Seminar on “Degradation of polymers in NPPs”
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Contents of the seminar

- Why is ageing of polymeric components of concern?
  - Basics of polymers & their degradation mechanisms
  - Areas of concern for components in NPPs
- Assessment of aged polymeric components
  - Condition monitoring methods
  - Fingerprinting of polymeric materials
  - Failure analysis of seals & special problem areas
- Lifetime prediction methods

The need for ageing management - why is ageing of polymeric components of concern?

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Why should we be interested in ageing of polymers in nuclear plant?

- Seals
  - Major equipment (e.g. valves, actuators) contain seals or gaskets
  - In AGRs, seals form part of the pressure boundary
- Cables
  - Typical NPP contains >1000 km of electrical cables
  - Cables provide the vital link for power, control and instrumentation for safety systems in a NPP. If the cable fails, the safety system cannot function
- Polymeric coatings used in many areas
- Seals, cable insulation and jacket materials, and many coatings are all polymeric.
  - Seals can often be replaced during routine maintenance of equipment, but cables need to operate for lifetime of plant
  - Cables are passive components, so maintenance is not an option. Replacement is expensive, and removal may be impractical

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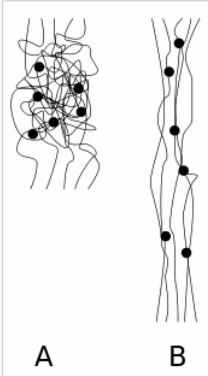
Polymers – what are they?

- Macroscopic properties determined by long chain structure
- Made up of long molecular chains, usually C, H and O based
- Other elements present can include S, Cl, F, N, Si
- Some crystallisation can occur in the simpler polymers (eg. PE) – this has implications for degradation



(A) is an unstressed polymer; (B) is the same polymer under stress. When the stress is removed, it will return to the A configuration. (The dots represent cross-links)

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Polymers commonly in use in NPPs

- Cable insulation
  - XLPE
  - EPR/EPDM
  - SiR
  - *PVC*
  - *PPO (Noryl)*
  - *ETFE (Tefzel)*
  - *PEEK*
- Cable jackets
  - EPR/EPDM
  - CSPE (Hypalon)
  - EVA
  - SiR
- Seals
  - EPR/EPDM
  - Nitrile rubbers
  - Fluoropolymers (eg. Viton)
  - SiR
- Coatings
  - Epoxy resins
  - Rubbers

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Basic structure of some polymer chains

- Polyethylene (simplest polymer)
  - CH2 - CH2 - CH2 - CH2 –
- Polypropylene
  - CH2 – CH - CH2 –
  |
  CH3
- Nitrile rubber
  - CH2 – CH = CH - CH2 – CH - CH2 -
  |
  CN
- Silicone rubber
  CH3 CH3
  | |
  - Si – O – Si – O -
  | |
  CH3 CH3
- Fluoroelastomer
  - CF – CF2 – CH2 – CF2 -
  |
  CF3

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What is in a polymeric component?

- In a commercial polymer formulation the polymer content can be relatively small, with fillers, additives, extenders, plasticisers
- Polymer properties can be varied by changing proportions of fillers, plasticisers etc.
- Formulations are specific to individual manufacturers and can vary over time
- A limited number of polymer types are in regular use in NPPs, **but** the properties and degradation behaviour are strongly dependent on the formulation used (particularly for radiation degradation)

e.g. Typical elastomer formulation

Base polymer	100 parts
Sulphur	2
Accelerator	1.5
Zinc oxide	5
Stearic acid	50
Carbon black	50
Plasticiser	10
Antioxidant	1

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Main degradation mechanisms

- Oxidative degradation, both scission and crosslinking (in most polymers)
- Radiation cross-linking
- Plasticiser loss (particularly in thermal ageing of PVC)
- Dehydrochlorination and defluorination (in halogenated polymers)

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Oxidative degradation – main mechanism for most polymers

Initiation

$$RH \rightarrow R\bullet$$

Propagation

$$R\bullet + O_2 \rightarrow RO_2\bullet$$
$$RO_2\bullet + RH \rightarrow RO_2H + R\bullet$$
$$RO_2H \rightarrow RO\bullet + OH\bullet$$
$$RO\bullet \rightarrow R\bullet + \text{-CO-}$$

Termination

$$2R\bullet \rightarrow RR$$
$$2RO_2\bullet \rightarrow RO_2R + O_2$$
$$\text{or} \quad ROH + \text{-CO-} + O_2$$

The kinetics of oxidative degradation are complex, with multistage reactions that can end in either scission of the long chains or cross-linking between chains

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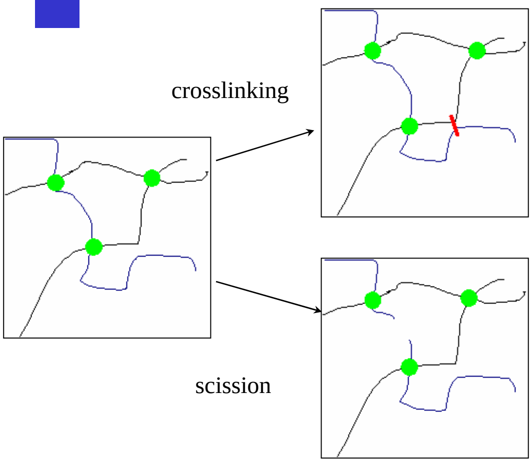
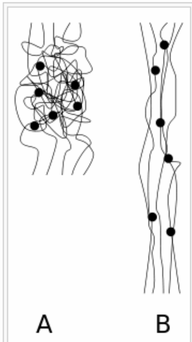
Scission and crosslinking - schematic

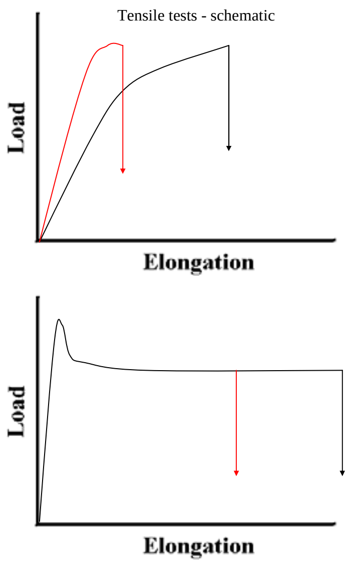




(A) is an unstressed polymer; (B) is the same polymer under stress. When the stress is removed, it will return to the A configuration. (The dots represent cross-links)

Effects of degradation on bulk properties of polymers

- Tensile elongation decreases
- Tensile strength decreases (may show initial increase)
- Hardness increases (usually)
- Density increases
- Compression set of seals increases
- Electrical properties show little change until material is significantly degraded (usually)
- Dielectric properties can change significantly
- Changes in colour and surface texture often visible



Degradation examples

- Loss of plasticiser after thermal ageing (example is for a PVC cable after 20 years at 60C)
- Mechanical stress can accelerate degradation – jacket failure on the outside of a tight bend in cables

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Degradation stressors

- Polymers are sensitive to environmental conditions within a NPP
- Main stressors –
  - Temperature
  - Radiation dose rate and total dose (unlike metals, polymers are susceptible to gamma irradiation)
  - Presence of oxygen
- Secondary stressors-
  - Moisture
  - Mechanical stress
  - Ozone
  - Chemical contamination

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Ageing of polymeric components

- Thermal ageing is dominant for most polymers in a NPP
- Radiation ageing is only significant for a small proportion of these
- Environmental qualification aims to demonstrate that cables can continue to fulfil their safety function throughout the lifetime of the plant
- Seal replacement intervals need to be known
- Requirement to simulate the ageing that would occur in the plant, using worst case environmental conditions
- Thermal and radiation ageing needs to be simulated in an accelerated time frame
- **Is this accelerated ageing an accurate simulation?**

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Accelerated thermal ageing

- Usually based on Arrhenius relationship, using following equation

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

  - Where t_1 is 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
- 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 value is known for specific polymer formulation

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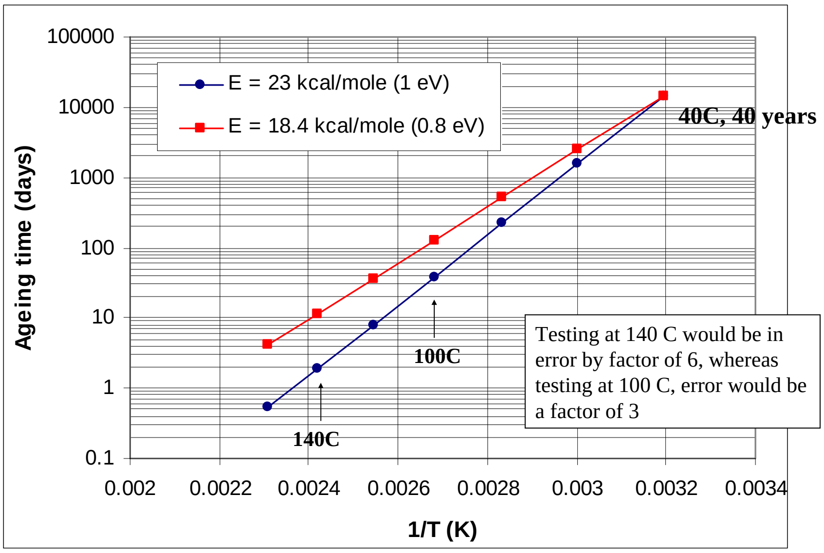
Activation energy - is the value appropriate?



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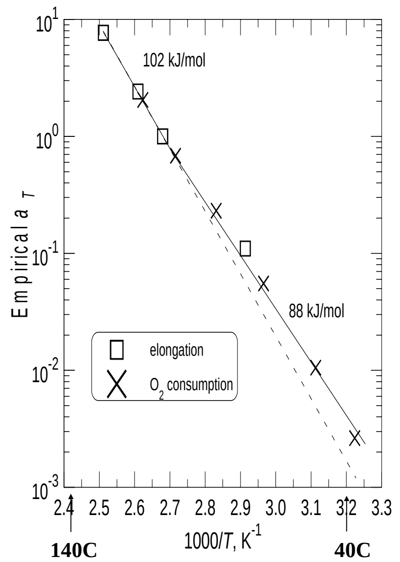
Variation of Ea with temperature



- Example for a CSPE cable jacket
- Oxygen consumption measurements used to access low temperature region
- Similar variations seen in many cable materials

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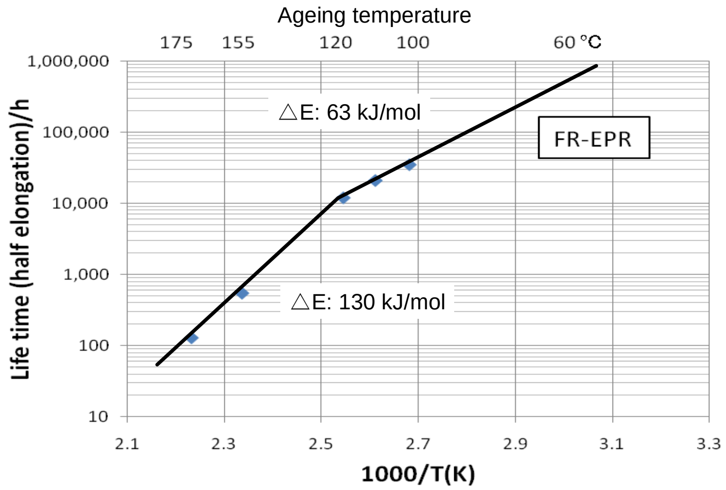
Variation of activation energy with temperature – example for EPR cable



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Are the degradation mechanisms the same?

- PVC cables – thermal ageing at < 90C is dominated by loss of plasticiser but > 90C mainly loss of HCl
- EPR and PE-based cables – can be semi-crystalline materials. Thermal ageing at T > crystalline melting point may not be representative of ageing in plant
- Important to use the lowest practicable temperature for the accelerated thermal ageing

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Factors affecting lifetime of polymeric components under irradiation

- Diffusion-limited oxidation
  - must be taken into account in any simulation of service conditions (both for thermal and radiation degradation)
- Radiation dose rate effects
  - particularly in accelerated testing
- Synergy between radiation and temperature
- Reverse temperature effect
- Polymer formulations

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Diffusion-limited oxidation

- Oxidative degradation is limited by diffusion of oxygen into sample
- Under service conditions (low temperature/dose rate, long times) oxidation is usually homogeneous
- In accelerated testing (high temperature/dose rate, short times) oxidation often heterogeneous
- Bulk measurements (eg. tensile tests, compression set) on heterogeneous samples likely to be non-representative

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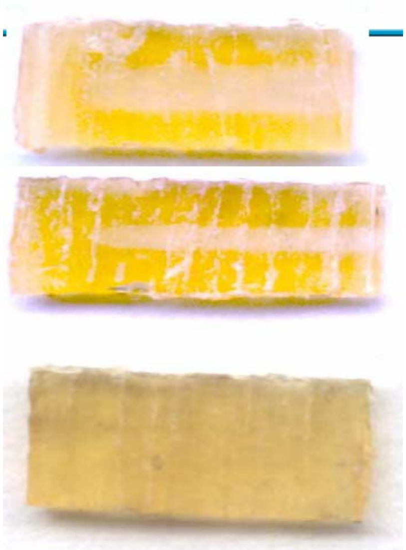
Diffusion – limited oxidation



- A visual example of heterogeneous oxidation (top 2 images) and homogenous oxidation (bottom image)
- The properties of the oxidised region (yellow) and unoxidised regions (clear) will be different

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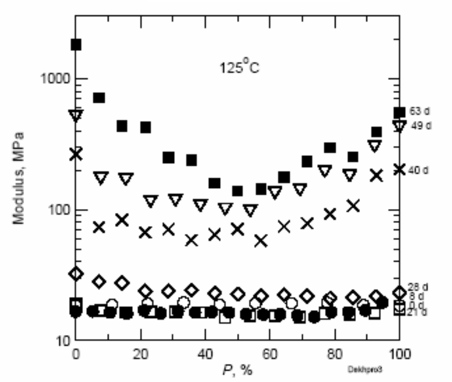
Example of heterogeneous oxidation – oxidative cross-linking

- Diffusion-limited oxidation can occur during both thermal and radiation ageing
- Edges of sample are more degraded than bulk of material
- Effects become more severe as ageing proceeds

CSPE jacket material



Relative distance through sample

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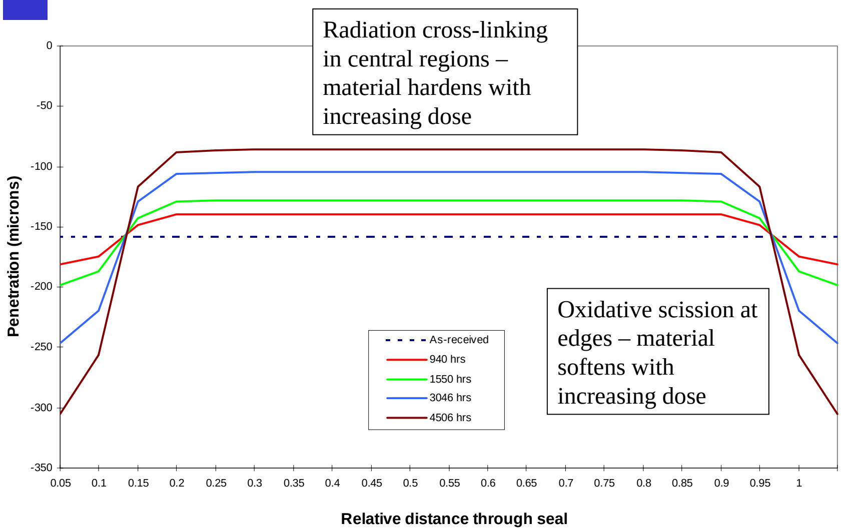
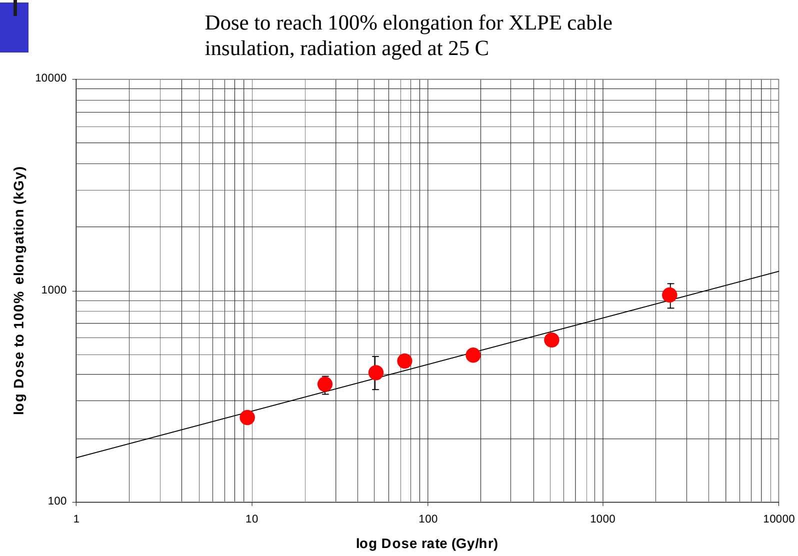
Example of heterogeneous oxidation –oxidative scission + radiation cross-linking (Viton seal)



Dose rate effects

- Assumption often made of equal dose = equal damage but many polymers are dose rate dependent
- Dose to equivalent damage (DED) decreases with decreasing dose rate
- Not seen in all polymers but can be significant in many
- Needs to be considered when simulating service conditions

Dose rate effect in a cable insulation material (XLPE)



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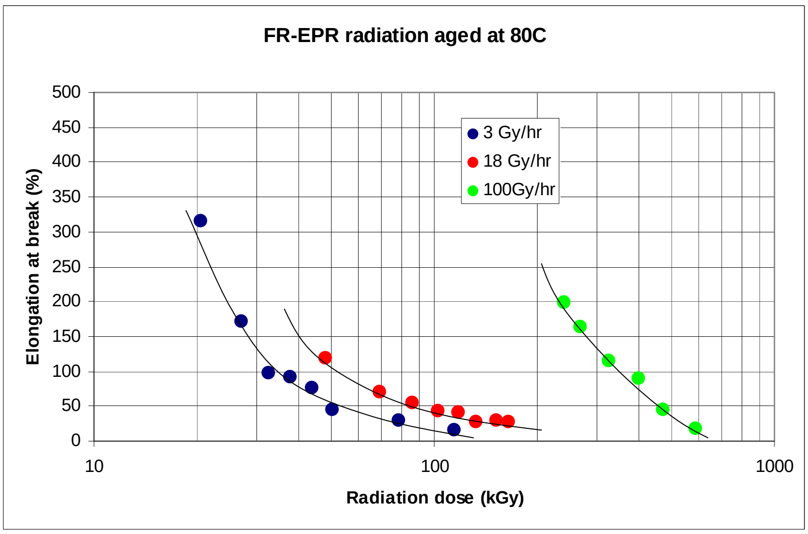
Dose rate effect in EPR insulation, radiation aged at elevated temperature



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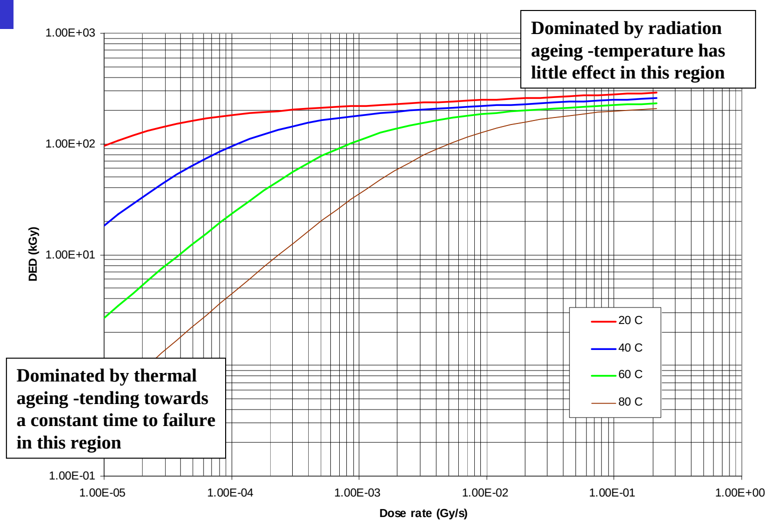
Synergy between radiation and temperature

- At low dose rates (typically seen in NPPs)
  - Degradation is dominated by thermal ageing
  - Degradation is determined only by time at temperature
- At high dose rates (typically seen in accelerated testing)
  - Degradation is dominated by radiation ageing
  - Degradation tends to show only a small effect of temperature

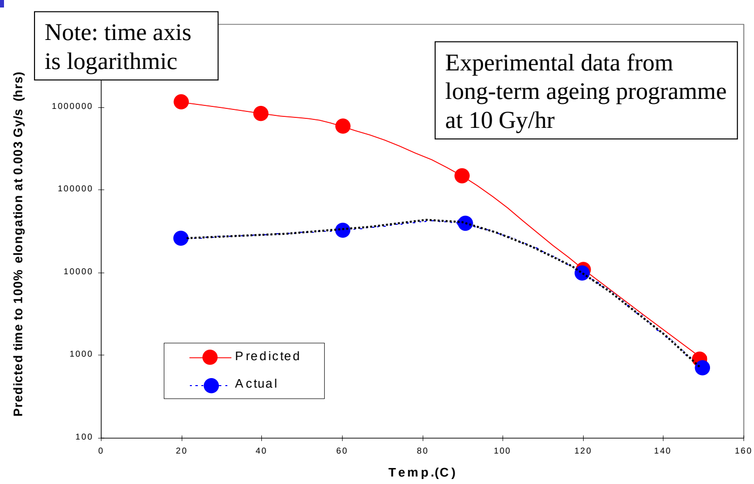
Effect of combined radiation/thermal ageing on DED – general trends



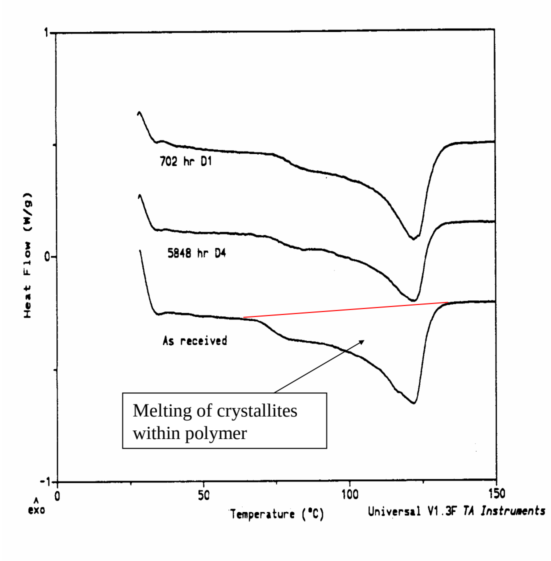
Reverse temperature effect in semi-crystalline polymers in radiation ageing

- Semi-crystalline polymers –
  - Tend to show reverse temperature effect, with degradation being greater at ambient temperature than elevated temperature in the presence of radiation
  - Arises from recrystallisation and recombination of radicals at higher temperatures
  - Only of concern where service and accelerated ageing temperatures span the crystalline melting point, e.g. in XLPE

Example of reverse temperature effect in XLPE cable insulation



DSC traces for same XLPE material



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Effect of formulation on degradation

- Differences in formulation can significantly affect the rate of degradation of a cable material
- Particularly important when radiation is present
- Changes in pigments, anti-oxidants, fillers or stabilisers, as well as the base polymer, can all affect component lifetime.

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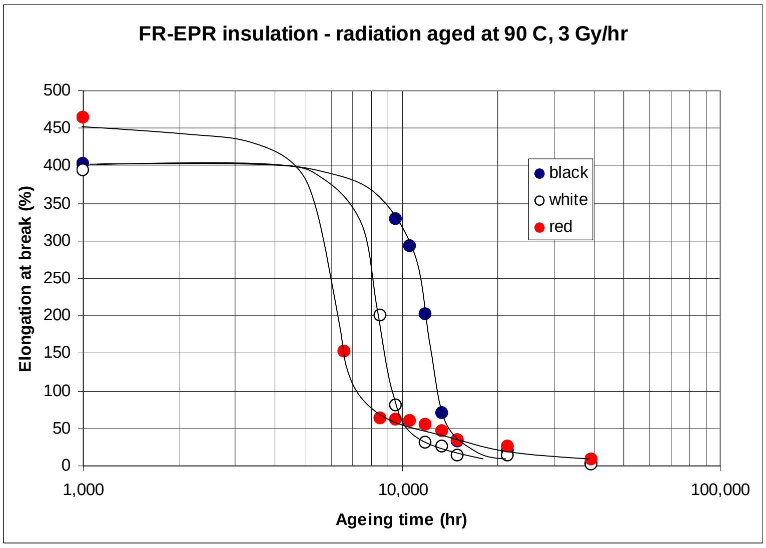
Pigment effects in an EPR insulation



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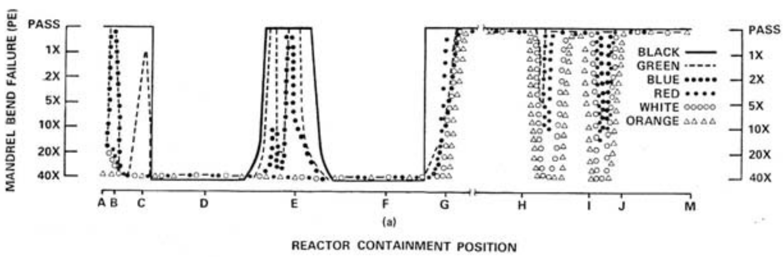
Effect of pigment on degradation



- Differences in formulation (e.g. pigments) can significantly affect the rate of degradation of a cable material
- The example above is for PE insulation from a USA reactor for a cable that ran through containment past several coolant lines for heat exchangers

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Factors to consider in accelerated ageing

Summary of factors that may need to be considered -

- Activation energy for thermal ageing
- Degradation mechanisms
- Diffusion-limited oxidation
  - for both thermal and radiation degradation
- Radiation dose rate effects
- Synergy between radiation and temperature
- Reverse temperature effect
- Polymer formulations

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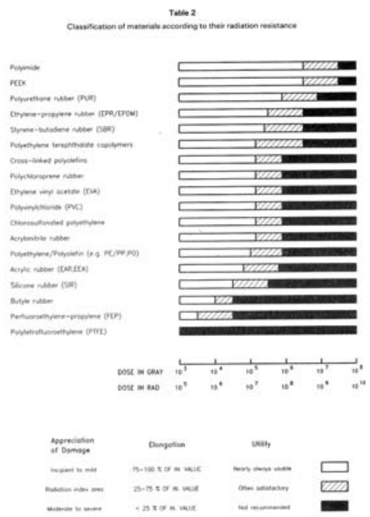
Radiation ageing of polymers – pitfalls!



- Be very wary of using tables such as this
- The data have been generated from very high dose rate irradiation tests
- Factors such as diffusion-limited oxidation and dose rate effects have **not** been considered
- Only indicate the relative radiation resistance of different polymers at high dose rates

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Special sealing situations

- Some seals may also need to cope with special situations, such as
  - High temperature transients
  - Low temperature transients
  - Impact or large vibrations

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High temperature transients

- Despite obvious damage, these EPDM seals continued to seal during a transient to 150 C
- Only the surface was damaged, interior of seal still flexible

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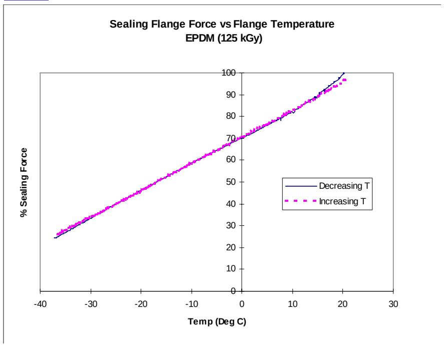
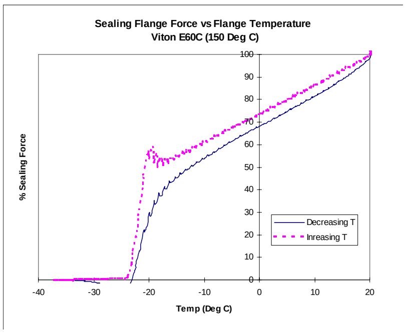
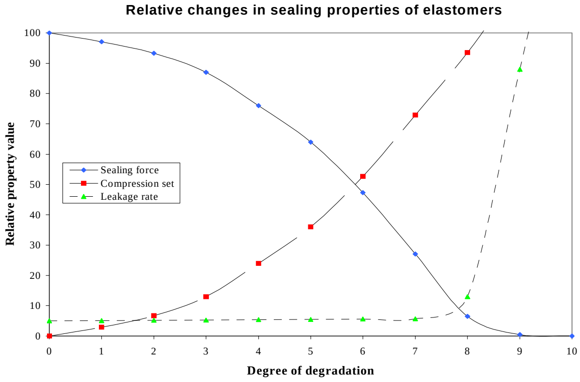
Low temperature transients - material selection is critical





EPDM seal continued to seal below -35 C, but Viton seal failed at -20 C because it has reached its glass transition temperature

Sealing after impact damage or with large vibrations



- Need to consider residual sealing force, allowing for operational degradation
- Need to assess whether seal is capable of bridging impact/vibrational gaps – from FE calculations on transport container design

Conclusions

- You should now have a better understanding of why polymer ageing is considered to be important
- Generic degradation processes and failure mechanisms are reasonably well understood
- Detailed behaviour of a polymer component is specific to its formulation

Thank you for listening

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