally <0.0023 Gy/h.

Subject to such threshold levels, only some specific NPP operational environments can be described as not significant in terms of radiation exposure. Most importantly, only specific low dose rate application environments without additional accident demands fall into this regime. Accident doses are usually defined as beyond such thresholds. In addition, any other applications with ongoing high dose rates cannot be covered with a threshold. There is a reason that materials for extended use under aggressive radiation-thermal conditions and/or accident scenarios must undergo comprehensive qualification testing and meet rigorous selection criteria.

Should radiation thresholds be embraced, it would also have consequences for qualification approaches and material testing/screening. Without combined environment evaluations, any ageing component due to added weak radiation levels is removed. Hence the question arises, what is the fractional damage contribution of the radiation threshold dose? For many materials 10 kGy is approx. 10% of what they should accommodate. Could this damage component be covered by adding testing demands in thermal evaluations? There could be a few options, perhaps higher temperature testing, but this is not attractive (just generates shorter times which do not offer best guidance). Another option could be to extend testing time and add moderate temperatures, in essence pursuing better aging studies. If the radiation dose contribution were to be removed, one would need to increase the required margins for predictions and performance expectations. An attractive option would be to demand longer lifetimes, simply adding performance margin. But many materials under thermal only conditions are already predicted to last longer than many decades. A suitable approach could therefore be to reduce uncertainty in predictions and justify that ~10% additional aging from radiation is inconsequential.

Final summary of the most important conclusions:

- Available data for polymer degradation in combined environments can be used to justify radiation threshold values.
- Highly conservative value for all common polymers is 1 kGy (0.1 Mrad) (high certainty of being inconsequential).
- 10 to 20 kGy (< 2 Mrad) is an acceptable threshold margin if polymer degradation is reasonably well-understood through published data.
- This represents ~ 10% of 'damage' accumulation which most polymers can accommodate without any reduction in their essential use properties.
- With radiation dose exposures less than such a threshold, the overall degradation will then be thermally dominated or through other processes.
- For extended material use with integrated radiation exposure below these thresholds, low doses should also NOT be a key determining factor for lifetime extension decisions.
- If radiation is eliminated from some qualification testing, then more meaningful and comprehensive thermal degradation studies should be pursued to compensate.
- Better understanding of materials aging and performance margins, i.e. meaningful 'aging science' will be helpful.
- Improved material qualification approach: Use threshold limits and justify extra operational long-term performance margins in the absence of radiation. Carefully document aging sensitivities and expected residual performance.
- However, if a material already thermally degrades over 50 years then radiation would not matter either way. This means safety margins and thresholds should be corroborated by well-understood thermal long-term ageing processes.
- Lastly, for generic materials where meaningful guiding data at low dose rates (non DLO) may not exist (nitrile, butyl, natural, styrene-butadiene rubbers or similar), the low most conservative threshold dose (1 kGy) should be applied initially unless data confirm otherwise.

6 Glossary of Abbreviations

DLO	Diffusion Limited Oxidation
EPR	Ethylene Propylene Rubber
Gy (kGy)	Unit for radiation dose
Hypalon	Trade name for chlorosulfonated polethylene
NPP	Nuclear Power Plant
PE	Polyethylene
PP	Polypropylene
Rad (Mrad)	Unit for radiation dose
RT	Room Temperature
RCP	Reactor Coolant Pump
XLPE	Crosslinked Polyethylene
XLPO	Crosslinked Polyolefins

7 Acknowledgments, author background and disclaimer

The discussion of radiation threshold data for the slow extended aging of polymers is based on actual published data which demonstrate that many polymers can accommodate minimum dose levels before physical properties may noticeably change. Existing published data from the work conducted at Sandia National Laboratories in Albuquerque, NM USA by numerous authors over decades of R&D activities are gratefully acknowledged.

The author of this report has spent > 30 years dealing with a broad range of material reliability challenges and the assessment of polymer degradation in many different application environments. He has contributed to the evaluation of radiation-thermal polymer degradation and authored/co-authored many research papers and reports on this topic. The author has also served the polymer material ageing community with many years of editorial support for the journal "Polymer Degradation and Stability'.

Note: This report is based solely on previously published data and describes objective technical results and analyses. Any subjective views or opinions that might be expressed do not represent the views of any government agency, research institution or working group. The opinions presented are of guiding nature and meant to open up discussions with the concept of threshold data to be further confirmed and corroborated by other experts in the field. There are no explicit warranties and justifications for expected material behaviour to be implied. As is the common approach for the use of materials/polymers in demanding applications, if in doubt and/or when specific reliability must be inferred, only dedicated materials reliability testing or comprehensive predictive aging studies may offer data-based guidance on actual material performance limits and hence meaningful operating margins in the desired application environments.

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9 Supplemental figures

Table I-1. Summary of cable samples contained in SCRAPS.

Material	Cable No.	Manufacturer	Trade Name	Material- common name
CPE-01	C-2	Anaconda	Flameguard FR-EP ("Y")	Chlorinated polyethylene
CPE-02	C-20	Anaconda	Flameguard FR-EP ("Y")	Chlorinated polyethylene
EPR-01A	C-14	Anaconda	Flameguard	Ethylene propylene rubber
EPR-01B	C-15	Anaconda	Flameguard	Ethylene propylene rubber
EPR-02	C-2	Anaconda	Flameguard FR-EP ("Y")	Ethylene propylene rubber
EPR-03	C-5	Eaton	Dekoron Elastoset	Ethylene propylene rubber
EPR-04	C-12	Anaconda	Durasheath	Ethylene propylene rubber
EPR-05	C-18	Okonite	EPR	Ethylene propylene rubber
ETFE-01		Teledyne	Thermatic	Tefzel
Hyp-01A	C-14	Anaconda	Flameguard	Hypalon
Hyp-01B	C-15	Anaconda	Flameguard	Hypalon
Hyp-02	C-6	Kerite	FR	Hypalon
Hyp-03	C-9	Samuel Moore	Dekoron	Hypalon
Hyp-04	C-10	Anaconda	Flameguard	Hypalon
Hyp-05	C-11	Rockbestos	Firewall III	Hypalon
Hyp-06	C-5	Eaton	Dekoron Elastoset	Hypalon
Hyp-07	C-3	Brand-Rex		Hypalon
Hyp-08	C-19	BIW	Bostrad 7E	Hypalon
Ker-01	C-6	Kerite	FR	EPR type
Neo-01	C-17	Okonite	Okolene	Neoprene
Neo-02	C-8	Rockbestos	Firewall III	Neoprene
Sil-01	C-7	Rockbestos	Firewall II	Silicone
XLPE-01	C-1	GE	Vulkene Supreme	Crosslinked polyethylene
XLPO-02A	C-3	Brand-Rex		Crosslinked polyolefin
XLPO-02B	C-3	Brand-Rex		Crosslinked polyolefin
XLPO-03	C-4	Eaton	Dekoron Polyset	Crosslinked polyolefin
XLPO-04	C-13	ITT Surprenant	Exane II (composite)	Crosslinked polyolefin
XLPO-05	C-16	Rockbestos	Firewall III	Crosslinked polyolefin

Cable materials and their polymers referred to in 'cable ageing reports' [17,19]

THRESHOLDS FOR RADIATION SENSITIVITY OF POLYMERS IN COMBINED RADIATION-THERMAL ENVIRONMENTS

Available data for polymer degradation in combined radiation-thermal environments can be used to justify radiation threshold values below which radiation effects are of little consequence to useful material properties. A highly conservative value for all common polymers is 1 kGy (0.1 Mrad) (high certainty of being inconsequential). 10 to 20 kGy (< 2 Mrad) is an acceptable threshold margin if polymer degradation is reasonably well-understood. Material performance subject to the upper threshold should be corroborated by well-understood thermal long-term ageing processes to confirm residual margin. With radiation dose exposure being less than such a threshold, the overall long-term degradation will be dominated by thermal and other processes. Radiation thresholds can guide improved material qualification testing, condition monitoring emphasis and extended use considerations.

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