RESEARCH REPORT

VTT-R-00037-19

Ageing of EPDM and Lipalon cable materials in high temperature and irradiation environments

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Confidentiality: Public

Report's title	
Ageing of EPDM and Lipalon cable materials in high temperature and irradiation environments	
Customer, contact person, address	**Order reference**
SAFIR 2018 Research Programme	
Project name	**Project number/Short name**
Condition Monitoring, Thermal and Radiation Degradation of Polymers inside NPP Containments	117751/COMRADE
Author(s)	**Pages**
Konsta Sipilä and Harri Joki	18
Keywords	**Report identification code**
Irradiation, thermal ageing, EPDM, CSM	VTT-R-00037-19

Summary

Ageing of polymer components in nuclear power plant applications are accelerated by elevated temperature and ionizing radiation. In this report the behaviour of two common polymer materials EPDM and CSM (Lipalon cable jacket material) in high temperature and irradiation environments are studied. According to the thermal ageing data, remaining lifetimes for CSM samples at 50°C and 25°C were estimated to be ca. 680 days and ca. 16 years, respectively. The sequence of the ageing treatments cannot be ignored in the case of the studied EPDM blend since the difference in elongation of break values can be seen when results from consecutive ageing treatments and simultaneous ageing treatments are compared. Application of a predictive model based on superposition were conducted in order to predict any existing dose rate effects. Based on the results, the chosen ageing environment (up to 400 kGy dose of gamma radiation and exposure to 125°C) did not yield required amount of degradation on EPDM that superposition principle could be successfully applied. Also in case of CSM the test matrix was too narrow to produce reliable predictions on dose rate effect.

Confidentiality	Public

Espoo 1.2.2019

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Distribution (customer and VTT)

SAFIR2018 website, VTT archive, VTT nuclear materials´ report archive.

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 of this study was to evaluate the thermal and irradiation effects on two common polymer based materials that are used in Nordic nuclear power plants. Finnish State Nuclear Waste Management Fund (VYR) and VTT Technical Research Centre of Finland Ltd are acknowledged for funding this work.

Espoo 21.2.2019

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1. Introduction

Different kind of polymeric components are used in nuclear power plant applications inside the containment building, e.g. in cables and sealants, where they can be exposed to elevated temperatures and ionizing radiation. Polymers are known to be susceptible to dose rate effects [Gillen et al. 1981, Reynolds et al. 1995, Placek et al. 2003], where the dose rate has an effect on the amount of degradation that the polymer is experiencing. Usually the situation involves a lower dose rate causing more damage to the material than a high dose rate with the same end dose. This kind of scenario can be problematic when the ageing of polymeric components is simulated with accelerated ageing where high dose rates are applied, possibly yielding in too low damage levels compared to a real service environment where irradiation dose is absorbed during a period of several years.

The mechanism governing the dose rate effect is strongly related to the diffusion of oxygen, which has an effect on the kinetics of the chemical reactions governing the ageing of polymers. The principle of the occurrence of dose rate effect is presented schematically in Figure 1, where the dose to equivalent damage (DED) parameter is plotted against dose rate. DED parameter is defined with an end-point criterion, which represents the condition of the polymer. Typical end-point criterion with cable materials is 50% absolute elongation of break but other criteria can be used as well, as long as they validly describe the condition of the polymer in its designed application. DED parameter is the absorbed dose at which the end-point criterion is reached, and as it is plotted against dose rate as illustrated in Figure 1, the dose rate effect can be visually examined.

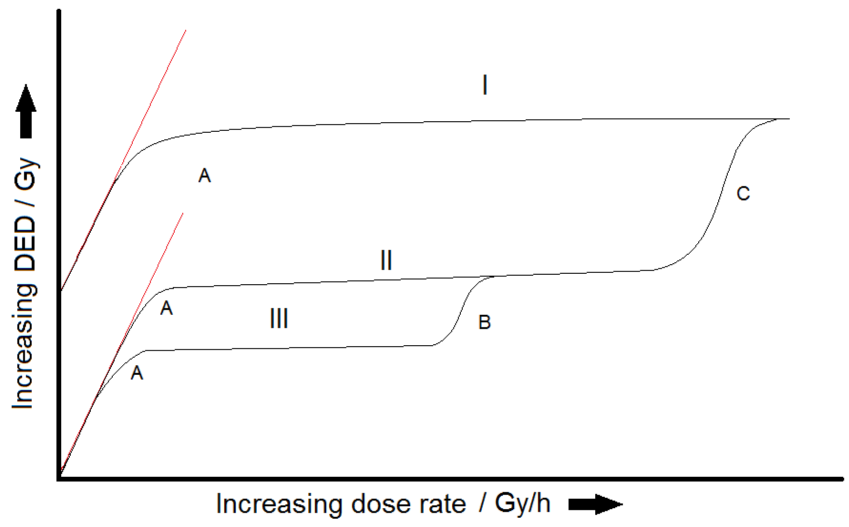

Figure 1. Schematic illustration of the dose rate effect.

Curve I in Figure 1 represents a situation where the polymer is irradiated in an inert atmosphere. The DED parameter has only a small decrease on very wide range of dose rates indicating a small dose rate effect. At the very low dose rates, a curvature can be seen in the figure, indicating an increase in the dose rate effect. The magnitude of the observed dose rate effect depends on the governing thermal and radiation degradation pathways [Gillen et al. 1993]. As the dose rate approaches zero value, the plot has slope of 1, which is the thermal ageing limit, i.e. dose rate at this stage is diminishingly small and only thermal ageing governs the ageing.

Curve II represents a situation where the irradiation is conducted in air atmosphere. In this case, the effects of diffusion limited oxidation (DLO) can be seen at very high dose rates.

DLO is closely related to the diffusion of oxygen and the ionizing radiation radicalizing the diffused oxygen. The interaction between an oxygen molecule and a high energy gamma quantum may result in oxygen radicals in polymer matrix, which react with surrounding polymer chains ultimately yielding in chain scission or crosslinking. As the dose rate is high, the oxygen is consumed in the vicinity of the surface of the polymer and thus the degradation of the polymer is concentrated on these surface layers. This heterogeneous oxidation can be less detrimental to the polymer than homogenous oxidation, where the oxygen has time to diffuse evenly in the whole volume of the polymer and thus degrade the polymer in wider volume.

Figure 1 has also a third curve which represents an additional type of dose rate effect that occurs at medium 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.

This report aims to study the behaviour of two polymer materials in thermal and irradiation environments. Some semi-empirical models exist that can be used to predict the degradation of polymers in thermal-radiative environments [Sipilä 2017]. Previous work estimated the use of power law model in predicting the severity of dose rate effect [Sipilä et al. 2018]. Application of a second model based on superposition is conducted based on the experimental data gathered within the COMRADE project.

2. Goal

The goal of the study is to evaluate how the chosen materials behave in high temperature and irradiation environments and estimate the use of semi-empirical model based on superposition in predicting the severity of the dose rate effect.

3. Methods

3.1 Samples

The studied materials included peroxide cured EPDM rubber manufactured by James Walker and CSM cable jacket material (tradename Hypalon, cable tradename Lipalon) provided from storage of the Finnish nuclear power company TVO. The EPDM samples were stamped out of two millimetre sheet delivered by the manufacturer and Lipalon samples were prepared from the jacket of the cable delivered by TVO.

3.2 Ageing of samples

The ageing of samples was conducted by subjecting them to high dose gamma radiation and/or elevated temperature. The irradiation treatments were conducted at ROZA irradiation facility and VTT gammacell. ROZA is located in UJV Řež, Czech Republic. The facility uses ^{60}Co as gamma radiation source. The planned and realized dose rates and absorbed total doses are shown in Table 1. The deviation from the required dose rates was satisfactory in most cases. In the case of 0,18 kGy/h the measured dose rate was however 44% higher than the required value. The deviation between the absorbed dose and target dose was mainly less than 10%, but in one case the absorbed dose was 18% higher than the required dose.

The low dose rate irradiation (<0,06 kGy/h) were conducted at VTT's gammacell (^{60}Co as gamma radiation source) at room temperature. The samples were prepared during the 2017 COMRADE project and they were irradiated with 20 kGy dose. As the results from 2017 indicated, the dose was rather small and the irradiation treatment was continued in fall 2017 for 309 days. During this irradiation treatment, the dose rate decreased from 54 Gy/h to 48 Gy/h. The irradiation treatment was performed in seven different stages as the gammacell was reserved for other irradiation treatments. The calculated absorbed dose for the samples was 400 kGy.

Table 1. Summary of the high dose rate irradiations at ROZA.

Temperature (°C)	Dose rate required (kGy/h)	Dose rate measured (kGy(h)	Absorbed dose required (kGy)	Absorbed dose measured (kGy)
25	0,36	0,38	400	418
25	0,18	0,27	200	209
100	1,0	0,71	400	470
100	0,36	0,44	400	401
100	1,0	0,75	200	219
100	0,36	0,41	200	200
100	1,8	0,26	200	201
125	1,0	1,11	400	411
125	0,36	0,41	400	406
125	1,0	1,02	200	203
125	0,18	0,26	200	202

The thermal ageing data on EPDM was produced by RISE during the previous years of the project.

3.3 Tensile testing

Tensile testing was conducted according to ISO 37 standard. From each ageing condition five samples were tested and the tensile stress and elongation at break values were extracted from the stress-strain curves. All measurements were conducted at room temperature and strain rate of 25 mm/min was used.

3.4 Hardness measurements

Shore-A hardness was measured from base of the tensile testing samples according to ISO 7619-1 standard.

4. Results and discussion

4.1 Mechanical properties of EPDM

The measured elongation at break (EaB) values for EPDM are shown in Figure 2 and Figure 3 and the measured tensile stress values in Figure 4 and Figure 5. From the results presented in Figure 2 it can be stated that the 200 kGy dose causes only slight decrease in EaB values. Similar observation can be done in tensile stress values, as they all seem to be close to the reference value.

The most interesting observation from Figure 3 is the measured EaB in case where a sample was irradiated in VTT gammacell with the dose rate of <0,06 kGy/h to the absorbed dose of 400 kGy. The increase in EaB is 51% compared to the reference value and 109% higher than the same irradiation conducted with the dose rate of 0,36 kGy/h. However, the measured tensile stress did not deviate from the reference value. An additional hardness measurement was conducted to this sample, and as a result, the Shore-A hardness was slightly increased from 73 to 76.

The samples irradiated at elevated temperatures had only small decreases in EaB values. In tensile stresses, the deviation from the reference value is very small in all cases, except with the sample irradiated at 125°C and 1 kGy/h. With this sample, the tensile stress decreased 29%.

The changes in EaB and tensile stress can be interpreted to conclude from chain scission and crosslinking [Scaliusi wt al. 2015, Šarac et al. 2016]. Increased EaB value and decreased tensile stress value are indicating chain scission dominating over crosslinking.

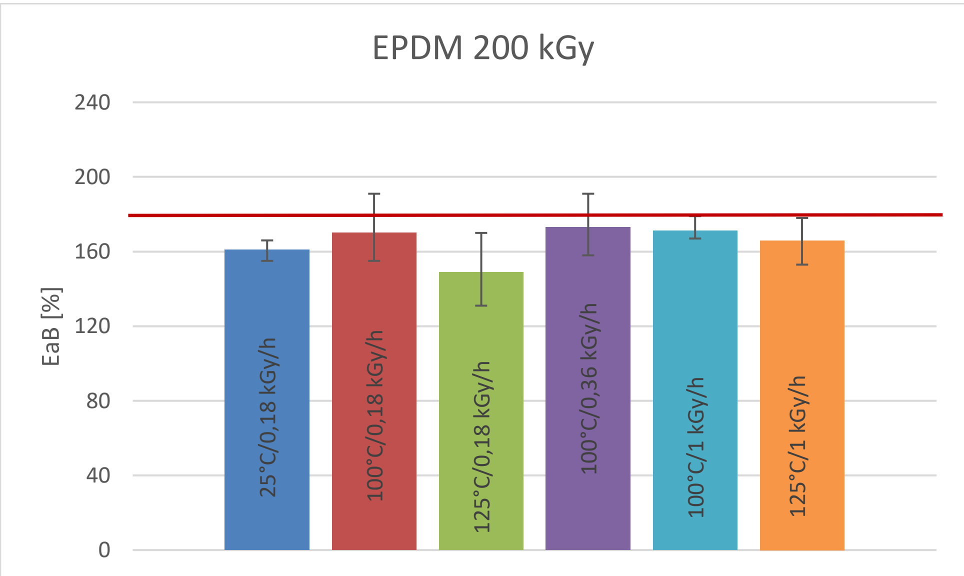

Figure 2. EaB results for EPDM samples irradiated with calculated dose of 200 kGy. The red horizontal line presents the non-aged material EaB value of 182%.

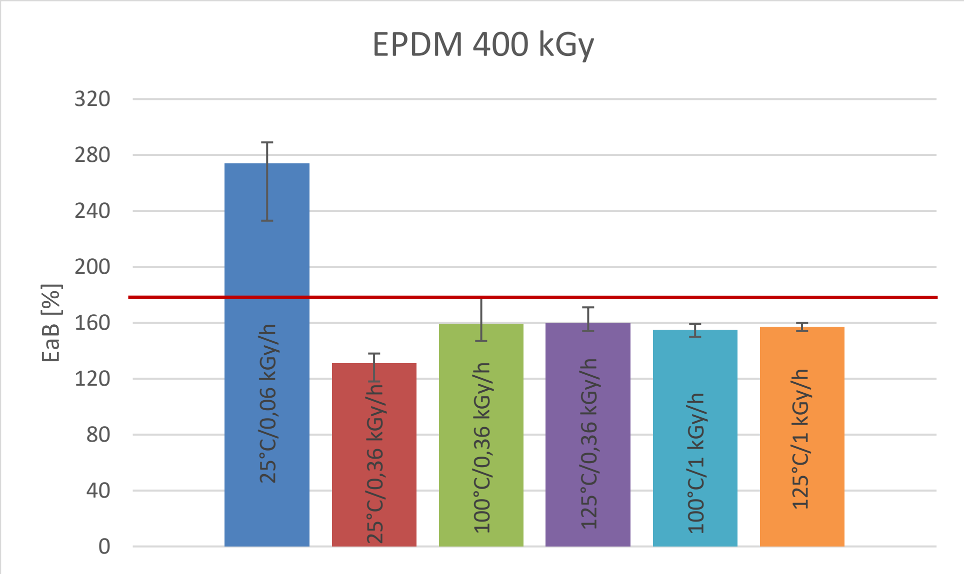

Figure 3. EaB results for EPDM samples irradiated with calculated dose of 400 kGy. The red horizontal line presents the non-aged material EaB value of 182%.

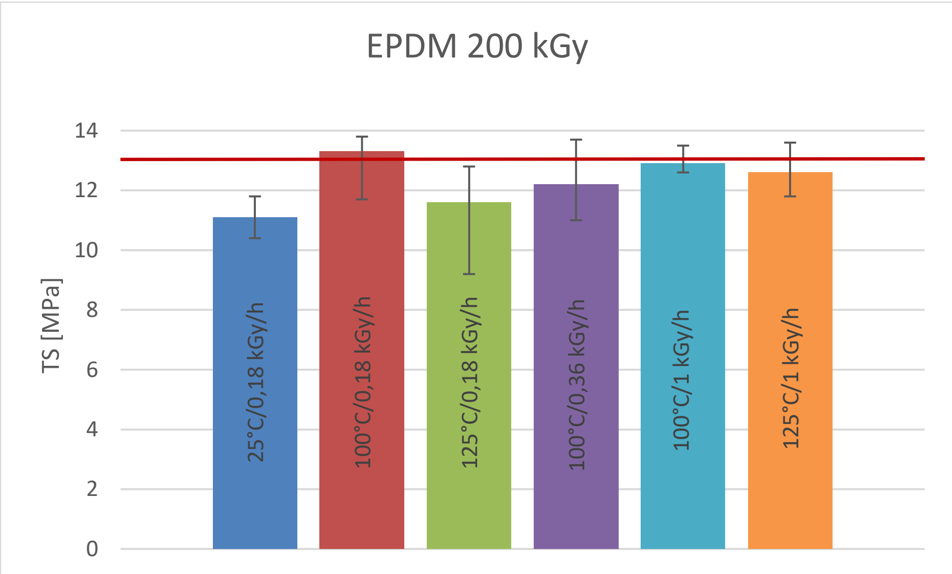

Figure 4. Tensile stress (TS) results for EPDM samples irradiated with calculated dose of 200 kGy. The red horizontal line presents the non-aged material TS value of 13,0 MPa.

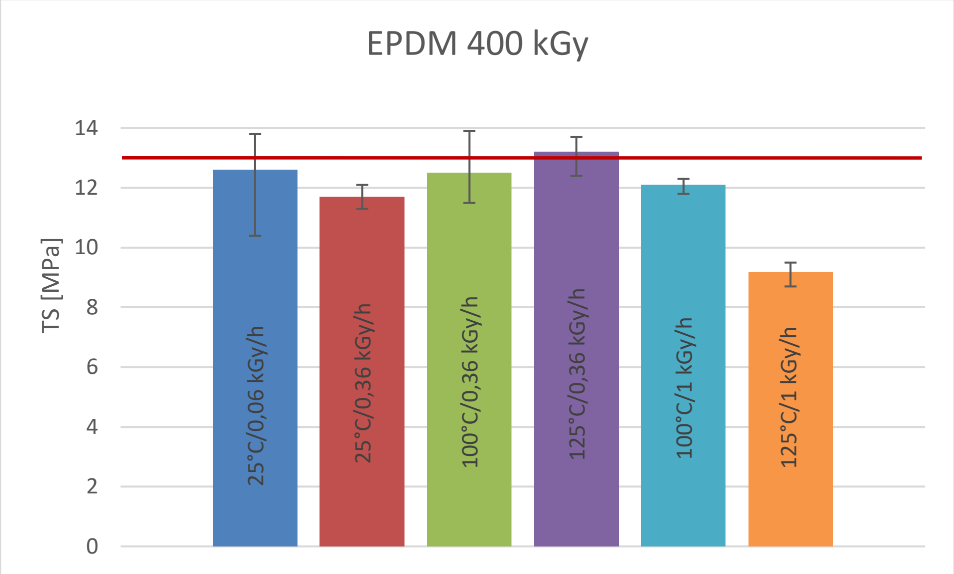

Figure 5. Tensile stress (TS) results for EPDM samples irradiated with calculated dose of 400 kGy. The red horizontal line presents the non-aged material TS value of 13,0 MPa.

4.2 The role of sequence in ageing of EPDM

During the COMRADE project, data on the role sequence on ageing has been gathered. In Figure 6 EaB data is presented after three different ageing procedures. The first ageing procedure included thermal ageing at 125°C for three weeks first and then irradiation at room temperature up to 200 kGy dose (blue column in Figure 6). The second ageing procedure (orange column in Figure 6) had the exact same thermal and irradiation ageing's, but their sequence was changed so that at first came the irradiation ageing and then the thermal ageing. In the third ageing procedure, both thermal and irradiation ageing were conducted simultaneously (grey column in Figure 6). The results indicate that the sequence does matter as simultaneous ageing and irradiation-thermal-sequence are compared.

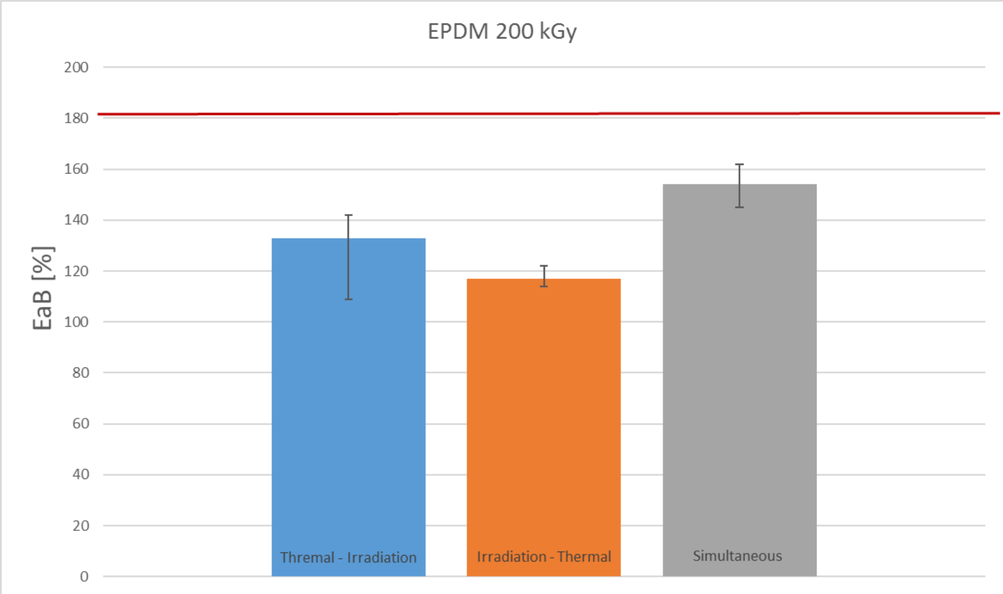

Figure 6. Comparison of sequence of ageing on EPDM samples. Blue column describes the decrease in EaB when sequence is thermal-irradiation, orange column irradiation-thermal and grey column simultaneous thermal and irradiation ageing.

4.3 Mechanical properties of CSM

The measured EaB values for CSM are shown in Figure 7 and Figure 8. The decrease in EaB is clear with both irradiation doses. The trend seems to be that the decrease in EaB increases as irradiation dose and temperature increases.

From the tensile stress values presented in Figure 9 and Figure 10, it can be seen that the tensile stress values are not changing significantly or are even slightly increasing with increasing absorbed dose.

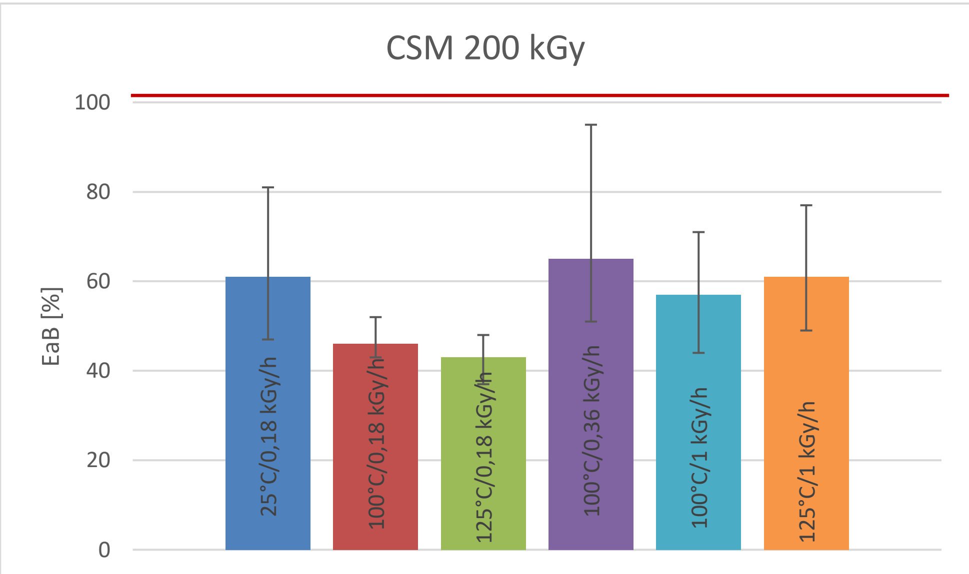

Figure 7. EaB results for CSM samples irradiated with calculated dose of 200 kGy. The red horizontal line presents the non-aged material EaB value of 102%.

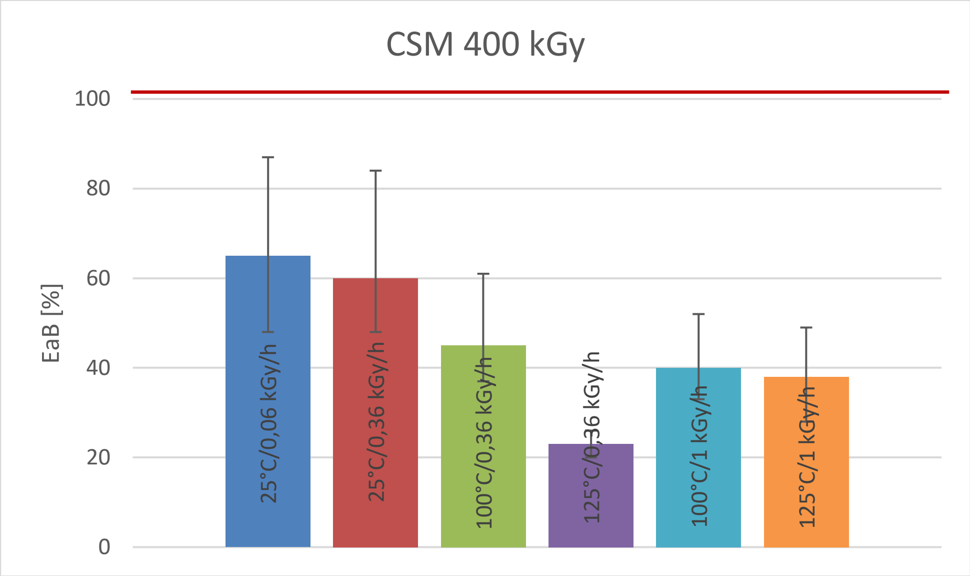

Figure 8. EaB results for CSM samples irradiated with calculated dose of 400 kGy. The red horizontal line presents the non-aged material EaB value of 102%.

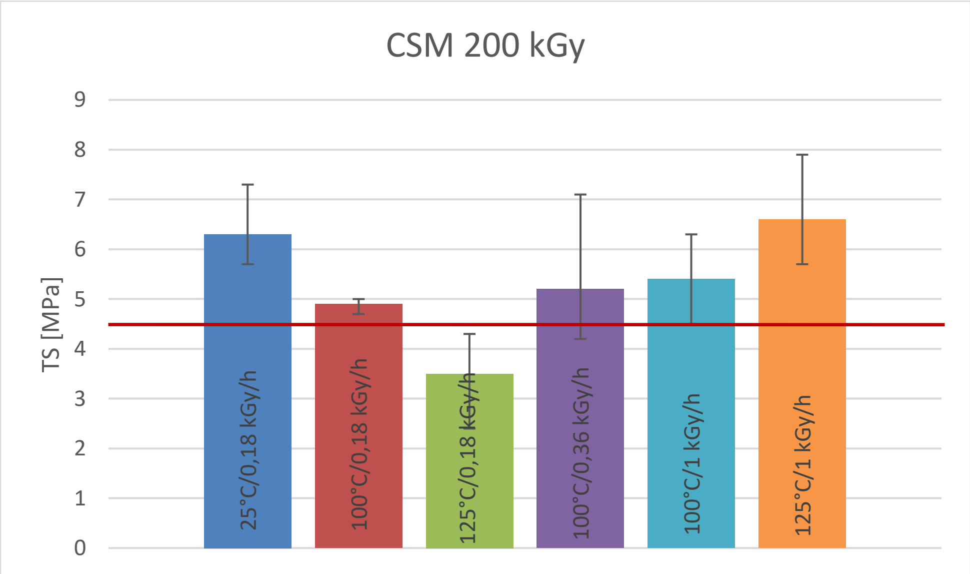

Figure 9. Tensile stress (TS) results for CSM samples irradiated with calculated dose of 200 kGy. The red horizontal line presents the non-aged material TS value of 4,5 MPa.

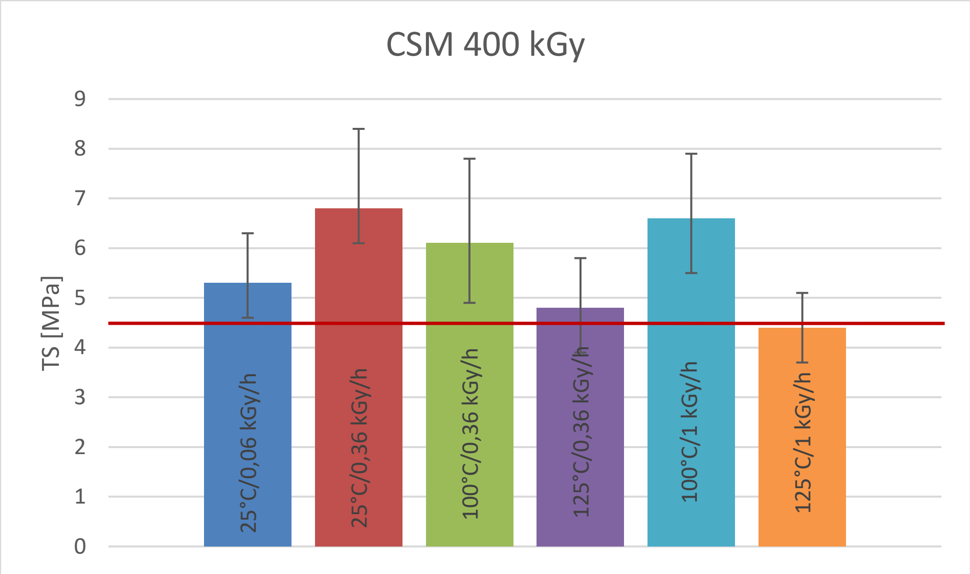

Figure 10. Tensile stress (TS) results for CSM samples irradiated with calculated dose of 400 kGy. The red horizontal line presents the non-aged material TS value of 4,5 MPa.

5. The effect of ageing environment to EaB

In this section, only the behaviour of CSM in thermal-radiative environments is studied since the damage induced in EPDM samples in radiative environments were too low to produce worthwhile predictions on its behaviour.

5.1 Application of superposition of time dependent data

Superposition of time dependent data makes possible to predict DED values as a function of dose rate i.e. the method offers a possibility to examine the dose rate effect. This procedure uses thermal and combined thermal-radiation data to predict the decrease of EaB or DED as a function of dose rate. The procedure is based on a semi-empirical model that relates shift factors to temperature and dose rate according to the following equation:

$$a(T,D) = e^{-\frac{E}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)} * \left[1 + kDxe^{\frac{Ex}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)}\right] \qquad (1)$$

Where T is the temperature in Kelvin, T_{ref} is the reference temperature, D is the dose rate, R is the gas constant, E is the activation energy, k and x are model parameters obtained experimentally. More detailed description of the procedure can be found in standard IEC-61244-2.

5.1.1 Definition of the shift factors and activation energy

Estimation for activation energy and shift factors was calculated from the thermal ageing data. CSM samples were aged in two temperatures (100°C and 115°C) and additional ageing data from previous year at 125°C was included in the calculations. Elongation at break was used as the damage parameter. In Figure 11 is shown the decrease of EaB as a function of exposure time at different temperatures.

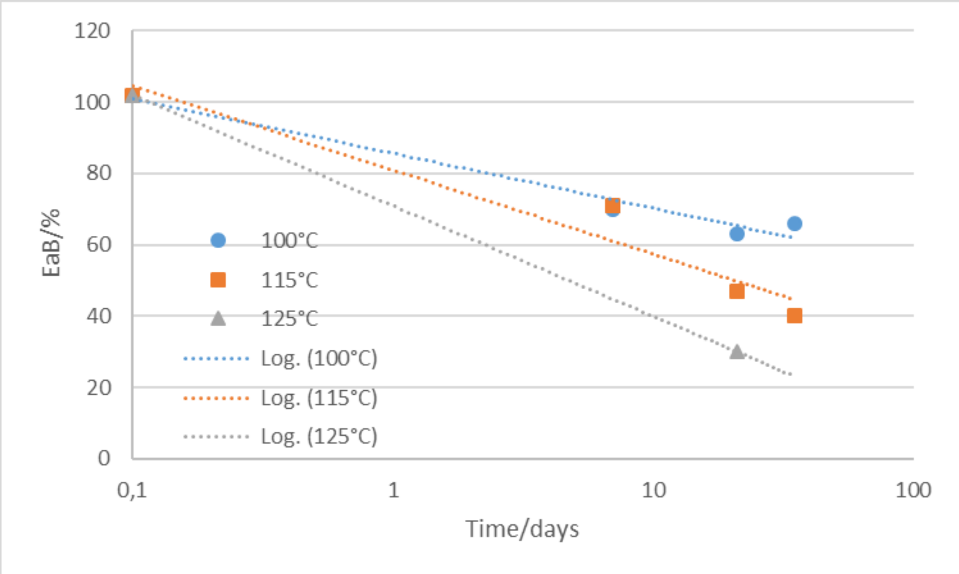

Figure 11. Evolution of EaB at three different temperatures as a function of exposure time.

At higher temperatures, the ageing is accelerated compared to lower ones. However, the same amount of ageing can be produced at lower temperatures, only with a longer time period. If it is assumed that the ageing mechanism does not change between the different temperatures, high temperature ageing data can be transformed to correspond ageing occurring at lower temperatures. The shift factors are multipliers that are used to shift the data gathered at higher temperatures to the reference temperature to form one master curve. Figure 12 shows the superposed ageing data on one master curve at 100°C. The calculated shit factors were 1,8 at 115°C and 4,2 at 125°C.

As the shift factor values have been extracted, they are plotted versus 1/T (T in Kelvins) in logarithmic scale. This is shown in Figure 13. The value of the activation energy is calculated from the slope of the formed line. Based on the data shown in Figure 13, the calculated activation energy value is 69 kJ/mol.

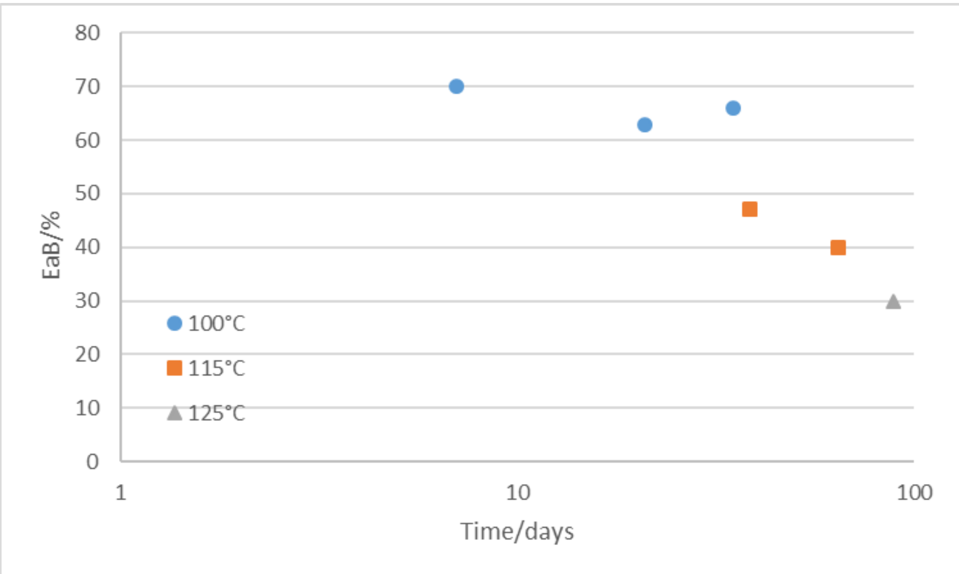

Figure 12. Master curve at 100°C.

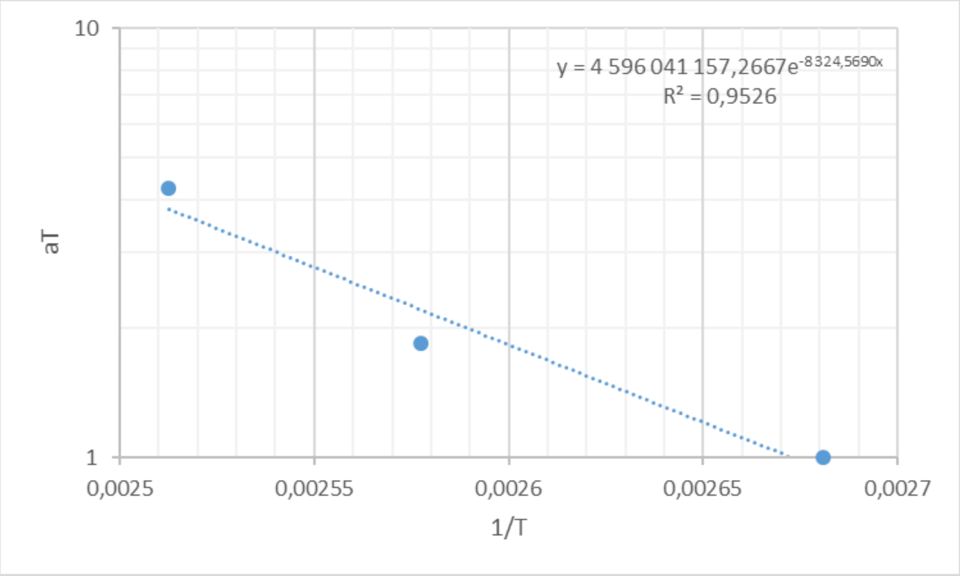

Figure 13. Extracted shift factor values versus 1/T.

5.1.2 Superposition of combined irradiation and thermal data

The data gathered in combined irradiation and thermal environments are plotted in EaB vs. log time plot. Similar superposition procedure is conducted as in the case of the thermal only ageing data. The combined irradiation and thermal data and the master curve at 100°C formed from the thermal only ageing data are shown in Figure 14.

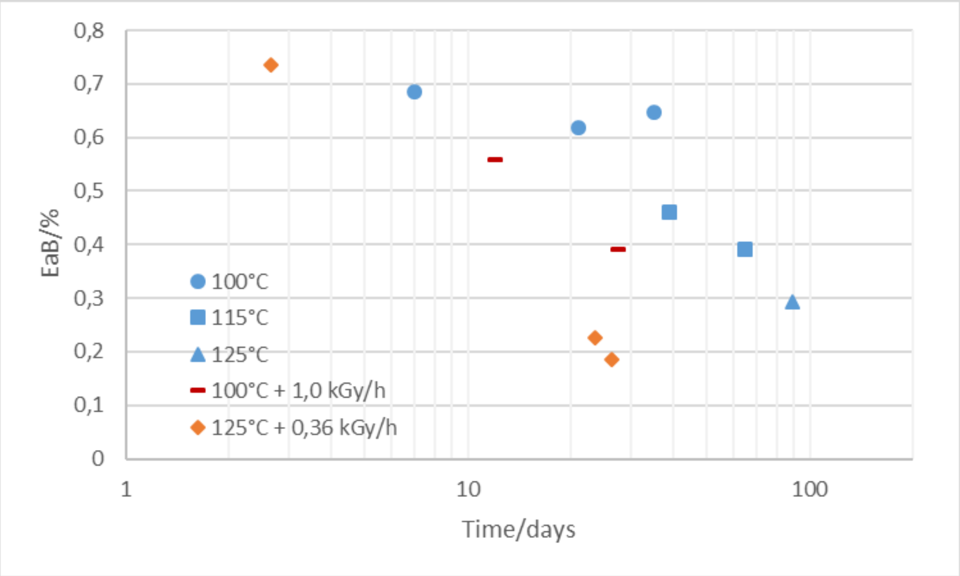

Figure 14. Ageing data from the combined thermal and irradiation environment (red and orange markers) and the formed master curve at 100°C from thermal only ageing data (blue markers).

According to the results presented in Figure 14 at 100°C/1,0 kGy/h and 125°C/0,36 kGy/h the shape of the curves seem to be a bit different to the one with the formed master curve in thermal only ageing. This is indicative to difference in ageing mechanism. The shift factors calculated for the combined ageing data at 100°C and 125°C were 2,3 and 4,8, respectively. Master curve at 100°C combining thermal and thermal-radiative data is presented in Figure 15.

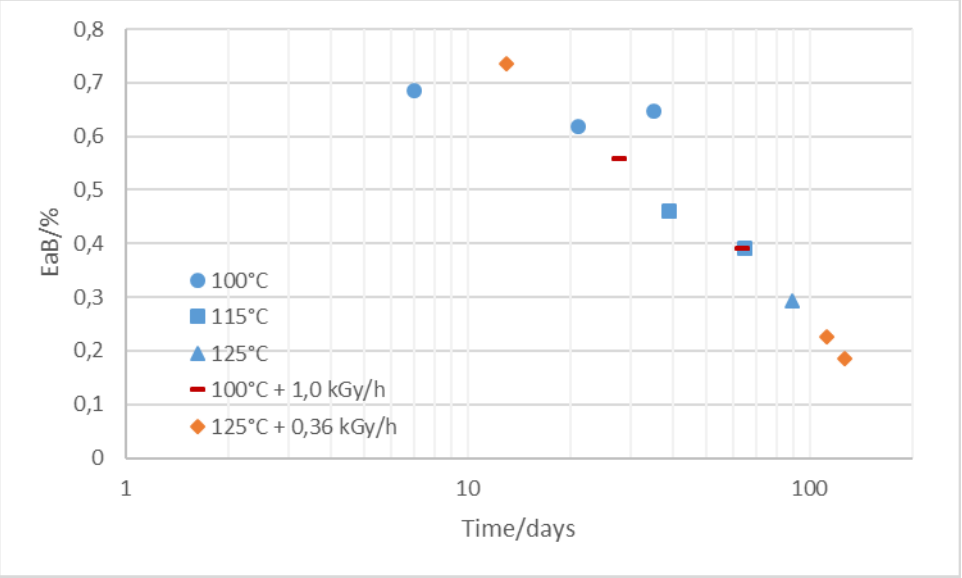

Figure 15. Master curve at 100°C combining thermal and thermal-radiative data.

The next step in the process would be plotting the calculated shift factors versus the dose rate. As the amount of experimental data is limited with respect to the number of temperature-dose rate conditions, reliable prediction of shift factors as function of dose rate was not possible.

5.1.3 Observations on predicting dose rate effect

Even though in this case the application of superposition model was not successful, the data makes possible to estimate radiation effects in combined thermal-radiative environments. For example, at 100°C the exposure to 1,0 kGy/h radiation increases the degradation by a factor of 2,3. At 125°C with dose rate of 0,36 kGy/h the ageing is accelerated only by factor of 1,6.

In addition, the thermal ageing data can be used to predict the ageing at lower temperatures. For example at 50°C, it takes ca. 680 days to achieve 50% of EaB and at 25°C the same time would be ca. 16 years.

Generally what comes to the superposition model and in 2017 studied power law model [Sipilä et al. 2018], it can be stated that the semi-empirical models require a lot of good quality data to function reliably. This data would consist of ageing samples at several temperatures, dose rates and absorbed doses, and producing such data is time consuming and expensive (power law model would need less data in this sense but it ignores the thermal ageing limit). There are ageing data available from public sources, but in the case of polymers, application of data is not that straightforward since the compositions vary and the ageing can be sensitive to any alterations of ingredients. In addition, it can be noted that very low dose rate data in the open literature is rather rare and would be essential to have when these semi-empirical models are applied.

6. Conclusions

EPDM and CSM samples were aged in thermal and irradiation environments. From the obtained test results, the following conclusions were made:

- Based on the thermal ageing data and calculated activation energy value, estimated remaining lifetimes for CSM samples at 50°C and 25°C can be provided (ca. 680 days and ca. 16 years, respectively).
- The sequence of thermal and irradiation treatments in ageing of the studied EPDM blend matter.
- The degradation levels in EPDM samples were too low after the ageing treatments that dose rate effect analysis could be conducted.
- Sufficient degradation levels were obtained with CSM samples, but still the dose rate effect analysis conducted based on superposition would not yielded in reliable results due to the narrow test matrix. These observations show that the predictive semi-empirical models based on superposition require a lot of experimental data to function properly.

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