DEGRADATION OF POLYMERIC COMPONENTS IN NUCLEAR POWER APPLICATIONS

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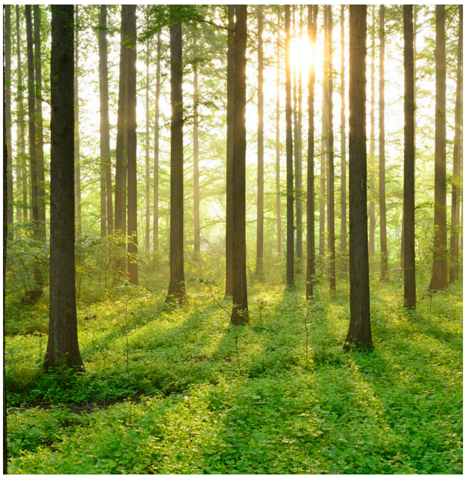
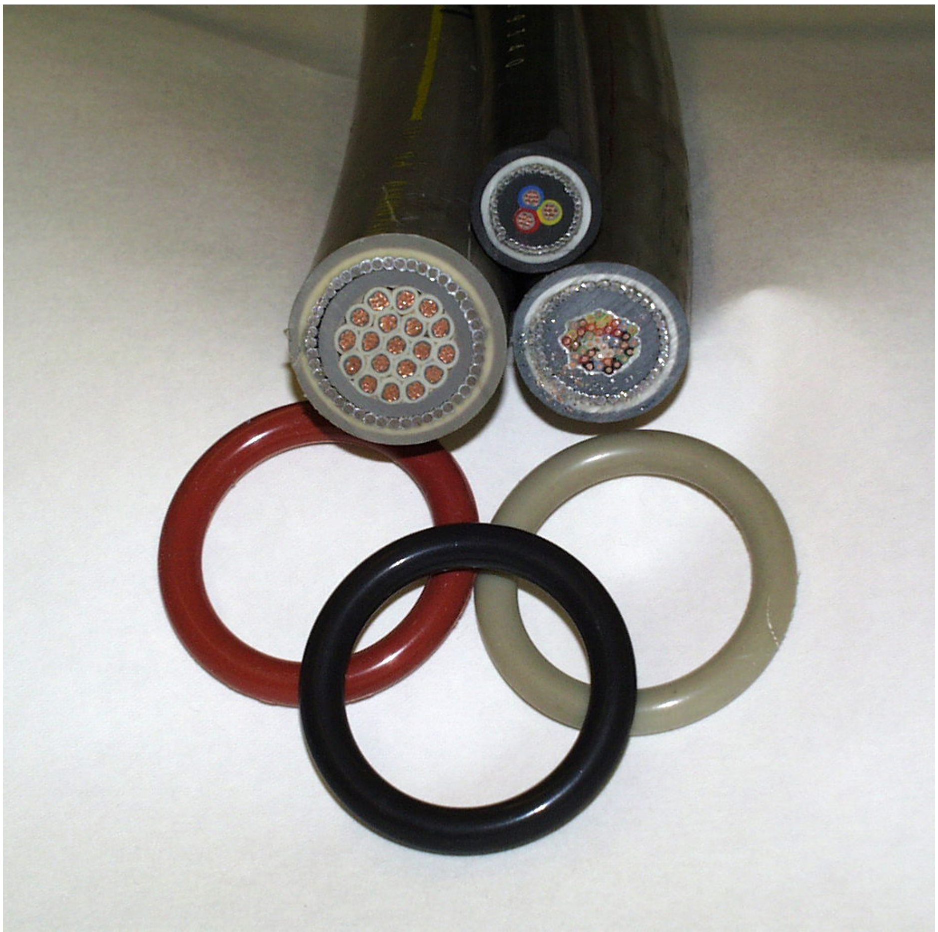


NUCLEAR



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Degradation of Polymeric Components in Nuclear Power Applications

Educational material for engineers

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Foreword

Aging of polymeric materials is very complex, especially for nuclear applications where radiation is involved. This report is designed as an educational material for polymer engineers at nuclear power plants. The aim is to give an applied support for maintenance and plant development involving polymeric materials at the nuclear power plants.

This material is compiled by Dr Sue Burnay, expert in applied aging of polymeric materials in nuclear applications. It is financed by the Energiforsk Nuclear Portfolio with the stakeholders Vattenfall, Sydkraft Nuclear, Fortum, TVO, Skellefteå Kraft and Karlstads Energi.

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Sammanfattning

Polymera komponenter, som tätningar, kabelisolering och ytbeläggningar, är viktiga komponenter i kärnkraftverk. Det är därför angeläget med en förståelse för hur dessa material bryts ned under de förhållanden som råder i anläggningen, för att kunna underhålla och förvalta sin anläggning på bästa sätt. Accelererad åldring av dessa komponenter (med högre temperaturer och / eller högre stråldoser) används ofta för att bestämma deras långtidsegenskaper och livslängd.

Graden av nedbrytning av polymera material är icke-linjär och är en funktion av såväl temperaturen som strålningsdosen. På grund av detta finns ett antal faktorer som måste beaktas vid genomförande av accelererad åldring av polymera material. Dessa belyses i denna rapport genom en rad exempel från polymerkomponenter som används i kärnkraftverk.

Det finns mycket kunskap om de allmänna nedbrytningsmekanismerna hos polymera material, men den specifika åldringen hos en komponent med en viss materialsammansättning och som är placerad i en miljö är komplex. Denna effekt belyses i en rad exempel. En möjlighet att minska denna komplexitet är att gå över till att använda ett begränsat antal standardmaterial i olika tillämpningar.

Rekommendationer har gjorts om hur man ställer samman lämpliga accelererade åldringstester för olika tillämpningar och vilka acceptanskriterier som skulle vara lämpliga för olika typer av komponenter.

Metoder för utvärdering av åldrade komponenter har diskuterats. Dessa inkluderar tillståndsövervakningsmetoder, felanalys och fingeravtrycksmetoder, som kan användas för att få en väl fungerande förvaltning och upphandling av polymera komponenter på kärnkraftverken.

Summary

Polymeric components, such as seals, cable insulation and coatings, are widely used in nuclear power plants. An understanding of how these materials degrade under the environmental conditions in the plant is critical, both in terms of environmental qualification and in determining maintenance intervals. Accelerated ageing of these components (using higher temperatures and/or higher radiation dose rates) is widely used to determine their ageing behaviour.

The rate of degradation of polymeric materials is non-linear and is a function of both the temperature and the radiation dose rate. Because of this, there are a number of factors which need to be considered when carrying out accelerated ageing of polymeric components. These are illustrated with examples from polymeric components used in NPPs.

The general degradation behaviour of polymeric components is well understood but the ageing of specific polymers is strongly dependent on their formulation. The magnitude of these formulation effects has been demonstrated using examples from components in actual use in NPPs. The use of standardised formulations to overcome some of these concerns has been discussed.

Recommendations have been made as to how to put together appropriate accelerated ageing tests for different applications and the acceptance criteria that would be appropriate for different types of component.

Methods for assessing aged components have been discussed. These include condition monitoring methods, failure analysis and ‘finger-printing’ methods that could be used as part of an informed procurement procedure.

List of content

1 Introduction

Polymeric components are used in many different areas throughout nuclear power plants. For example, equipment such as valves and actuators contain seals and gaskets, which are polymer-based. Electrical cables provide vital links for power, control and instrumentation to many safety-related systems. The insulation and jacket materials for these cables are primarily polymer-based. Polymeric coatings are also used in many areas in the form of paints, protective liners in pipes and coatings on pond walls.

Seals can be replaced during maintenance in many cases, but cables and coatings are passive components and can be difficult and expensive to replace or remove. For these reasons, it is important to understand how polymeric components degrade under the conditions seen in NPPs to avoid unplanned outages and to enable informed maintenance.

This report provides educational material on the behaviour of polymeric components in nuclear power applications, in a format suitable for engineers who do not have a materials science background. Section 2 covers the basics of polymer ageing, highlighting specific areas of concern that can affect the rate of degradation. Section 3 discusses the effect of formulation changes on the behaviour of polymeric components and how this may be overcome for critical components. How to put together appropriate ageing test programmes is discussed in section 4 and methods for assessing aged components are covered in section 5. Appendices have been used to cover some additional topics that could be relevant to some users. Appendix A covers methods for lifetime prediction and their limitations and Appendix B covers approaches that could be used to improve environmental qualification. Finally, Appendix C includes some recommendations for further reading for those who would like to extend their knowledge of ageing of polymeric components.

2 Why is ageing of polymers of concern?

Unlike metals and ceramic materials, polymers can degrade at relatively low temperatures and are susceptible to gamma radiation. To understand how polymers degrade, initially it is important to look at the basics of polymer degradation and what factors affect the rate of degradation.

2.1 BASIC POLYMER SCIENCE

All polymers are based on long chain molecules and their properties are determined by this structure. Figure 1 illustrates this schematically, with the long polymer chains entangled and linked periodically with crosslinks. When stress is applied to the polymer the chains extend, the limit of extension being determined by the presence of crosslinks. When the stress is removed, the chains return to their original position. This structure of long chains and crosslinks give polymers their particular elastic nature. For most polymers, the long chains are spatially random and are regarded as having an amorphous structure. In a few types of polymer that have a relatively simple chain structure with no large side groups, there can be some localised organisation of the chains to form crystalline sections linked by more amorphous areas. These are known as semi-crystalline polymers and have some properties that are different from the amorphous polymers.

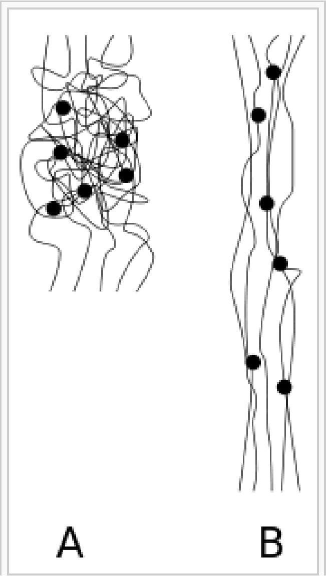


Figure 1. A is the unstressed polymer; B is the same polymer under stress (the dots represent crosslinks)

Polymeric materials can also be described as rubbers (or elastomers), thermoplastics or thermosets, partly dependent on their normal operating temperature range. Elastomers are highly elastic and can be stretched and return to their original shape. Thermoplastics have some elasticity (not as much as elastomers) but on further stretching do not return to their same shape. Thermosets are rigid and have little elasticity and will break on further stretching.

There are two temperatures of importance when describing polymeric materials. These are the glass transition temperature T_g and the crystalline melting point T_m. The glass transition temperature is the point at which the polymer becomes a glassy material and loses its elastic properties. Rubbers should not be used below T_g (this is what went wrong with the seals on the Challenger shuttle). In semi-crystalline polymers the crystalline melting point is the temperature at which the polymer chains in the crystallites lose their organised structure. It is not the melting point of the polymer itself.

Rubbers are usually amorphous structures with their normal operating temperature being above T_g. Thermoplastics can be amorphous or semi-crystalline and are used above their T_g but below T_m. Thermoplastics can be melted at higher temperatures and reformed into other shapes. Thermosets are heavily cross-linked polymers used below their T_g and cannot be melted and reformed.

Most polymers chains have a backbone of C-C links, with side groups containing other elements. The most common elements are O and H, with some polymers also containing N, S, Cl or F in the side groups. The exceptions are the silicone elastomers that have Si-O groups forming the main backbone. Nowadays, halogenated polymers (i.e. containing Cl or F) are avoided in NPPs, where possible. The only common polymer containing S is CSPE (see table below), which is widely used as a cable jacket material. The specific properties of the polymer (such as its mechanical properties, chemical and thermal resistance) are determined by the basic structure of the long chains and the degree of crosslinking.

The most common polymer types found in NPPs are the following –

Abbreviation	**Polymer type**	**Used in**
EPR and EPDM	Ethylene propylene based	Seals, cable insulation and jacket
XLPE	Crosslinked polyethylene	Cable insulation
CSPE (Hypalon)	Chlorosulphonated polyethylene	Cable jacket
Viton	Fluoroelastomer	Seals
NBR	Nitrile rubber	Seals
SiR	Silicone rubber	Seals, occasionally cables
EVA	Ethylene vinyl acetate	Cable jacket
Epoxy (Araldite)	Epoxy resins	Paints and coatings
NR	Natural rubber	Coatings
Less commonly used		
PVC	Polyvinyl chloride	Cable insulation and jacket
PEEK	Polyether ether ketone	Cable insulation (specialist types)
PPO (Noryl)	Polyphenylene oxide	Cable insulation (specialist types)
ETFE (Tefzel)	Ethylene trifluoroethylene	Cable insulation (specialist types)

The basic chain structures of the most commonly used polymers are shown below.

- Polyethylene (the simplest polymer): $-CH_2-CH_2-CH_2-$
- Propylene: $-CH_2-CH(CH_3)-CH_2-$
- Nitrile rubber: $-CH_2-CH=CH-CH_2-CH(CN)-CH_2-$
- Silicone rubber: $-Si(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_2-$

In reality, the polymer content in a commercial polymer formulation can be relatively small, with fillers, additives, extenders, plasticisers making up a large proportion of the overall materials. The specific properties of a polymeric component can be varied by changing the proportions of fillers, plasticisers etc. An example for an EPDM component is shown in below. Such formulations are specific to individual manufacturers and can vary over time unless a fixed formulation is specified during procurement. Although a limited number of polymer types are in regular use in NPPs, the properties and degradation behaviour are strongly dependent on the specific formulation used (this is covered more thoroughly in section 3 of this report).

Formulation of a commercial EPDM seal -

Base polymer	47 wt. %
Sulphur	1
Accelerator	1.5
Zinc oxide	1
Carbon black	40
Plasticiser	7
Antioxidant	2.5

2.2 EFFECT OF DEGRADATION ON BULK PROPERTIES OF POLYMERS

Since the macroscopic properties of a polymer are determined by the long chain structure, changes to these chain structures have significant effects on polymer behaviour. One of the most important parts of the polymer structure is the density of crosslinks between the chains. If additional crosslinking occurs then the polymer tends to harden whereas if degradation tends to break chains i.e. chain scission, then the material tends to soften.

The effect on the mechanical properties of typical polymers is shown schematically in Figure 2. For an elastomeric material (such as most seal materials), the tensile elongation decreases and the hardness or modulus tends to increase (Figure 2 a). Tensile strength may increase initially at early stages of degradation but will decrease with further degradation. For plastic materials (such as cable insulation and jackets), the elongation at break decreases but the modulus and tensile strength tend to show little change (Figure 2 b).

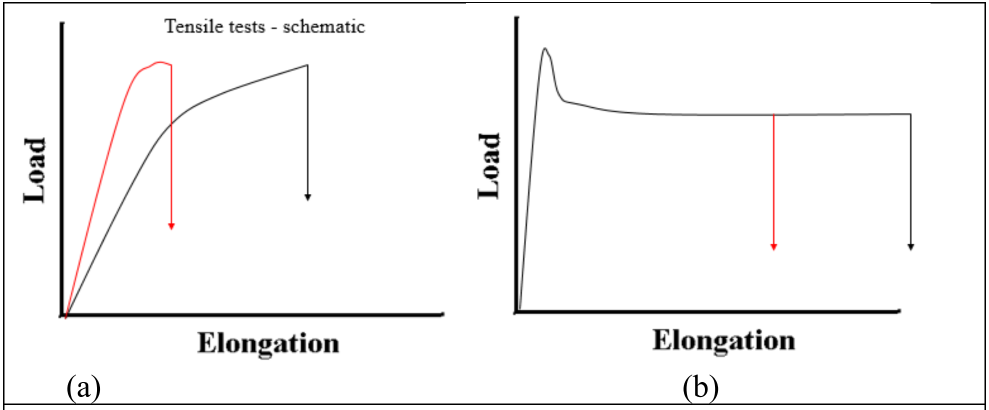


Figure 2. Effect of degradation on tensile behaviour of an elastomer (a) and a plastic (b) – red is aged material

For seal materials, compression set increases with increasing degradation and hardness usually increases, but a few materials soften where chain scission dominates degradation. Most electrical properties of cable insulation materials tend to show little, if any, change until the material is severely degraded, to the stage that mechanical failure occurs. The exception are dielectric properties (such as Tan delta) which can change significantly, but this is generally only of concern for a few specific cables. Changes in colour or surface texture are often visible in aged polymeric components – this can be a useful qualitative indicator of damage in cables.

2.3 AGEING MECHANISMS AND DEGRADATION STRESSORS

The most important mechanisms for ageing of polymeric components are the following –

- Oxidative degradation, both crosslinking and chain scission (in most polymers)
- Radiation crosslinking (in most polymers)
- Loss of plasticiser (particularly in PVC but can be important in other polymers)
- Dechlorination and defluorination (in halogenated polymers)

Oxidative degradation is important in both thermal and radiation ageing, whenever oxygen is present in the environment surrounding the polymer. This process is complex, with multi-stage chemical reactions that can end in either crosslinking or chain scission. Each of these reactions has its own reaction rate and activation energy. A simplified reaction scheme is shown in Figure 3 to illustrate the complexity. Free radicals generated during these reactions are shown generically as R• in Figure 3. These are generated during the initiation stage, react with oxygen in the propagation stage to form additional radicals and finally are terminated to form more stable species.

$$\begin{array}{lrcl}
\text{Initiation} & RH & \rightarrow & R\bullet \\
 & & & \\
\text{Propagation} & R\bullet + O_2 & \rightarrow & RO_2\bullet \\
 & RO_2\bullet + RH & \rightarrow & RO_2H + R\bullet \\
 & RO_2H & \rightarrow & RO\bullet + OH\bullet \\
 & RO\bullet & \rightarrow & R\bullet + \text{-CO-} \\
 & & & \\
\text{Termination} & 2R\bullet & \rightarrow & RR \\
 & 2RO_2\bullet & \rightarrow & RO_2R + O_2 \\
 & & \text{or} & ROH + \text{-CO-} + O_2
\end{array}$$

Figure 3. Simplified reaction scheme for oxidative degradation

Radiation crosslinking is important in nearly all polymers exposed to radiation. The free radicals generated by radiation result in direct crosslinking between molecular chains.

Loss of plasticiser by diffusion is particularly important in materials such as PVC, which have a high proportion of plasticiser in their formulation. In PVC, this is the main mechanism for degradation at low temperatures (< 90ºC) resulting in hardening of the material. At higher temperatures degradation of PVC is dominated by dechlorination. Even in polymers with relatively small proportions of plasticiser (such as the EPDM formulation shown in section 2.1), this mechanism can still contribute to the observed changes in hardness.

In halogenated polymers, such as PVC and Viton, loss of halogen can be significant particularly during thermal ageing at relatively high temperatures. In PVC, this mechanism dominates at temperatures >90ºC. Viton is a fluoropolymer that is often used at relatively high temperatures because of its inherent thermal stability. However, if thermally degraded in the presence of moisture there is the risk of hydrofluoric acid (HF) being generated as fluorine is lost from the chain structure.

[NB. When handling aged Viton seals, any visible fluid on the surface should be assumed to be HF and suitable precautions taken].

CSPE (Hypalon) contains S in its side-groups, so there is the potential for loss of S on degradation of the polymer. However, in practical terms this does not appear to be a significant issue.

The main degradation stressors for polymeric components in NPPs are –

- Temperature – increasing temperature increases the observed degradation (with a few exceptions – see section 2.5.4)
- Radiation dose rate and the total dose – unlike metals, polymers are susceptible to gamma radiation and are sensitive to the dose rate. The dose required to reach a specific level of degradation (e.g. 50% compression set) decreases as the dose rate decreases
- Presence of oxygen in both thermal and radiation ageing

Secondary stressors are –

- Moisture – this is generally only a concern in a limited number of hydrophilic formulations but has been a factor in some specific Hypalon cable jacket materials
- Mechanical stress – this is of particular concern in cable materials which have been installed with too tight a bend radius or are connected to vibrating equipment.
- Ozone – enhanced degradation has been observed in some polyethylene wiring insulation
- Chemical contamination – in most cases where polymers are exposed to chemicals, the material has been specifically selected to withstand those chemicals. However, spillages can occur and may have an effect on the ageing of components

In this report the emphasis is on the main stressors of temperature, radiation and oxygen, but in some cases the secondary stressors may need to be considered.

Thermal ageing is the dominant degradation process for nearly all polymeric components in NPPs. Only a very small proportion are exposed to significant radiation ageing. For those components which form part of safety related equipment, there is a requirement for environmental qualification (EQ). This aims to demonstrate that the equipment will continue to fulfil its safety function throughout the lifetime of the plant. For equipment that contains polymeric seals, the replacement intervals need to be known. EQ requires a simulation of the ageing that would occur during the lifetime of the plant, using the worst case environmental conditions. Both thermal and radiation ageing need to be simulated over an accelerated timescale. The main question that needs to be answered is –

"Is the accelerated ageing an accurate simulation?"

Some of the factors that need to be considered when carrying out accelerated ageing are discussed in sections 2.4 and 2.5.

2.4 THERMAL AGEING

Thermal ageing of polymeric components is normally carried out at elevated temperatures, making use of the Arrhenius relationship to calculate the ageing time required at the ageing temperature. The relationship is usually used in the form of the following equation.

$$t_1 = t_2 \exp [E/R\ (1/T_1 - 1/T_2)] \qquad (1)$$

Where t_1 is the ageing time required at a temperature T_1 to simulate a service life of t_2 at a temperature T_2. E is the activation energy for thermal ageing and R is the gas constant.

Although this equation has been in use for a long time, not everyone understands the assumptions that underlie the relationship. Equation (1) assumes that –

- A single degradation mechanism is in operation

- Degradation mechanisms are the same at the higher temperature used for accelerated ageing
- Activation energy E is constant, and the value is known for the specific polymer formulation being tested

These assumptions are discussed in more detail in sections 2.4.1 and 2.4.2 with their implications for the accuracy of accelerated thermal ageing.

2.4.1 Activation energy for thermal ageing

The original Arrhenius equation only described the reaction rate of a single chemical reaction, but as has been shown in Figure 3, oxidative degradation of a polymer is a complex process involving several different chemical reactions. Each of these reactions will have its own reaction rate and activation energy. Usually there will be one reaction that dominates the overall rate of degradation, but the dominant reaction can change with temperature. This is one of the reasons why the ageing temperature should be as close to the service temperature as practicable, to minimise the extrapolation required.

To illustrate the importance of the activation energy E in thermal ageing let us take an example of trying to simulate the degradation that would occur for a service life of 40 years at 40ºC (Figure 4). The usual approach is to plot an ageing parameter (e.g. time) against 1/T, where T is the ageing temperature in ºK. If the activation energy is a constant, this plot will be a straight line.

On the assumption that the activation energy E has a value of 1 eV, the blue line in Figure 4 shows the time required at different ageing temperatures to simulate 40 years. According to the Arrhenius relationship, ageing at 140ºC would require 2 days to simulate 40 years at 40ºC. If the temperature was decreased to 100 ºC, then 40 days of ageing would be required. However, if the activation energy was actually only 0.8 eV, the ageing times would be shown by the red line in Figure 4. Then the ageing time required would be 12 days at 140ºC or 120 days at 100 ºC. So, a difference of only 20% in the value for E would result in a factor of 6 difference in ageing time at 140ºC, but only a factor of 3 at 100ºC. This shows how important an accurate value for E is in carrying out accelerated thermal ageing. It also illustrates another reason for keeping the ageing temperature as low as practicable, since the error is reduced significantly by using the lower temperature.

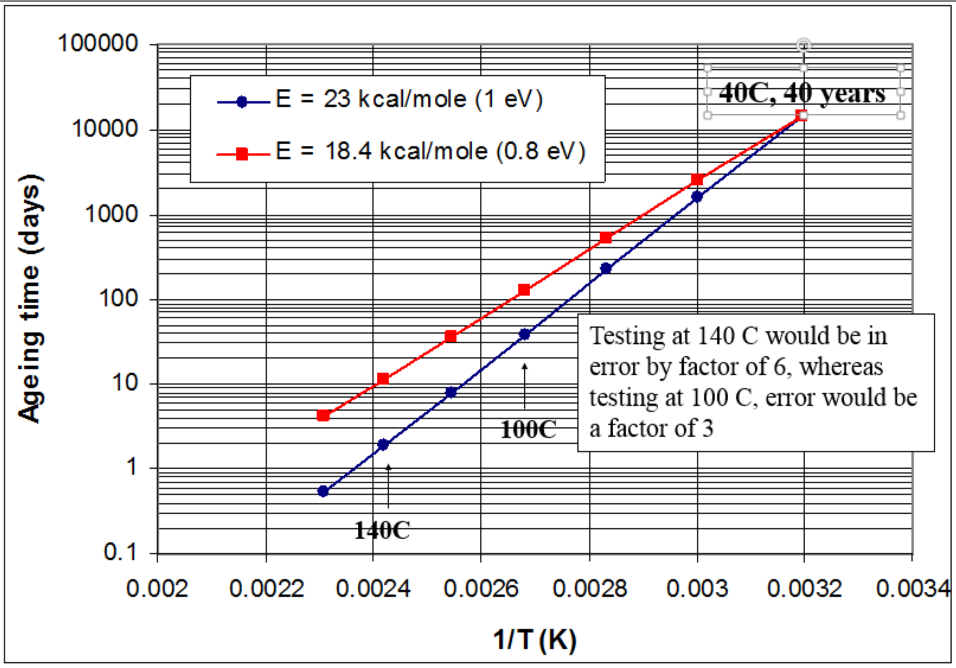


Figure 4. Effect of different activation energy values on the time required to simulate a service life of 40 years at 40ºC

The other basic assumption that underlies the Arrhenius equation is that the activation energy is constant over the temperature range between the ageing and service temperature and that the actual value is known for the specific polymer formulation that is being tested. In reality the value of E does change with temperature for many polymers, with lower values at lower temperatures. Two examples are shown in Figure 5 and Figure 6, for a CSPE (Hypalon) cable jacket material and an EPR cable insulation respectively. Figure 5 is from work carried out at Sandia Labs, USA, where they were able to use ultra-sensitive techniques to measure degradation down to temperatures near those seen in service. The change in E for the CSPE over the temperature range from 120ºC to 40ºC is about 20%. Larger changes in E are seen in the EPR in Figure 6, but here the upper temperature used for ageing is much higher than would normally be used in accelerated ageing.

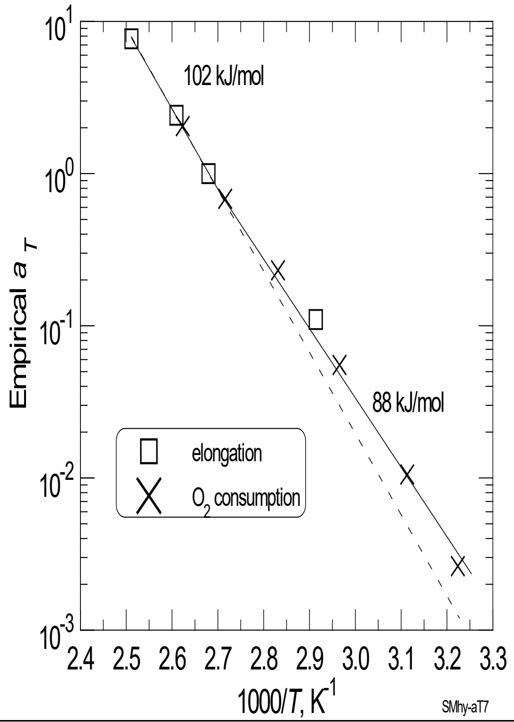


Figure 5. Variation of ageing time as a function of 1/T for CSPE jacket material (1)

When calculating the ageing time and temperatures required for accelerated ageing, the assumption is made that the value of E is known for the specific polymer being tested. However, too often a value is taken from the literature for a material of the same generic type, e.g. an EPR. But this will not necessarily be the same formulation and therefore not have the same E value. Ideally, the activation energy for the specific material should be measured directly. Sometimes this information is available from the manufacturers, but not always. So, it may be necessary to use a conservative value for E if the actual value is not known. For most of the polymer types used in NPPs, the value of E is usually within the range 0.8 to 1.2 eV – very few will have realistic values higher than this. If too high a value is assumed then the material will be significantly under-aged, as illustrated in Figure 4.

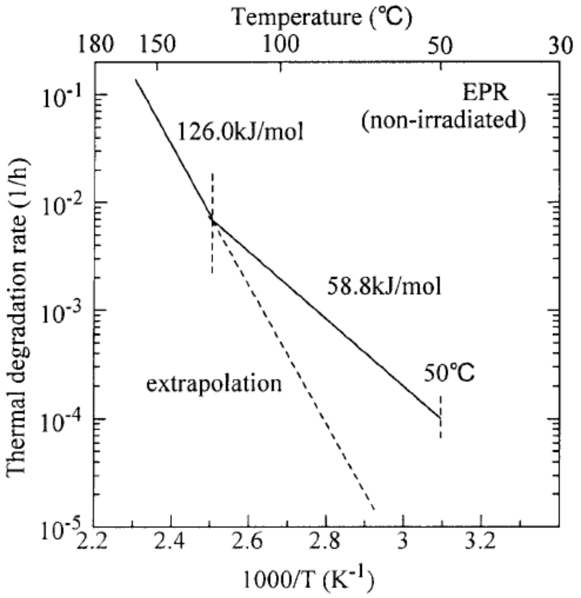


Figure 6. Variation of ageing time as function of 1/T for EPR cable insulation (2), (3)

2.4.2 Changes in ageing mechanism

Another reason for keeping the ageing temperature as low as possible is that the degradation mechanism can be different at the higher temperatures. The classic example here is for thermal ageing of PVC, which degrades by loss of plasticiser at the temperatures used in service but at temperatures > 90ºC PVC degrades by dechlorination.

For some EPDM elastomers used in inert atmosphere, loss of plasticiser can be a significant degradation mechanism as the more usual oxidative degradation is suppressed. A recent study of an EPDM cable transit seal during thermal ageing (4) showed that at 110ºC, ageing occurs via 3 different mechanisms

- Surface oxidation – formation of carbonyl groups and oxidative crosslinking
- Loss of plasticiser
- Anaerobic crosslinking

Each of these has its own temperature dependence and comparison with real-time aged sample showed that loss of plasticiser is a more important degradation process in-service compared with accelerated testing.

A different concern arises in some EPR and polyethylene-based polymers. In these materials which have a relatively simple chain structure, some crystallisation can occur. These crystalline areas can melt into the amorphous phase at quite low temperatures, e.g. for XLPE crystallite melting peaks at about 120ºC but melting starts as low as 60ºC (Figure 7).

[Note that this is not melting of the polymer itself, just the conversion of crystalline to amorphous structure].

In this type of semi-crystalline polymer, the temperatures used for thermal ageing would often be above the crystalline melting point, so the material is aged in its amorphous state. However, in service it would be ageing in the semi-crystalline state and the degradation would be expected to be different.

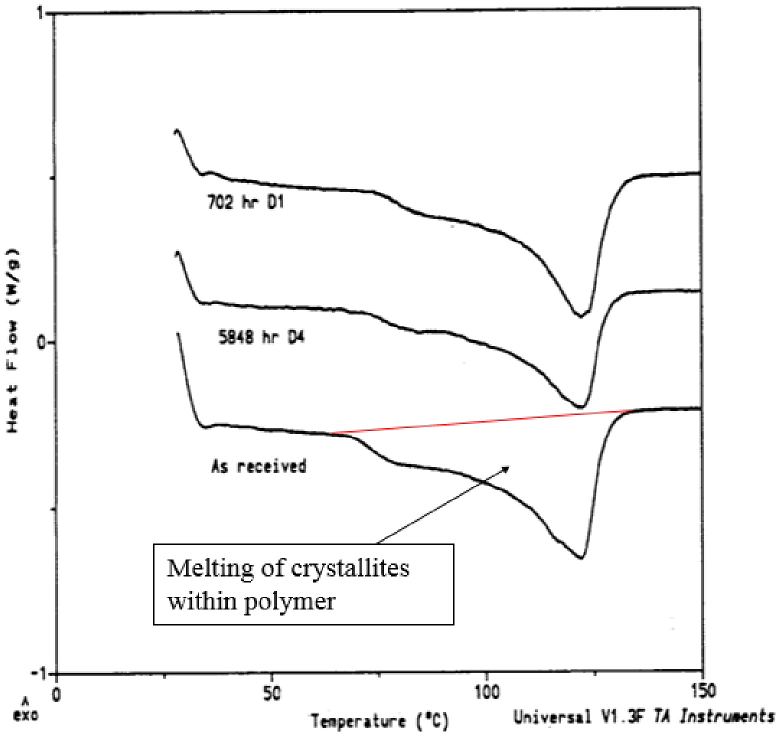


Figure 7. Melting endotherm for a XLPE cable insulation material

2.5 RADIATION AGEING

As with thermal ageing, there are a number of factors that need to be considered when carrying out accelerated radiation ageing on polymeric materials. Unlike metals, polymers are susceptible to gamma radiation and the degradation is also **dose rate** dependent. It is particularly important to be very wary of some of the tables of radiation resistance of polymers that appear in some older publications. The data in these tables were obtained at very high dose rates and do not take into account the various factors that can affect the observed degradation. The main factors that need to be considered are –

- Diffusion-limited oxidation
- Dose rate effects
- Synergy between radiation and temperature
- Reverse temperature effect

These factors are discussed in more detail in the following sections.

2.5.1 Diffusion-limited oxidation (DLO)

As discussed earlier, one of the most important ageing mechanisms in polymers is that of oxidative degradation. This will be determined by diffusion of oxygen into the component under both thermal and radiation ageing. Under normal conditions in service in NPPs (i.e. low temperatures, low dose rates and long times) there is ample time for oxygen to diffuse into the material and the observed oxidation is homogeneous through the full thickness of the component. In accelerated ageing (i.e. higher temperatures, higher dose rates, shorter times), oxygen dissolved in the polymer is consumed much more rapidly than can be replaced by diffusion into the material. In this case the oxidation is often heterogeneous, with the surfaces being fully oxidised and the interior effectively ageing in anaerobic conditions.

Bulk measurements, such as compression set or tensile elongation, are likely to be unrepresentative in materials that show heterogeneous oxidation. This diffusion-limited oxidation is of concern in both thermal and radiation ageing. The degree of heterogeneity becomes more pronounced as ageing increases. An example for thermal ageing of an EPDM seal material is shown in Figure 8. In this example, the indenter modulus (related to hardness of the material) has been measured through the thickness of the sample. At the edges of the sample, the modulus increases rapidly with increasing ageing time whereas in the centre the increase in modulus is much less.

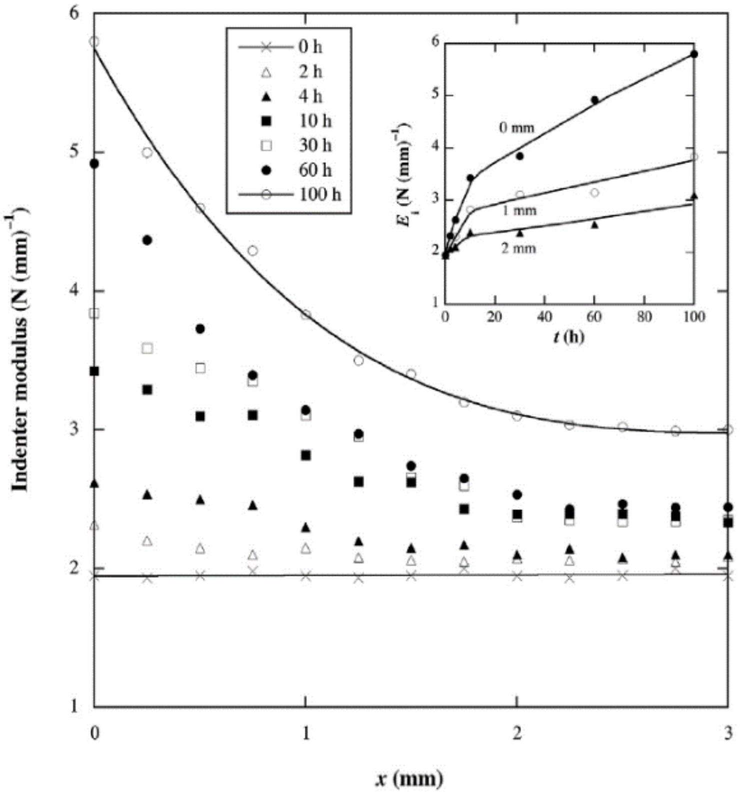
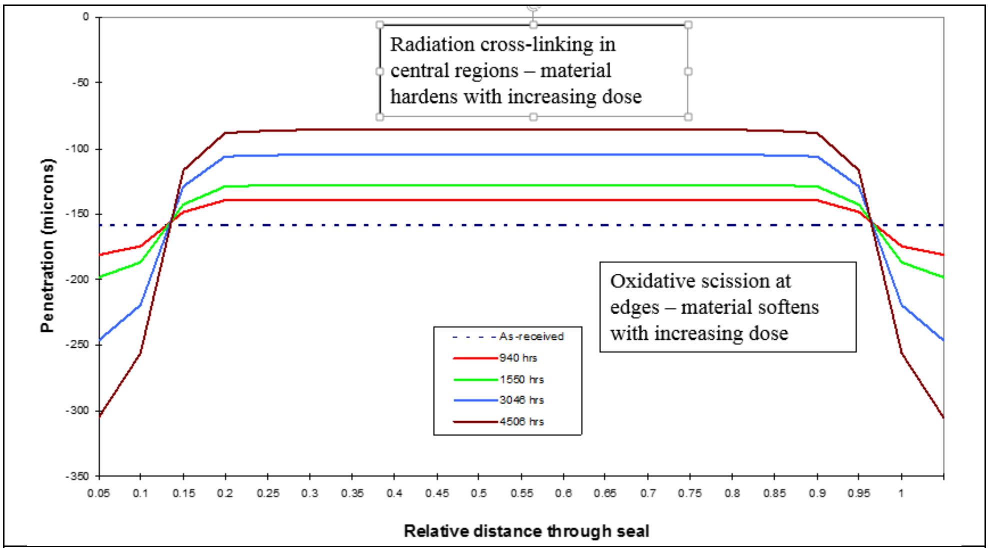


Figure 8. Modulus profile through thickness of an EPDM seal material aged at 150ºC (5)

A second example illustrates that oxidation does not always result in hardening of a polymer. In this case a Viton seal has been radiation aged and the depth profile measured using penetration depth as an indicator (Figure 9). At the edges of the sample the material has softened significantly as it undergoes oxidative scission. However, in the centre of the seal the material has hardened due to radiation crosslinking in the absence of oxygen.



Radiation cross-linking in central regions – material hardens with increasing dose

Oxidative scission at edges – material softens with increasing dose

Figure 9. Hardness profiles in a Viton seal radiation aged (6)

The effects of DLO can be reduced by using thinner samples or by reducing the temperatures or dose rates used in accelerated ageing. There are methods for calculating the thickness of sample that can be used in radiation ageing to minimise DLO effects (7) .

2.5.2 Dose rate effects

The assumption is often made that equal dose will produce equal damage, irrespective of dose rate. Even when diffusion-limited oxidation is eliminated, many polymer types show a dose rate effect, with the dose required to reach a specific level of degradation decreasing with decreasing dose rate. Some examples for various materials of interest in NPPs will indicate how important dose rate effects can be. Figure 10 shows the dose required to reduce the tensile elongation of a XLPE cable insulation material to 100% absolute. Note that the dose required decreases from 600 kGy at 400 Gy/hr to 150 kGy at 9 Gy/hr. So, for this particular polymer, using dose rates that are typically used for accelerated ageing can give an error by a factor of 4.

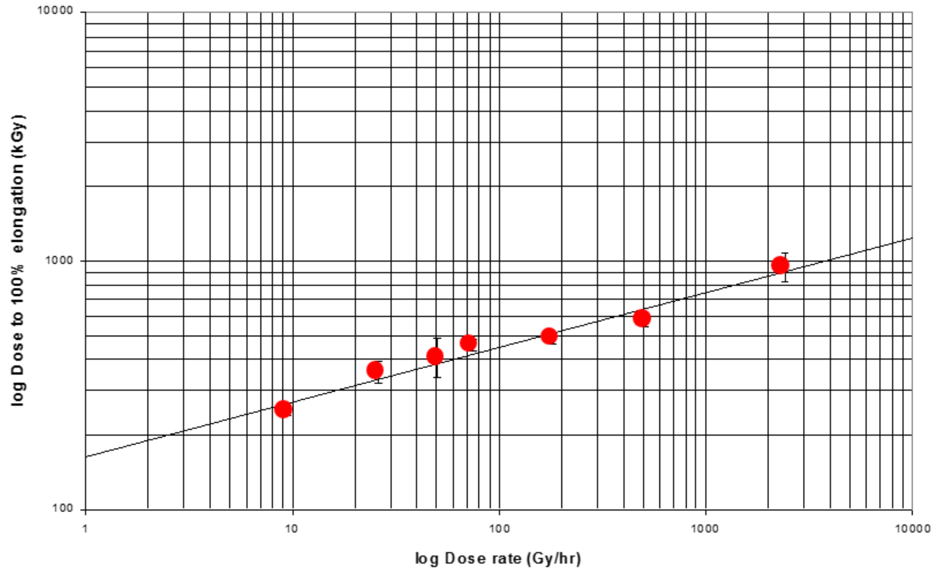


Figure 10. Radiation ageing of an XLPE cable insulation at 25ºC (6)

Not all polymers show such a large dose rate effect. An example for a nitrile elastomer used as a seal material shows very little dose rate effect over a large dose rate range at 25ºC (Figure 11). However, if the same material is radiation aged at a higher temperature, then dose rate effects are significant (Figure 12) for the lowest dose rates. A similar pattern of behaviour is seen in an EPDM elastomer, also used as a seal material (Figure 13) that has been radiation aged at elevated temperature. At high dose rates, typical of those used for accelerated ageing, there is little dose rate effect but once the dose rates decrease to levels closer to those seen in NPPs there is a large effect.

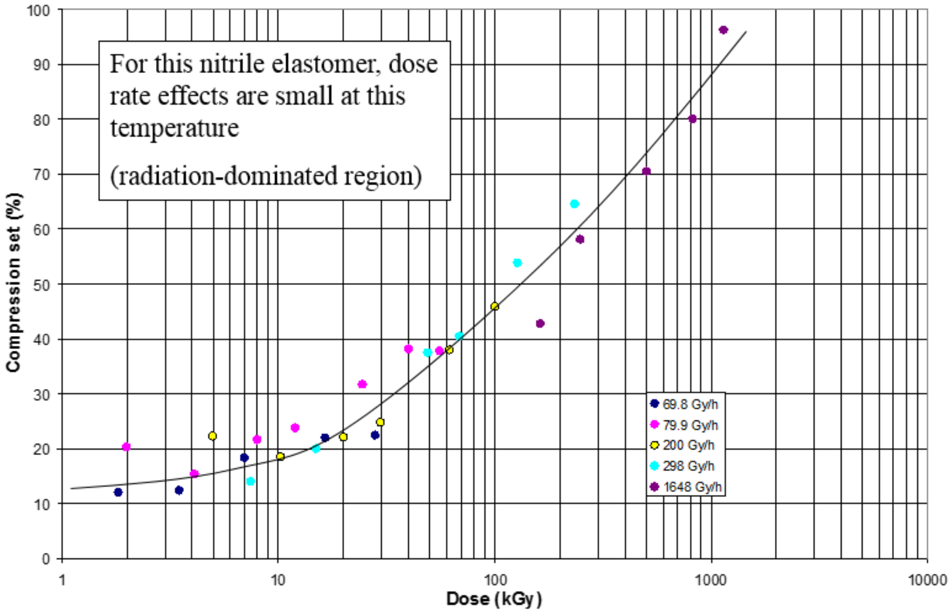


Figure 11. Change in compression set of a nitrile elastomer radiation aged at 25ºC (6)

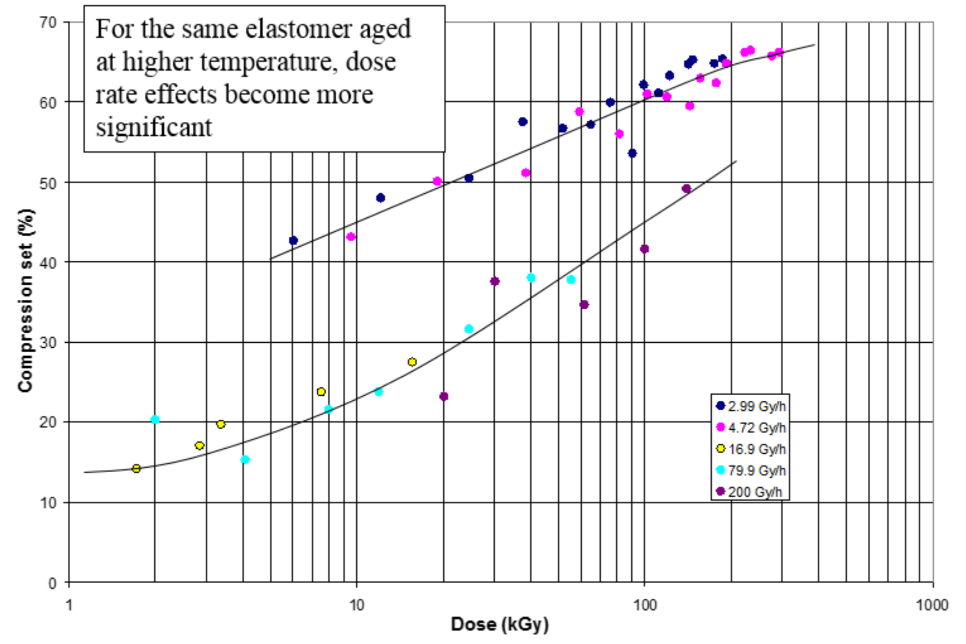


Figure 12. Change in compression set for a nitrile elastomer radiation aged at 55ºC (6)

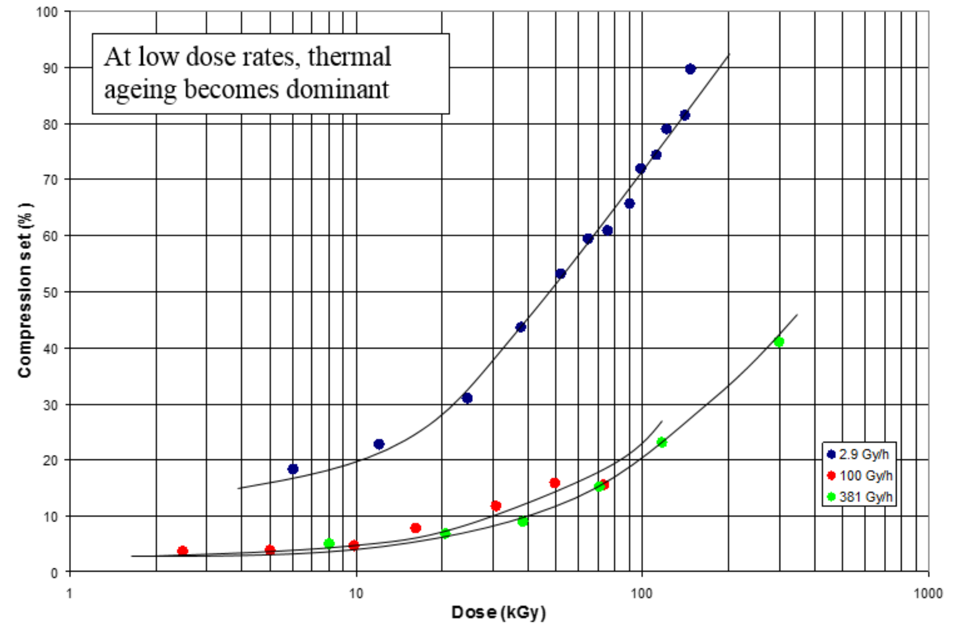


Figure 13. Change in compression set for an EPDM elastomer radiation aged at 92ºC (6)

2.5.3 Synergy between radiation and temperature

The reason why dose rate effects change with temperature is that there is a synergy between the two stressors. At high dose rates, as usually used in accelerated ageing, degradation is dominated by radiation ageing and temperature has little effect. At low dose rates, more typical of conditions in NPPS, degradation is dominated by thermal ageing and is determined only by the time at temperature. Under these conditions, temperature has a significant effect.

This synergy can be illustrated by the schematic shown in Figure 14. This shows the general behaviour of a polymeric material when exposed to radiation and thermal ageing. In this diagram the radiation dose required to reach a specific level of degradation (DED, dose to equivalent damage) is shown as a function of dose rate for different temperatures. The spacing of the curves and their position along the axes will be dependent on the specific polymer, but the figure can be used to illustrate the concept of synergy.

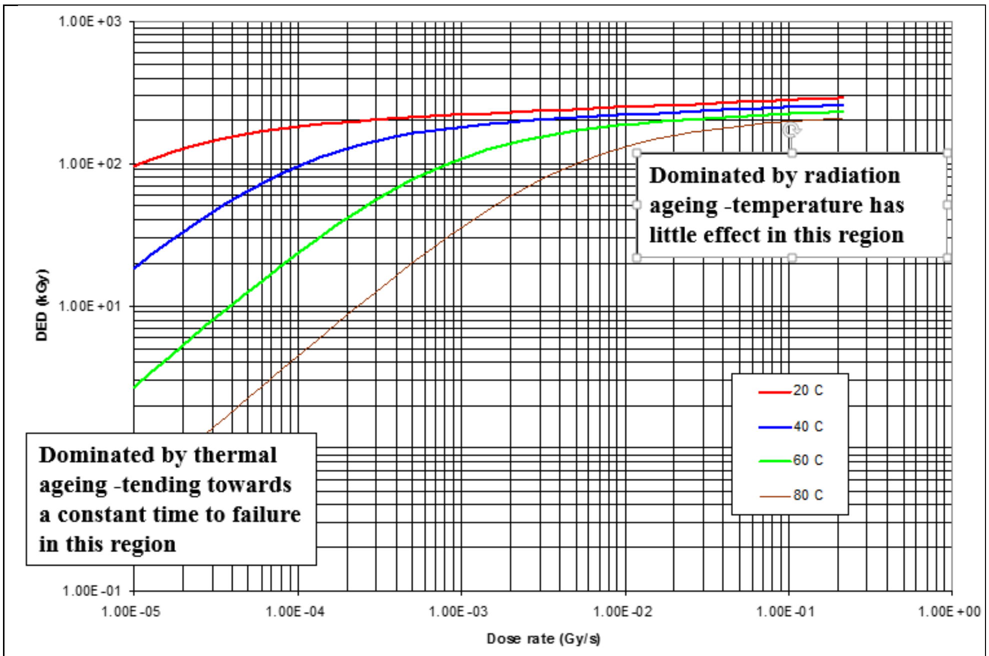


Figure 14. Effect of combined thermal/radiation ageing on a polymeric component – general trends

Note that the curves for different temperatures are closely spaced at the right-hand side of the diagram (at high dose rates), indicating that temperature has little effect on the degradation observed. The slope of the curves in this region give an indication of the level of dose rate effect that arises purely from radiation ageing. This is the region that is dominated by radiation ageing.

At the left-hand side of the diagram (at low dose rates), the curves for different temperatures are widely spaced indicating that thermal ageing is dominant. The curves also tend towards straight lines with a slope of 1, indicating that ageing is determined only by time at temperature.

At intermediate dose rates, both radiation and temperature are important, and the curves vary in spacing and slope. Although the diagram shown in Figure 14 appears to be complex, it can be readily described by a relatively simple model. This is described in more detail in Appendix A.

2.5.4 Reverse temperature effect

The general behaviour of most polymeric components under radiation and thermal ageing can be described by the diagram shown in Figure 14. But there are a few polymer types that show a different behaviour, with a reverse temperature effect. In this case, degradation is greater at lower temperatures than at higher temperatures in the presence of radiation. The temperature range 20ºC to 120ºC is where this effect is of particular importance, so it occurs in the range of specific interest to NPPs.

The only polymers that exhibit this behaviour are those that are semi-crystalline and where the service and accelerated ageing temperatures span the crystalline melting point. This means that the effect is only seen in polyethylene-based polymers, i.e. XLPE and some EPR materials. An example is shown in Figure 7, which shows a thermal analysis scan of an XLPE cable material that is known to show a reverse temperature effect. In this figure, a decrease in heat flow at about 60ºC indicates the start of melting of the crystallites, the peak melting point at about 120ºC.

Figure 15 illustrates the reverse temperature effect seen in this same XLPE material, showing the predicted dose required for the tensile elongation to reduce to 100% absolute compared with the measured value. The predicted values were obtained from model parameters obtained under accelerated ageing. The actual data was from long term ageing tests carried out at 10 Gy/hr. At temperatures < 120ºC, the measured degradation is significantly greater than predicted – note that the y-axis in this plot is logarithmic. This is not a small effect – at near ambient temperature the actual dose required is more than an order of magnitude less than predicted.

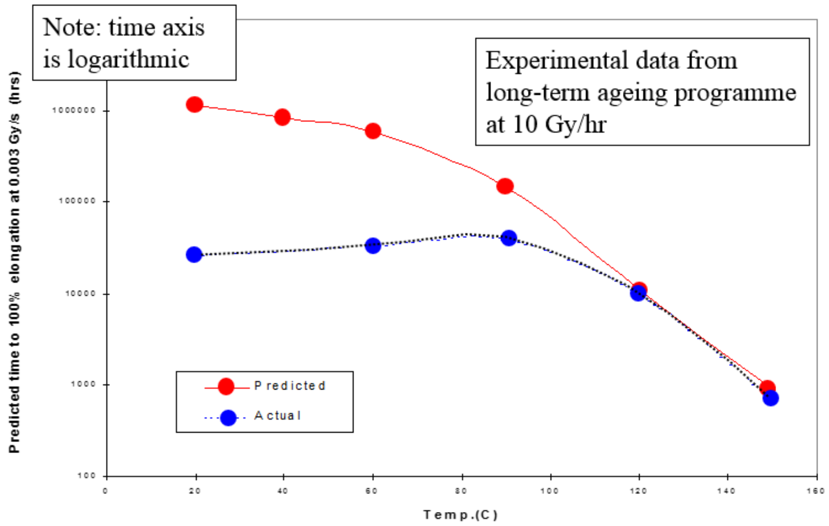


Figure 15. Comparison of predicted and actual radiation dose required to reach 100% elongation for an XLPE insulation (3)

2.5.5 Post-radiation effects

It is not always possible to test radiation aged samples immediately after their exposure to radiation e.g. when samples have to be shipped back from a radiation facility to the test laboratory. During irradiation, some of the free radicals generated can be trapped in the polymer matrix. These will gradually react post-irradiation, dependent on the temperature and oxygen availability. It is therefore important to carry out any measurements as soon as possible after irradiation, preferably within a few days.

If you are carrying out sequential ageing so that thermal and radiation ageing are carried out separately, it is important to check whether post-radiation effects are relevant to your particular materials. Thermal ageing after radiation ageing is preferred as this will enable any trapped radicals to react. If thermal ageing is carried out first, the trapped radicals would not be present and the overall degradation is likely to be less.

2.6 SUMMARY OF FACTORS TO CONSIDER IN ACCELERATED AGEING OF POLYMERS

To summarise, there are a number of factors that may need to be considered when carrying out accelerated ageing of polymers. You need to ask the following questions –

- Is the material being tested the same formulation as that used in the NPP?
- Are you using an appropriate value for the activation energy for thermal ageing?
- Are the degradation mechanisms the same at the ageing temperature and in service?
- Diffusion limited oxidation needs to be assessed for both thermal and radiation ageing
- Have dose rate effects been taken into account?
- Has the synergy between temperature and radiation been considered when establishing the appropriate conditions for accelerated ageing?
- If the polymer being tested is semi-crystalline, has the reverse temperature effect been taken into account?
- Have you tested the samples as soon as possible after radiation ageing?

You should now have a better understanding as to why polymer ageing is considered to be important. The generic degradation processes and failure mechanisms are reasonably well understood but the detailed behaviour of any specific polymeric component is dependent on its formulation.

3 Effect of polymer formulation on ageing

As discussed in section 2.1, commercial polymers contain additional components, such as fillers, additives, plasticisers etc. These are used to adjust the physical properties of the polymer, e.g. changing the filler and/or the plasticiser content will affect the mechanical properties of a polymer. These formulations are specific to the individual manufacturer and can vary over time. During procurement of polymeric components, it is normal to specify the physical properties required but how that is achieved is up to the manufacturer.

Although only a limited number of basic polymer types are used in NPPs, their degradation behaviour is strongly dependent on the specific formulation, particularly for radiation degradation. The formulation is usually regarded as commercially sensitive, so it is rarely possible to obtain specific details of the exact composition of a particular polymer. So, what are the most important parts of the formulation?

- Fillers and plasticisers will affect the mechanical properties
- Anti-oxidants, pigments (particularly in cable insulation) and the curing system used will affect the degradation rate
- In some cases, the long chain structure of the polymer base can be important e.g. determining whether the reverse temperature effect will be significant

3.1 EXAMPLES OF EFFECT OF FORMULATION CHANGES ON DEGRADATION

Because of the differences in the detailed formulation, polymeric components that are nominally the same material can degrade very differently. Figure 16 shows the changes in elongation after thermal ageing at 120ºC for 3 fire-retardant EPR cable insulation materials from different manufacturers. Although they are nominally the same type of polymer, there is an order of magnitude difference between them. For this particular example, there was no information available as to the differences in formulation.

In other cases, more is known about the formulations and it is easier to assess the effect of changing particular aspects of the formulation. In Figure 17, the effect of changing the curing system for an EPDM seal material is shown. During radiation ageing at 381 Gy/h, the peroxide cured variant of this seal shows very similar degradation behaviour for radiation ageing at 3 different temperatures (indicated by the circles and solid line in Figure 17). This is typical of a material being tested in the radiation dominated region of dose rate. In contrast, the sulphur-cured variant of the same material tested under the same conditions (indicated by the triangles and dotted lines in Figure 17), shows a large difference between each temperature and is degrading much more rapidly than the peroxide-cured formulation. The behaviour of the S-cured variant is more typical of a material being tested in the thermally dominated region of dose rate.

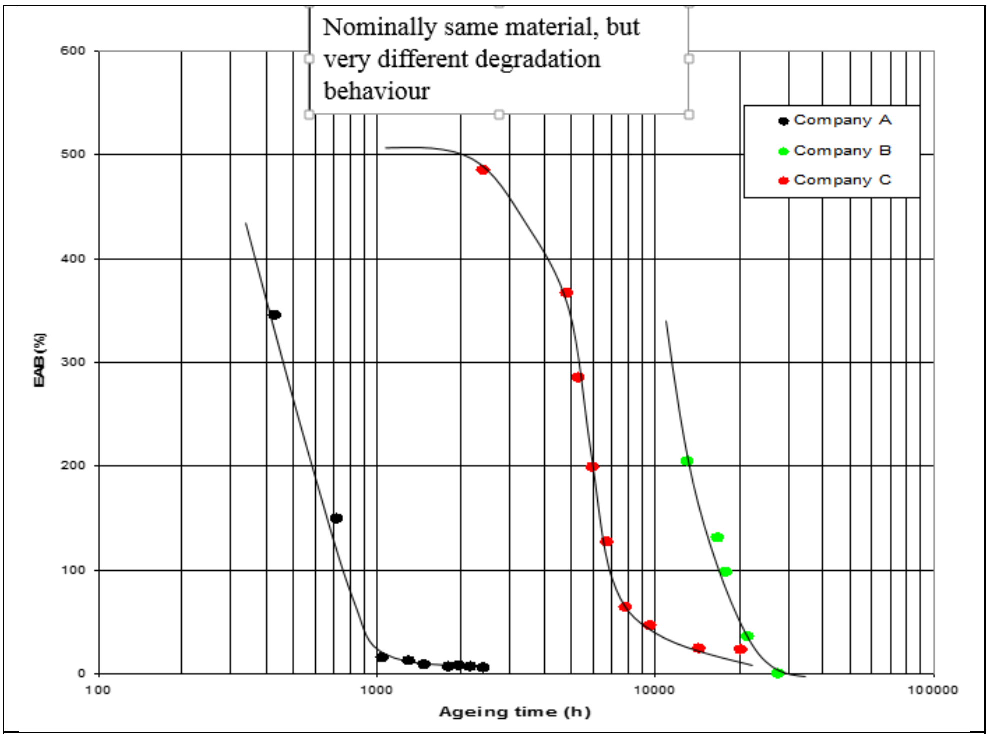


Figure 16. Variation in thermal ageing behaviour of FR-EPR cable insulation from 3 different manufacturers (8)

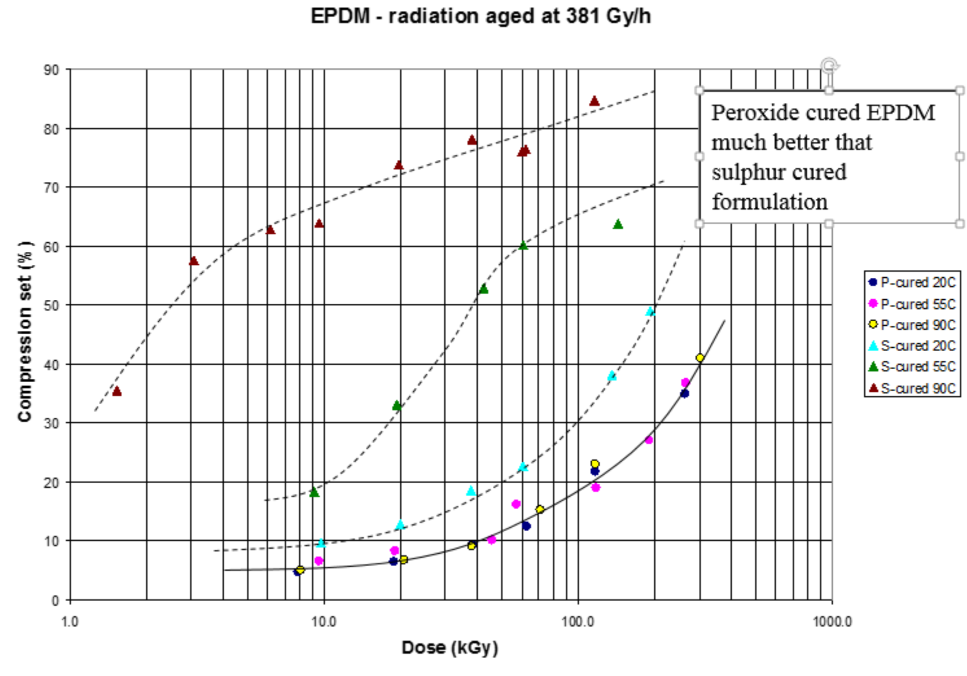


Figure 17. Effects of changing the curing system in an EPDM seal (6)

Note the importance of radiation testing at elevated temperature. Had these seal materials only been compared at room temperature, it would have indicated that the S-cured formulation was only slightly worse than the P-cured. Comparing the dark blue dots with the light blue triangles in Figure 17 would indicate only a factor of 2 difference in dose required to reach the same level of degradation at 20ºC. However, at the higher temperature of 90ºC there is more than 2 orders of magnitude difference.

Not all changes in formulation have such a large effect as shown in Figure 16 and Figure 17. The effect of changing the filler content of a nitrile seal material is shown in Figure 18. These nitrile formulations were radiation aged at low dose rate (3 Gy/h) and elevated temperature (55 ºC) and would be expected to be in a dose rate region where both radiation and thermal ageing are important. In this case, the soft variant which had less filler content initially looks to be the better material but as ageing proceeds the degradation curves cross over and the harder material is shown to be better at higher radiation doses.

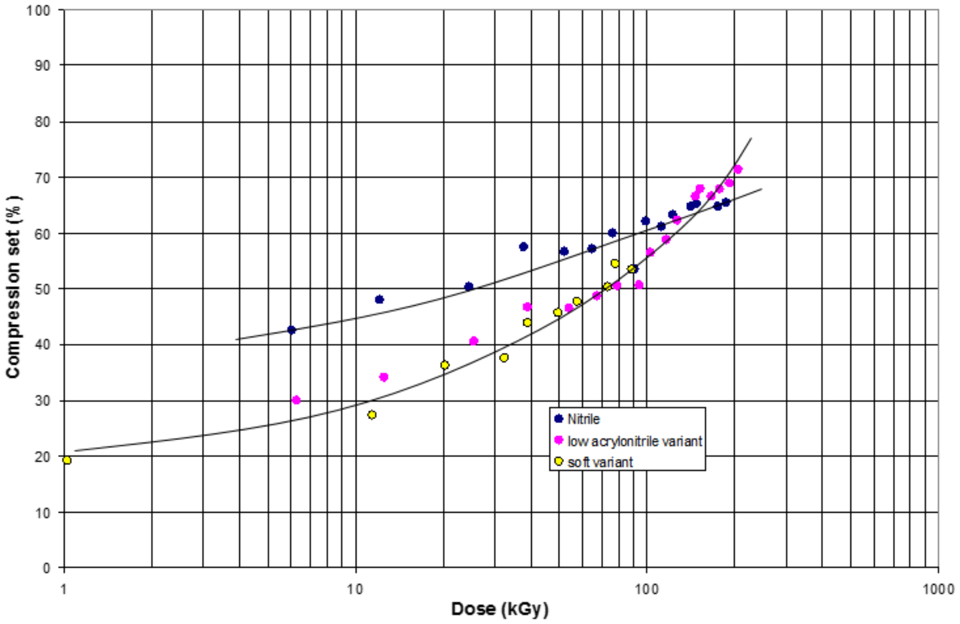


Figure 18. Effect of changes to filler content and polymer structure in a nitrile seal (6)

Figure 18 also illustrates what happens when the polymer structure is changed, all other components being unchanged. The low acrylonitrile variant behaves in a similar manner to the soft variant.

Pigments are not often found in formulations for seal materials, but are frequently used in cable insulation materials to distinguish between different wires in a complete cable. Different pigments can affect the degradation rates in both thermal and radiation ageing. Figure 19 shows the effect of 3 different pigments on the degradation of a FR-EPR cable insulation, thermally aged at 120 ºC. Usually a black material (using carbon black as pigment) shows the least degradation, whereas red pigments often show enhanced degradation.

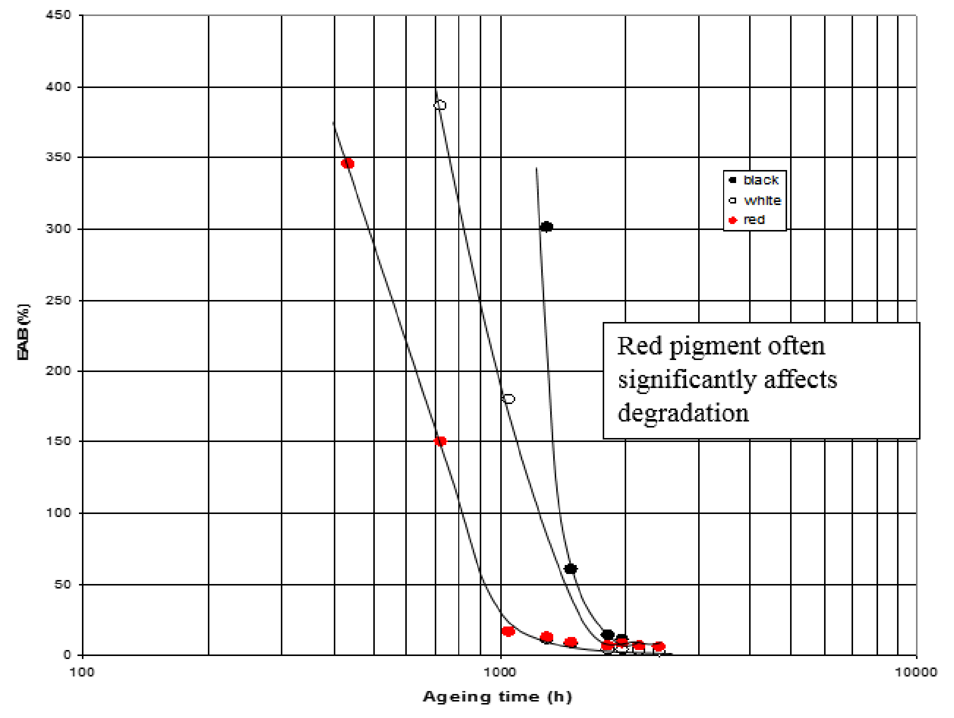


Figure 19. Pigment effects in a FR-EPR thermally aged at 120ºC (8)

During radiation ageing, pigment effects can also be dose rate dependent. Figure 20 shows the effect of ageing at 2 different dose rates (3 and 100 Gy/h) at 80ºC. The black wires are the least degraded at both dose rates, but the worst colour is red at the higher dose rate and white at the lower dose rate.

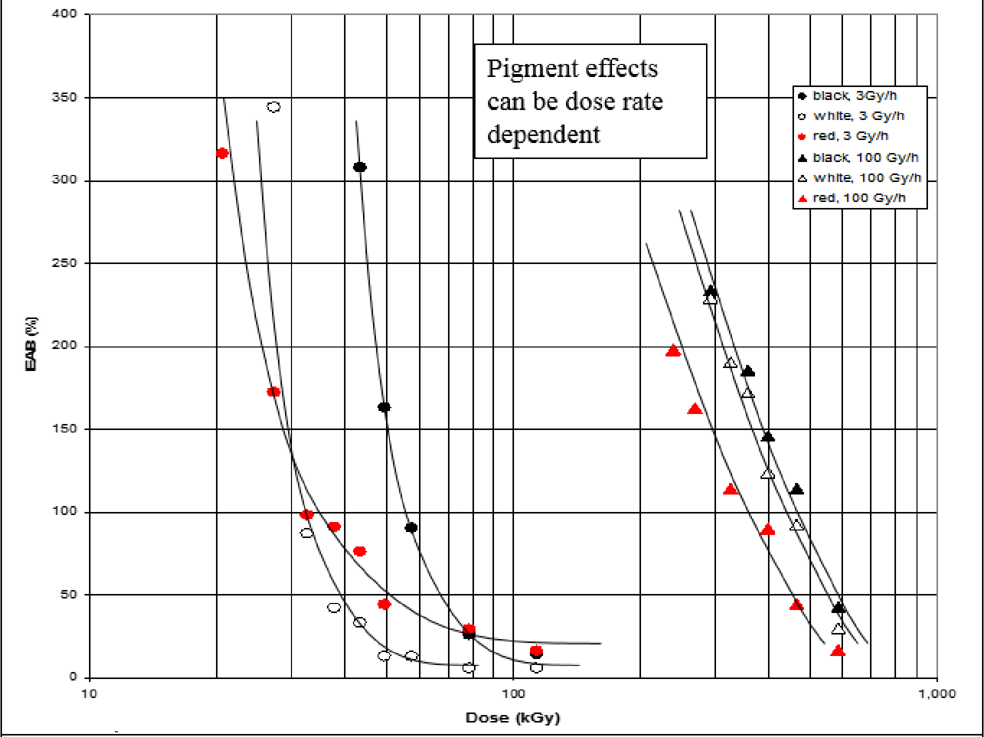


Figure 20. Pigment effects in a FR-EPR radiation aged at 80ºC (8)

3.2 USING STANDARDISED FORMULATIONS

So how do you handle the concerns over the variations in ageing behaviour with changes in formulation? One way is to use a limited number of standardised formulations that have a known ageing behaviour. This requires a change in procurement procedures to purchase components from a single manufacturer who guarantees to keep the formulation fixed. A programme of testing on these fixed formulations will then give you confidence in their long-term behaviour.

This approach is mainly appropriate for those components which are most important to the plant, e.g. seals in safety related equipment. The cost of the components will be higher than those bought under normal procurement procedures and there will be additional costs in carrying a testing programme to evaluate ageing. But these costs can be off-set against improved maintenance procedures in the long-term.

In the UK, this approach has been used for seals in the advanced gas-cooled reactors (AGRs), where seals are critically important in equipment like the on-line refuelling machine. A set of four fixed formulations are in use, available from a very limited number of manufacturers, covering different types of seal material. These are Viton, silicone, nitrile and EPDM seals, each of which is colour coded by using different fillers. This ensures that maintenance people cannot accidentally use the wrong seal type (one black seal looks very similar to another black seal even if they are different polymers) since the replacement procedure would include a specification of the seal colour. All four types have been subjected to an extensive ageing programme and predictive models developed for ageing. The degradation behaviour is well understood and is accepted by the regulator for determining maintenance intervals for seal replacement. This has been cost effective in the long term as extension of replacement schedules has significantly reduced maintenance costs for some of the critical equipment.

4 Accelerated testing of polymeric components

One of the important reasons for developing an understanding of how polymeric components degrade is to be able to carry out accelerated testing that is a reasonably accurate simulation of degradation in service. To do this you need to identify an appropriate test matrix for the ageing programme.

4.1 DEVELOPING AN APPROPRIATE TEST MATRIX

The first item you need to consider is - what are you trying to achieve with the test programme? You need to identify the aims of the test – some typical types of test programme are shown below for example.

- Simulation of service life as part of a qualification programme
- Simulation of accident conditions for a qualification programme
- Developing data for predictive modelling to address replacement intervals for components
- Generation of correlation curves between a condition monitoring method and degradation of the component
- Proof tests on new supplies of replacement components

Each of these would have a different emphasis and set of requirements. The number and type of tests and test conditions will depend on what you are trying to achieve. This will also determine the timescale required for the test programme, although the optimum time may not be possible because of the constraints of budget or availability of test facilities.

Proof tests tend to need only a limited number of test conditions, whereas data for predictive modelling will require a large matrix of test conditions and times. Correlation curves usually only require an intermediate number of conditions. Simulation of service life and accident conditions for qualification are usually only carried out under a single test condition, but it is important that this condition has been determined from an understanding of the degradation behaviour of the specific polymer material.

4.2 FACTORS TO CONSIDER FOR THERMAL AND RADIATION AGEING TESTS

Good accelerated ageing tests take time – this is because of the need to minimise the acceleration factors used, where practicable.

- As pointed out in section 2.5.1, diffusion-limited oxidation (DLO) becomes an issue in both thermal and radiation ageing. Keeping the ageing temperature or radiation dose rate low will minimise the effects of DLO.
- Keeping the ageing temperature as low as practicable will also help to avoid the effects of variations in activation energy (section 2.4.1) and help to reduce the possibility of non-representative degradation mechanisms (section 2.4.2)

- The measurements taken during the test need to be appropriate for the type of component being tested, e.g. adhesion tests for coatings.

For seals, the prime property of interest is leakage rate, but this generally does not change significantly until the seal is heavily degraded. Instead, compression set is used as the main indicator of degradation since it changes monotonically with ageing (Figure 21). Sealing force also changes monotonically with ageing, but it is more difficult to measure than compression set which can be measured with simple equipment (Figure 22). In some cases, it may be necessary to measure leakage rates or sealing force, e.g. for functional tests.

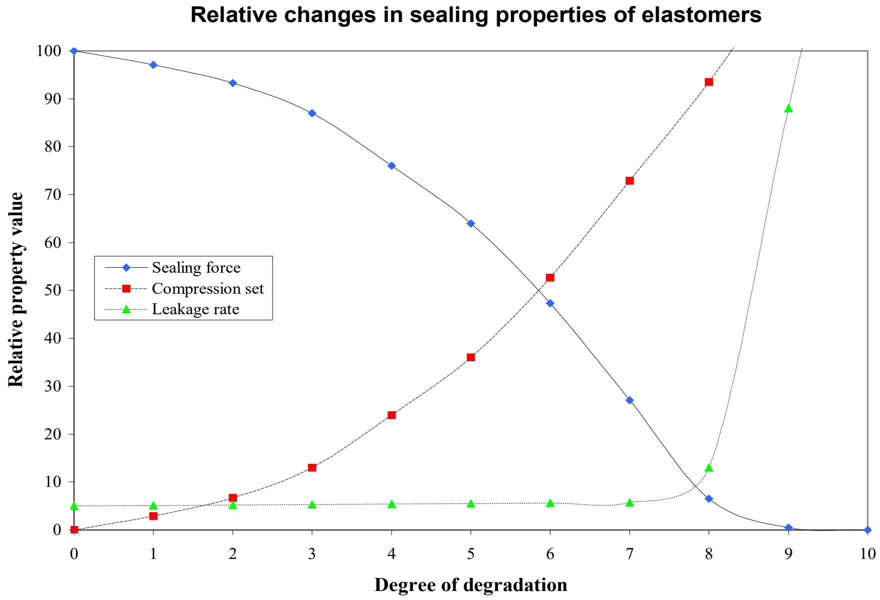


Figure 21. Schematic indication of relative changes in sealing properties of elastomers

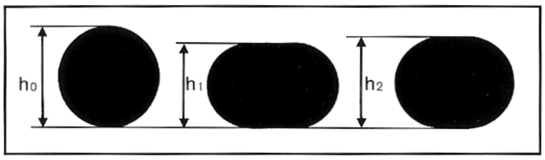


Fig. 6.1

$$\text{Compression set C.S} = \frac{h_0 - h_2}{h_0 - h_1} \cdot 100\ (\%)$$

where: h_0 = O-ring cross-section or original height of the test piece
h_1 = height of deformed test piece
h_2 = height of released test piece (after a definite time delay)

Figure 22. Measurement of compression set

For cable materials, tensile elongation at break is the usual indicator of degradation since electrical properties do not usually change significantly until the material is heavily degraded. There a number of condition monitoring methods that have been developed for cable materials, some of which are non-destructive or are easier to measure than elongation at break. There is no single technique that is applicable for all cable types, but a 'tool box' of methods are available. These are discussed in more detail in section 5. For the most developed of these methods, standards are being established e.g. IEC 62582 series (9).

For thermal ageing tests, if the activation energy is not known, a minimum of 3 ageing temperatures are required. The lowest ageing temperature should be as close to the service conditions as is practical. Extrapolation from this temperature should ideally be < 25°C but in practice this is often not possible.

For radiation ageing tests, the lowest dose rate that is practicable should be used. However, if simulation of accident conditions is being carried out, then a high dose rate is acceptable. If the tests are to generate data for predictive modelling, then a minimum of 3 different dose rates are required and there should be at least one test condition where the radiation ageing is carried out at elevated temperature. For those materials where the reverse temperature effect could potentially be a concern, some of the tests need to be carried out at the **lowest** temperature seen in service.

For both thermal and radiation ageing tests on seals, the ageing must be carried out in the compressed state, using compression levels that are representative of actual use. For all tests being carried out in air (rather than an inert atmosphere), it is important that there is good air access to the samples and it is replenished during the tests. This is of particular concern when using radiation facilities which use a sealed container. Even with good air access to the samples, diffusion-limited oxidation is likely to occur in large cord diameter seals or whole cables.

Typical test matrices for different types of programme are shown below. Examples of actual test matrices that have been used in different types of test programme are discussed in section 4.3.

Test type	**Radiation dose rates**	**Temperature**
Predictive modelling	25, 50, 100, 200 Gy/hr	20 C
	100 Gy/hr	40, 60 C
	0 Gy/hr	80, 95, 110 C
CM correlation curves	50, 200 Gy/hr	20 C
	100 Gy/hr	40 C
	0 Gy/hr	100 C
Proof tests	200 Gy/hr	20 C
	plus 0 Gy/hr	110 C

4.3 EXAMPLES OF ACTUAL TEST MATRICES

During the 1980s and 1990s, a large number of radiation ageing programmes were carried out by AEA Technology, UK. Many of these were on seal materials as part of programmes to understand how seals degrade under conditions relevant to NPPs. Examples of the test conditions that were used are shown below.

A programme aimed at developing data for predictive modelling of seal degradation used measurements of compression set under the following ageing conditions.

- Thermal ageing at 120°C, 125°C, 135°C and 150°C
- Radiation ageing in air at 20°C at dose rates of 70, 100, 300 and 1500 Gy/h
- Radiation ageing in air at 55°C and 90°C at 17, 80 and 200 Gy/h

Later, this was supplemented by a long-term ageing test at 55°C and 92°C at 3 and 5 Gy/h to validate the predictive models developed from the original data. These long-term tests were at dose rates much closer to service conditions.

Another type of programme was one aimed at checking the behaviour of a modified formulation of one of the seal materials that had been tested earlier in a programme similar to the one shown above. In this case, compression set measurements were made at 20°C and 90°C at a dose rate of 140 Gy/h and compared with the predictive model.

An example of a proof test is one where leakage measurements were made on a large seal during a thermal transient (up to 310°C), to simulate a fire test requirement for transport flask seals.

In the early 2000s, JNES (Japan) carried out a major cable test programme aimed at developing data for predictive modelling and correlation of condition monitoring (CM) methods with ageing (8). This programme included measurements of tensile elongation at break, indenter modulus and several other CM methods on a wide range of cable insulation materials. The test conditions used were as shown below.

- Thermal ageing at 100°C, 110°C and 120°C
- Radiation ageing at 80°C, 90°C and 100°C at each dose rate of 3, 18 and 100 Gy/h

Unfortunately, because no radiation tests were carried out at room temperature, the effects of the reverse temperature effect were not observed in the JNES programme.

During the period 2012 to 2015, an IAEA co-ordinated research programme tested a wide range of cable insulation and jacket materials for developing condition monitoring correlation curves and for inter-laboratory comparison of the different CM methods (10). In this case, the only test conditions used were thermal ageing at 120°C, 135°C or 190°C (one temperature only, dependent on the material being tested) and radiation ageing at 273 Gy/h at room temperature.

These examples of actual test matrices that have been used do illustrate how test programmes have evolved as a better understanding of ageing of polymers has developed. The early AEA Technology programmes did not take into account diffusion-limited oxidation, as this area of concern had not been established at that time. Luckily, measurements of compression set on most of the seal materials being studied at that time were not very sensitive to DLO. Similarly, the conditions for the JNES cable test programme were formulated at a time when the reverse temperature effect was not well known, and so this was missed in the design of the test programme and in their analysis of the data.

4.4 ACCEPTANCE CRITERIA

For seal materials, the critical functional parameter is the leakage rate, but this is not very easy to measure routinely as part of a large ageing test programme. Elastomeric seals rely on the sealing force exerted on the face of the seal housing to create a seal. This sealing force gradually decreases as the seal ages but the leakage rate does not change significantly until a critical minimum sealing force is reached. The critical value of sealing force will be determined to a certain extent by the surface roughness of the sealing face. Sealing force is also not easy to measure routinely. The most practical condition indicator for seals is compression set, which is easily measured with simple equipment. Compression set gradually increases as the seal ages, mirroring the behaviour of the sealing force (Figure 21).

So, what is an acceptable level of compression set for an elastomeric seal? For static seals, leakage rates do not change significantly for set values <90%. In some cases, e.g. at high temperatures, the differential thermal expansion between the seal and its housing means that compression set can be >100% and still maintain a seal. Even when severely degraded, with considerable loss of material from extrusion, some seals can continue to operate satisfactorily (Figure 23). Under these conditions, the seal would be expected to fail once it cools down.

Figure 23. Extrusion of an EPDM seal after a high temperature transient, but still sealing (6)

For static seals, a compression set value of 75 to 80% would still be conservative. If the seal is subject to large thermal variations or significant vibration, a slightly lower value may be appropriate. Dynamic seals are usually compressed to a much lower level than static seals and failure is more usually associated with wear rather than set.

For cable insulation materials, electrical properties are of prime importance functionally, but these do not tend to change much until the material is severely degraded, e.g. to the stage where the insulation cracks. For example, Figure 24 shows the measured values of insulation resistance of an EPR cable insulation after thermal ageing at 135ºC. Note that there is no significant trend in this property even though the elongation had decreased to <100% after 6000 hours of ageing. Tensile elongation at break (EAB) is therefore the main parameter used as an indicator of cable degradation. Most condition monitoring methods for cables are therefore correlated to changes in EAB.

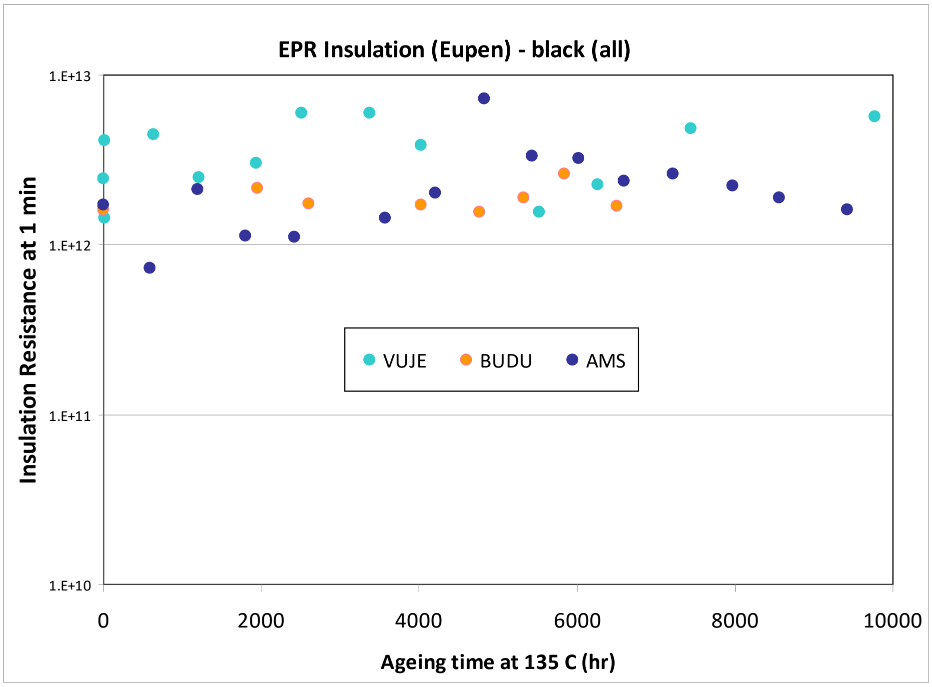


Figure 24. Insulation resistance of an EPR insulated cable after thermal ageing at 135ºC

For cables that are not required to survive accident conditions (e.g. a loss of coolant accident) an EAB value of 50% is recognised as a useful acceptance criterion (Note: this is 50% absolute, not relative to the initial elongation). At 50%, the cable material would still retain some flexibility and could be handled without the risk of cracking. If the cable is required to survive accident conditions, then 50% absolute EAB may not be adequate. For these materials, the limiting value must be determined during qualification tests.

For other polymeric components, e.g. coatings, acceptance criteria will need to be established dependent on their service requirements. This is likely to be based on some form of adhesion or other mechanical property measurement for coatings. Very little work has been published in this area.

5 Assessment of aged polymeric components

Assessment of aged polymeric components covers a number of possible activities that could be used as part of an ageing management system. These include –

- Condition monitoring methods, for assessing the current state of ageing and potentially for assessing residual life
- 'Fingerprinting' methods, as part of procurements procedures for confirming that components are as required
- Failure analysis of components

These areas are covered in more detail in the following sections.

5.1 CONDITION MONITORING – GENERAL PRINCIPLES

Condition monitoring (CM) is mainly used for assessing the current state of ageing of a component. There are different methods available for different types of component, some of which may only be appropriate for specific polymer types. Each CM method will give data on a specific condition indicator which is usually cross-correlated to an indicator of degradation, e.g. compression set in seals or elongation at break in cable materials.

In principle, CM methods could be used for assessing residual lifetime of the component, but this is not straightforward since the rate of degradation is non-linear and dependent on several environmental stressors. However, if sufficient accelerated ageing data is available to enable the use of lifetime prediction models (see Appendix A), then it is possible to estimate residual life.

Any CM method needs to fulfil a number of requirements to be of practical use in an ageing management programme. These requirements are –

- It must correlate with a functional property so that acceptance criteria can be set
- It must change significantly with degradation and that change must be monotonic, i.e. always increasing or always decreasing
- It must be reproducible under different ageing conditions
- Ideally, the method should be applicable to a number of different polymer types and be usable in areas of limited access

In practice, no single CM method satisfies all of these requirements, but there are a number of techniques available which are of practical use, forming a 'tool box' that can be used as part of ageing management. Some of the best developed of these methods now have standards, specifically for CM e.g. the IEC 62582 series of standards (9).

Most of the work that has been carried out on the development of CM methods has concentrated on cable materials, so there are limited options for condition monitoring of other types of component.

5.2 CONDITION MONITORING METHODS FOR CABLES

There a number of CM methods that have been developed for polymeric cable materials. These can be grouped into various types of test method –

- Qualitative methods, that give a broad indication of cable condition across a wide range of materials
- Methods that require sample removal or intrusion, usually used on sacrificial samples in cable deposits or on cable removed from service
- Methods not requiring sample removal, applied to cables in service or in deposits
- Electrical methods that can be applied to in-service cables, but may require disconnection from the end device

These are described in more detail in the following sections.

5.2.1 Qualitative methods

Planned walk-downs, specifically to look at cables, can be a very valuable method of obtaining a broad indication of the state of degradation of cables within a NPP. Visual and tactile inspection can be used to look for changes in colour or texture, indications of hardening or loss of flexibility, signs of cracking or damage, surface contamination etc.

Such inspections can help to identify where more sophisticated methods should be applied and are very useful in locating and identifying ‘hot-spots’, where degradation is significantly higher than in the general area. These ‘hot-spots’ can arise from original installation procedures which did not consider the particular concerns of polymer ageing or could be from faulty maintenance procedures, e.g. thermal insulation not being replaced correctly.

Some examples of potential problem areas are shown in Figure 25 to Figure 28. There are more photographs of examples in the Appendices of EPRI reports EPRI-103663 (11) and EPRI-TR-109369 (12), which cover a wide range of potential ‘hot-spot’ problem areas.

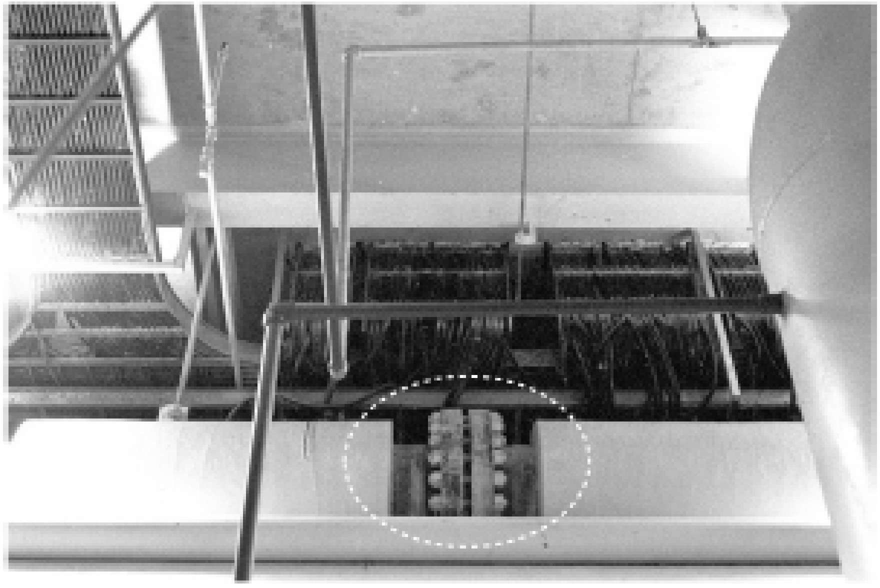


Figure 25. Missing thermal insulation (11)

Figure 26. Displaced thermal insulation on a valve operator (11)

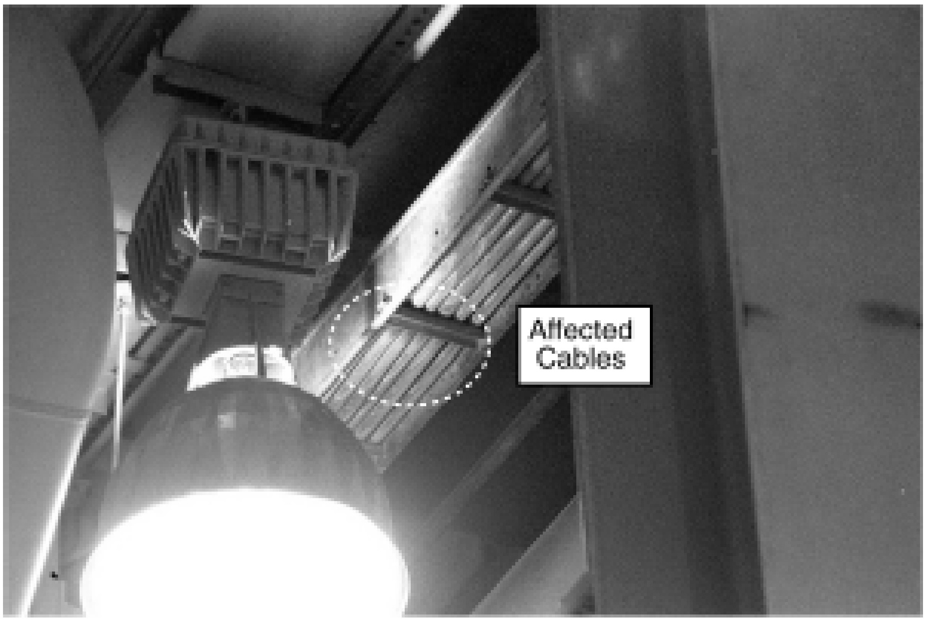


Figure 27. Heat from high intensity lamps (11)

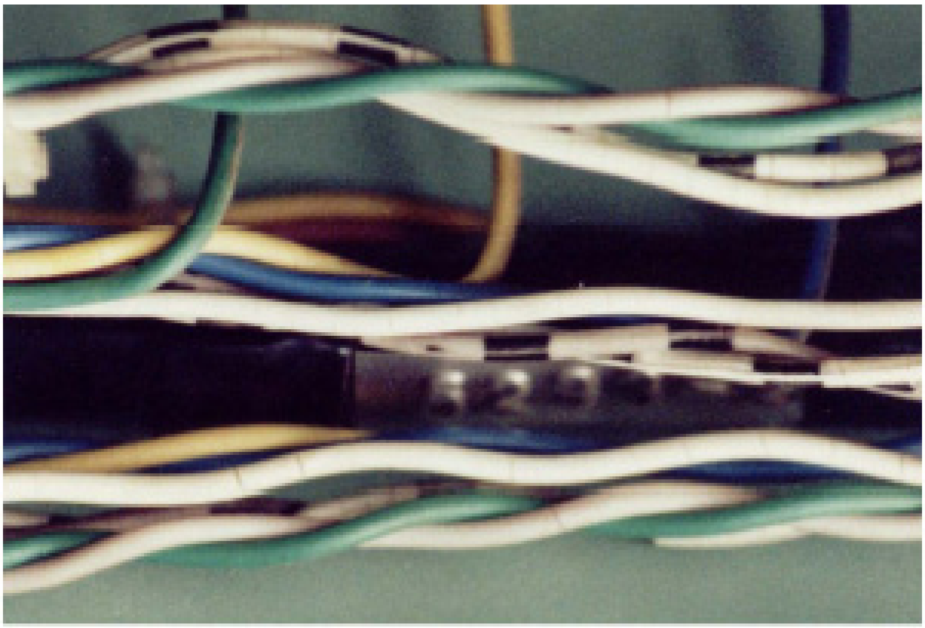


Figure 28. Cracking of PE wiring from fluorescent lights (11)

5.2.2 Methods requiring sample removal

The amount of material required for these methods varies. For some methods, only micro-samples (10 mg) are required and it may be possible to apply them to in-service cables, providing an approved repair method is available in the plant. Other methods, which require larger samples, are best applied to sacrificial samples in a cable deposit. The CM methods included in this group are as follows

- Elongation at break
- Density
- Oxidation induction
- Thermogravimetric analysis

Elongation at break (EAB) is typically used as the benchmark which is used to evaluate other CM methods. For most cable jacket materials, EAB decreases steadily with increasing ageing. For insulation materials, there is sometimes little change in EAB until near the end of life. For all cable materials, the standard deviation of measurements of EAB tend to be quite large (e.g. Figure 29 shows typical standard deviation for EAB data). Some examples of the shape of the degradation curves are shown in Figure 30. There many more examples to be found in the report on the Japanese cable ageing programme, JNES-SS-0903 (8).

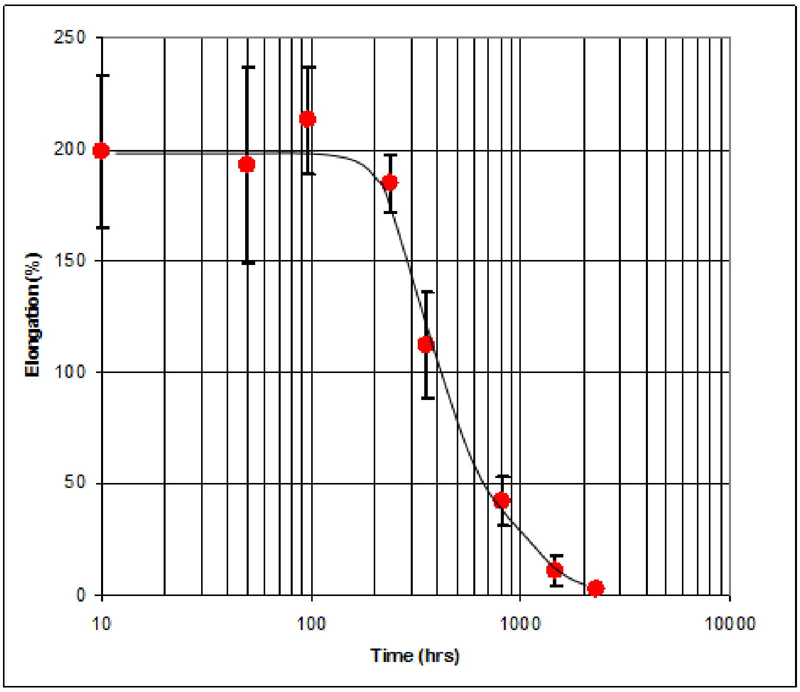


Figure 29. Radiation ageing of a PVC cable jacket at 295 Gy/h at 40°C (6)

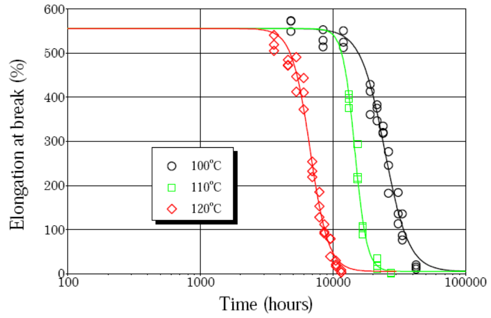


Fig. 1.1-4 Thermal aging characteristics of the FR-XLPE insulator made by Company B

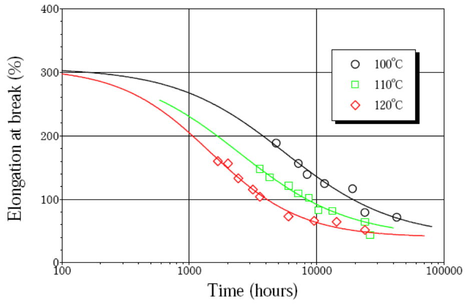


Fig. 1.1-5 Thermal aging characteristics of the XLPE insulator of triaxial cable made by Company C

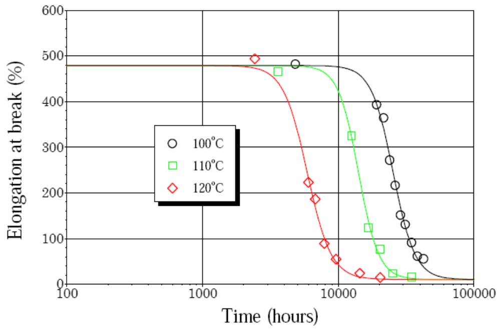


Fig. 1.1-13 Thermal aging characteristics of the FR-EPR insulator (black core) made by Company C

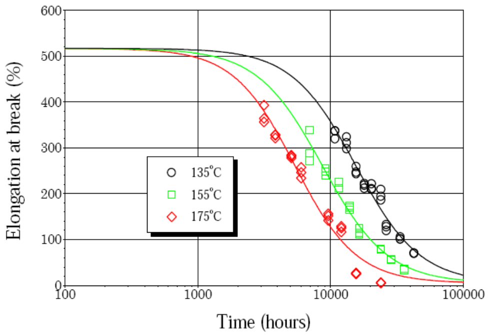


Fig. 1.1-17 Thermal aging characteristics of the SIR insulator made by Company B

Figure 30. Thermal ageing of several different cable insulation materials (8)

EAB measurements require significant amounts of material and so are only used on sacrificial samples or on cables removed from service.

Density measurements require a much smaller amount of material, but approximately 1 g of material is needed to get sufficiently accurate results, that would be representative of the bulk material. This limits its use to cable deposits or cables not in service. Density needs to be correlated with changes in EAB for the specific polymer formulation being tested. Density is very sensitive to the filler content and changes in density with ageing are quite small. For EPR and CSPE materials, density correlates quite well with ageing, but for XLPE the changes tend to be much smaller. An example for a radiation aged EPR cable insulation is shown in Figure 31.

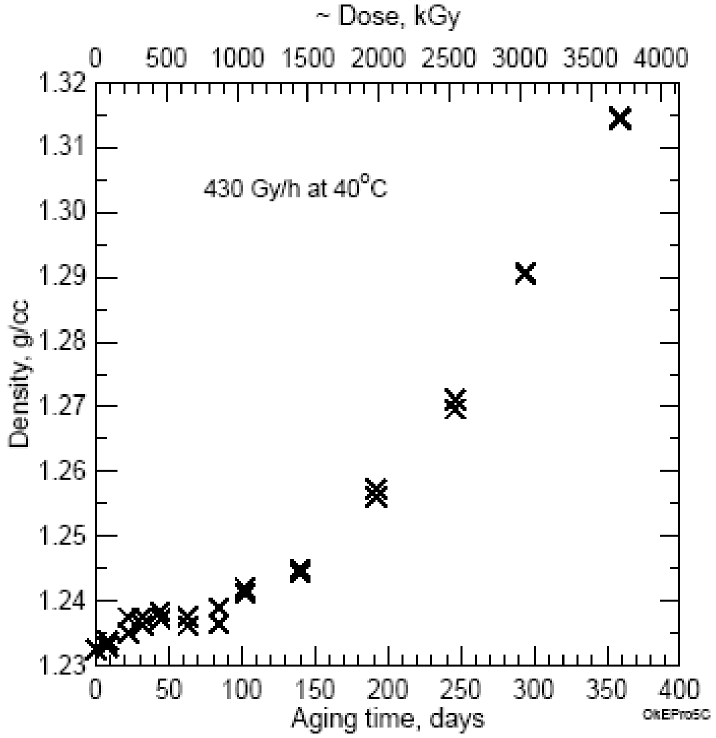


Figure 31. Density changes in an EPR insulation radiation aged at 430 Gy/h at 40°C (13)

Oxidation induction methods include two types of test – oxidation induction time (OIT) and oxidation induction temperature (OITP). Both make use of standard laboratory thermal analysis instruments and require approximately 10mg per test. OIT measures the time required for the onset of oxidation at constant temperature, whereas OITP measures the temperature of the onset of oxidation as the temperature is increased at a constant rate. The two methods are complementary.

OIT tends to be particularly sensitive to the early stages of degradation and so can be a useful 'early warning' method for those materials that show little change in other properties (e.g. elongation) in this region. OITP tends to be more useful in the later stages of degradation, so the two methods used together can be particularly useful. As an example, Figure 33 and Figure 34 show the change in OIT and OITP respectively for a thermally aged EVA cable jacket. For PE and EPR based components, OITP trends well with ageing (Figure 32).

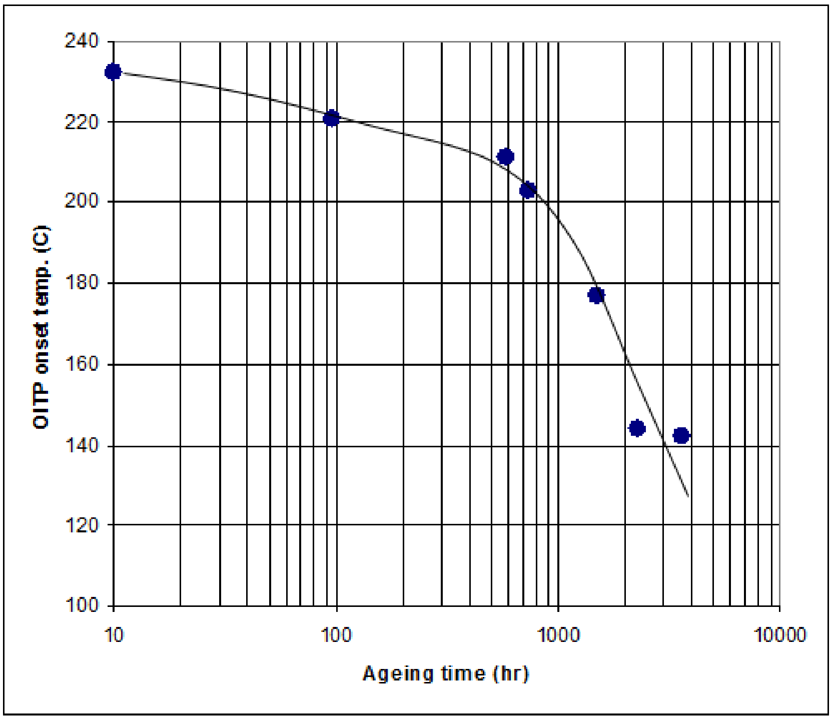


Figure 32. Change in OITP during radiation ageing of an EPR cable insulation at 200 Gy/h at 25°C

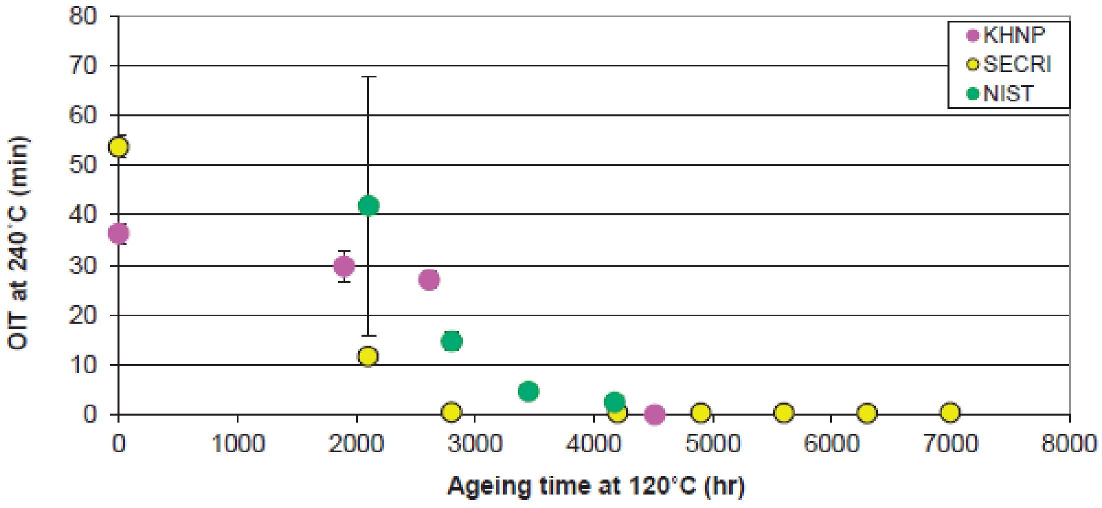


Figure 33. OIT data for thermally aged EVA jacket material

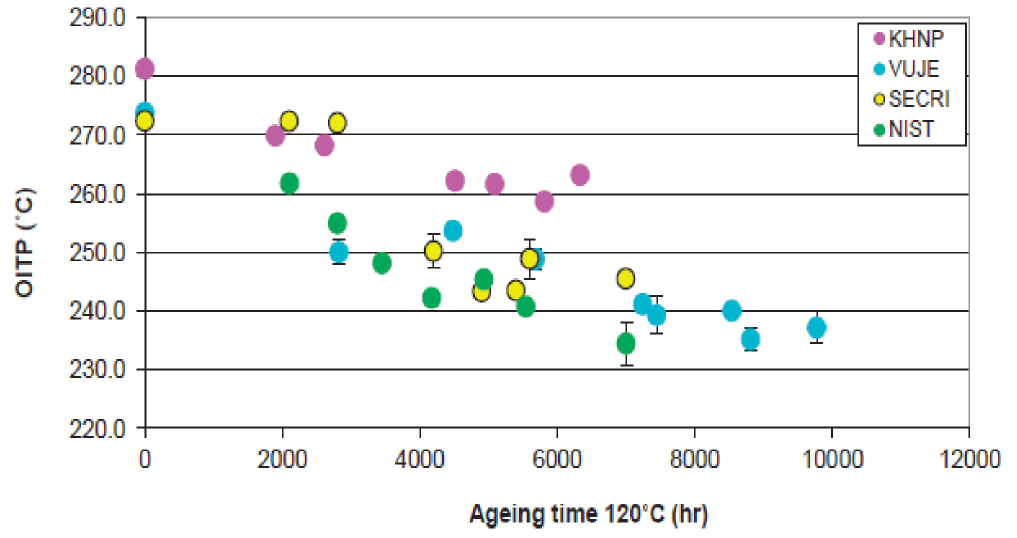


Figure 34. OITP data for the same thermally aged EVA jacket material

Thermogravimetric analysis (TGA) also uses standard thermal analysis equipment and requires approximately 10 mg per test. The weight loss of the sample is monitored as the temperature is ramped up, usually at 10°C per minute. This method is less useful than the oxidation induction methods although it does trend reasonably well for a few materials (Figure 35). More recent studies indicate that TGA has the potential to be more useful if the test method is changed so that analysis is carried out in oxygen rather than nitrogen, as is the usual method (14).

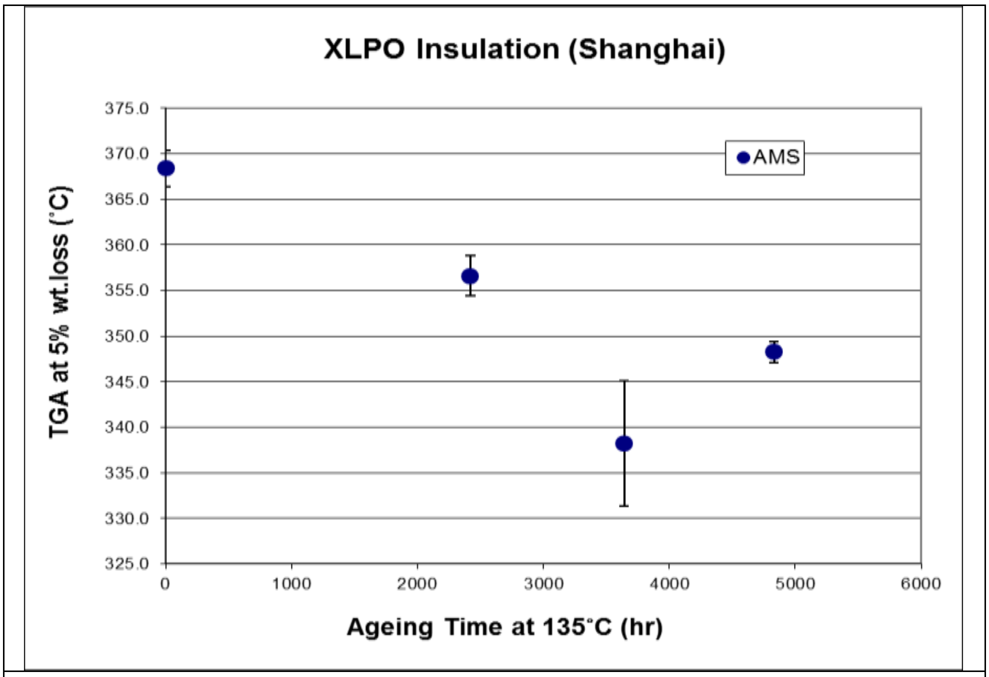


Figure 35. TGA for thermally aged XLPO cable insulation

5.2.3 Methods not requiring sample removal

There are a number of methods that do not require the removal of samples for testing. In principle these could be applied to cables in service or on samples in deposits. These methods include the following –

- Indenter modulus
- Recovery time
- Sonic velocity
- Infrared reflectance

The indenter is the most established of these methods and consists of a portable instrument that measures the load exerted on a probe tip as it is pressed into the surface of a material under controlled conditions. The slope of the load-displacement curve is an indicator of the modulus of the material. The indenter modulus (IM) is defined as the change in load $F_2 - F_1$ divided by the change in displacement $d_2 - d_1$ (Figure 36).

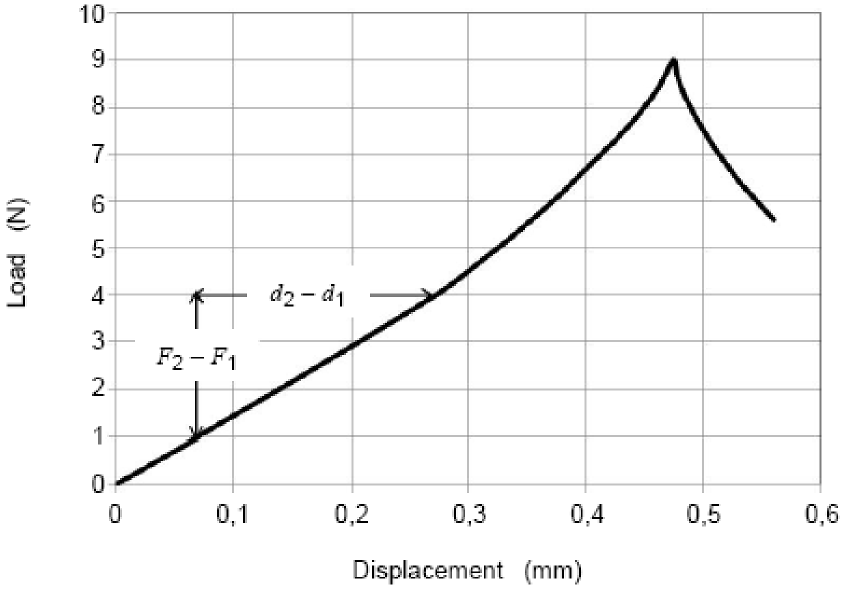


Figure 36. Typical load-displacement curve for indenter measurements

IM measurements correlate well with ageing degradation in many polymeric materials used in cables, e.g. EPR cable insulation (Figure 37). The changes observed tend to be largest in soft materials such as silicone rubbers (Figure 38). For the harder semi-crystalline polymers, such as XLPE and PEEK, the correlation with elongation is poor and the method is not useful.

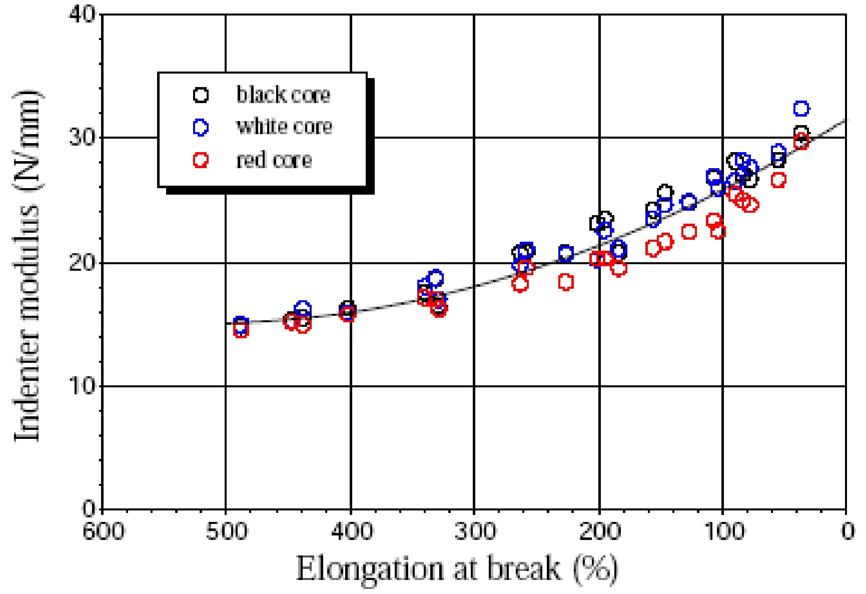


Figure 37. Correlation curve between IM and EAB for an EPR cable insulation (8)

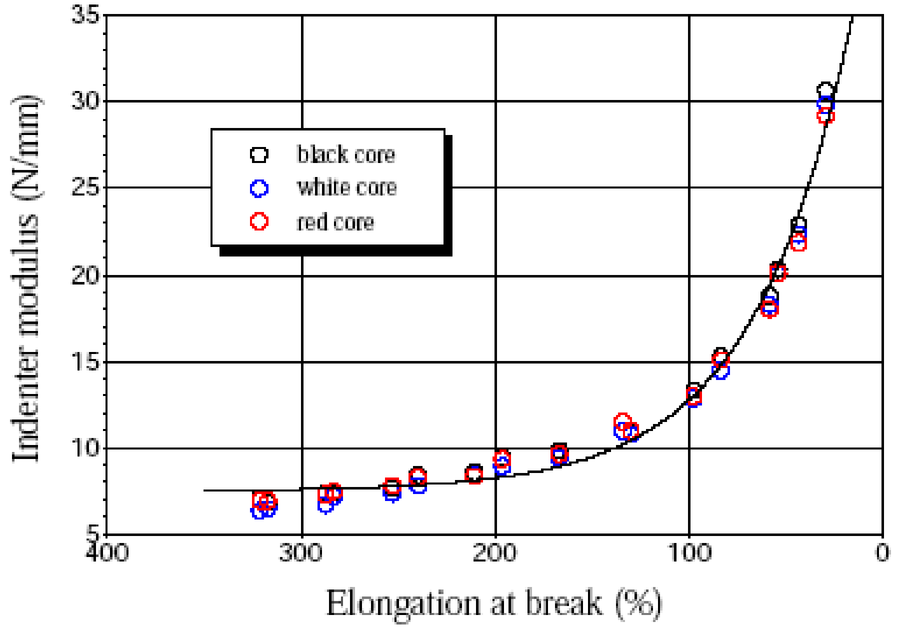


Figure 38. Correlation curve between IM and EAB for a SiR cable insulation (8)

Recovery time is a variation of the indenter method that is potentially much more useful than the indenter for harder polymers such as XLPE and PEEK. It uses a modified version of the indenter to measure the time required for the polymer to recover from a fixed displacement (Figure 39), using a probe tip similar to that used in the indenter (15). An example of indenter versus recovery time measurements is shown in Figure 40.

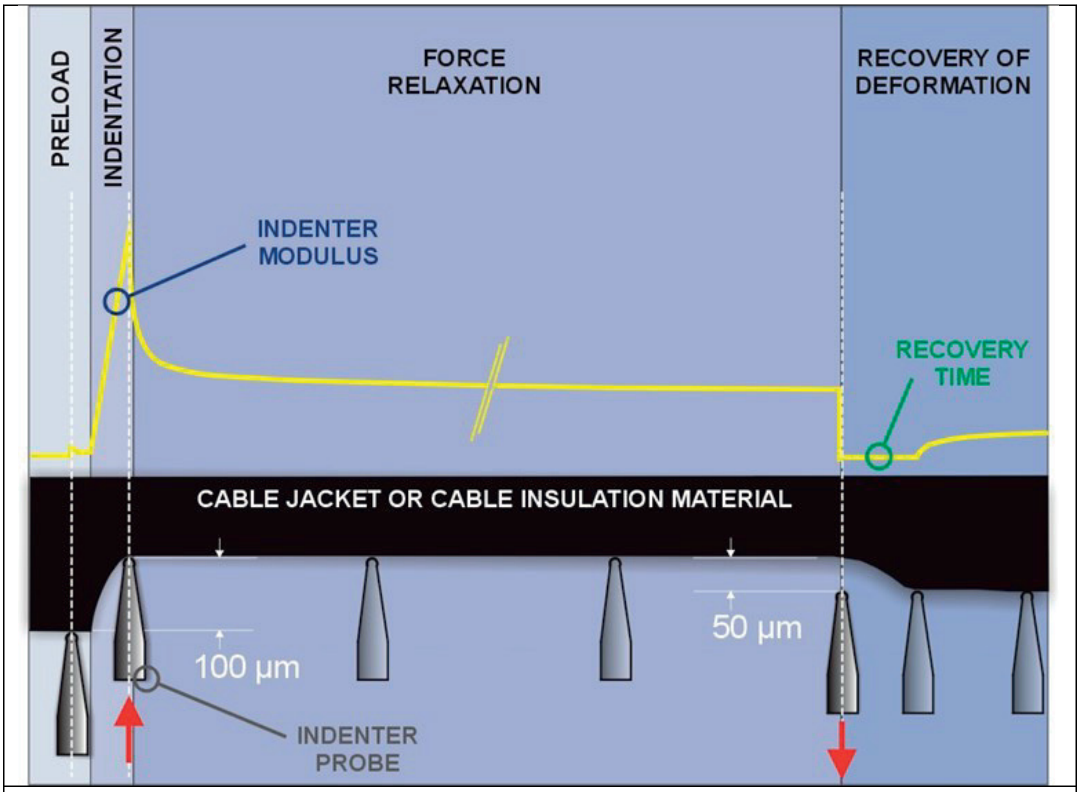


Figure 39. Test method for measurement of recovery time.

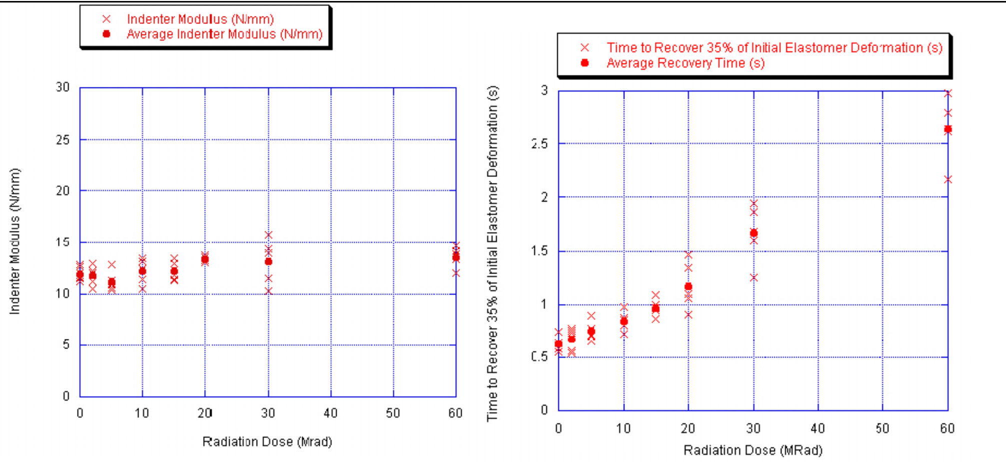


Figure 40. Comparison of IM and recovery time measurements for radiation aged PVC (15)

Sonic velocity measurements have also been used as a potential condition monitoring method, using an ultrasonic pulse between two probes attached to the cable surface. The optimum probe space and pulse frequency are still to be established but the technique looks promising for some cable materials (Figure 41). The main disadvantage of the method is that it needs to be correlated for different sizes of cable, not just different materials, and can be disturbed by the presence of metallic armour layers in a cable.

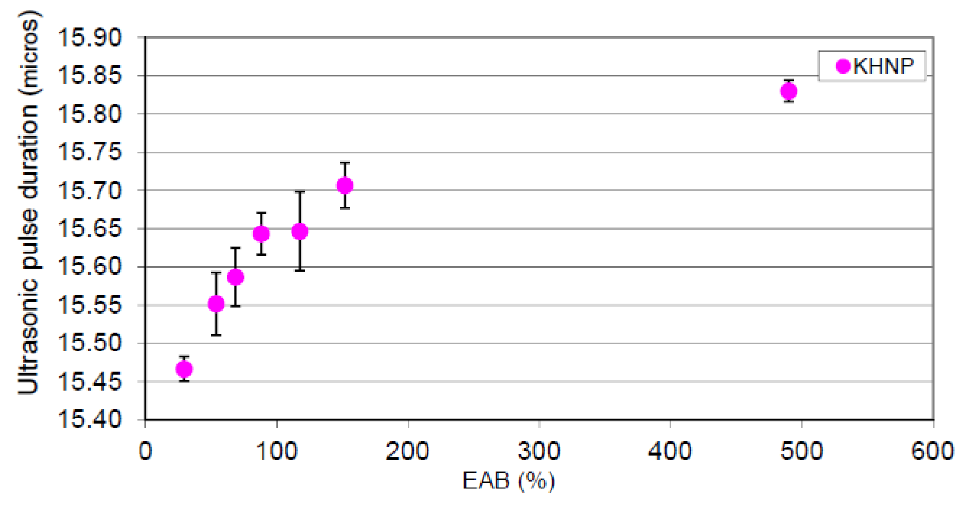


Figure 41. Sonic velocity measurements after thermal ageing of CSPE cable jacket material (10)

Infrared analysis in reflectance mode is another potentially useful method that could be used on cable in service. The method uses a portable instrument to measure the ratio of absorbance peaks in the infrared spectrum that are representative of polymer degradation. It cannot be used on black material but shows a reasonable correlation with changes in elongation for EPR and XLPE materials (Figure 42).

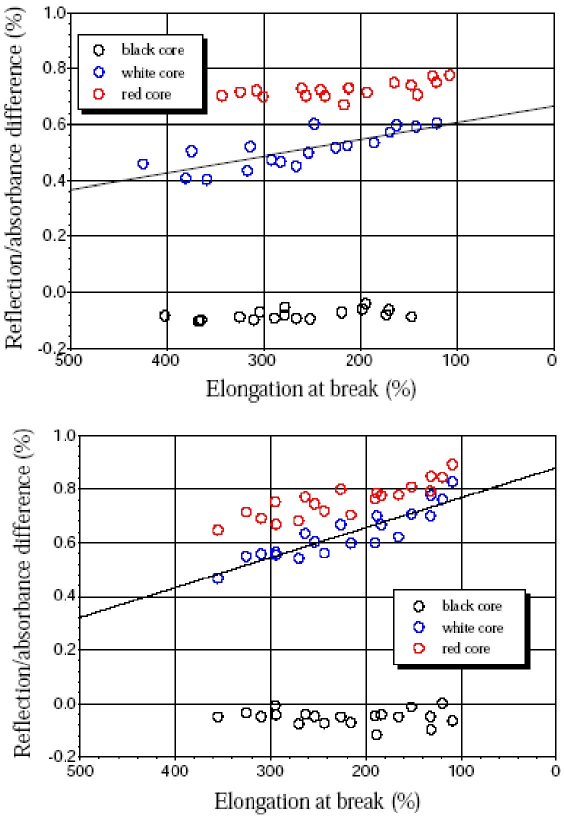


Figure 42. Correlation of infrared absorbance with EAB for EPR and XLPE cable insulation of different colours (8)

5.3 ELECTRICAL METHODS

There are a number of electrical property measurements that have been studied as possible condition monitoring methods for polymeric cable materials. Potentially these could be used on in-service cables. The methods that have been tested include –

- Dielectric loss
- Time domain reflectometry
- Frequency domain reflectometry
- Insulation resistance

Although some of these methods are quite good for fault location or troubleshooting, recent studies have demonstrated that they do not trend significantly with ageing (10).

5.4 CONDITION MONITORING METHODS FOR SEALS AND COATINGS

Less research has been carried out on CM methods for components other than cables, so this is an area which is not as well developed. For seal materials, the prime property of interest is leakage rate but the main property that is usually measured is compression set. The measured set correlates well with the sealing force (Figure 21) and changes monotonically with ageing degradation, so can be used as a practical method for CM of seals.

Recent research (4) has shown that a portable NMR probe has some potential as a non-intrusive method for CM of seals. Preliminary results show a good correlation with changes in elongation and indenter modulus for an elastomeric seal material (Figure 43).

For coatings, the mechanical properties and adhesion are the prime properties of interest. Very little research has been published on potential methods for CM. At present, only destructive tests such as adhesion strength have been used to assess ageing in coatings, but interpretation is difficult because of the large standard deviation of adhesion measurements (6). The NMR relaxation time method could possibly be of use for these materials as well, since it samples the properties at a selectable depth with a thickness of about 200μm. So far, no work has been done on correlation of these NMR measurements with adhesion or other mechanical properties in coatings.

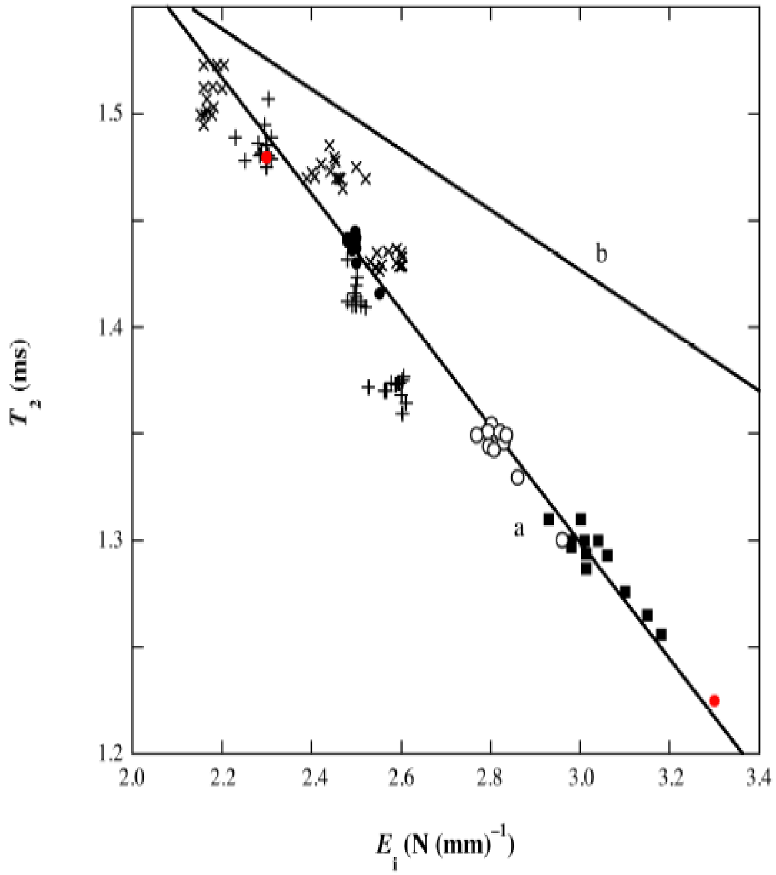


Figure 43. Correlation of NMR relaxation time T2 with indenter modulus for an EPDM transit seal (4)

5.5 POTENTIAL PROBLEM AREAS IN CONDITION MONITORING

Each formulation of a polymer will have its own response to condition monitoring methods, some methods being more sensitive to formulation changes than others. The appropriate CM method will depend on both the polymer and component type. There are some common potential problem areas that you should be aware of when considering which CM method to use. These are –

- ‘Cliff edge’ behaviour
- Heavily aged before significant change in condition indicator
- Changes too small relative to scatter of data
- Sensitivity to test environment
- Sensitivity to variations in test method or analysis

Some examples of these common problem areas are shown in the following sections.

5.5.1 ‘Cliff edge’ behaviour

This type of behaviour is associated with a condition indicator that does not change significantly during the early stages of ageing, but then changes rapidly at the later stages of degradation when the material is close to failure. In this situation, it is very difficult to obtain sufficient data during the rapid change (Figure 44). This type of measurement is not very useful for CM as there is little warning of the onset of failure - like approaching a cliff edge. It is often associated with polymers that contain anti-oxidants that are consumed during ageing, such as XLPE.

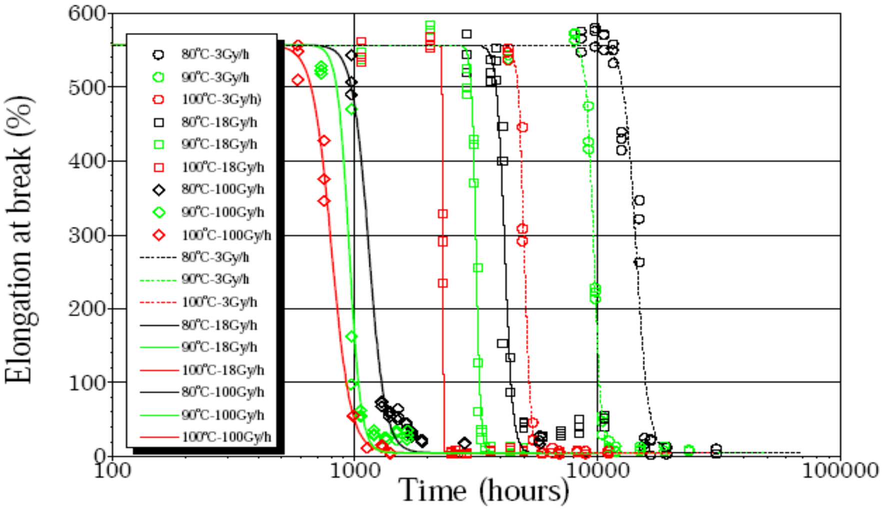


Figure 44. Radiation ageing of a XLPE cable insulation at elevated temperature – elongation at break measurements (8)

It is far preferable to have a condition indicator that changes more gradually during ageing as seen for elongation measurements in a silicone rubber cable insulation (Figure 45).

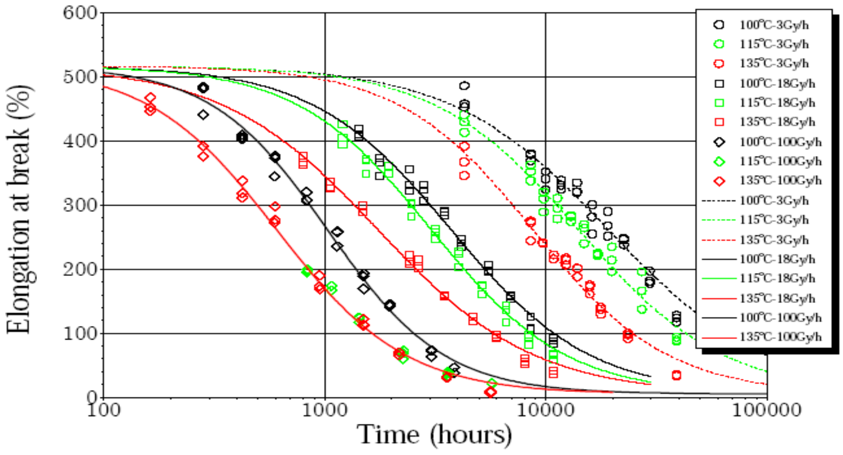


Figure 45. Radiation ageing of a SiR cable insulation at elevated temperature – elongation at break measurement (8)

5.5.2 Heavily aged before significant change in condition indicator

In some cases, a condition indicator appears to show a marked change with ageing but only changes significantly once the material is heavily degraded, as shown when the data are cross-correlated with a prime indicator. An example of this is shown in Figure 46 for density measurements carried out on a thermally aged XLPE. Although the density changes are large after 5000 hours at 135°C, the cross-correlation with elongation data shows that these changes only occur once the elongation has dropped below 50% absolute.

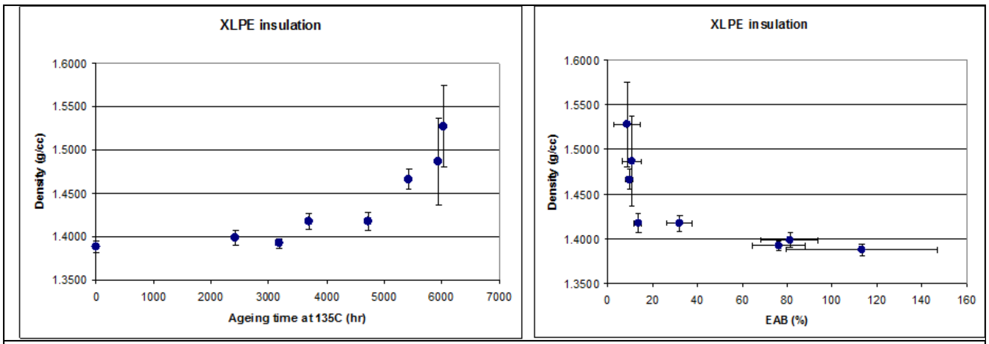


Figure 46. Density changes in a XLPE cable insulation during thermal ageing (10)

5.5.3 Changes too small relative to scatter of data

A condition indicator may show a reasonable trend with ageing but if the data scatter is too large relative to the changes with ageing, then the indicator will not be particularly useful for CM. An example is shown in Figure 47for infrared absorbance measurements made on a thermally aged FR-EPR cable insulation. For both the red and white wires, there is a distinct trend with ageing but the scatter is too large. This method may be made more useful if the test method can be refined to reduce the measured variation.

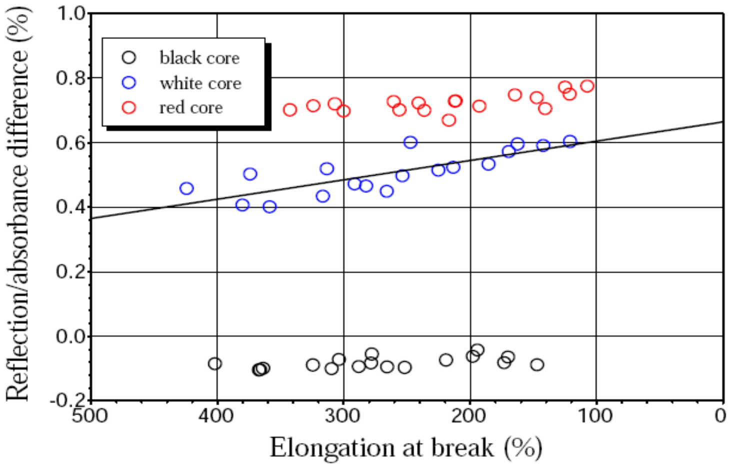


Figure 47. Correlation of infra-red absorbance measurements with changes in elongation in a thermally aged FR-EPR (8)

5.5.4 Sensitivity to test environment

When carrying out condition monitoring it is important that the measurements are not sensitive to the environmental conditions under which the test is carried out. For example, in some polymeric materials indenter measurements can be sensitive to the test temperature (Figure 48). Also, many electrical measurements are sensitive to the moisture content of the material. This can have a significant effect on data generated after thermal ageing, since the materials will have very low moisture content after ageing. It is necessary to allow sufficient time for the materials to equilibrate to normal humidity levels before useful measurements are made.

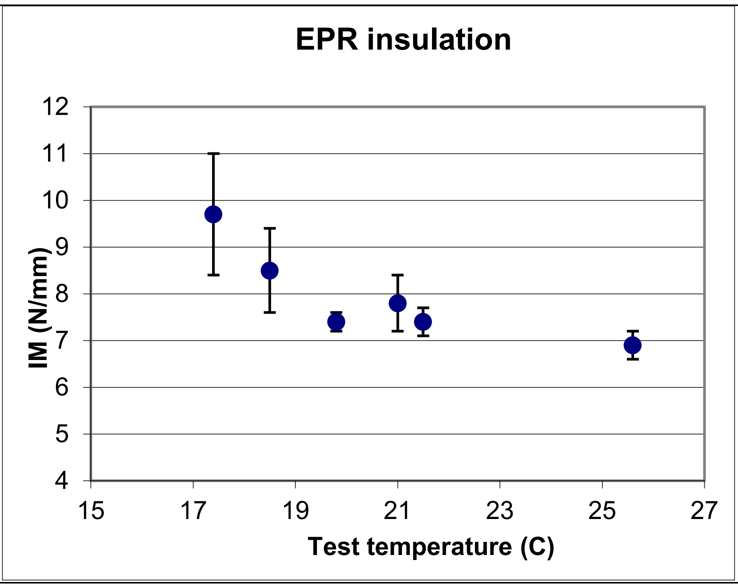


Figure 48. Variation of indenter modulus with test temperature for an EPR cable insulation (3)

5.5.5 Sensitivity to variations in test method or analysis

In any practical condition monitoring programme, it will be essential that the measurement method is consistent, since this sort of programme may cover decades. The test method must be rigorously defined, including the method for data analysis, to ensure consistency.

A recent study comparing CM measurements made by different laboratories on the same materials has highlighted how important this is (10). Figure 49 shows indenter data from 3 different laboratories on a thermally aged EPR cable insulation material. Note that one of the lab measured values significantly different from the other laboratories. Examination of the test procedures used by the laboratories showed that part of this had arisen from the use of a different tip diameter by the one lab. Figure 50 shows the same data set after correcting for the difference in tip diameter. The remaining differences between the laboratories were primarily due to the use of different force ranges for calculating the indenter modulus.

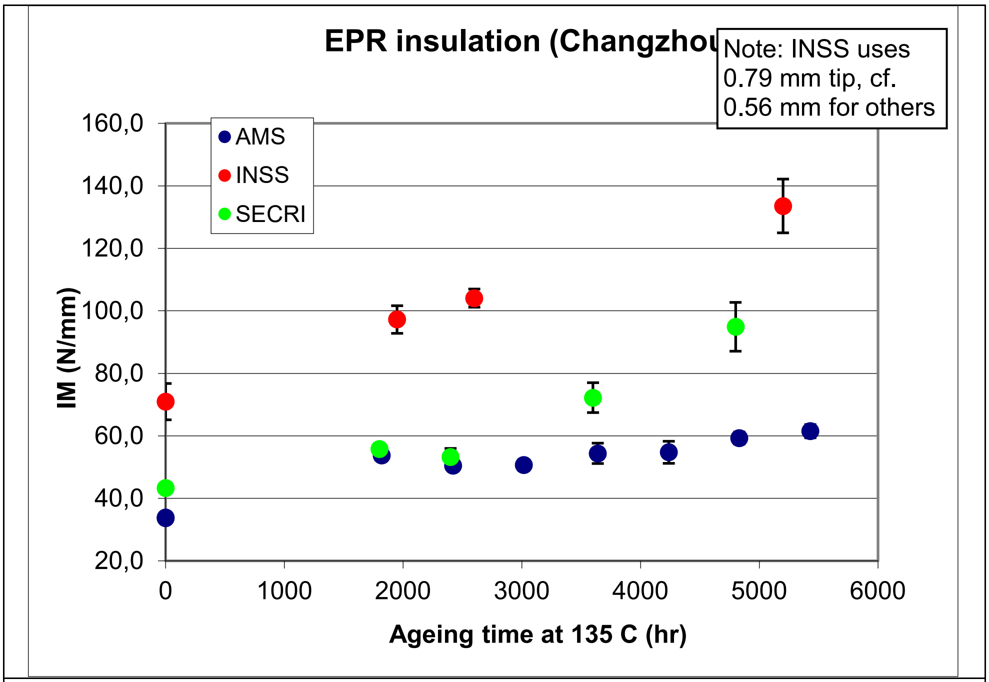


Figure 49. Indenter modulus measurements on a thermally aged EPR cable insulation (10)

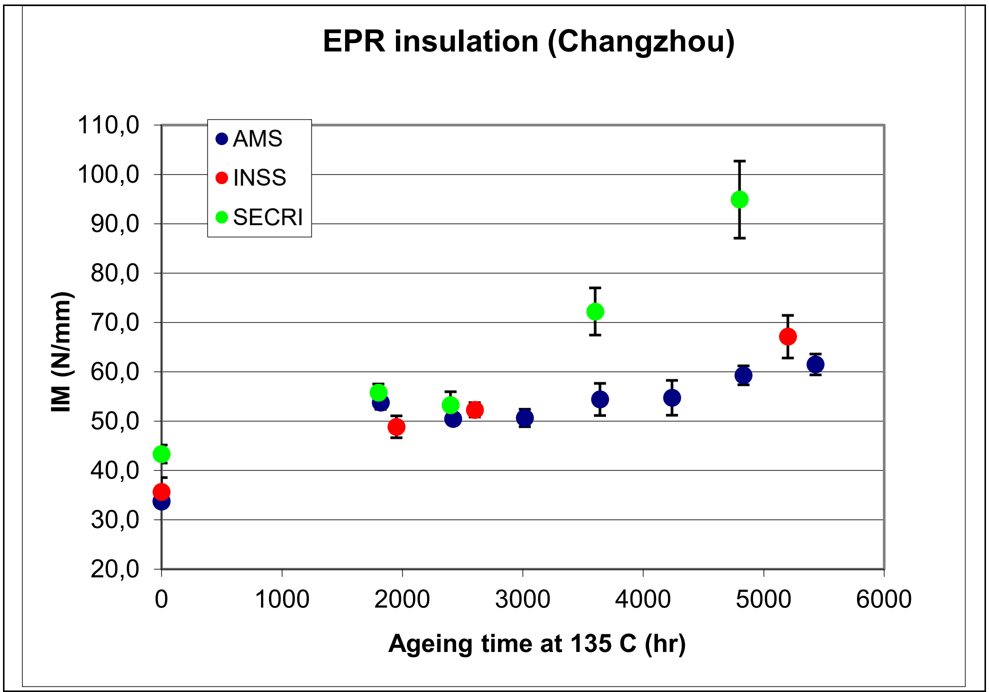


Figure 50. Indenter modulus measurements on the same material after correction for tip diameter (10)

5.6 ENSURING RELIABILITY AND REPRODUCIBILITY OF CM METHODS

So, in view of the potential problem areas in condition monitoring, how do you ensure the reliability and reproducibility of the CM methods being used? As pointed out in section 5.4.3, it is important that the scatter in repeated measurements is small relative to the changes that occur on ageing. Using a very well-defined test method can help to reduce these measurement variations. For example, changes in density are quite small but the reproducibility of data (as indicated by error bars of ± one standard deviation) can be good enough for the method to be viable for some materials (Figure 51).

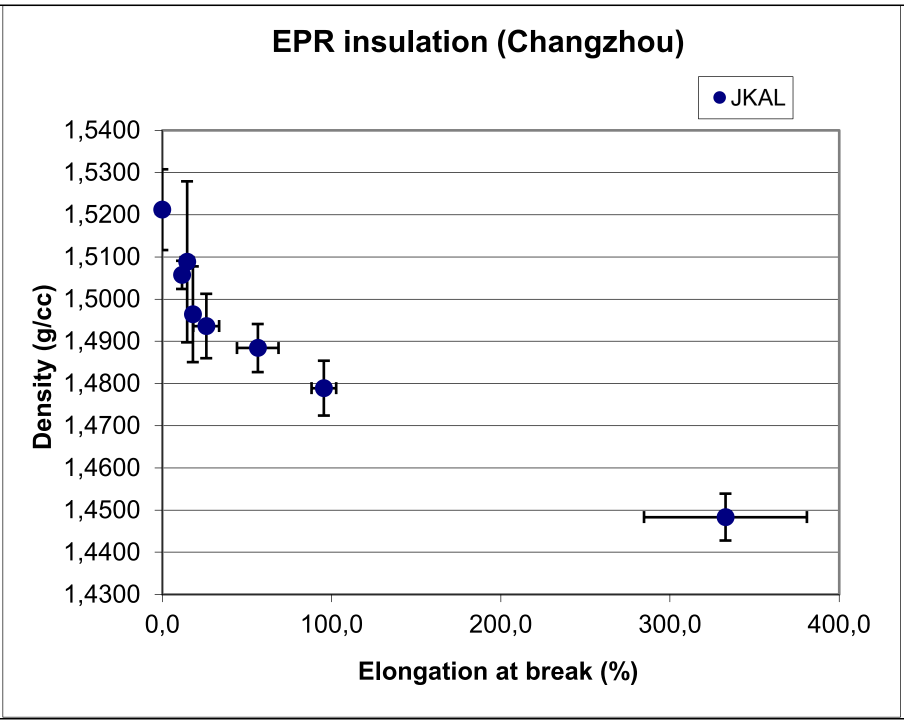


Figure 51. Correlation of density measurements with elongation for an EPR cable insulation (10)

One important area that must be checked is whether the correlation between the condition indicator and the prime indicator (e.g. elongation for cables, compression set for seals) is dependent on how the ageing has been carried out. The correlation curves should be the same, whether the degradation is from thermal ageing or radiation ageing. Figure 52 illustrates this for density measurements on a XLPE cable insulation. For thermal ageing at 100°C and radiation ageing at 2.9 Gy/h (low dose rate), the curves are the same, but at a higher dose rate there is a discrepancy between the curves. This is a useful illustration of the need to determine correlation curves under conditions that have a low acceleration factor relative to in-service conditions.

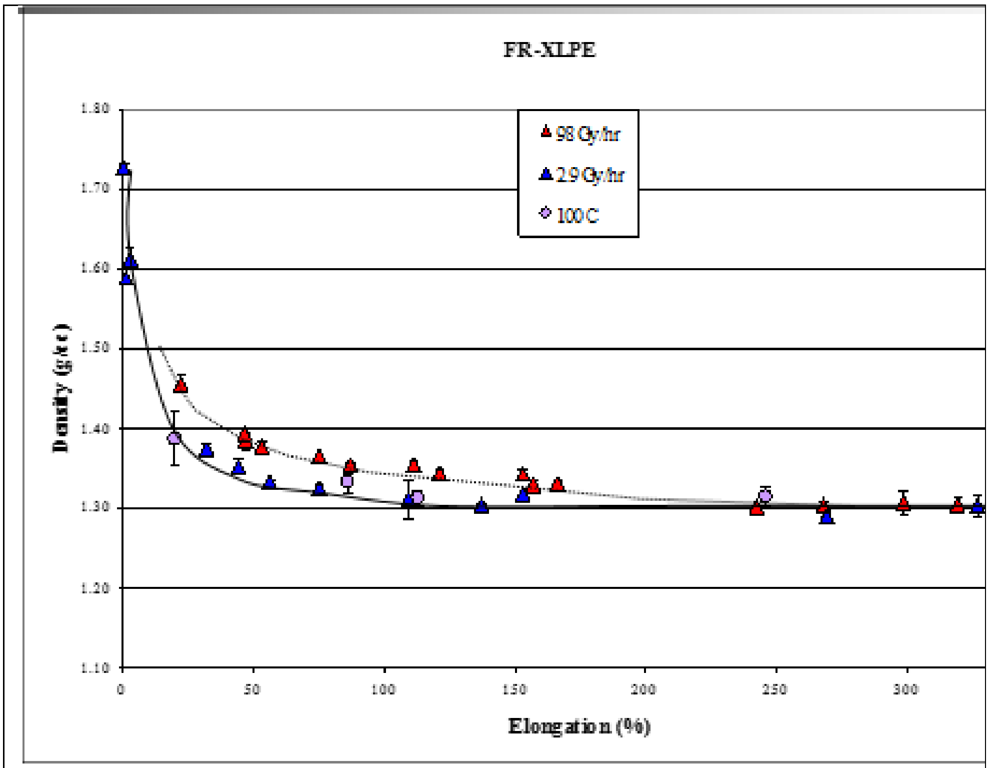


Figure 52. Correlation curves for density versus elongation for a FR-XLPE cable insulation (6)

Another point that needs to be addressed is whether the CM method being used is particularly sensitive to variations in formulation. For example, in cable materials you will often find that the insulation in multi-core cables are of different colours even though the basic polymer formulation is the same. Methods based on mechanical properties (such as the indenter) are relatively insensitive to the pigment used whereas infrared absorbance is very sensitive (Figure 53). So, for these types of components it is important to select CM methods that are independent of the pigment used.

[Note that it is the correlation curve that is independent of variations in pigment, but the actual degradation rate may still be pigment-dependent.]

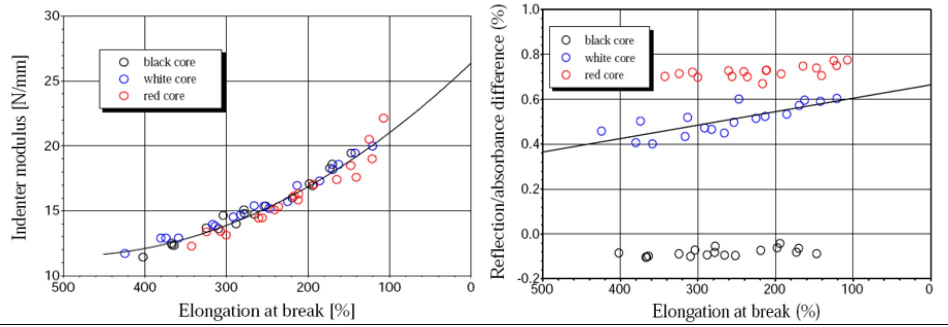


Figure 53. Comparison of correlation curves for FR-EPR cable insulation using indenter and IR absorbance methods (8)

Practical ageing management programmes in NPPs will need to operate over long periods of time, typically decades. Over this time period it is unlikely that exactly the same people or equipment will be used for condition monitoring. So, it is very important to understand which parameters in the CM test method are critical to getting reproducible results. This is an area that has been specifically addressed in a recent IAEA co-ordinated research programme (10). The following examples from that programme help to illustrate how important this is, using data from elongation measurements and other CM methods made on thermally aged cable materials.

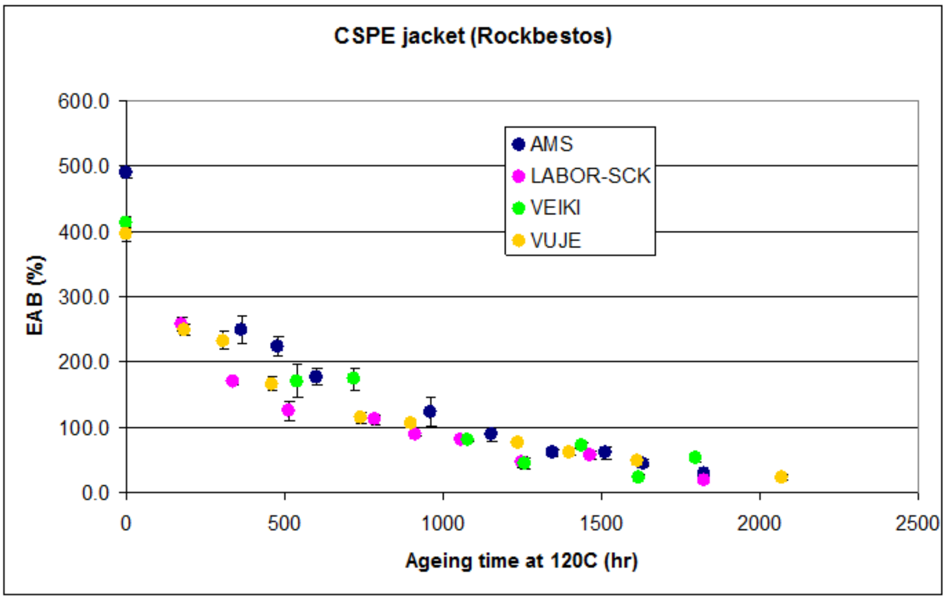


Figure 54. Elongation measurements for a thermally aged CSPE cable jacket material (10)

Figure 54 shows elongation data from 4 different laboratories on a CSPE jacket material. This particular material was of relatively even thickness so that there was no problem in cutting dumbbell shaped tensile specimens using a standard cutter. The error bars on the individual data points indicate ± 1 standard deviation for batches of 5 specimens. There is little variation in the measured values of elongation between laboratories. The main variations were determined to be from the different methods used to measure the elongation. Most of the laboratories used optical extensometers but one used the separation between the cross-heads to measure elongation.

Not all of the cable materials tested in this programme were as easy to prepare for elongation measurements. Figure 55 shows elongation data from 6 different laboratories who tested an EPR cable insulation material that was particularly difficult to strip from its wire. Note that the error bars are much larger than those for the CSPE material shown in Figure 54 and the measured values are very different between laboratories, particularly for the unaged material. The approach used to prepare samples varied significantly between the laboratories. Some used standard wire strippers, which tended to damage the insulation. Some tried stretching the conductor to break the bond between the insulation and the conductor. Others tried slitting the insulation along the wire and then peeling the insulation off the conductor. All of these methods tended to introduce some mechanical damage to the polymer insulation, but the most consistent data for this particular material was obtained by stretching the conductor. This illustrates that the test method also has to specify the sample preparation method very closely.

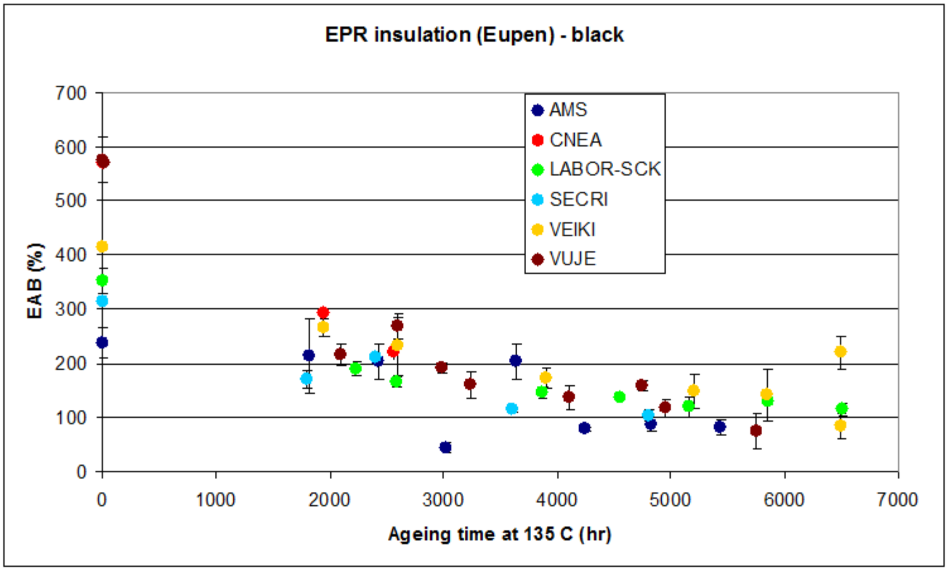


Figure 55. Elongation measurements for a thermally aged EPR cable insulation (10)

Another example of the importance of the sample preparation method is shown in Figure 56. This EVA jacket material could be easily separated from the cable insulation but was of very variable thickness as it had been moulded around the wires in a 4-core cable. Most of the laboratories tested this material without any further preparation, so the elongation results had large standard deviations. One laboratory removed the variations in thickness by slicing and buffing the samples to provide a more uniform thickness, which gave more reproducible results in terms of standard deviation but very different absolute values when compared with the other laboratories.

Sample preparation is also important in other CM methods. For the methods based on thermal analysis (OIT, OITP and TGA) the method used to prepare the samples has a strong influence on the measured results. To prepare samples for thermal analysis it is necessary to chop up the material into small pieces before inserting these into the sample pan. The size of the particles and the degree of contact with the pan affects the measured test values (Figure 57). The variations between laboratories are very large compared with the standard deviation of the measurements. The current standard for this method does not stipulate the sample preparation method in sufficient detail for reproducible measurements to be made, and so does need updating.

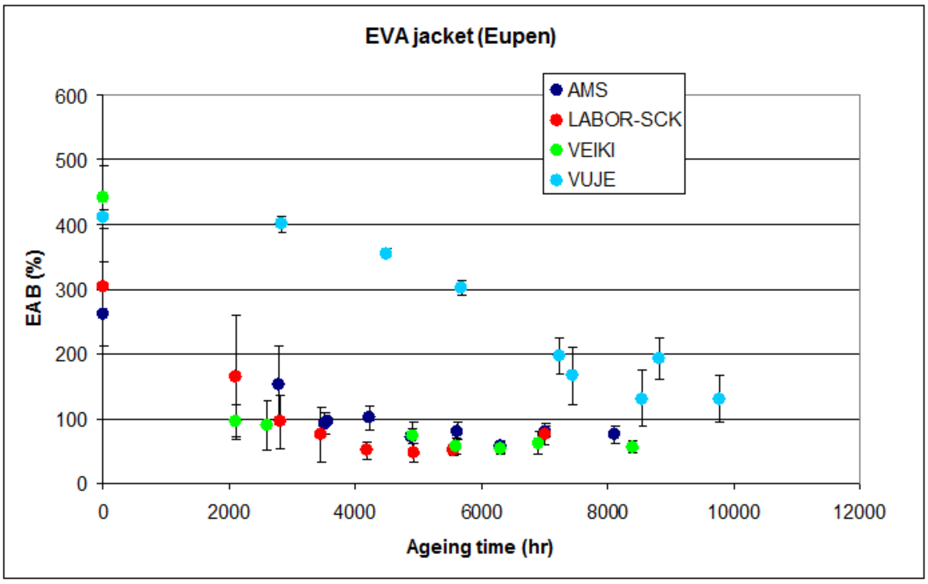


Figure 56. Elongation measurements for a thermally aged EVA cable jacket material (10)

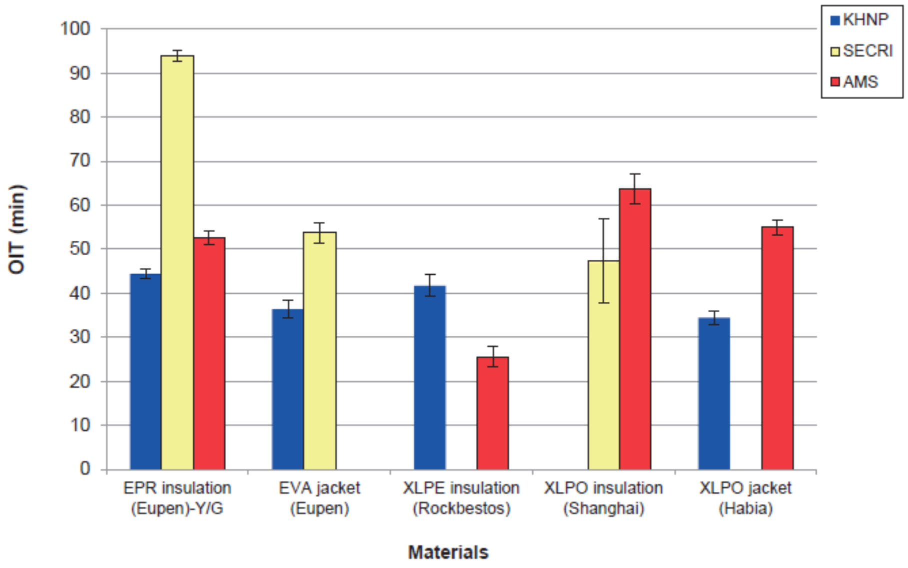


Figure 57. Example of variability of OIT measurements on unaged samples (10)

Variations in the test equipment itself may also be important in comparison of data between laboratories. The indenter is a relatively well-defined CM method but there are still variables that are not controlled. The main variable that seems to have a significant effect on the absolute values measured is the force used to clamp the sample. In most indenter equipment this clamping force is determined manually by the operator, so although consistent data can be obtained by the same operator, different values may be obtained with a different operator of the same equipment. This is starting to be addressed by several laboratories that have built their own indenter equipment. Within the IAEA cable test programme, this can be illustrated by comparing the data obtained from 3 different laboratories which used different indenter equipment (Figure 58). In this figure, the data points in blue are from a standard commercially available indenter instrument that is widely used, but does not have a specific control of the clamping force. The brown and pink data points are from two laboratories that developed their own instruments that included some form of control over clamping force. All three data sets show the same general trend with ageing but the two with controlled clamping are slightly more consistent, with lower standard deviation of the measurements.

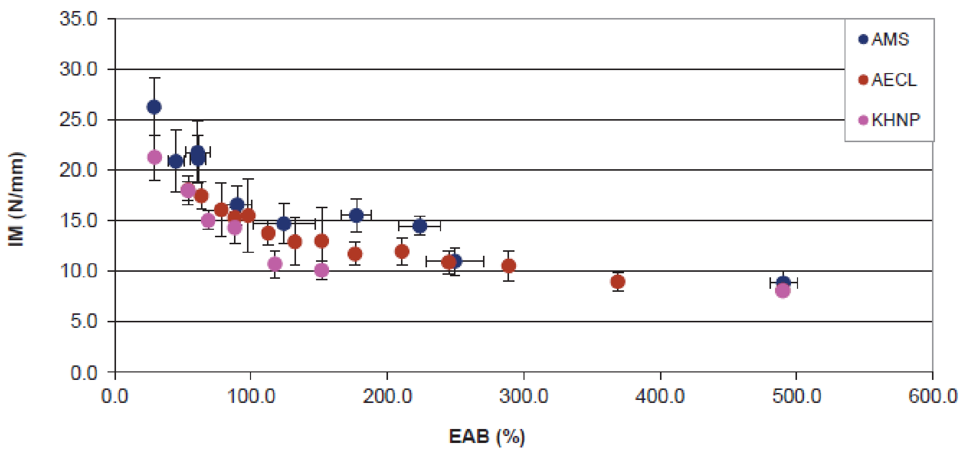


Figure 58. Cross-plot of indenter modulus versus elongation for a CSPE cable jacket material (10)

The other area for potential variations in measurements between laboratories is in the method used for analysis. This is particularly important for those methods where the data point recorded has to be extracted from a large data set, e.g. indenter modulus and thermal analysis methods. The indenter modulus is taken from the slope of the force - displacement curve (Figure 36), which is often non-linear. It is therefore important to define the force range to be used for analysis in the test method specification. Similarly, the oxidation induction methods (OIT and OITP) require extrapolation of the oxidation part of the test profile back to a baseline at a specified threshold level (Figure 59). How this should be done needs to be specified in the test method, particularly since the in-built analysis methods within the instruments vary between manufacturers. [Note in Figure 59, the exothermic oxidation reaction is shown as a negative heat flow, i.e. going down the graph].

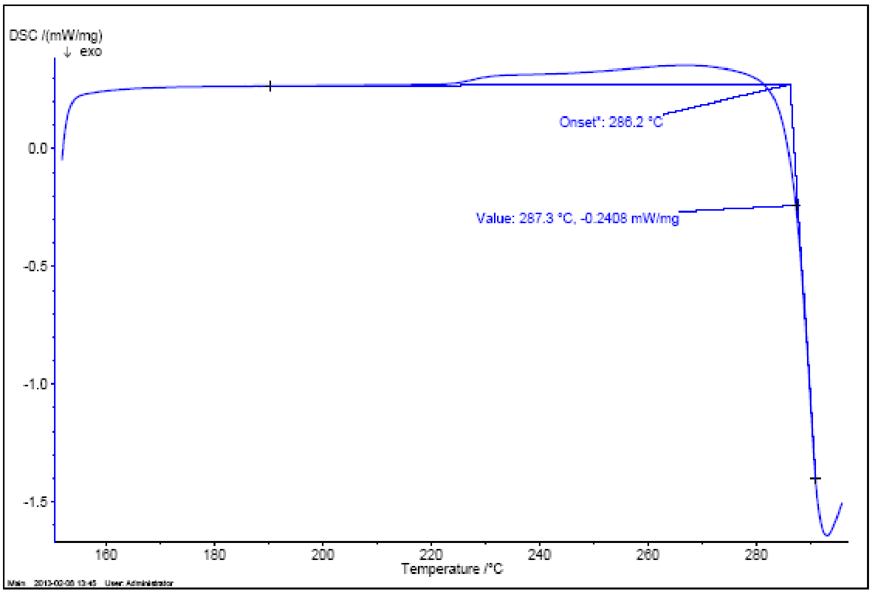


Figure 59. Example of an OITP plot showing method for calculating the oxidation temperature

5.7 ESTIMATION OF RESIDUAL LIFE

It is possible to make an estimation of the residual life of a component making use of condition monitoring measurements provided that sufficient background data is available. You need to know the shape of the ageing curve as a function of time for the main degradation parameter under conditions that are a good simulation of the service conditions. This might be obtained during the pre-ageing phase of environmental qualification, provided that the acceleration factors are small enough. In addition, the correlation curve between the chosen CM method and the main degradation parameter is needed.

If the CM method chosen is the main degradation parameter (e.g elongation for cables, compression set for seals), then an example of estimation of residual life is shown schematically in Figure 60. Let us assume that a measured value of 200% elongation has been determined after 25 years of operation in the NPP. According to the degradation curve, this is equivalent to 18 years under the conditions assumed in EQ, indicating that the material is ageing slower than predicted. The curve also shows that elongation would reach a limiting value that would fail the DBE after 30 years under EQ conditions. The estimated residual life L_R could then be described as

$$L_R = L_{op} / L_{eq} \cdot (L_f - L_{eq}) = 25/18 * (30\text{-}18) = 16.7 \text{ years}$$

where L_{op} is the actual time it has been in operation, L_{eq} is the equivalent age under EQ conditions, L_f is the age at failure under EQ conditions.

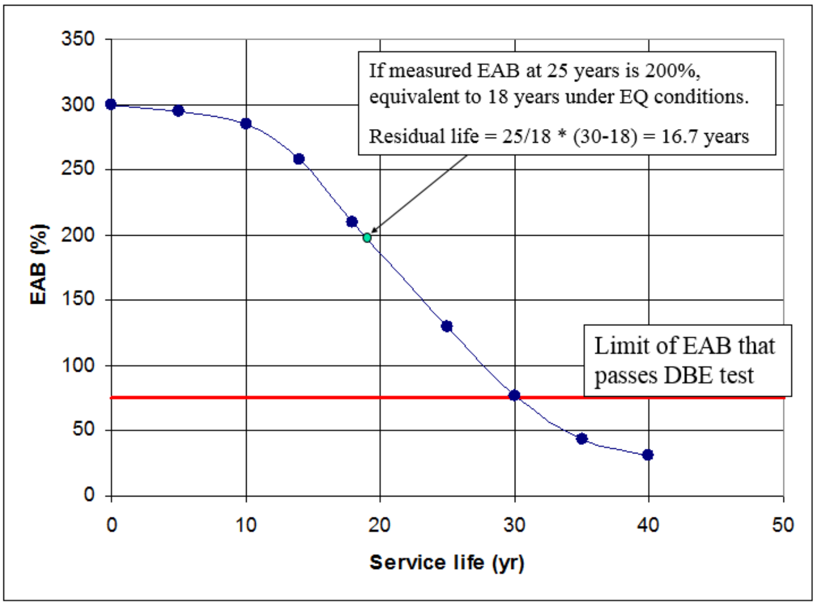


Figure 60. Degradation curve as function of service life (schematic)

If the CM method chosen is not the main degradation parameter, then a correlation curve between the CM parameter and the degradation parameter is required. This is shown schematically in Figure 61, using indenter modulus as the example. Let us assume that an indenter modulus of 16 N/m has been measured after 25 years in the NPP. The correlation curve can then be used to estimate the elongation value to which this is equivalent, 225%. This elongation value is then compared with the degradation curve as before, giving an equivalent age of the sample as 17 years. For this example, the estimated residual life would therefore be 19.1 years.

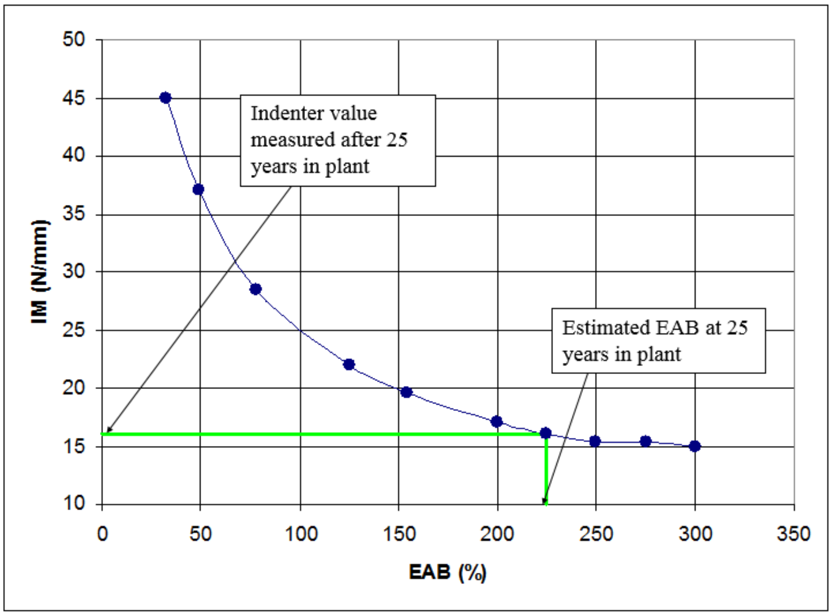


Figure 61. Using a CM correlation curve to estimate elongation

These schematic examples use a large change in CM parameter over the full range of elongation and assumes that the variation of the CM value is negligible. In reality, the variability of both the CM value and the degradation parameter need to be taken into account, e.g. using the standard deviation. If the change in CM value is quite small relative to the degradation parameter, then any estimate of residual life will be very approximate. However, you can use several different CM methods to get a better estimate of residual life.

If there is sufficient data available for a predictive model to be developed for the specific formulation being tested, then an analytical approach to estimating residual life can be made. This only possible for those materials with a suitable model but has been used successfully on some seal materials. Plots of the shift factor versus dose rate at different temperatures can be developed from the model and combined with a master curve for degradation to calculate the change in ageing parameter under the temperature and dose rate conditions in the NPP. This modelling approach is described in more detail in Appendix A.

5.8 ASSESSING USED SEALS

Seals are one type of polymeric component that are often replaced under a maintenance programme for equipment in a NPP. In some cases, degradation of the seal material will determine the maintenance interval for that equipment. It is therefore very useful to assess the state of seals when they are removed from equipment to determine whether the maintenance interval can be re-evaluated. For those cases where seals have failed, analysis of the seal will help to understand the reason for failure.

After removal of the seal from equipment, it is very useful to make a visual inspection of the seal to look for any signs of cuts, splits, wear marks or any surface deposits. The type of damage can be characteristic for different failure types e.g. extrusion failure will show up as a loss of material from the seal on the low-pressure side (Figure 62). Note that there can be a significant extrusion of seal material without loss of sealing, particularly at high temperatures, partly due to the differential thermal expansion between the seal material and its housing. Figure 61 illustrates this for an EPDM seal exposed to a high temperature transient.

Another type of failure with characteristic damage is spiral failure, usually seen in reciprocating seals where one part of the seal is sliding but the rest has rolled. This leaves characteristic spiral cuts or marks (Figure 63). This type of failure is also seen occasionally in static seals with a small cross-sectional area and a large internal diameter that have been twisted during assembly. Observation of this type of failure is indicative of a need to reassess the lubrication of reciprocating seals or the assembly procedures for static seals.

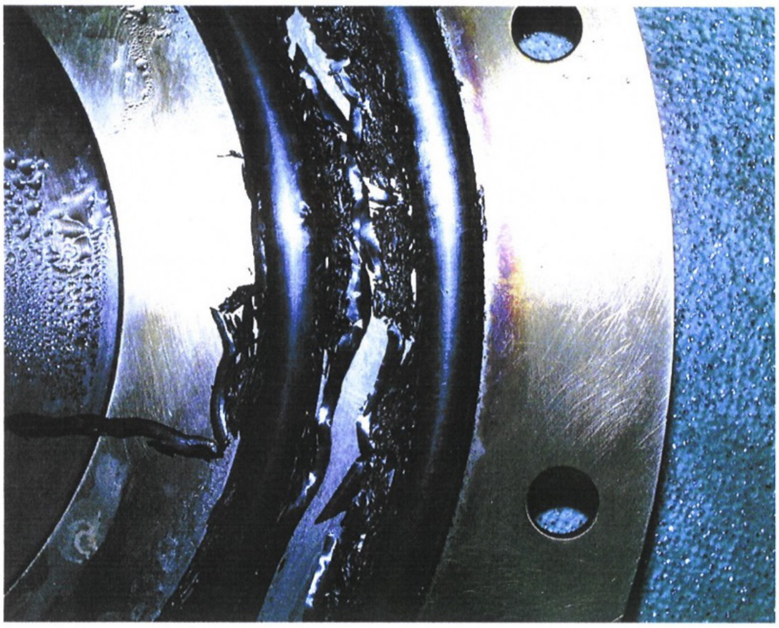


Figure 62. EPDM seals after a thermal transient, showing loss of material by extrusion (6)

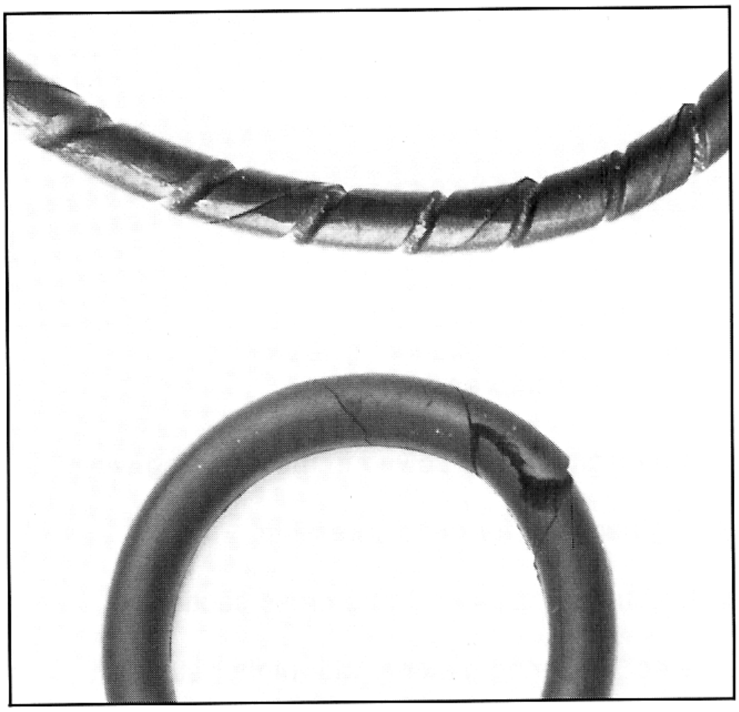


Figure 63. Spiral failure of reciprocating seals, showing characteristic marks and cuts

Wear failure of a seal usually shows as a flattening of the seal on one side and often occurs in dynamic seals where there is excessive friction (Figure 64). It can also occur in static seals exposed to fluctuating pressures. Compression set also shows as a flattening of the seal, but the seal is usually flattened on both sides (Figure 65).

It is always worth making an estimate of compression set on any seal that has been removed during maintenance as this is an important indicator of ageing. The measurement can be made with simple equipment and even if the time between removal and measurement is much longer than that required by standards, an estimate will still be useful. Static seals can continue to seal satisfactorily with set values of >90%, provided that there is no mechanical disturbance or large fluctuations in temperature or pressure. The change in compression set with ageing time tends to approximate to a power law, where the exponent is <1. So, for static seals with a compression set of <50%, a rough 'rule of thumb' is that the seal could withstand double the current exposure time. For equipment where seal ageing determines the maintenance interval, this could be very valuable information.

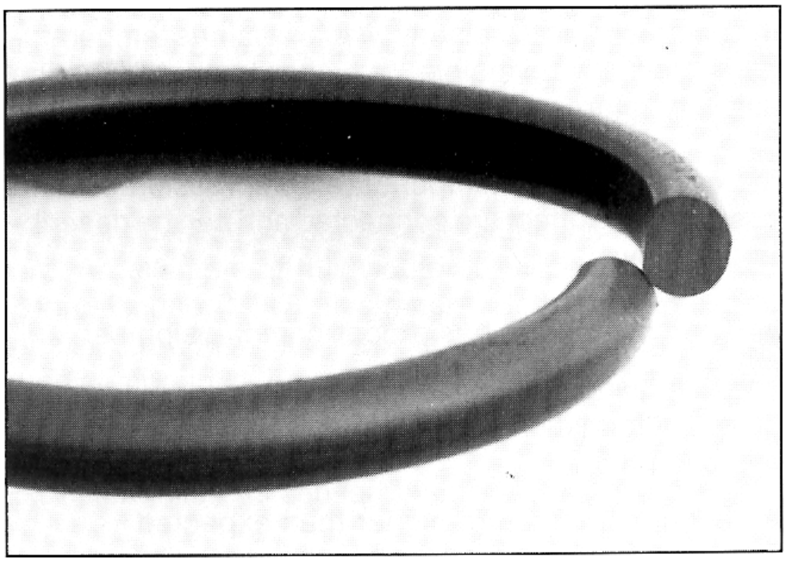


Figure 64. Wear failure of a dynamic seal -seen as a flattening on one side of the seal

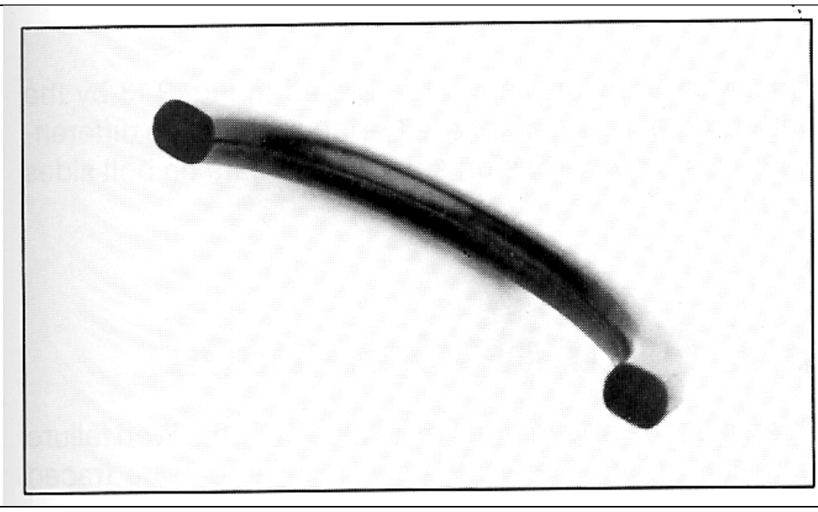


Figure 65. Characteristic shape of compression set in a static seal – flattened on both sides

The hardness of seals can also change with ageing, but you should be aware that thermally aged seals tend to be harder than radiation aged seals for the same level of compression set. Surface deposits should also be noted when examining used seals as these can be indicative of excessive temperatures during operation. Be particularly careful if any liquid or sticky deposits are observed on fluorocarbon (Viton) seals as these potentially could be hydrofluoric acid generated from degradation of the polymer at high temperature.

6 ‘Finger-printing’ of polymeric components

As has been pointed out in earlier sections, the degradation of polymeric components is strongly dependent on the specific formulation being used. If an ageing management programme is to be of practical use it is necessary to know which materials are being used. How do you know that the replacement seals you have purchased are the same as those used before? For the most important components, e.g. for use in safety-related equipment, you may need to check that exactly the same material has been supplied. This may require the use of a series of ‘finger-printing’ tests on newly procured components.

Details of polymer formulations are usually regarded as sensitive information by the manufacturers, so it is rarely possible to know exactly what is in the polymeric component. Some of the information that you would like to know could be –

- Base polymer type and structure
- Filler type and content
- Anti-oxidant type and concentration
- Pigments
- Plasticisers and other additives
- Degree of crystallinity (where appropriate)
- Macroscopic properties e.g. hardness, density

Some of these can be relatively straight forward to determine with standard tests but in many cases, you will need to make use of data that can be compared with earlier tests in a more qualitative approach.

The base polymer type can be determined using infrared spectroscopy (FTIR) or Raman spectroscopy. These are difficult to interpret in detail but do provide a ‘finger-print’ of the material, so are useful for comparison with earlier measurements. FTIR is the more common of the two techniques but only samples a few microns depth of the material and can be problematic with black materials. Raman spectroscopy samples a greater depth and is better suited to black materials. An example of an FTIR spectrum is shown in Figure 66 for an EVA cable jacket material. In principle, either of these techniques could also be used to identify additives but with multiple additives present it is difficult to quantify without a considerable amount of additional data.

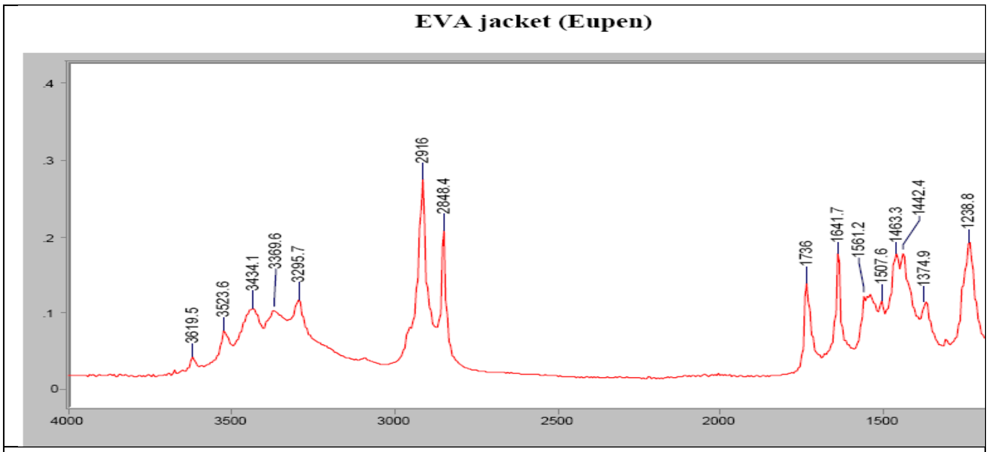


Figure 66. FTIR spectrum of an EVA cable jacket material

Thermal analysis using standard laboratory test equipment can provide quite a lot of information on a formulation. For those materials that are semi-crystalline e.g. XLPE and some EPR materials, an oxidation induction test using DSC will give the degree of crystallinity and an oxidation onset temperature that will be determined by the presence of anti-oxidants (Figure 67). Thermogravimetric analysis (TGA) can be used to determine the filler content since the residual weight at the end of the test is usually that of the filler alone, since most fillers are thermally inert. The derivative plot of TGA data (the rate of weight change as a function of temperature) is characteristic of the specific formulation and so also acts as a 'finger-print' for comparison with earlier tests (Figure 68).

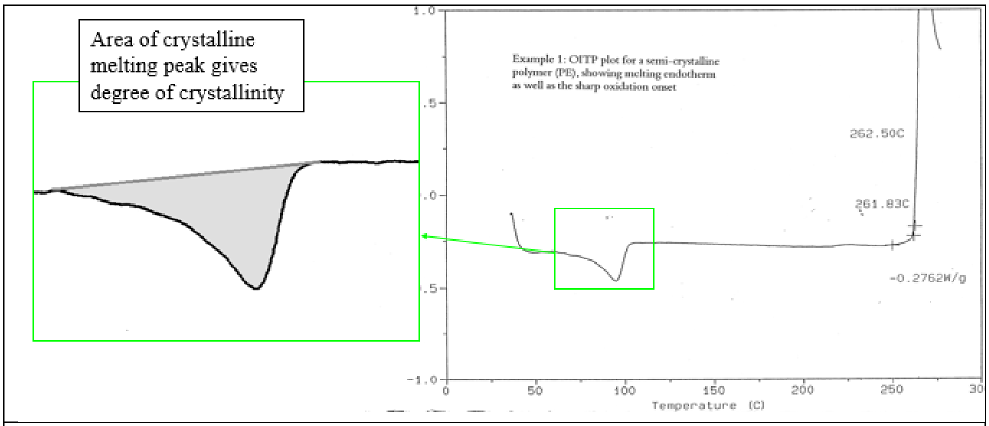


Figure 67. Using DSC to determine the degree of crystallinity and oxidation onset in an XLPE cable insulation material

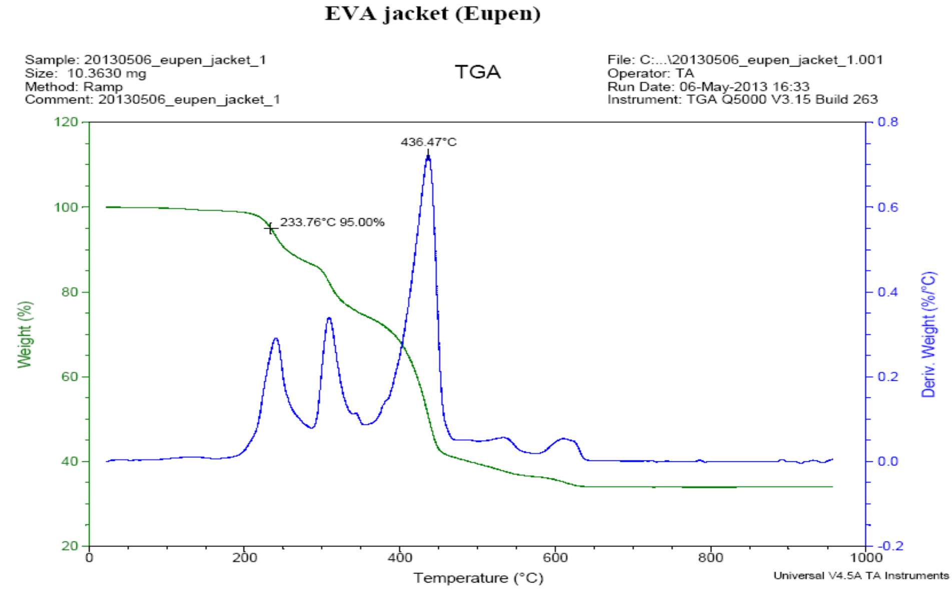


Figure 68. TGA (green) and differential TGA (blue) for an EVA cable jacket material

Measurements of hardness and density can also be used to confirm that the filler content is as expected since these properties are strongly dependent on the filler. Pigments are a bit more difficult to determine from laboratory tests but comparison with standard colour charts would give at least some indication as to whether the pigment type or content has been changed.

Since changes in formulation can significantly affect the ageing behaviour of polymeric components, it could also be appropriate to carry out a standardised ageing test for those components that are of most importance. This could be a compression set measurement after thermal ageing, say for 4 days at 120°C for example. You would need to have some background data as to the likely variability of measurement expected for the specific component, but this would be true for all of the 'finger-printing' methods.

Overall, there are a number of techniques that could be used for 'finger-printing' as part of the procurement process, particularly for those components which form part of safety-related equipment.

7 Recommendations for best practice

The development of an understanding of the behaviour of polymeric components in NPPs can be of practical use throughout the plant life cycle. With the right kind of guidelines and procedures you can move towards optimisation of lifetime for these components.

The initial procurement of components should have traceability and be based on a knowledge of which specific materials are appropriate. Quality control may need to include a number of ‘finger-printing’ tests to confirm that formulations have not been changed and ensure that acceptance criteria have been met.

In the long term, a move towards using a limited number of specific formulations can be effective. These would be materials whose ageing behaviour has been well characterised and are suitable for use in areas with worst-case environmental conditions but can also be used in mild environments. Ideally, enough ageing data will have been generated to enable lifetime prediction models to be developed. These models can then be used to optimise replacement schedules or assess residual life. Limiting the number of materials in use in plant has the added benefit of reducing the possibility of using the wrong material in equipment.

To support the aim of informed maintenance, knowledge of the actual environments in the plant are needed. These should be the actual temperatures and radiation dose rates at the positions where the components are being used, including information on the chemical environment and any mechanical stressors (e.g. vibration).

To help with the development of informed maintenance, it is very useful to assess the ageing of any component removed from the plant since these will have aged in real-time. Combined with appropriate end of life criteria, such assessments may enable longer replacement intervals to be justified for those equipment where the polymeric component is the limiting factor.

8 Summary

Polymeric components, such as seals, cable insulation and coatings, are widely used in nuclear power plants. An understanding of how these materials degrade under the environmental conditions in the plant is critical, both in terms of environmental qualification and in determining maintenance intervals. Accelerated ageing of these components (using higher temperatures and/or higher radiation dose rates) is widely used to determine their ageing behaviour.

The rate of degradation of polymeric materials is non-linear and is dependent on a number of degradation stressors. The most important stressors for the majority of polymeric components are temperature and radiation. There are a number of factors which need to be considered when carrying out accelerated ageing of polymeric components. These are –

- The specific formulation being used
- The value of the activation energy for thermal ageing
- Degradation mechanisms – both during accelerated ageing and during normal operational conditions
- Diffusion-limited oxidation in both thermal and radiation ageing
- The effects of dose rate and the synergy between temperature and dose rate
- Reverse temperature effects for semi-crystalline polymers (e.g. polyethylene-based materials such as XLPE and some EPRs)
- Post-radiation ageing

The general degradation behaviour of polymeric components is well understood but the ageing of specific polymers is strongly dependent on their formulation. The magnitude of these formulation effects has been demonstrated using examples from components in actual use in NPPs. The use of standardised formulations to overcome some of these concerns has been discussed.

Recommendations have been made as to how to put together appropriate accelerated ageing tests for different applications and the acceptance criteria that would be appropriate for different types of component.

Methods for assessing aged components have been discussed. These include condition monitoring methods, failure analysis and ‘finger-printing’ methods that could be used as part of an informed procurement procedure.

Appendices covering modelling methods for lifetime prediction (Appendix A) and improved qualification procedures (Appendix B) have been included for completeness. Finally, some recommendations for further reading have been provided (Appendix C) for those who wish to delve deeper into the background of the subject.

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Appendix A: Lifetime prediction methods

There are a number of reasons why predictive modelling of ageing is important. For those components which need to undergo environmental qualification (EQ) tests, there is a requirement for the component to continue to fulfil its safety function throughout the qualified life. To do this a simulation of the ageing under worst case environmental conditions must be carried out. This simulation uses accelerated thermal and radiation testing, so it is important to know whether the simulation is accurate. Modelling of the service conditions can be used to determine appropriate simulation conditions. Predictive modelling can also be used to optimise replacement schedules for components, using actual environmental conditions.

As has been discussed in section 2.5.3, the balance between thermal and radiation ageing is a complex function of the radiation dose rate and temperature (Figure 69). Any predictive model will need to take this into account, sometimes by modelling only a small but important part of this complex behaviour. The following sections describe the most developed of the modelling approaches that have been used for ageing of polymers and their limitations.

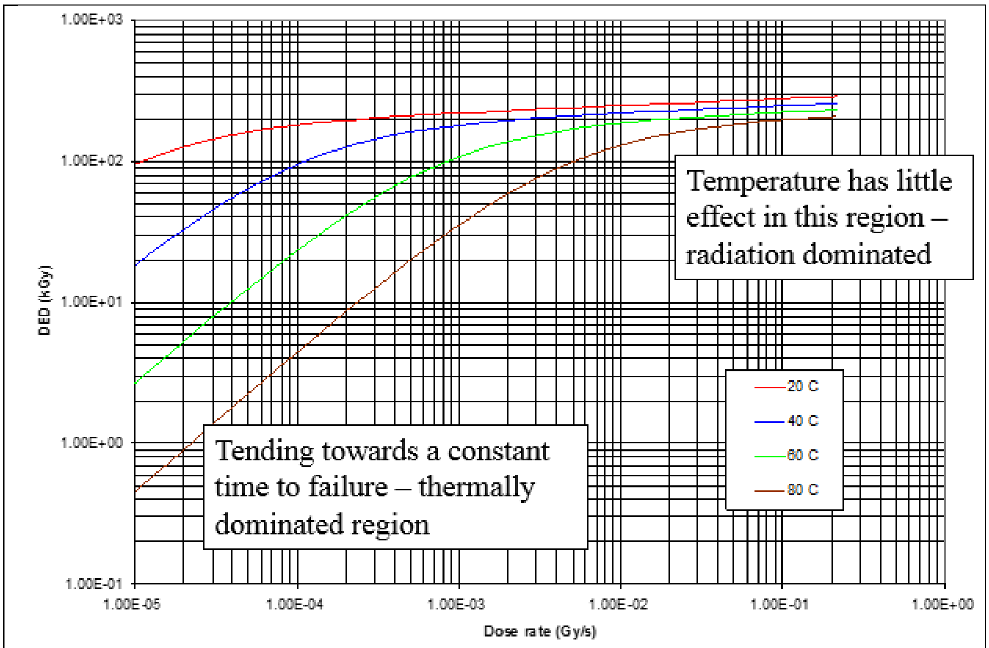

Figure 69. General trends for polymer ageing as a function of temperature and dose rate

There are four models currently in use that are sufficiently well developed to be of practical use in ageing management programmes.

- Arrhenius equation for thermal ageing
- Power law extrapolation for radiation ageing
- Time - temperature superposition for combined thermal and radiation ageing
- Dose - temperature superposition for combined thermal and radiation ageing

The three models used for lifetime prediction under radiation ageing conditions are described in detail in an IEC standard (16). A summary of each of the methods are given in the following sections.

Most of these approaches make use of the principle of superposition to some extent. Superposition makes use of all of the data generated during ageing tests. The data are plotted as a function of log (ageing time) to form a series of curves taken under different ageing conditions (Figure 70). These curves can be superposed to form a single curve by multiplying the time at each ageing condition by a factor known as the shift factor. This will be a function of temperature and/or dose rate and is usually shown as *a(T,D)*, where *T* is the ageing temperature and *D* is the dose rate. The single curve is referred to as a master curve at a reference temperature T_{ref} for which the shift factor is set at a value of 1.

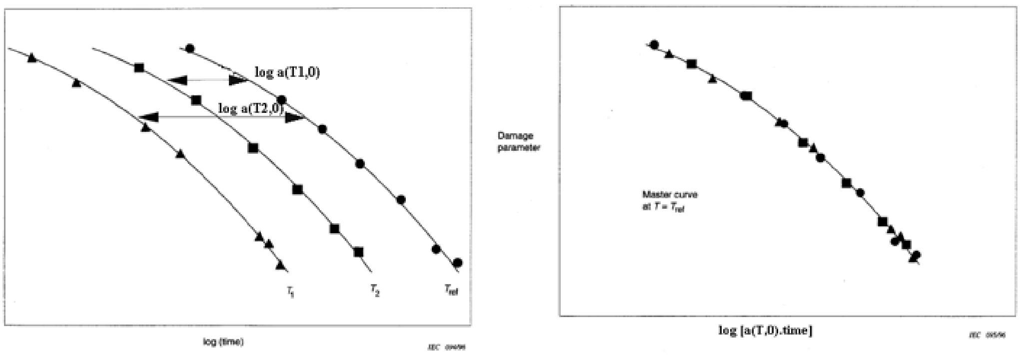

Figure 70. Principle of superposition approach

MODELLING THERMAL AGEING USING ARRHENIUS EQUATION

The Arrhenius equation has been used for many years to model thermal ageing behaviour in polymers and is described in detail in section 2.4. Provided that the assumptions underlying the equation are understood, then it is a very valuable tool. These assumptions are –

- A single degradation mechanism is in operation
- Degradation mechanisms are the same at the higher temperature used for accelerated ageing
- Activation energy E is constant, and the value is known for the specific polymer formulation being tested

When carrying out tests to determine the value of the activation energy for the specific polymer formulation of interest, it is important to check that these assumptions are valid.

To make best use of the data it is useful to make use of the superposition principle. By plotting the ageing parameter (e.g. elongation at break) as a function of log (ageing time), you should check that the curve shapes are the same (Figure 71). If the shapes are different, the plot against 1/T will also be non-linear (Figure 72), indicating a possible change in degradation mechanism. This can be checked by determining the time required to reach different degradation levels and comparing the slope of the plots of log(time) against 1/T for each level. If the degradation mechanism is the same over the temperature range tested, then these slopes should be the same. In some cases, you may not have enough data to interpolate to the degradation level required. If so, make use of the superposition principle and plot log (shift factor) against 1/T.

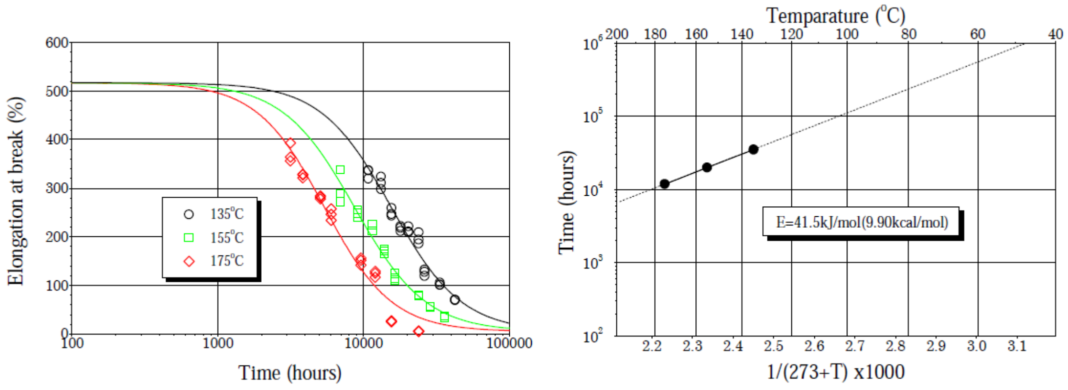

Figure 71 Example of parallel degradation curve shapes, giving a good Arrhenius plot – SiR insulation (8)

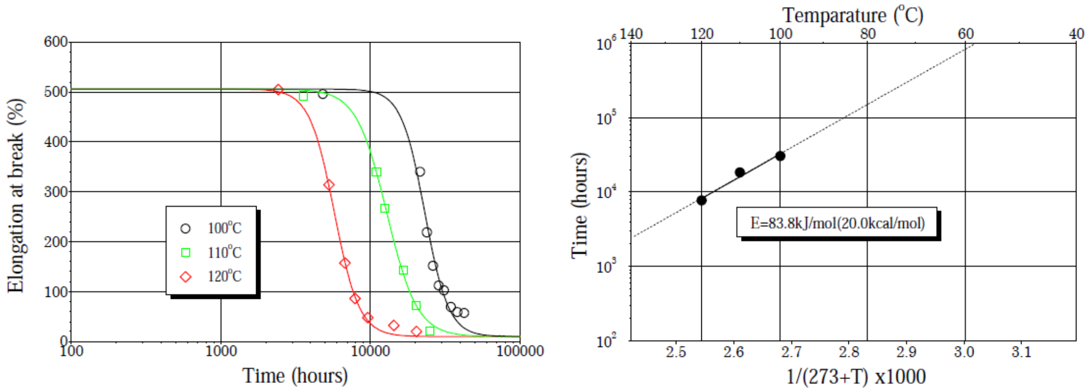

Figure 72 Example where curve shapes are different (FR-EPR), and Arrhenius plot indicates there may be a change in mechanism (8)

POWER LAW EXTRAPOLATION

This is the simplest modelling approach for radiation ageing at a single temperature and uses the concept of dose to equivalent damage (DED). This is the dose required to reach a specific degradation level, e.g. 80% compression set or 50% elongation. DED is determined at several different dose rates at a constant temperature and can be described by a simple power law –

$$DED = C \cdot D^x$$

Where D is the dose rate, the exponent x is < 1 and C is a constant for the specific material at the temperature tested.

DED values are extracted from the ageing data at each of the dose rates. Plots of log (DED) against log (dose rate) should be linear. The analysis process is shown schematically in Figure 73.

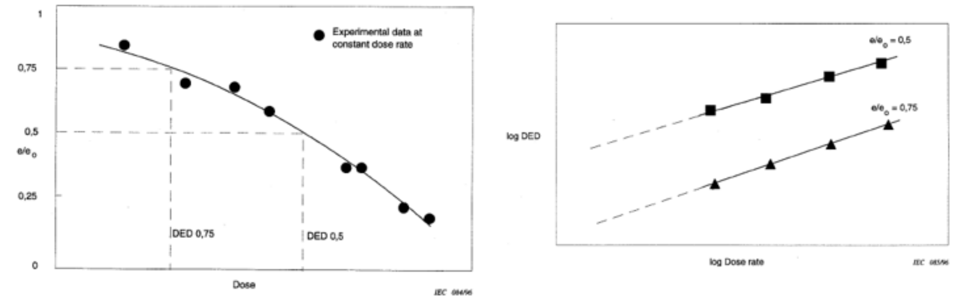

Figure 73. Using radiation ageing data to determine power law parameters (schematic)

For some polymers, this can be a very useful method. An example is shown in Figure 74 for a XLPE cable insulation aged at room temperature over a wide range of dose rates. But at low enough dose rates the method will break down, since the region dominated by thermal ageing will be reached (Figure 75), particularly for radiation ageing at higher temperatures.

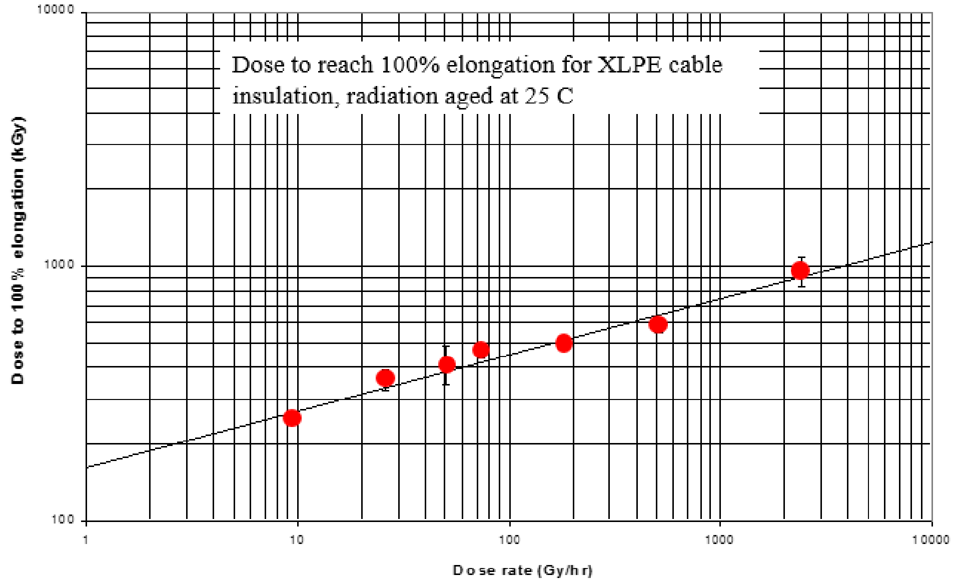

Figure 74. Dose required to reach 100% absolute elongation for a XLPE cable insulation (6)

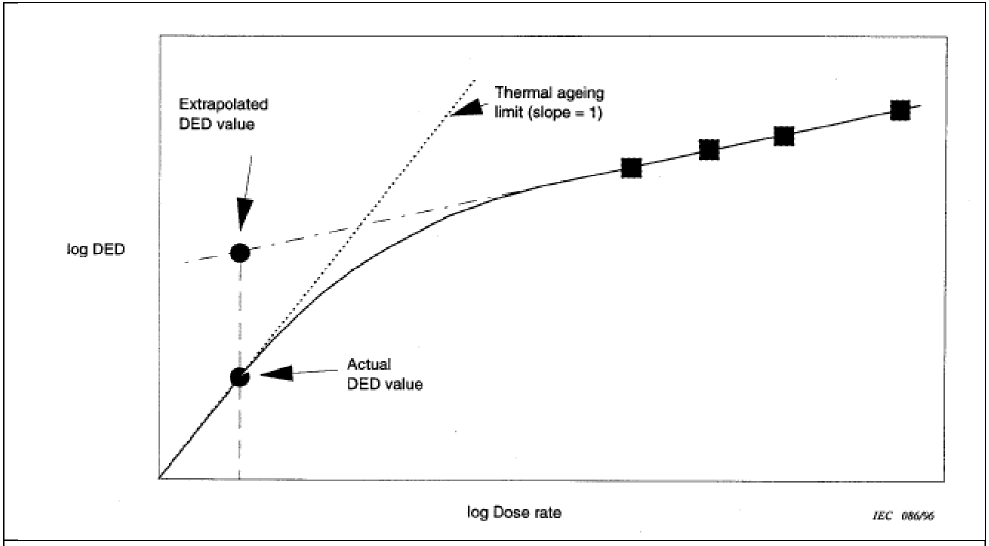

Figure 75. Limitations of the power law extrapolation method.

As a rule of thumb, extrapolation of more than an order of magnitude below the lowest dose rate tested should be regarded as very approximate. As can be seen in Figure 75, if the region dominated by thermal ageing is reached then the extrapolated estimate of DED is **not** conservative.

TIME – TEMPERATURE SUPERPOSITION

This model requires a large matrix of radiation ageing data at several different temperatures over a range of dose rates. These data are superposed to generate shift factors *a(T,D)* for each combination of temperature *T* and dose rate *D* tested. A semi-empirical model links these *a(T,D)* values to the temperature and dose rate, as shown in the equation below.

$$a(T,D\ ) = \exp\{-E/R\ (1/T - 1/T_{\mathrm{ref}})\}\ [1 + k \cdot D^{x} \cdot \exp\{Ex/R\ (1/T - 1/T_{\mathrm{ref}})\}]$$

where E is the activation energy, R is the gas constant, T is the test temperature (in degrees K), T_{ref} is the reference temperature, D is the dose rate, and k and x are empirical constants for the specific formulation tested.

Although this looks complicated, the equation simplifies to the Arrhenius equation for D=0

$$a(T,0) = \exp\{-E/R\ (1/T - 1/T_{\mathrm{ref}})\}$$

and at the reference temperature T_{ref} it simplifies to

$$a(T_{\mathrm{ref}}, D) = 1 + k \cdot D^{x}$$

An example of use of this model for an EPDM seal material is shown in Figure 76. Note that for this material, radiation ageing at elevated temperatures has little effect at the dose rates usually used for accelerated testing. But at lower dose rates, where the model predicts that thermal ageing will be significant, elevated temperature has a large effect on the ageing.

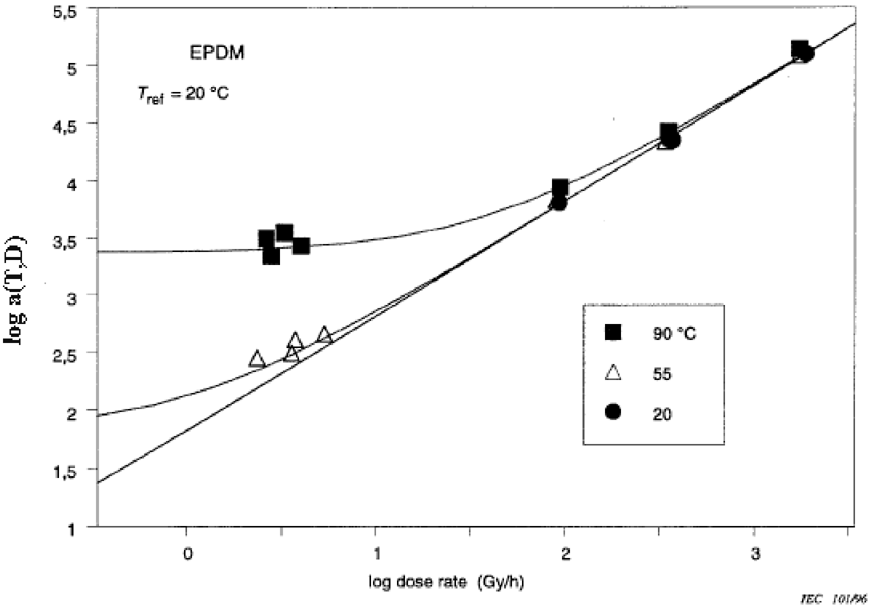

Figure 76. Fitting of shift factors to superposition model for an EPDM seal material (6)

In general, on a plot of log (shift factor) against log (dose rate), the slope of the line through the lowest temperature data will give the value of the exponent *x*. Where the slope is 1, the curves for different temperatures will also be close together. The parameter *k* is determined by the location of the curves along the dose rate axis. At low enough dose rates, the curves will tend to fixed values of *a(T,D)* which are determined by the activation energy.

Since this model is based on superposition of time-dependent data, it can only be applied if the curve shapes remain the same over the whole temperature and dose rate range tested. This will be true if there is a single degradation mechanism operating. The model has proven to be particularly useful for amorphous materials such as elastomeric seals but is less useful for polyolefins or semi-crystalline materials. An example is shown in Figure 77 for a XLPE cable insulation material, where the curve shapes are definitely not the same. For this polymer the model should not have been used and would give misleading predictions of lifetime under service conditions.

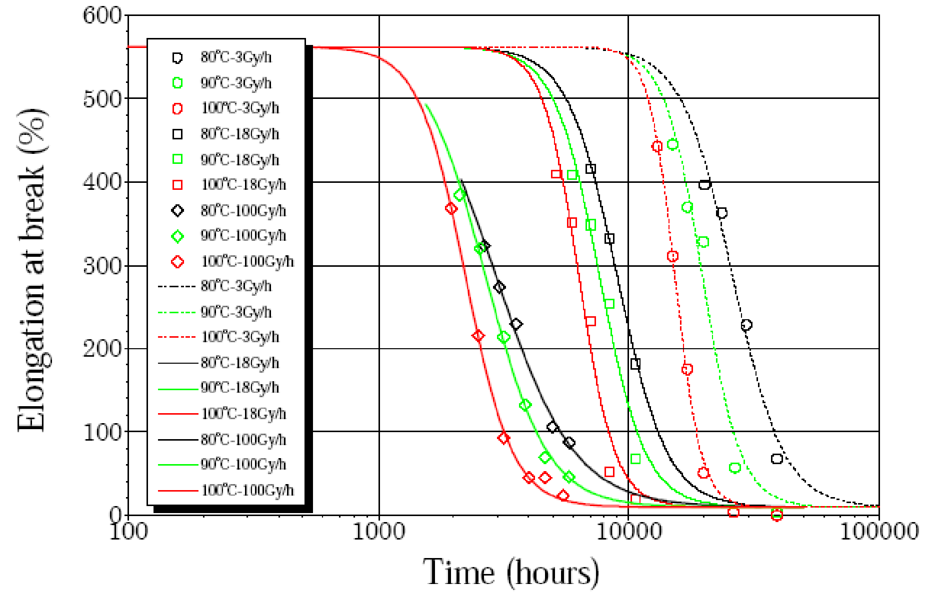

Figure 77. Ageing data for a FR-XLPE that show marked variation in curve shape (8)

DOSE – TEMPERATURE SUPERPOSITION

This model also requires a large matrix of data over a range of temperatures and dose rates. It also uses the superposition principle, but in this case DED values are superposed using a shift factor *a(T)* which is only dependent on temperature. These shift factors will usually be determined by the Arrhenius equation with an activation energy that is often (but not always) equal to that for thermal ageing.

The basic process for using the model is shown in Figure 78. DED values for each temperature and dose rate tested are extracted from the test data and plotted against log (dose rate). These DED values are superposed to form a single curve which will tend towards the thermal ageing curve at T_{ref} at low enough dose rates.

An example where this has been successfully applied to actual test data is shown in Figure 79 for a FR-EPR cable insulation material. The test data from radiation ageing at elevated temperature has been combined with thermal ageing data (the straight line in Figure 79) to determine the predicted behaviour of this material at 60ºC (the red curve).

The model has proved to be useful for a wide range of polymeric materials, including cable insulation and jacket compounds. It does require a large matrix of data but can be used in some cases where the time-dependent superposition does not work. The model does not work for those materials that show the reverse temperature effect but its use on such materials will highlight that the effect exists. Figure 80 illustrates this for a XLPO cable insulation material where the DED data have been superposed to give a predicted curve at 50 ºC. In this case, the radiation ageing data for temperatures >60ºC superpose well (open squares) but using the same activation energy for lower temperatures shows that they are degrading much faster (solid squares, with temperature values alongside). For this material, the ageing at low temperatures would be significantly under-estimated.

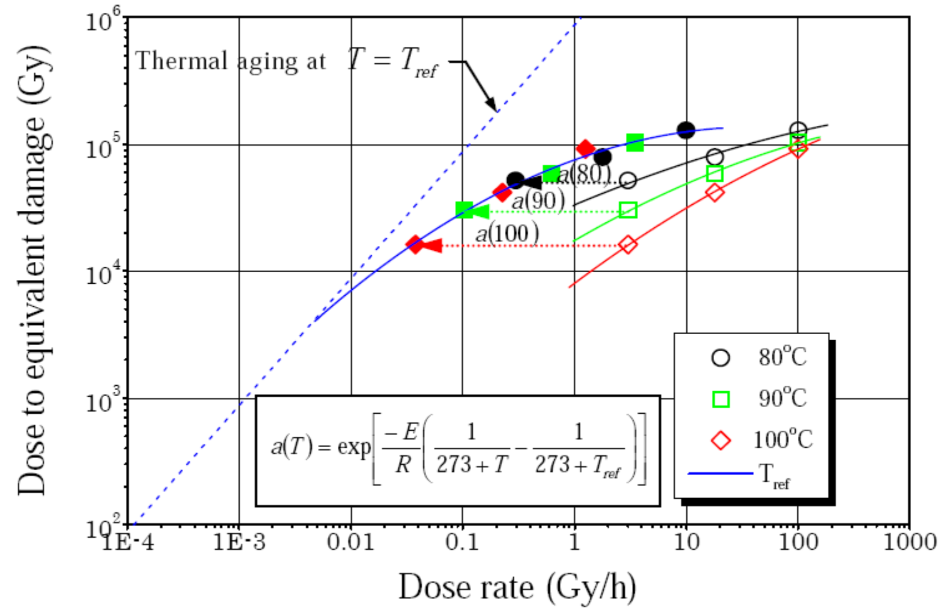

Figure 78. Using superposition of DED values (schematic)

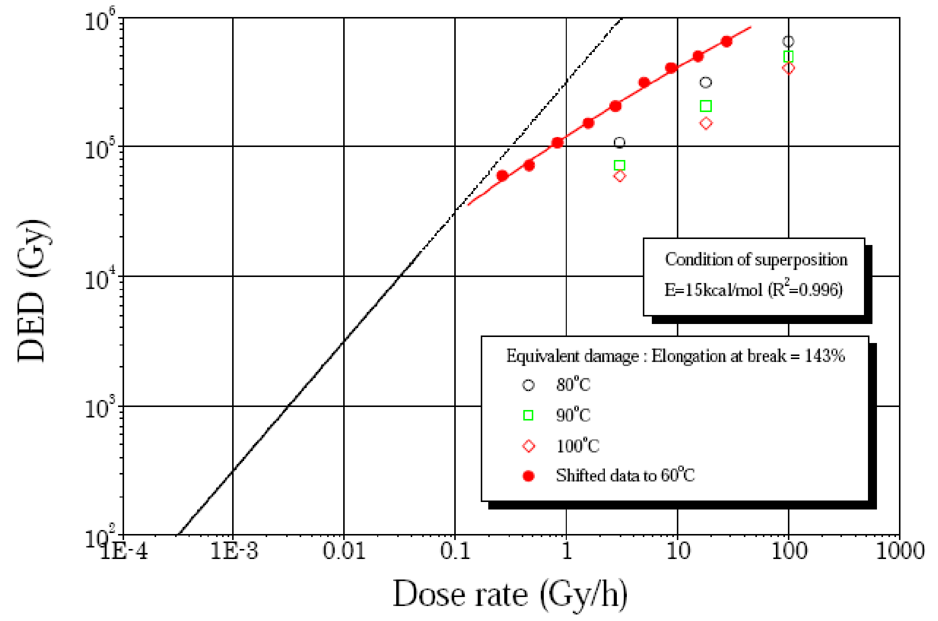

Figure 79. Superposition of DED data for a FR-EPR cable insulation (8)

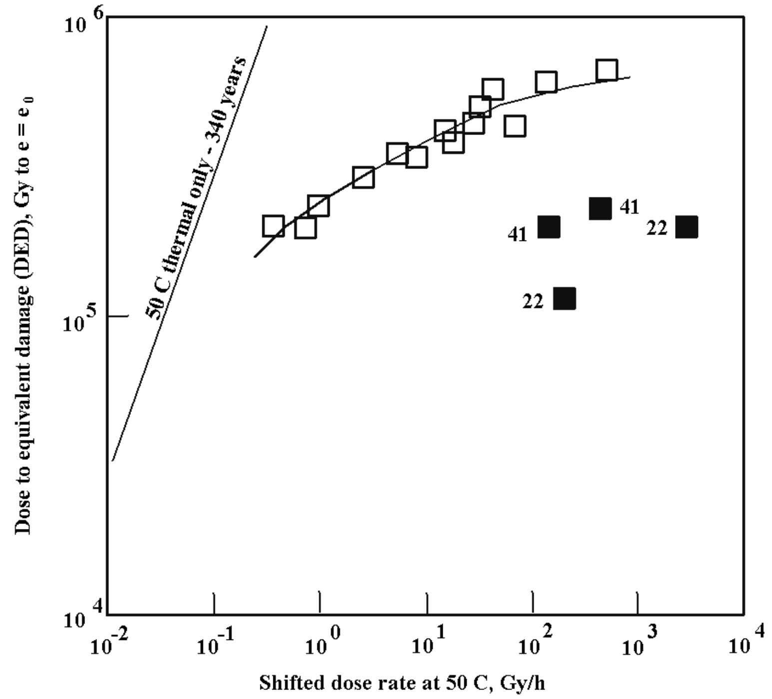

Figure 80. Example of reverse temperature effect in a XLPO cable insulation (13)

Identifying the presence of the reverse temperature effect will only be possible if there are some radiation ageing data available at lower temperatures. Figure 81 is an example where the effect was missed because all of the data were obtained at elevated temperature. This example was for a XLPE cable insulation which would be expected to be semi-crystalline and so liable to the reverse temperature effect, but no data were obtained at temperatures below the crystalline melting point.

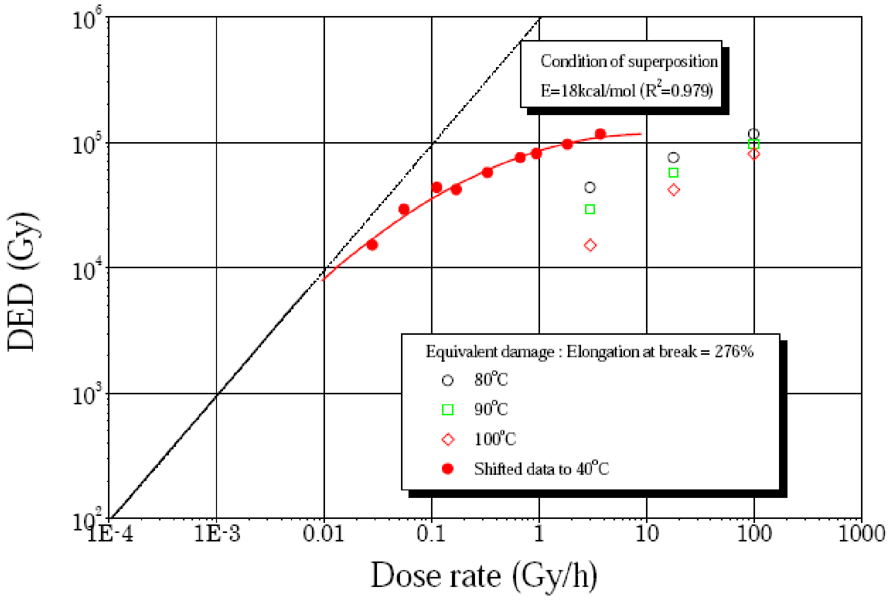

Figure 81. Superposition of DED data for a XLPE cable insulation (8)

SUMMARY

For all of the predictive modelling methods it is essential to understand the underlying assumptions and the limitations of each method.

For thermal ageing, the Arrhenius equation is widely used and has proved to be very useful provided that an accurate value of the activation energy is used, and the ageing temperature is kept as low as is practicable.

The power law extrapolation method can be applied to many different polymers and is currently the only way to predict the behaviour of those materials that show a reverse temperature effect.

The two superposition models have both proved to be useful but do require large data sets which tend to limit their use to the most important materials. Superposition of time-dependent data is particularly useful for elastomeric materials, such as seals. Superposition of DED data is more useful for the polymer types used in cable insulation and jacket materials and can identify the presence of reverse temperature effects.

Appendix B: Improved EQ methods

The traditional approach to environmental qualification (EQ) has been based on general standards (such as IEEE 323, IEC 60780), National standards or equipment-specific standards (such as IEEE 383 for cables). These EQ tests are intended to demonstrate that the equipment can continue to fulfil its function throughout the life of the plant, including after a design basis accident, for those equipment that are safety-related. There are usually 3 basic stages to the EQ process. These are –

- Pre-ageing to simulate in-service ageing, typically for 40 or 60 years for long-lived equipment
- Simulation of accident conditions e.g. loss of coolant accident (LOCA)
- Simulation of post-accident conditions, for those equipment required to operate post-accident

The pre-ageing stage usually consists of thermal ageing at elevated temperature to simulate the worst case environmental conditions for the equipment in the NPP. This is usually followed by radiation ageing at a high dose rate for the total dose expected during the lifetime of the plant. This service dose is often assumed to be negligible compared to the accident dose and so is often combined with the accident radiation dose for practical reasons. The accident conditions are usually simulated using a steam profile that may include a chemical spray. The profile is usually specific to the type of NPP in which the equipment is to be installed.

Functional tests are usually carried out during the accident simulation phase but typically no other component properties are measured during the EQ test. These functional properties (e.g. electrical tests for cables, leakage for seals) determine whether or not the equipment has passed the EQ test.

AREAS OF CONCERN IN TRADITIONAL EQ

There are a number of areas of concern in this traditional approach to EQ, particularly during the pre-ageing stage. The main areas of concern are –

- The use of high acceleration factors that do not take into account changes in degradation mechanisms, dose rate effects, diffusion-limited oxidation
- The use of sequential testing – is thermal followed by radiation more conservative than radiation followed by thermal ageing? Simultaneous thermal and radiation ageing may be the worst case
- Is the assumption correct that the operational dose is negligible compared with the accident dose? This can be strongly dependent on dose rate effects since operational dose is usually very low dose rate whereas accident dose is very high dose rate.
- The value of activation energy used for the thermal ageing stage needs to be appropriate to the specific formulation being tested
- Worst case environmental conditions in service may not be the highest temperature for those materials that show a reverse temperature effect under irradiation

- Simulation of accident conditions is typically carried out in a closed chamber which may have limited oxygen present, which could reduce the degradation observed during the steam profile
- Margins are usually included in the test procedures. These margins are intended to cover manufacturing tolerances when testing only a limited number of samples, but they are often used to account for all of the other uncertainties.

CONDITION – BASED QUALIFICATION

Determination of a qualified life using the traditional EQ approach is subject to many uncertainties, as indicated above. One way to overcome at least some of these uncertainties is to use condition-based qualification (CBQ) rather than a qualified life. This is based on knowing the condition of a component that would survive the accident condition, i.e. a qualified condition. The condition of the component in the NPP can then be compared with the qualified condition to determine whether it is still acceptable.

This type of condition-based qualification requires a different approach to the EQ test, particularly during pre-ageing (17). It is necessary to know how the condition changes with ageing during the pre-ageing stage, which requires additional measurements to be made. The pre-ageing should be carried out using as low acceleration factors as is practicable and using the worst-case sequential testing, or simultaneous ageing (if this is possible). The basic principle is shown schematically in Figure 82.

Note that the pre-ageing has to be carried out in stages with a condition indicator being measured after each stage. This indicator must be a property that trends with ageing but is not necessarily a functional property. For example, it could be compression set for a seal, but could be any suitable mechanical, electrical or chemical property that is known to trend with ageing. The qualified condition would be the condition of the component at the point before it passes the accident test, with a margin to allow for measurement variations for the condition indicator.

[Note that it is the functional test carried out during the accident stage of EQ that determines whether the component has passed the EQ test, **not** the condition indicators.]

The same concept can be used for components in mild environments that do not require an accident test. In this case, the qualified condition is determined by the minimum acceptable value of a functional property. The condition indicator would need to be correlated to the functional property e.g. for seals it might be a compression set value of 75%.

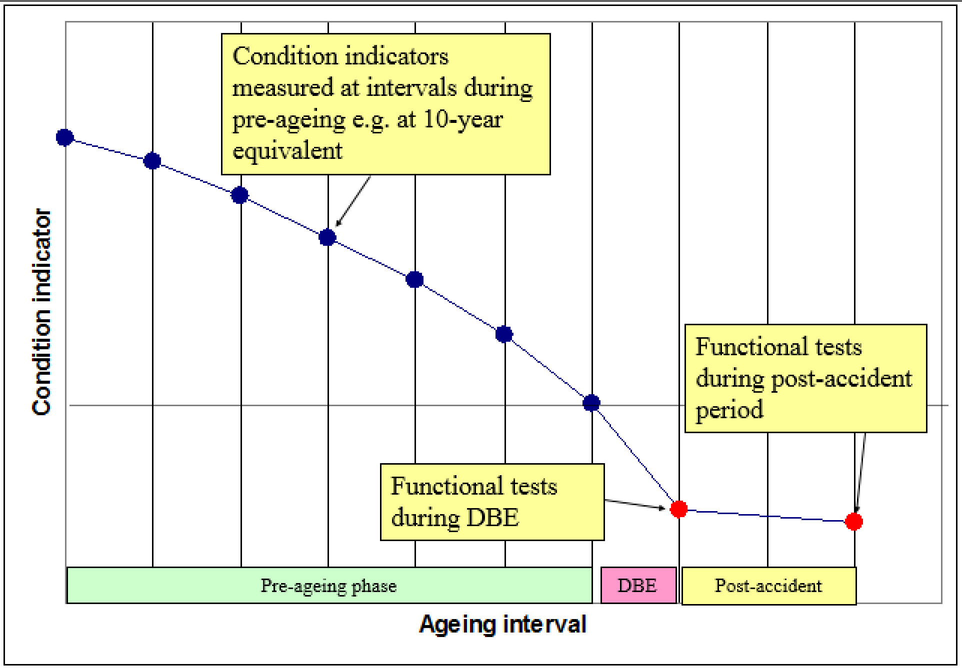

Figure 82. Basic principle for condition-based qualification

USE OF DEPOSITS IN AGEING MANAGEMENT

The use of condition monitoring methods as part of an ageing management programme based on qualified condition can be problematic. In many NPPs, it is not possible to carry out such tests on actual components, either because of access problems or the concern that the component might be damaged during the measurement of a condition indicator. This is a particular problem for some of the condition monitoring methods used for cable materials that require samples to be removed for testing.

One way around this that is particularly valuable is the use of deposits. These are sacrificial samples that age under real-time conditions in the plant and are specifically for taking condition monitoring measurements at intervals, e.g. during outages. Because the samples are ageing in real-time, the uncertainties associated with accelerated ageing tests are avoided. Deposits can be placed in a range of locations, including areas with higher temperatures and/or dose rates to give accelerated ageing with very low acceleration factors. For those materials which may show reverse temperature effects, the locations should include areas where radiation is present, but the temperature is low.

The use of deposits is particularly advantageous for cable materials and small electrical equipment but can also be used in principle for seal materials. If seals are to be included in a deposit, they need to be placed in holders that provide the correct level of compression, as they need to be aged in a compressed state.

In a new NPP, deposits can be installed before commissioning. This is the most cost effective and efficient time to set them up. In older NPPs, deposits can still be installed but the samples will need to be pre-aged to simulate the age of the NPP. This should be done using low acceleration factors to minimise uncertainties.

An example of the use of cable deposits in a new NPP is shown in Figure 83 and Figure 84. This is for the Temelin plant where a range of cable samples have been installed in various locations around the plant. It is important that the actual dose rate and temperature are known for each of the deposit locations (Figure 84). The samples in these deposits will be used for measurement of electrical properties, elongation, OIT and density and additional cable samples have been included for future testing e.g. re-qualification, life extension.

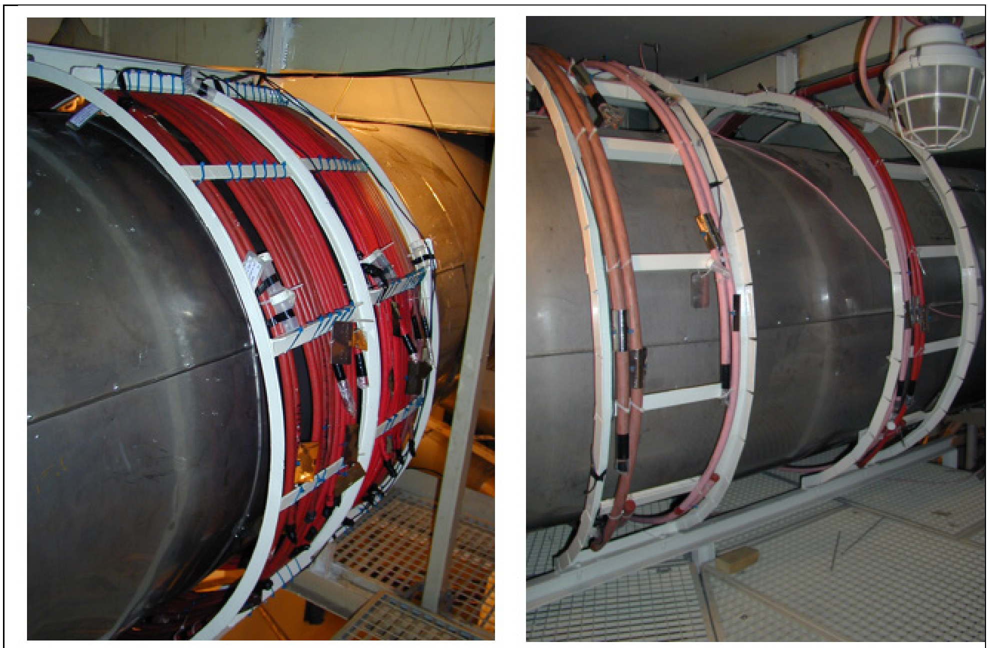

Figure 83. Cable deposit installed around the primary loop line in Temelin (photo courtesy of Vit Placek, UJV Rez)

An example of deposits installed in older plant is that for Dukovany which started operation in 1985 (Figure 85). The cable deposits were installed in 2005 after ageing at very low acceleration factors for 2.5 years. The laboratory ageing was carried out at 2.4 Gy/h at 70ºC to simulate 20 years of operation.

A different approach was used at the Beznau plant in Switzerland. In this case their regulator required a minimum elongation value of 50% absolute for the cable materials. Rather than installing whole cables for these tests, pre-prepared elongation samples were installed for testing (Figure 86). These samples were pre-aged for 2 years in the laboratory and installed in 1998 together with pre-aged whole cable samples. The elongation samples are removed every 5 years for testing. Once the elongation decreases to 50%, the whole cable samples will be removed for LOCA testing and cable replacement scheduled if necessary.

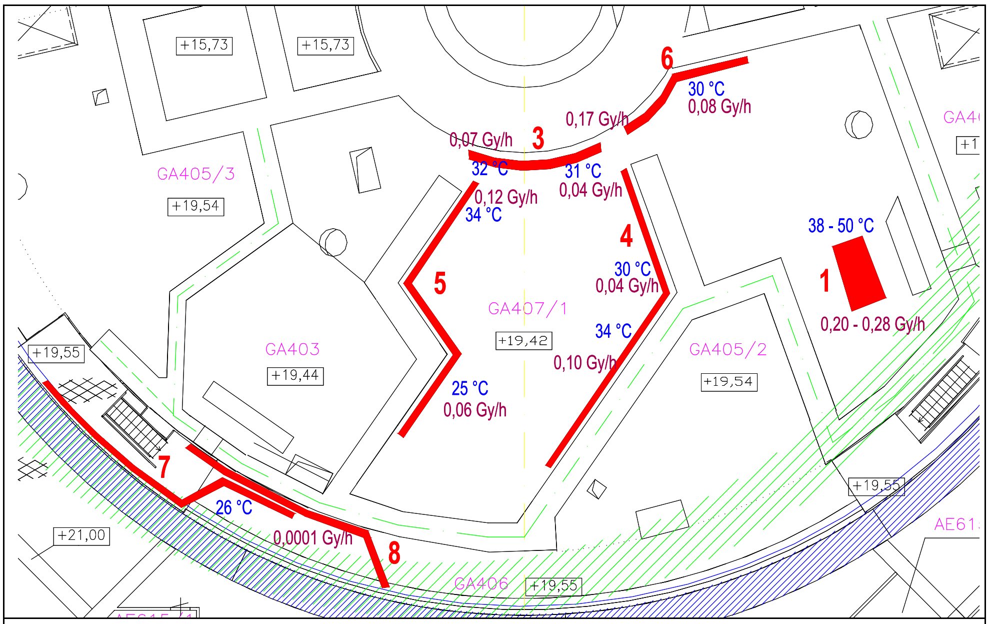

Figure 84. Cable deposits installed in various locations around the NPP (courtesy of Vit Placek, UJV Rez)

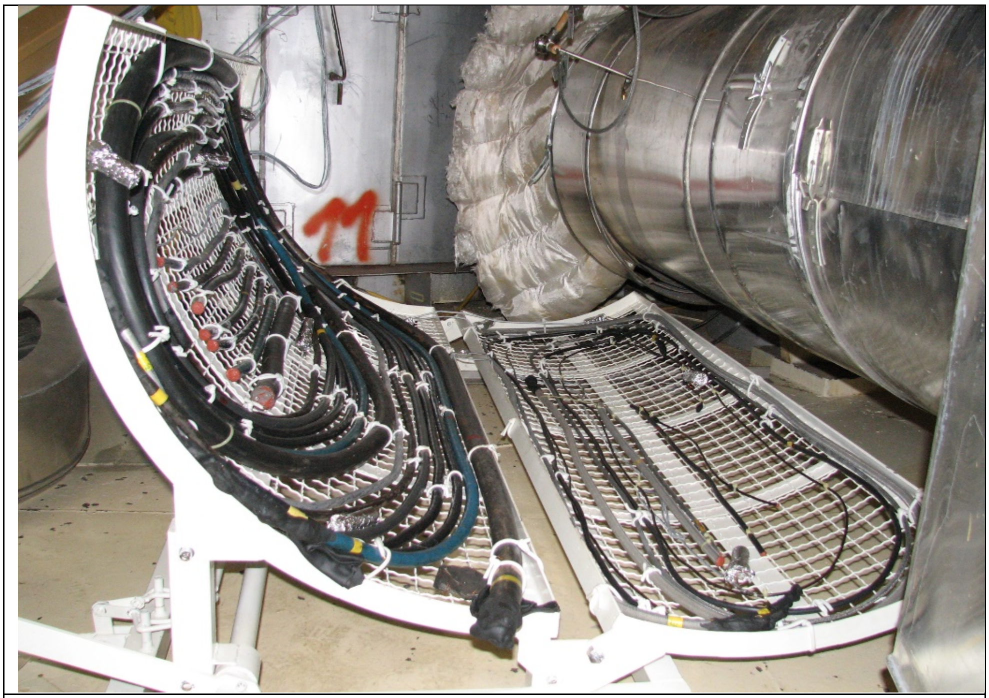

Figure 85. Cable deposit at Dukovany after pre-ageing (photo courtesy of Vit Placek, UJV Rez)

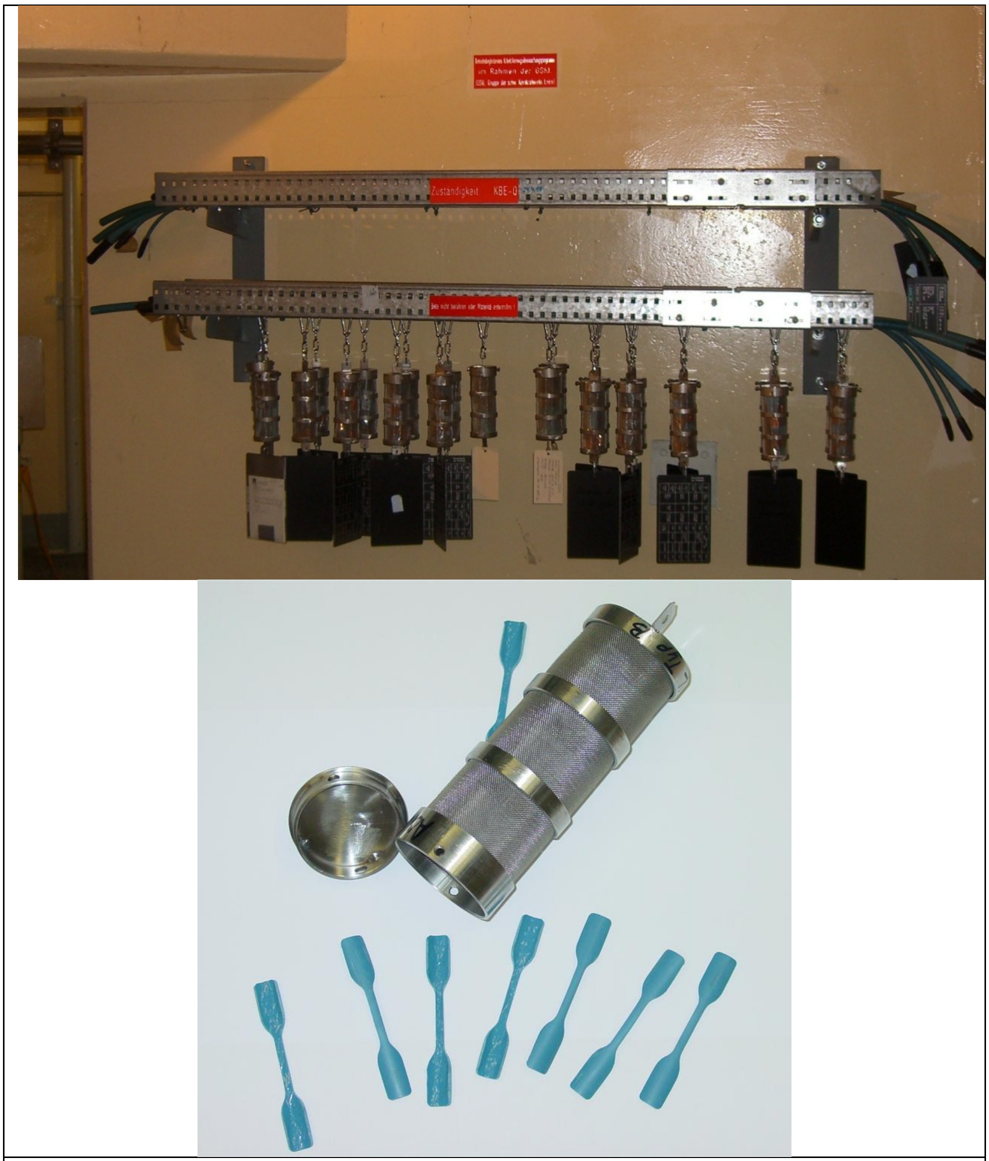

Figure 86. Cable deposit at Beznau NPP – mesh cages containing prepared elongation test samples plus whole cable samples for future testing (photo courtesy of Kurt Thoma, Beznau NPP)

Deposits are a practical way of approaching the condition monitoring aspect of ageing management. There are many ways in which they can be used, dependent on the specific requirements of the NPP. Ideally, deposits should be installed in new plant before commissioning, with samples of all of the types of cable in use. It is still possible to use deposits in older plant, but the pre-ageing needs to be done with low acceleration factors. Ageing over a period of about 2 years is a typical timescale to keep acceleration factors sufficiently low.

Appendix C: Recommendations for further reading

There are a number of reports referenced in the main body of the text which are worth examining in greater depth. These can be used to get a further understanding of the research work and practical experience with ageing of polymeric components that has been carried out in recent years. All of these reports are freely available on-line.

The 3 IAEA reports in the reference list will give you a background of how the current approaches to ageing management of polymeric cable materials have developed. The first report (3) from 2000 gives a general description of mechanisms and areas of concern and a preliminary assessment of possible approaches to ageing management. The second report (17) from 2012 specifically deals with improvements to the qualification process (as summarised in Appendix B). The third report (10) is specifically on methods for condition monitoring of cable ageing. Although all 3 reports deal only with cables, much of the material is equally applicable to other polymeric components.

IAEA-TECDOC-1188 (2 volumes)	https://www-pub.iaea.org/MTCD/publications/PDF/te_1188v1_prn.pdf https://www-pub.iaea.org/MTCD/publications/PDF/te_1188v2_prn.pdf
IAEA-NP-T-3.6	https://www-pub.iaea.org/MTCD/Publications/PDF/Pub1554_web.pdf
IAEA-TECDOC-1825	https://www-pub.iaea.org/MTCD/Publications/PDF/TE-1825web.pdf

There are 2 major reports from the Sandia Laboratories in USA, summarising the extensive research work that has been carried out there over many decades (1) (13). The work primarily covers laboratory studies of the behaviour of cable materials under both thermal and radiation ageing, with many examples of their behaviour and modelling. This body of work has been instrumental in the development of an understanding of how polymers degrade under NPP conditions.

SAND 2010-7266	http://prod.sandia.gov/techlib/access-control.cgi/2010/107266.pdf
EPRI-1011873	https://www.epri.com/#/pages/product/1011873/

The report on the large Japanese study on thermal and radiation ageing of cable materials (8) is particularly valuable for the tabulation of many of the data determined during their test programme. This included some LOCA testing of their cables as well as long term ageing data.

DEGRADATION OF POLYMERIC COMPONENTS IN NUCLEAR POWER APPLICATIONS

Aging of polymeric materials is very complex, especially for nuclear applications where radiation is involved. This report is designed as an educational material for polymer engineers at nuclear power plants. The aim is to give an applied support for maintenance and plant development involving polymeric materials at the nuclear power plants.

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