# Assessment of aged polymeric components in NPPs

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## Ageing assessment

- Condition monitoring (CM) methods
  - CM for cables
  - CM for seals
  - CM for other components
- “Finger-printing” methods
- Failure analysis of seals

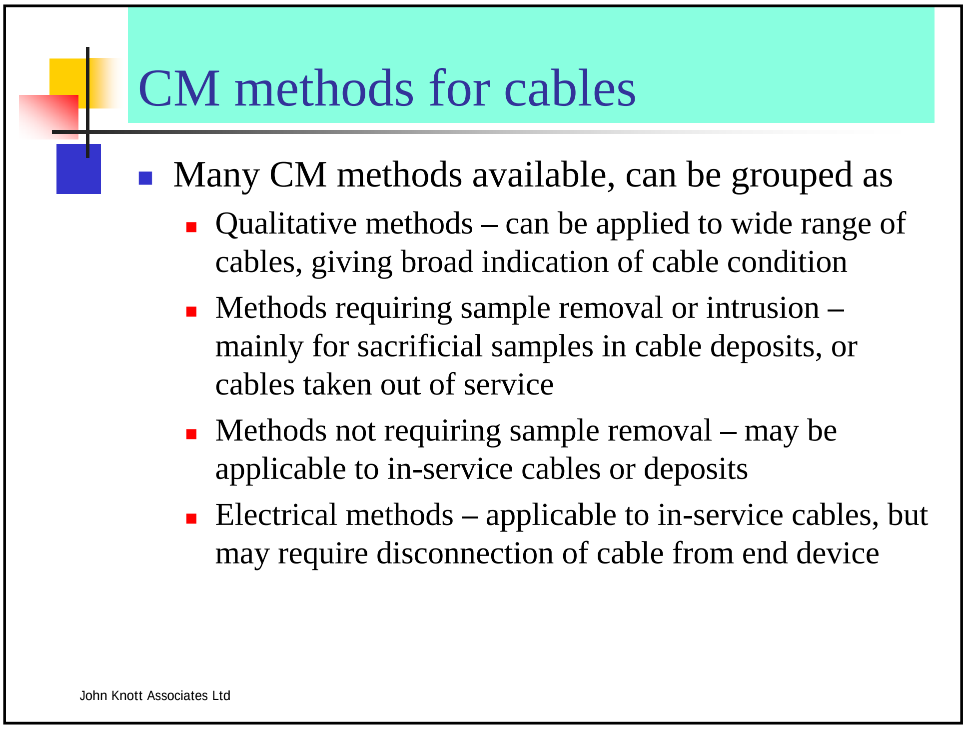
# Condition monitoring (CM)

Objectives:

- Assessment of current state of degradation
  - Compression set used as a reference indicator of degradation for seals – 90% set is a possible end-point for static seals
  - Elongation at break often used for cables – 50% absolute is indicator of some remaining flexibility but not necessarily a good indicator of DBE survivability
- Prediction of remaining lifetime
  - Not straight forward, as rate of degradation is non-linear & dependent on several environmental stressors, but estimates can be made

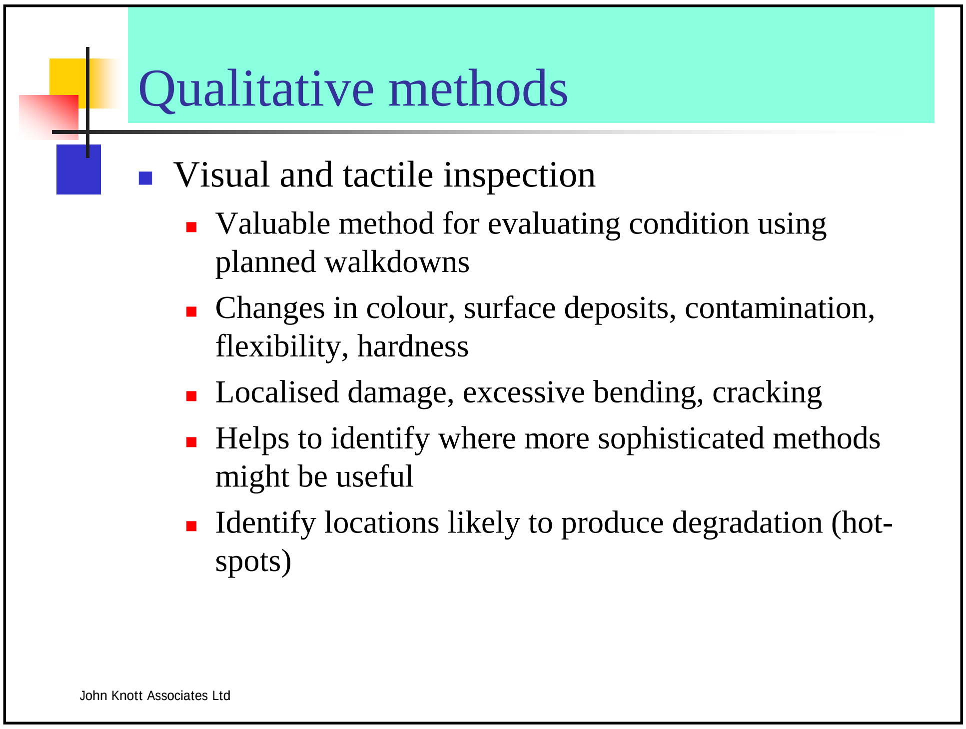
# Condition monitoring requirements

- Any CM method must
  - Be an indicator of structural integrity
  - Change significantly with ageing degradation
  - Be reproducible under different ageing conditions
- Ideally, a CM method should also
  - Be applicable to wide range of materials
  - Be usable in areas of limited access
- No current CM method satisfies all of these requirements
  - For cables, a number of useful methods have been evaluated and found to be potentially useful
  - Limited CM methods available for seals and coatings



## CM methods for cables

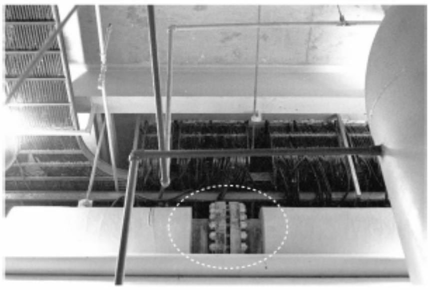
- Many CM methods available, can be grouped as
  - Qualitative methods – can be applied to wide range of cables, giving broad indication of cable condition
  - Methods requiring sample removal or intrusion – mainly for sacrificial samples in cable deposits, or cables taken out of service
  - Methods not requiring sample removal – may be applicable to in-service cables or deposits
  - Electrical methods – applicable to in-service cables, but may require disconnection of cable from end device



## Qualitative methods

- Visual and tactile inspection
  - Valuable method for evaluating condition using planned walkdowns
  - Changes in colour, surface deposits, contamination, flexibility, hardness
  - Localised damage, excessive bending, cracking
  - Helps to identify where more sophisticated methods might be useful
  - Identify locations likely to produce degradation (hot-spots)

# Some examples of potential problem areas identified in walkdowns (from EPRI report 1003663)



Missing thermal insulation

Displaced thermal insulation on valve operator

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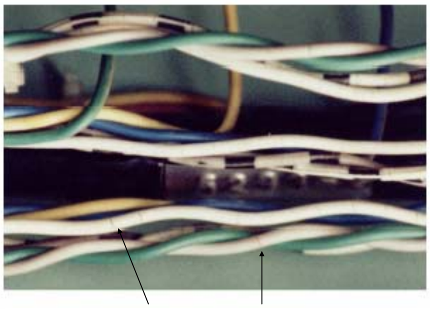
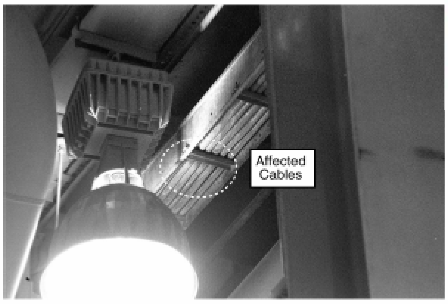
# Some examples of potential problem areas identified in walkdowns (from EPRI report 1003663)



Cracking of PE wiring from fluorescent lights

Heat from high intensity lights



# Some examples of problem areas identified in walkdowns (from UJV, Rez)

Excessive bending stresses
on cable installation

Poor clamp design producing excessive
compressive forces on cables

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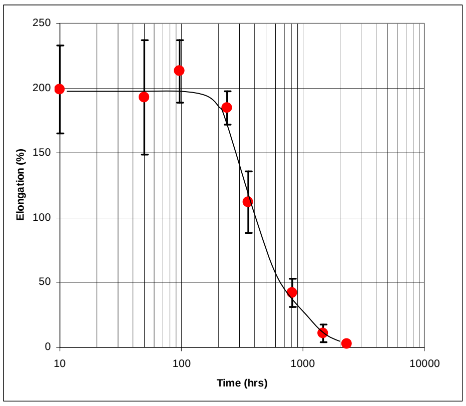
# Methods requiring sample removal

- Some methods can use micro-samples but most methods are best applied to deposit samples
- Methods currently available
    - Elongation at break
    - Oxidation induction methods (OIT/OITP)
    - Thermogravimetric analysis (TGA)
    - Density
    - Infra-red analysis

## Elongation at break (EAB)

- Typically used as benchmark for evaluating other CM techniques
- For elastomeric materials, e.g. most cable jacket materials, EAB decreases steadily with ageing
- For some polymeric insulation materials, little change in EAB until near end of life
- Measurements tend to show quite large standard deviation



PVC cable jacket, aged at 295 Gy/hr at 40C

## Examples of changes in EAB after thermal ageing (from JNES-SS-0903)

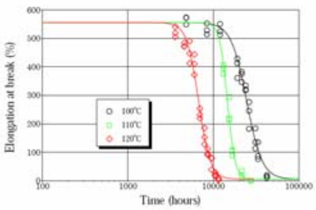


Fig. 1.1-4 Thermal aging characteristics of the FR-XLPE insulator made by Company B

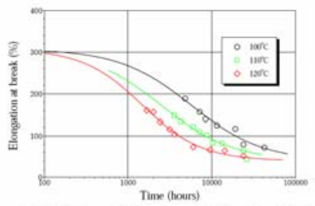


Fig. 1.1-5 Thermal aging characteristics of the XLPE insulator of triaxial cable made by Company C

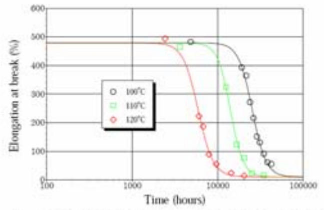


Fig. 1.1-13 Thermal aging characteristics of the FR-EPR insulator (black core) made by Company C

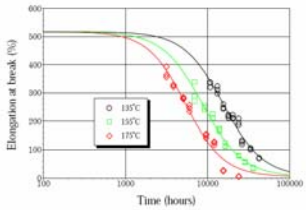


Fig. 1.1-17 Thermal aging characteristics of the SIR insulator made by Company B

# Micro-sampling methods

- These methods require only small samples (typically 10-20 mg of material)
- Some NPPs will allow sampling of operational cables, with approved repair methods
- Other NPPs may only allow sampling on deposit cables

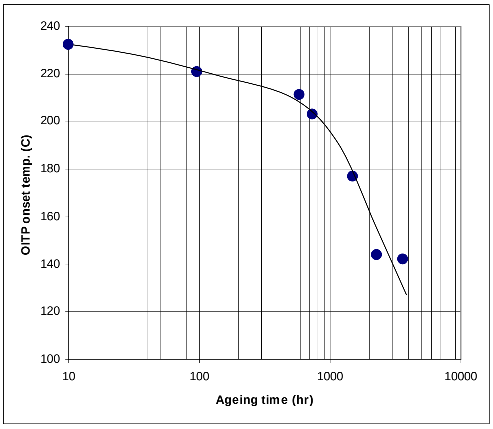
Photos courtesy of UJV, Rez

# Oxidation induction methods

- Two types of test used – oxidation induction time (OIT) and oxidation induction temperature (OITP)
- Both use samples of approx. 10 mg, using standard laboratory equipment – differential scanning calorimeter
- OIT measures the time for onset of oxidation in oxygen at a constant temperature
- OITP measures the temperature of oxidation onset as temperature is increased at a constant rate (typically 10C/min)

# Oxidation induction (OIT/OITP)

- OITP trends well with ageing in EPR and PE-based materials
- OIT trends well at early stages of ageing when other CM methods show little change
- Both methods need to be correlated with changes in EAB for specific formulation tested



EPR cable insulation, aged at 200 Gy/hr at 25C

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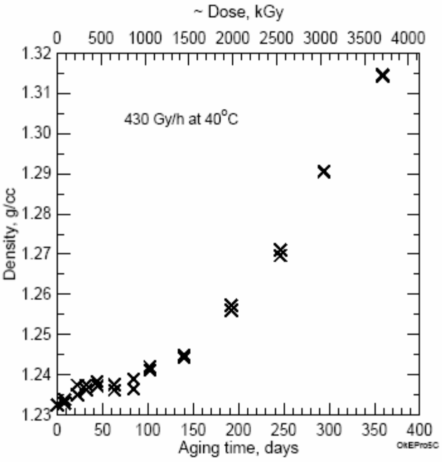
# Density measurements

- Simple measurement using small samples (<1 g)
- Correlates well with ageing for CSPE and EPR materials; changes in XLPE tend to be quite small
- Needs to be correlated with changes in EAB for specific formulation tested



EPR cable insulation, radiation aged

# Infrared analysis

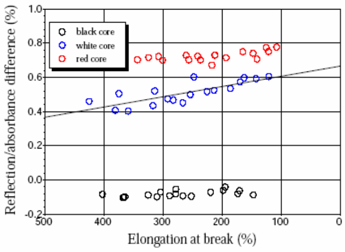


Fig. 3-19 The FR-EPR insulator made by Company C
Optical diagnostic method: R=0.80
(Linear regression is for white core only)

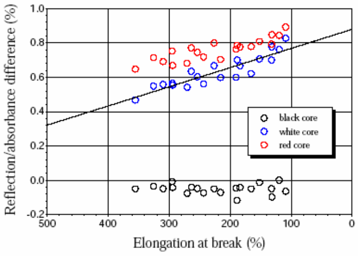


Fig. 3-3 The FR-XLPE insulator made by Company A
Optical diagnostic method: R=0.85
(Linear regression for white core only)

- Uses the ratio of absorbance peaks in the infra-red spectrum representing molecular changes to monitor ageing.
- Portable instrumentation so could be used in-plant
- Cannot be used on black material but gives a reasonable correlation with changes in elongation at break for most EPR and XLPE materials

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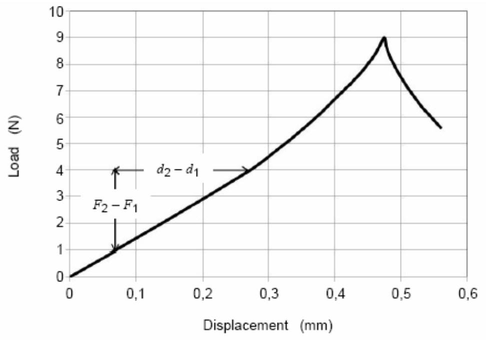
# Methods not requiring sample removal

- These can be used on deposit samples or on in-service cables.
- Methods available include
  - Indenter modulus
  - Recovery time
  - Sonic velocity
  - Infrared analysis (reflectance mode)

# Indenter modulus

- Portable instrument that can be used in-plant
- Measures load exerted on a probe tip pressed into surface under controlled conditions
- Slope of load-displacement curve is a measure of the modulus of the material
- Considerable data available on correlation with ageing degradation



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# Indenter modulus – examples of correlation with EAB (from JNES-SS-0903)

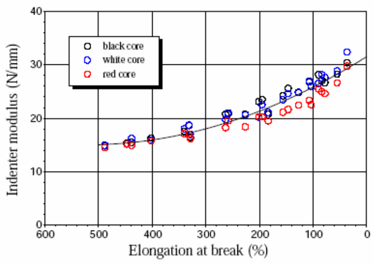


Fig. 3-6 The EPR insulator made by Company C
The Indenter: $R^2$=0.93

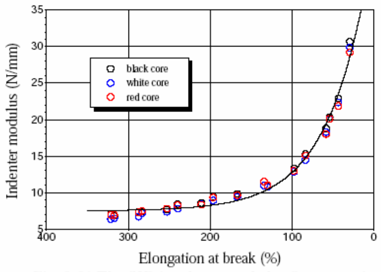


Fig. 3-21 The SIR insulator made by Company A
The indenter: $R^2$=0.99

- Indenter modulus values correlate well with elongation for most EPR materials
- For softer materials such as SiR, changes tend to be much larger
- Correlation is poor for harder materials such as XLPE and PEEK

# Electrical methods

- Potentially could be used on in-service cables
- Methods available include
  - Frequency domain reflectometry (FDR)
  - Time domain reflectometry (TDR)
  - Dielectric loss
  - LCR measurements
  - Insulation resistance
- Currently these methods are used more for fault location and troubleshooting, but research is on-going to evaluate them for trending ageing

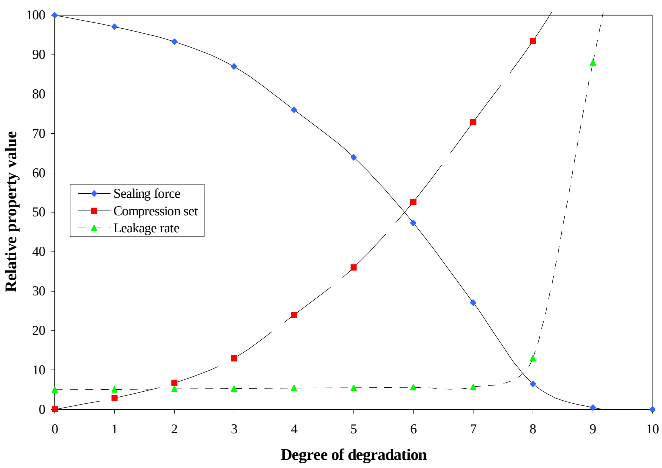
# CM methods for cables - summary

- Wide range of CM methods available but there is no single technique suitable for every cable type
- Some techniques are well developed, with standards for the test method (e.g. IEC 62582 series)
- Other techniques are still being evaluated
- Overall, there is a ‘tool-box’ of CM methods that can be applied – some to measure ageing degradation, some to locate faults

# CM for seals and coatings

- Seals
  - Prime property of interest is leakage rate
  - Seal needs to be compressed to maintain the sealing force – initial compression is typically 20-25% (but should not be >30%)
  - Sealing force decreases as seal ages, but leakage rate generally unchanged until critical level reached
  - Compression set is usually used as the benchmark test of degradation
- Coatings
  - Mechanical properties and adhesion are the prime properties of interest

# Important properties of seals (schematic)


Relative changes in sealing properties of elastomers

# Compression set measurement

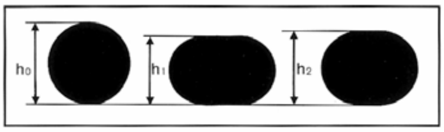


*Fig. 6.1*

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

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)

*Fig. 9.9 Characteristic compression set. High deformation*

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# Potential problem areas in CM

- Each formulation has its own response to ageing
- Appropriate CM methods will depend on the material and component type
- Common problem areas
    - “Cliff edge” behaviour
    - Heavily aged before significant changes
    - Changes too small relative to data scatter
    - Sensitivity to test environment
    - Variations in test method/analysis

# Problem 1: “Cliff edge” behaviour

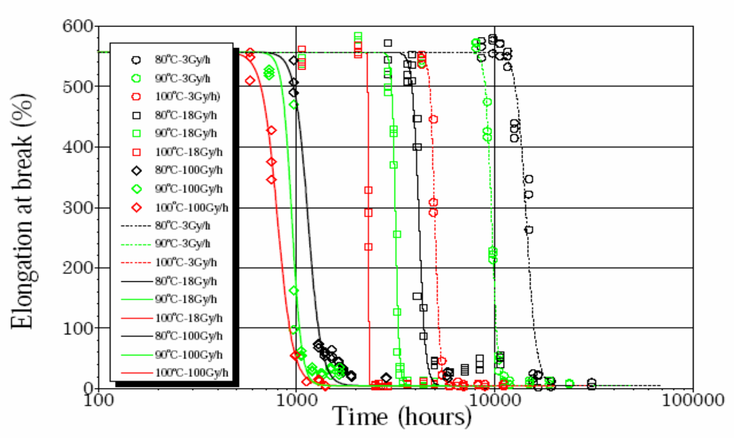
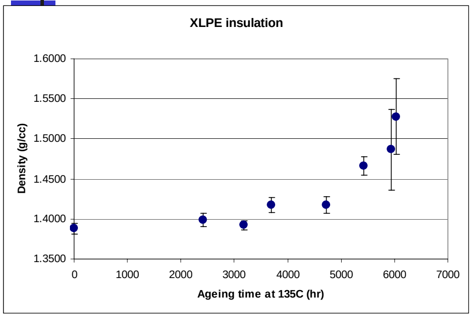
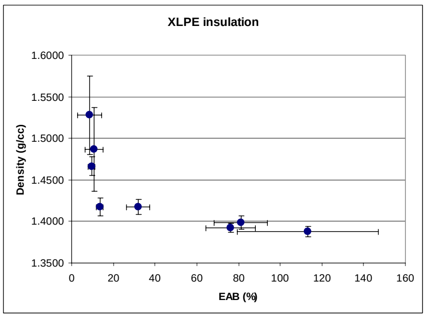


**Fig. 1.2-1 Simultaneous aging characteristics I of the XLPE insulator made by Company A**

# Problem 2: Heavily aged before significant changes





- Density changes appear to be useful condition indicator
- Cross-plot shows that changes only occurring when material is heavily aged

# Problem 3: Changes too small relative to scatter

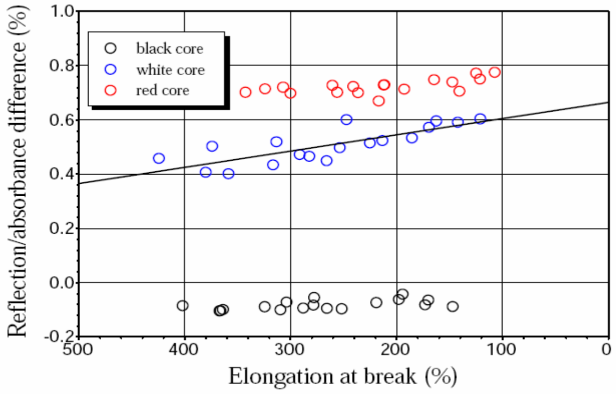


**Fig. 3-19 The FR-EPR insulator made by Company C**
**Optical diagnostic method: R=0.80**
(Linear regression is for white core only)

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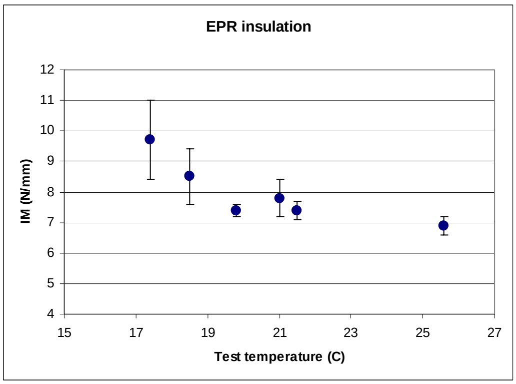
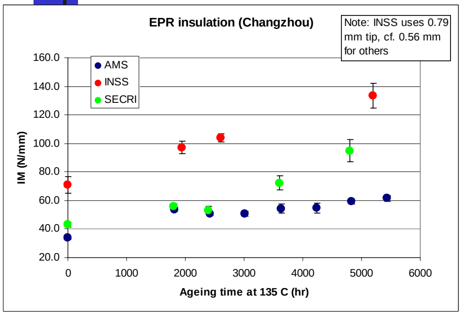
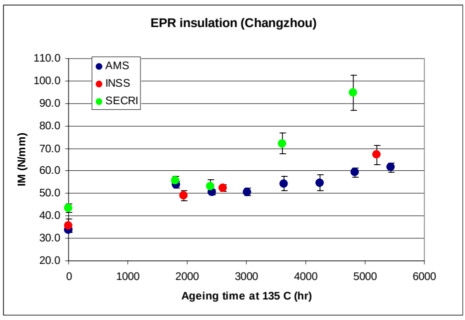
# Problem 4: Test environment variability

- The condition indicator can be sensitive to test temperature (e.g. IM in some materials) or moisture (e.g. most electrical methods)



# Problem 5: Variations in test method





- Essential that the test method is rigorously defined, including method of analysis
- Example for indenter – INSS used different diameter probe tip
- Once corrected for tip diameter, data variation then from different force ranges used for IM

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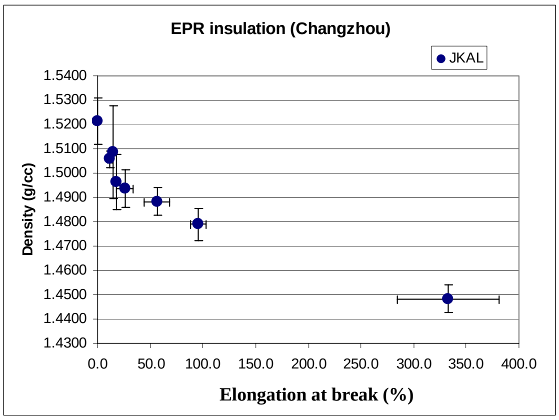
# Reliability and reproducibility of CM data

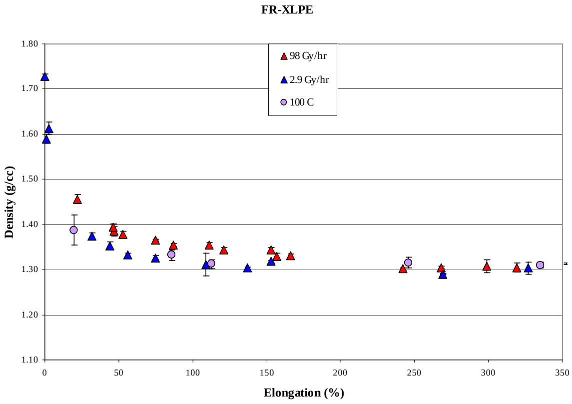
- Is the scatter of data small relative to change with ageing?
- Are the changes consistent with different ageing environments?
- How do variations of formulation (e.g. pigments) affect the parameter measured?
- How much variation do you get between labs?

# Is the scatter of data small relative to change with ageing?



- Changes in density are not large, but the variation is small enough for method to still be viable

# Are the changes consistent with different ageing environments?



- Thermal ageing and low dose rate radiation ageing lie on same curve, but higher dose rate does not

## Do variations of formulation (e.g. pigments) affect the parameter measured?

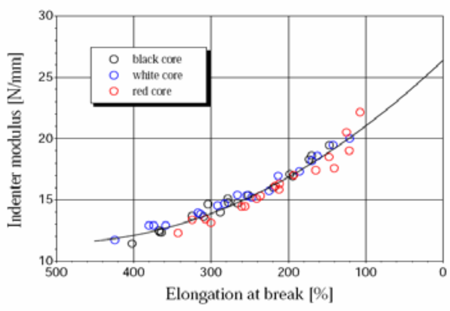


Fig. 3-17 The FR-EPR insulator made by Company C
The indenter: $R^2$=0.96

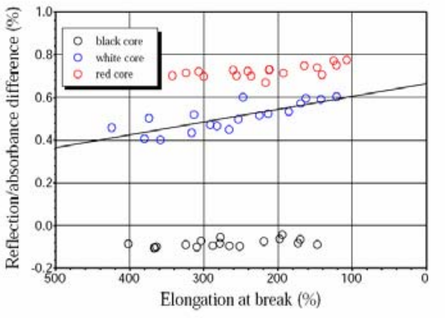


Fig. 3-19 The FR-EPR insulator made by Company C
Optical diagnostic method: R=0.80

- Pigments have little effect on indenter measurements but significant differences for FTIR values

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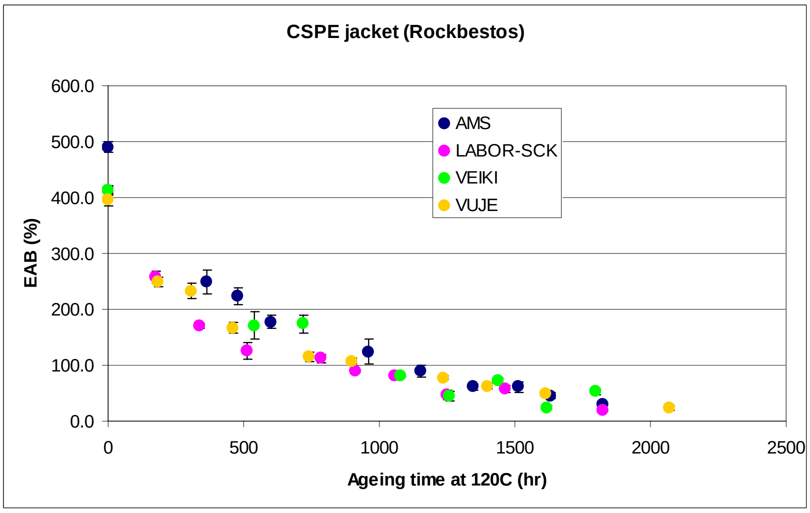
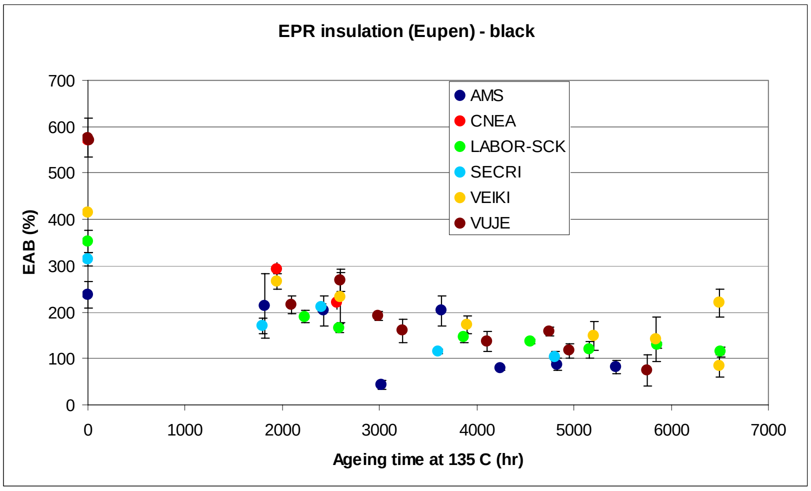
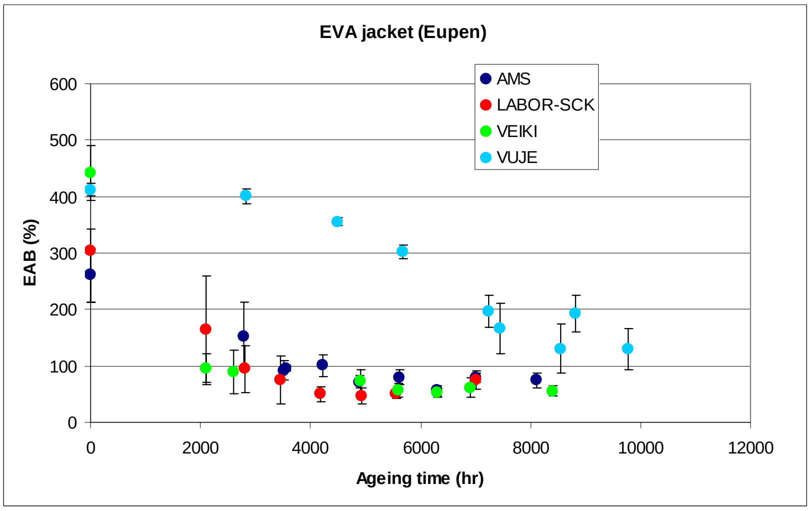
## How much variation do you get between labs? – test equipment



# How much variation do you get between labs? – sample preparation



# How much variation do you get between labs? – sample preparation



# Important lessons learned

- CM test method must be very well defined, including
  - Sample preparation
  - Test environment & sample conditioning
  - Test equipment
  - Analysis method
- Standards are being developed, but existing CM ones may need updating and new standards written for other methods

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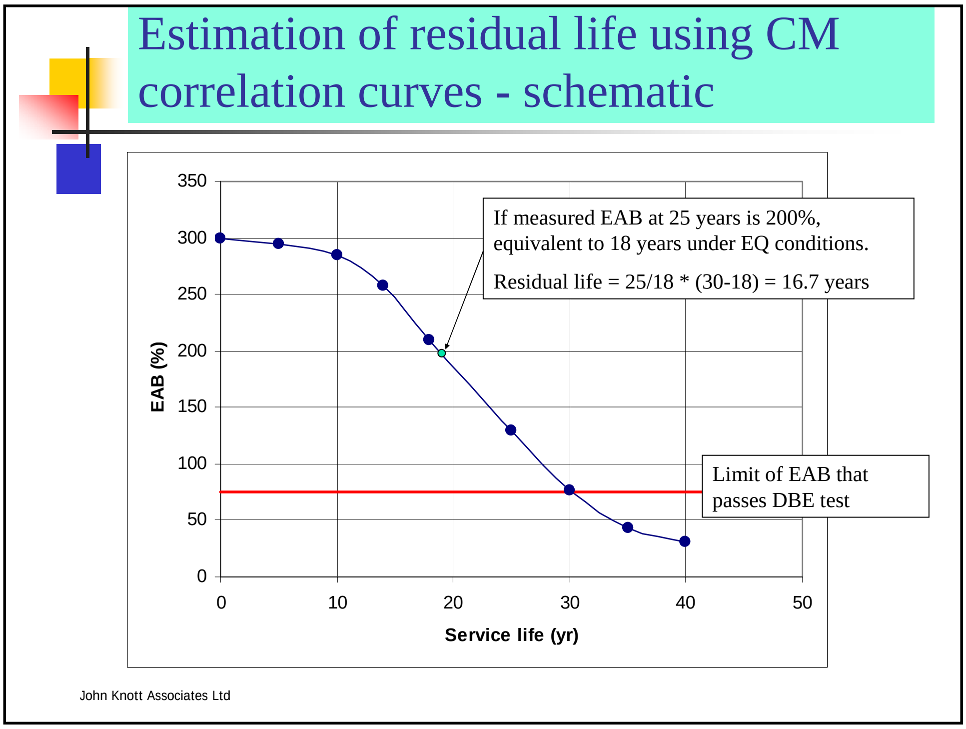
# Estimation of residual life

- Using CM correlation curves
  - Need to know the shape of the CM parameter versus ageing time curve (e.g. in pre-ageing phase of EQ – using low acceleration factors)
  - Need correlation curves between CM method used and changes in prime indicator of degradation (e.g. EAB, compression set)
- Analytical approach
  - Only possible if the model is suitable for the material and model parameters are known for specific formulation
  - Has been used successfully for seal materials



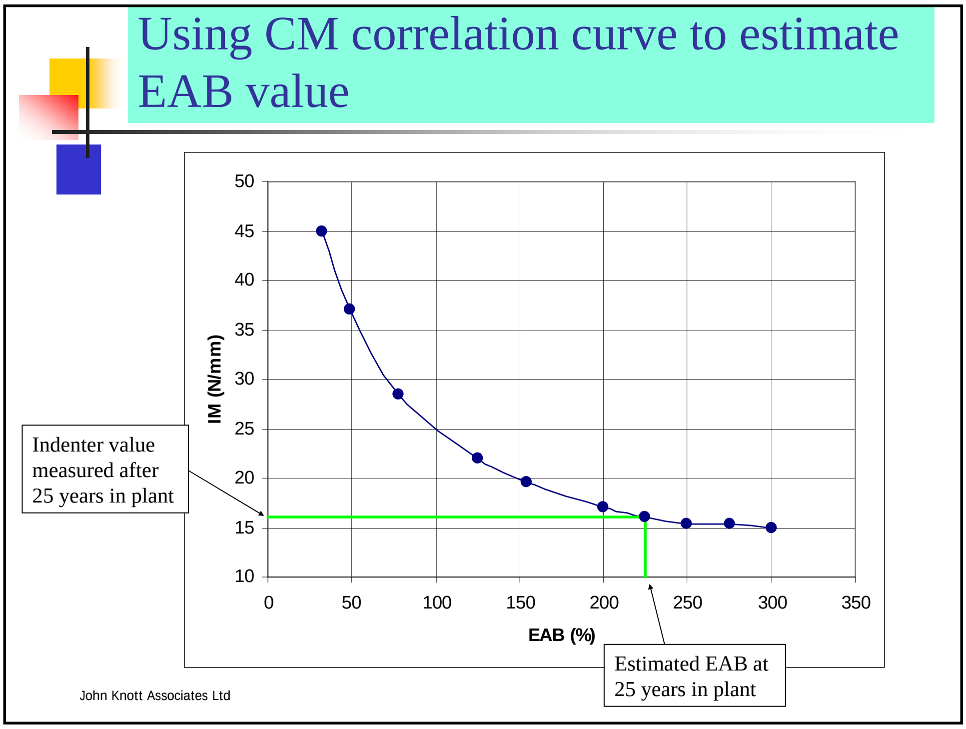
# Estimation of residual life using CM correlation curves - schematic

If measured EAB at 25 years is 200%, equivalent to 18 years under EQ conditions.

Residual life = 25/18 * (30-18) = 16.7 years

Limit of EAB that passes DBE test

John Knott Associates Ltd



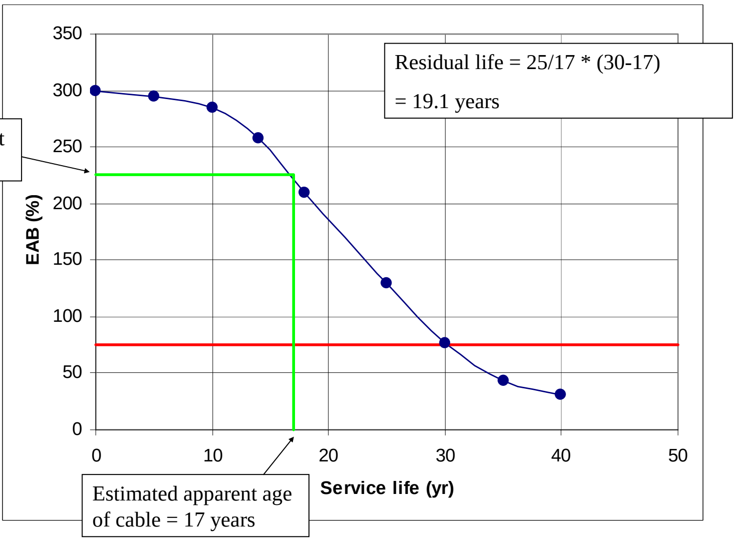
# Using CM correlation curve to estimate EAB value

Indenter value measured after 25 years in plant

Estimated EAB at 25 years in plant

John Knott Associates Ltd

# Estimate residual life



Residual life = 25/17 * (30-17)

= 19.1 years

Estimated EAB at 25 years in plant

Estimated apparent age of cable = 17 years

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# Real life situations

- Schematic uses CM with a large change in value over full EAB range
- Assumes variation of CM value is negligible
- In reality, must take into account the variability of CM measurements, e.g. using its standard deviation
- If the change is CM value is relatively small compared with change in EAB, then estimate of residual life will be very approximate
- Can use several CM methods to get best estimate of residual life

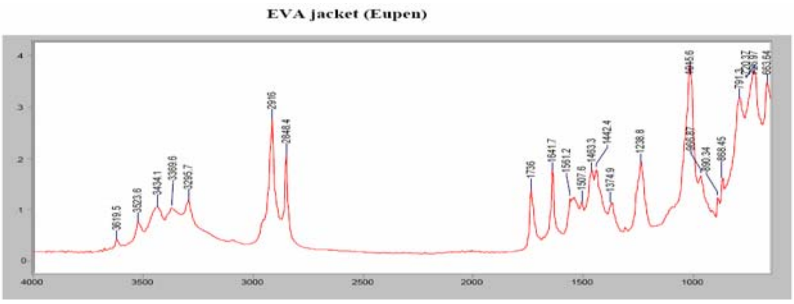
## Condition monitoring - summary

- You should now have an idea of what is possible in condition monitoring
- Which CM methods are suitable will depend on specific material formulation
- It is possible to make an estimation of residual life

## “Finger-printing” of polymeric components

- What needs to be identified?
  - Base polymer type and structure
  - Filler type and content
  - Antioxidant type and concentration
  - Pigments
  - Plasticisers
  - Flame retardents
- Is it the same material as previously used?
  - Macroscopic properties – hardness, density etc.
  - Degree of crystallinity (where applicable)

# Identifying polymer type



- FTIR potentially can identify polymer type but
  - Samples only a few microns depth
  - Black materials can be problematic but possible
  - Difficult to interpret
- Raman spectroscopy possibly a better method
  - No sample preparation needed
  - Samples greater depth
  - Easier to get data from black samples

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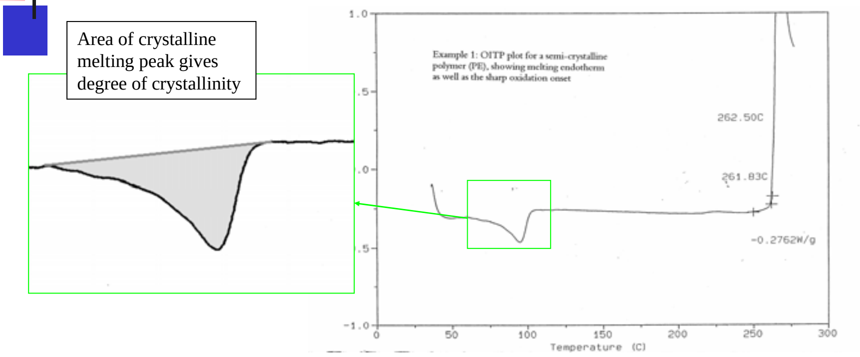
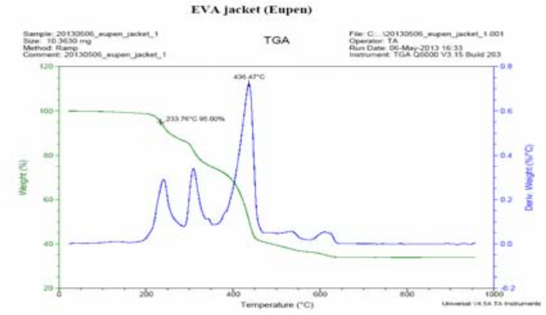
# Polymer structure


Area of crystalline melting peak gives degree of crystallinity

- Thermal analysis
  - DSC will identify degree of crystallinity of semi-crystalline polymers
- Gel content and solvent uptake
  - Indicator of crosslink density

# Filler type and content



- Thermogravimetric analysis (TGA)
  - Residual weight at end of test should give filler content (since this is usually thermally stable)
  - Derivative curve characteristic of specific formulation

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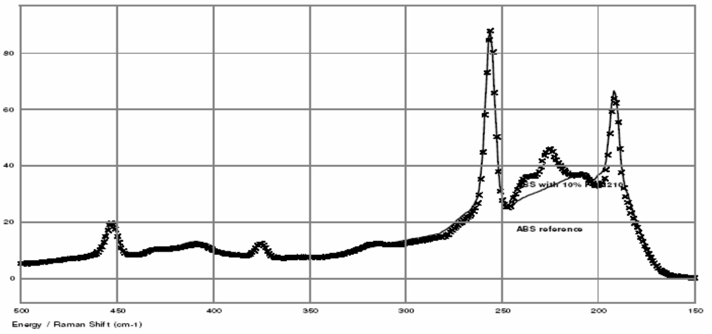
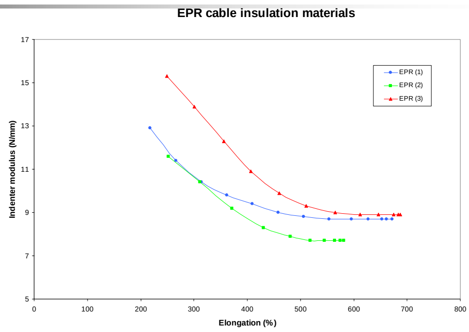
# Other additives – antioxidants, flame retardents etc.

Figure 5. ABS and 10% FR-1210 in ABS matrix, all to the same scale.



- Raman spectroscopy
  - Identification of additives
  - When calibrated can also measure concentration of additives

# Non-specific methods



Note: EPR2 (green) and EPR3 (red) are from the same manufacturer but with different fillers; EPR1 (blue) is from a different manufacturer

- Many CM methods potentially could be used to characterise a specific formulation
  - Density and IM both strongly dependent on filler content
  - TGA at different temperature ramp rates can be used to measure activation energy for decomposition (ASTM E1641 method)
  - Frequency dependence of dielectric loss and permittivity (cables)

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# “Finger-printing” - summary

- Combination of techniques can be used
  - Identify polymer type
  - Presence of additives
  - Amount of filler
  - Comparison with known materials

# Assessing used and failed seals

- Visual inspection - examine seal for any signs of cuts, splits, wear marks or surface deposits
  - Type of damage can be characteristic for different failure types – e.g. extrusion, spiral failure, explosive decompression
  - Surface deposits can indicate excessive temperature (be particularly wary of fluorocarbon seals)
- Measurement of compression set
- Changes in hardness

# Extrusion failure of seals

- Extrusion failure – material on low pressure side of seal is lost
- Can have significant amounts of material extruded and damaged with seal still functioning

*Fig. 9.6 Extruded O-ring*

*Fig. 9.7 "Nibbled" O-ring*

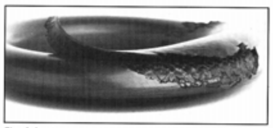

*Fig. 9.8 Peeled O-ring*

# Extrusion of EPDM seals after high temperature transient – but still sealing

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# Spiral failure of dynamic seal

- Spiral failure occurs in reciprocating seals when part of the seal rolls while the rest slides
- In static seals, spiral failure can occur if seal is twisted on assembly (particularly with a small cross-section seal with large internal diameter)

*Fig. 9.10 and 9.11 Twisted O-ring with spiral marking, (9.10) or with spiral cuts in surface (9.11)*

# Wear failure of seals

- Mainly in dynamic seals from excessive friction
- Can also occur in static seals with pulsating pressures

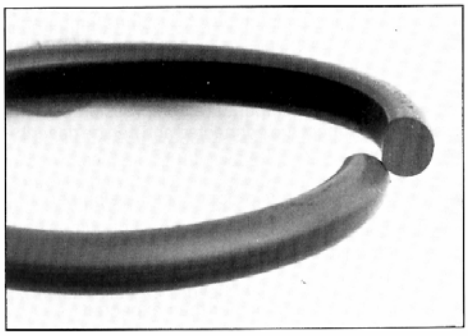

*Fig. 9.13* Wear is seen as flattening of O-ring on one side

# Explosive decompression

- In high pressure applications, gas will diffuse into seal and become trapped in the seal material
- Under rapid decompression the bubbles will expand and may rupture the seal
- Can be a particular problem with gases such as carbon dioxide and methane, where solubility is high but diffusion coefficient is relatively low

# Explosive decompression - example

- Typically, observe blisters on the surface immediately after decompression
- Surface ruptures are irregular and may not be obvious – flexing the seal will sometimes make them more visible


EXPLOSIVE DECOMPRESSION

FIGURE A9-4

# Compression set measurement

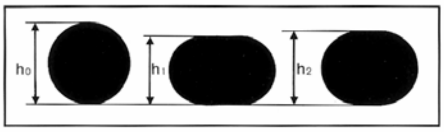

*Fig. 6.1*

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

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)


*Fig. 9.9 Characteristic compression set. High deformation*

## Compression set

- Static seals can continue to seal satisfactorily at > 90% set, provided temperature and pressure are constant and mechanical movement is negligible
- The change in set with ageing time tends to approximate to a power law, where the exponent is <1
- So, for static seals with set <50%, a rough rule of thumb indicates current exposure time can be doubled

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## Hardness measurements

- Changes in hardness will often occur – thermally aged seals are usually much harder than unaged material
- But radiation aged seals can have high compression set but still be flexible

## Joule effect in dynamic seals

- An elastomer under tension **contracts** when heated (cf. an unstressed elastomer which expands according to coefficient of thermal expansion)
- A particular concern for dynamic seals – a seal with ID less than shaft diameter, seal is warmed by friction and contracts onto shaft causing increased friction and higher temperatures
- Seal dimensions need to be chosen so that it will slide over shaft without stretching – compression is provided by groove dimensions

## Seal compatibility with fluids (summary)

- Nitrile – hydraulic and pneumatic systems, mineral oils, water, air – temperatures <90 C
- Ethylene propylene – steam, water, dilute acids, phosphate ester-based hydraulics – **not mineral oils**
- Fluorocarbon – high temperatures, aromatic solvents, oils, many chemicals
- Silicone – high temperatures, low temperatures – **not for dynamic seals** (low strength)

## Seal compatibility

- For more detailed compatibility tables for a wide rang of fluids, see “Fluid compatibility tables” in the O-ring Handbook from Parker Seals

Thank you for listening