Ageing and lifetime estimation of rubber materials by stress relaxation

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Factors influencing lifetime

- Heat
- Light
- Oxygen
- Humidity
- Mechanical influence
Ageing tests for Rubber

- Heat ageing, ISO 188
- Ageing in liquids, ISO 1817
- Relaxation in compression, ISO 3384
- Relaxation in tension, ISO 6914
Important ageing factors

- Temperature
- Air exchange rate
- Air speed
Temperature influence

Temperature tolerances in ISO 23529 are
± 1 °C up to and including 100 °C
± 2 °C 100 °C and up
± 2 h time tolerance at test times 1 week or longer

1 °C wrong temperature corresponds to 10 % in testing time at an Arrhenius factor of 2, or 15 % at a factor of 2,5.

This means that two laboratories can be 60 % from each other at a test at 125 °C and still be within the specification.
Air exchange rate influence

An Interlaboratory Test Program was done in ISO TC 45 Rubber and Rubber Products many years ago with different air change rates.

0, 3 and 10 changes per hour were tested by hardness change and change in tensile properties.

The results showed very small differences between 3 and 10 changes, but dramatic difference at 0 changes.

This means that it is very important to keep the Oxygen concentration constant and to ventilate away degradation products.

The ISO 188 ageing standard specifies 3 to 10 air changes per hour.
Air speed influence

The air speed in the ageing oven influences the ageing. An investigation of this influence was done by me in the early nineties and published in Polymer Testing.

What happens in the oven is that a higher air speed increases the oxidation and ventilates away softeners and antioxidants and this changes the ageing conditions.
Ageing, different air speeds

NBR

- Weight loss, %
- Time, weeks

0,001
0,3
3 m/s
Ageing, different air speeds
EPDM

Time, weeks
Weight loss, %
0 1 2 3 4 5 6
-2.0
-1.5
-1.0
-0.5
0.0
3 m/s
0.3
0.01

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Instruments for ageing

- Cell ovens
- Cabinet ovens
- Containers for testing in liquids
- Rigs for Relaxation in compression
- Rigs for Relaxation in tension

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Ageing ovens

Cabinet ageing oven

Cell ageing oven
Stress relaxation methods

Relaxation in compression, ISO 3384
a) measurement at test temperature
b) measurement at room temperature
c) measurement in liquids (rings)

The measurements can be done discontinuous or continuous
Stress Relaxation methods

Relaxation in tension, ISO 6914

a) continuous elongation

b) intermittent elongation

*this is not relaxation, but measurement of the change in modulus*
Stress Relaxation

What happens in the material

- Physical relaxation
- Thermal degradation
- Oxidative degradation
- Continued crosslinking
History

The first relaxation rig for continuous testing
Discontinuous relaxation
Wallace instrument
Discontinuous relaxation
Elastocon compression tester
ISO 3384 method B, reading at 23 °C
SAE 2979 determination of force
Instruments continues relaxation

Relaxation rig and amplifier
Relaxation system
Relaxation rigs

Compression, Tension, in liquids
Stress Relaxation – ALE
Aeration and Liquid Exchange
ALE-rig details
ALE-test, standard test compared to test with aeration

Conventional test in closed container

With aeration

Temperature
## ITP ISO 3384 Stress relaxation, 1998

### Table 1 Precision

Method A 168 h at 23 °C; % relaxation

<table>
<thead>
<tr>
<th>Material</th>
<th>Mean</th>
<th>Sr</th>
<th>r</th>
<th>SR</th>
<th>R</th>
<th>(R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10.9</td>
<td>0.80</td>
<td>2.22</td>
<td>1.21</td>
<td>3.40</td>
<td>31</td>
</tr>
</tbody>
</table>

Method A 168 h at 100 °C; % relaxation

<table>
<thead>
<tr>
<th>Material</th>
<th>Mean</th>
<th>Sr</th>
<th>r</th>
<th>SR</th>
<th>R</th>
<th>(R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>50.5</td>
<td>0.85</td>
<td>2.37</td>
<td>2.15</td>
<td>6.03</td>
<td>11.9</td>
</tr>
</tbody>
</table>

Method B 168 h at 100 °C; % relaxation

<table>
<thead>
<tr>
<th>Material</th>
<th>Mean</th>
<th>Sr</th>
<th>r</th>
<th>SR</th>
<th>R</th>
<th>(R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>67.5</td>
<td>2.07</td>
<td>5.80</td>
<td>8.66</td>
<td>24.3</td>
<td>36</td>
</tr>
</tbody>
</table>

Sr = repeatability standard deviation, measured units
r = repeatability, in measured units (i.e..%relaxation)
SR = reproducibility standard deviation, measured units
R = reproducibility in measured units (i.e..%relaxation)
(R) = reproducibility in %
Repeatability

One rig different test periods
Repeatability

Two rigs the same test period
Important factors

• Keeping a constant deformation
• Keeping a constant temperature
Manual compensation
Calculated compensation
Relaxation test in room temperature

Influence of temperature variations

![Graph showing force and temperature over time](image)
Relaxation test at elevated temperature

Influence of room temperature variations
Stress Relaxation system
with draught hood and room temperature box

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Relaxation Test
Sealing rings 70 °C

Relaxation, %

Time, h

G-ring
M-ring

0 1 5 10 50 100 500 1000 5000 10000

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ISO 11346 Estimation of Lifetime

At a chosen test temperature, the variations in the numerical value of a chosen property, for example a mechanical or viscoelastic property, are determined as a function of time.

The testing is continued until the relevant threshold value of that property has been exceeded.

Further tests are carried out at at least two other temperatures.

For the Arrhenius procedure, the measures of the reaction rates obtained are plotted logarithmically as a function of the reciprocal of temperature and the straight line obtained is extrapolated back or interpolated to the temperature of use.
Relaxation - sealing rings

Relaxation index

Time, h

1 5 10 50 100 500 1000 5000 10000

0,0
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9
1,0

Relaxation - sealing rings
Stress Relaxation b:22  2007-10-04Elastocon AB
70 °C
85 °C
100 °C

t1 t2 t3

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Arrhenius plot

Temperature, °C

Ln time, h

0 10 20 30 40 50 60 70 80 90 100 110 120

1e2
5e2
1e3
5e3
1e4
5e4
1e5
5e5
1e6

Max temperature of use

Lifetime

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Stress Relaxation b:23  2007-10-04
Relaxation in compression - Greene Tweed FFKM 545

- Force 180 °C
- Temp 160 °C
- Temp 180 °C
- Temp 200 °C
- Force 160 °C
- Force 200 °C

Time, h

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Arrhenius plot

FFKM 545

Ln time, h

10 M
1 M
100 k
10 k
1 k
100
10

Temperature, 1/T

50 °C
100 °C
150 °C
200 °C

180 000 h

40 % reduction in force

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Arrhenius plot for FKM
Relaxation 50 % reduction in force

Temperature, $1/T$
Ln time, h

Temperature, $1/T$
50 °C
100 °C
150 °C
200 °C

Relaxation 50 % reduction in force

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ISO 3384-1 changes

• Divided into two parts
  Part 1 at constant temperature
  Part 2 at cycling temperatures

• Technical revisions

• Addition of a calibration schedule
ISO 3384-2
Testing with temperature cycling

• Method A, Once a week at low temperature

• Method B, Continuous cycling
Temperature cycle for method A
Temperature cycle for method B
Example of a cycling test
Oven for cycling tests
Automatic instrument

Control and measurement of:

- Temperature 0,1 °C
- Force 0,1 N
- Displacement 0,001 mm
- Servo motor driven movement of the test rig
Relaxation test
Creep test
Stress Relaxation Tests

Stress relaxation tests are very effective for conducting ageing tests, as substantial amounts of information result with little effort, especially when using the continuous measurements system.
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Testing with precision