Stress Relaxation

Test methods, instruments and lifetime estimation

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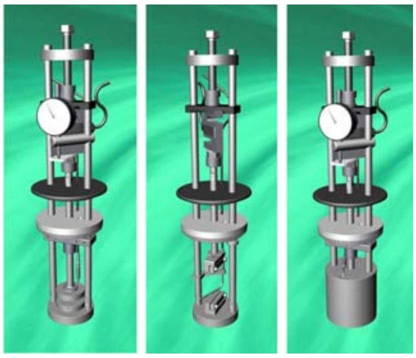

"Stress relaxation tests are very effective for conducting ageing tests, as substantial amounts of information result with little effort, especially when using the continuous measurement system"

Introduction

Stress relaxation tests are becoming more and more popular for determination of rubber properties. From the beginning stress relaxation tests were used mainly in scientific projects at universities, but a growing use has been shown in recent years and this may be caused by the introduction of stress relaxation tests in product standards, such as sealing rings for pipes (1). The automotive industry has also started to specify stress relaxation tests for critical sealing products in the cars. This paper will describe the test methods, the instruments, test results and how to use the test data for lifetime estimations.

Definitions

When a constant strain is applied to a rubber sample, the force necessary to maintain that strain is not constant but decreases with time, this behaviour is called ”stress relaxation”. Conversely, when a a rubber sample is subjected to a constant stress, an increase in the deformation takes place with time, this behaviour is called ”creep”.

The processes causing stress relaxation may be physical or chemical in nature, and under all normal conditions both types of process will occur simultaneously. However, at normal or low temperatures and/or short times, stress relaxation is dominated by physical processes, whilst at high temperatures and/or long times chemical processes are dominant.

Standardised test methods

More than 25 years ago ISO TC 45 started to standardise test methods for stress relaxation tests. As a result the standard ISO 3384 was published (2). Later the standard ISO 6056 concerning testing of ring test pieces in liquids was published. Another standard, ISO 6914 (3), describes the testing of relaxation in tension.

Later ISO 3384 and ISO 6056 were combined into one standard ISO 3384, dealing with tests in both air and liquids. ISO 3384 has now been revised several times with the objective of improving the precision when doing relaxation tests.

The present standard **ISO 3384,** includes two methods A and B which both can be used in air or liquids. The test pieces are either a cylindrical disc of diameter 13 mm, height 6,3 mm or a ring with square cross section 2 x 2 mm and ID 15 mm .

In method A, the compression is applied and all counter force measurements are made at the test temperature.

In method B, the compression is applied and all counter force measurements are made at standard laboratory temperature (23 °C). The test pieces are stored at the test temperature.

ISO 6914 describes the testing of stress relaxation in tension. This can be done by two methods, either on continuously stretched samples or intermittent stretched samples. The test piece is a 1 mm thick strip elongated 50%.

What happens in the tested rubber material

In a rubber material, tested during time, the following processes can be observed:

Physical relaxation, due to relocation of the molecular chains and the fillers, when subjected to deformation. Most of the physical relaxation happens during the first moments after a deformation.

Thermal degradation, due to increased movements of the molecular chains at increased temperature, causing chain scission.

Oxidative degradation, causes chain scission due to oxidation.

All the above processes cause a reduction in the counter force when doing relaxation tests.

Cross linking - the cross linking can continue in a rubber material, depending on the cure system and the state of cure. There are always some remains of curing agent and in the case of sulphur cures, polysulfide cross links can brake and form new cross links in the tested material.

When doing continuous stress relaxation tests new cross links formed are considered not to cause any new stress. However the cross linking will show if testing intermittent stress relaxation, which is in fact measuring the change in stiffness of the material. The cross linking will also clearly show when doing compression set tests, as the new cross links formed in the deformed state will restrain the rubber from recovering.

Instruments for testing of stress relaxation

There are mainly two types of instruments for the testing of stress relaxation available on the market.

Continuous measurement

One type of relaxation instrument is measuring continuously and consists of a small rig with a load cell. When testing at elevated temperature the rig is placed in a cell oven and when testing at room temperature the rig is placed in a room temperature box, as temperature stability is of great importance for this test.

The rigs are connected to a data acquisition box connected to a computer, storing the force and temperature data, see figure 1, 2 and 3.

Figure 1 *Stress relaxation system for continuous measurements*

Figure 2 *Relaxation rigs in a cell oven*

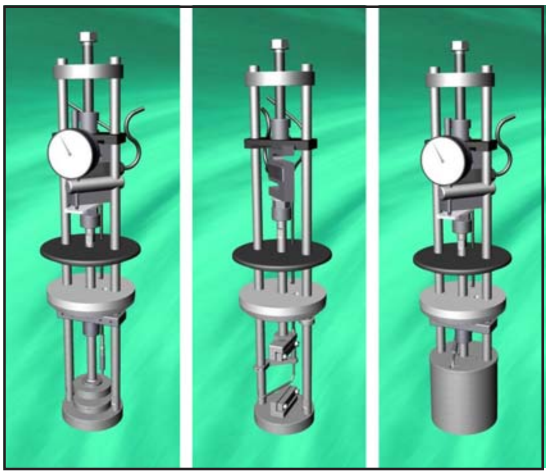

Figure 3 *Relaxation rigs, arranged for testing in compression, tension and in liquids*

Figure 4 *Stress relaxation system for discontinuous measurements using jigs*

ITP ISO 3384 Stress relaxation,1998
Table 1, Precision

Method A 168 h at 23 C°; % relaxation

Material	Mean	Sr	r	SR	R
A	10,9	0.795	2.22	1.21	3.40

Method A 168 h at 100 C°; % relaxation

Material	Mean	Sr	r	SR	R
A	50.5	0.845	2.37	2.15	6.03

Method B 168 h at 100 C°; % relaxation

Material	Mean	Sr	r	SR	R
A	67.5	2.07	5.8	8.66	24.3

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)

Discontinuous measurement.

The other type of relaxation instrument is using test jigs, like compression set. The counter force is measured in a tensile tester or a special relaxometer, figure 4, before placing the jigs at the test temperature. The jigs are taken out of the test temperature at intervals and the counter force is measured. To measure the counter force in these type of jigs it is necessary to apply a slight increase in compression.

Precision

In the beginnining of the 90's an Interlaboratory Test Program, ITP, was done within ISO TC 45 for stress relaxation tests according to ISO 3384. The intention was to be able to include a precision clause in the standard. The result from this ITP was very disappointing and showed great variation between participating laboratories. As a result of this, some work was done in Sweden at the University of Borås (4), where different factors influencing the test result were investigated. The investigation showed that the two most important factors influencing the test result were to keep the temperature and the compression constant during the test.

The importance of keeping a constant temperature within ±0,25 °C during the test, can be explained by the different thermal expansion of rubber and steel. The rubber sample is placed in a steel rig and as rubber expands about 20 times more than steel when the temperature increases, it is of vital importance to keep the temperature constant during the test.

ISO has during 1988 repeated the ITP with the new information included in the revised standard. The results are now much better (but not good), see table 1. A general conclusion made when analysing the test results, was that commercial instruments showed much better reproduceability than home build instruments.

Precision with the continuous type of instrument

Figure 5 and 6 shows the repeatability of the relaxation rigs. Figure 5 is a graph from two tests of the same compound run at different test periods. Figure 6 is a graph from two samples of the same compond run at the same test period in different rigs.

Figure 7 and 8 shows how to correlate for the spring effect in the load cell and rig, when doing very accurate tests. The spring effect is caused by the expansion of the load cell and rig when the force decreases with time. Figure 7 shows a manual correction done twice during the test, by manual adjustment of the compression. Figure 8 shows a correction done in the software by a mathematical calculation. The correction may not be necessary when doing comparative tests.

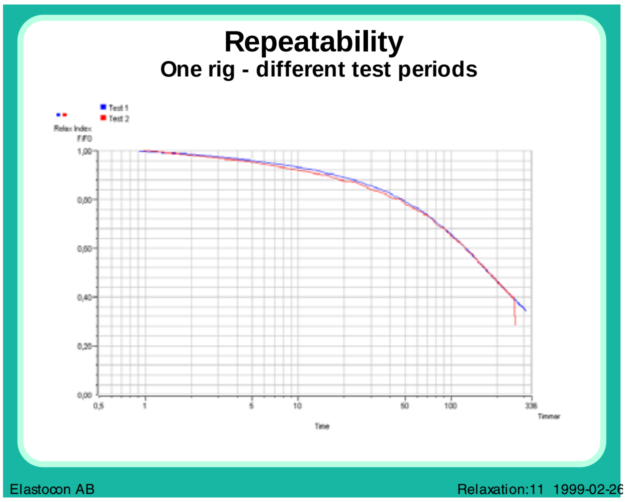

Figure 5

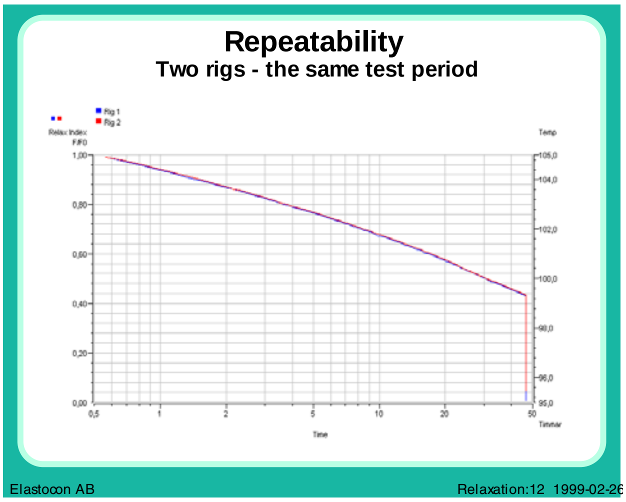

Figure 6

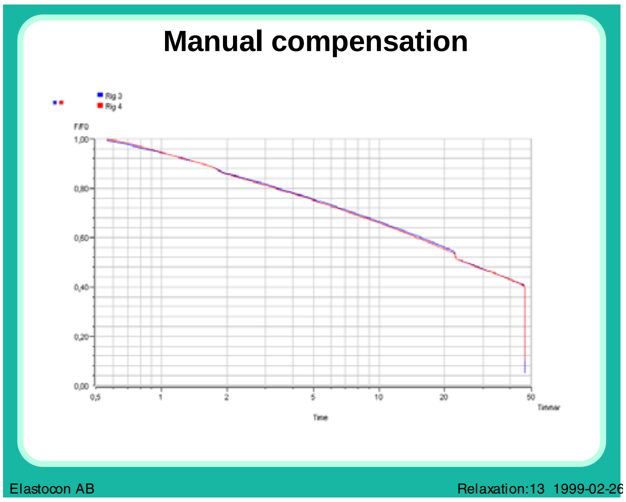

Figure 7

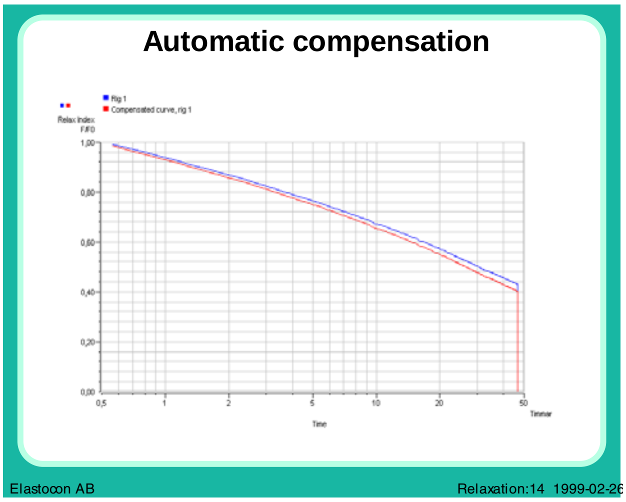

Figure 8

Estimation of lifetime from relaxation tests

Stress relaxation tests are ideal for making lifetime estimations using an Arrhenius plot.

How to do an estimation of lifetime of rubber materials using an Arrhenius plot is described in the ISO standard ISO 11346 (5).

When doing an Arrhenius plot, tests are made of a critical property at different times and at least at three test temperatures. The tests are normally run until the properties are reduced to 50 % of the original value, see figure 9. The time to reach this level is determined for each temperature. The test temperatures are chosen so the test time for the highest temperature is at least one week and the time for the lowest temperature is at least 9 months.

The times to reach the ”end of life” time for each temperature are plotted in an Arrhenius plot, which is a diagram with ln time on the Y-axis and 1/T on the X-axis, where T is the temperature in Kelvin, see figure 10. A straight line is drawn through the points and extrapolated to the temperature of use, to get an estimation of the lifetime of the tested material.

Testing of products

For determination of the lifetime for a product with thin walls and exposed to air, the stress relaxation test in tension with a thin strip, extended 50 % is the best test. This test is very sensitive for broken molecular chains, showing as a decrease in force.

For thicker products and seals of different kinds, stress relaxation in compression is more suitable.

The standards normally prescribe the relaxation tests to be done on cylindrical test pieces. Relaxation tests are however also easy to do on products or parts of products, such as O-rings, sealing rings for pipes, weather strips, hoses etc.

Figure 11 shows a test run on the inner tube of hydraulic hoses made of three different compounds. The test pieces were 40 mm long parts of the inner tube compressed 75 % and the test was done in Oil no. 1.

Stress relaxation tests are very suitable for doing ageing tests as they give a lot of information with very little operator time, especially when using the continuous measurement system, compared to make e.g. tensile tests at different times.

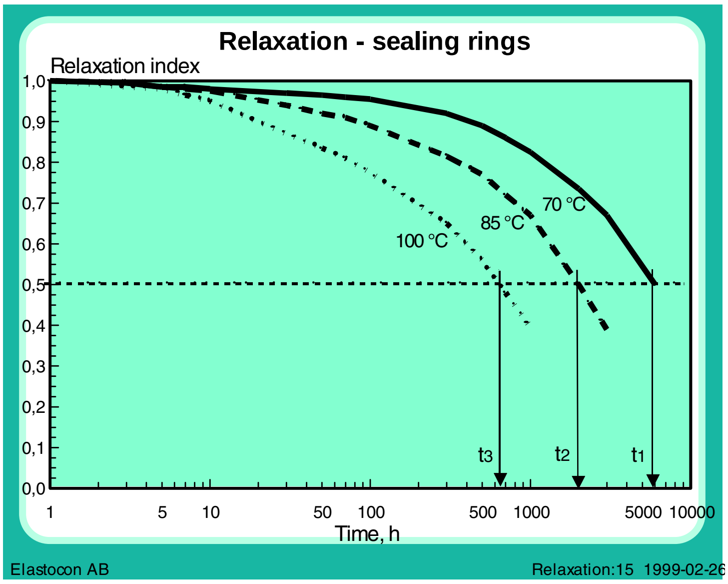

Figure 9 *Stress relaxation test on sealing rings*

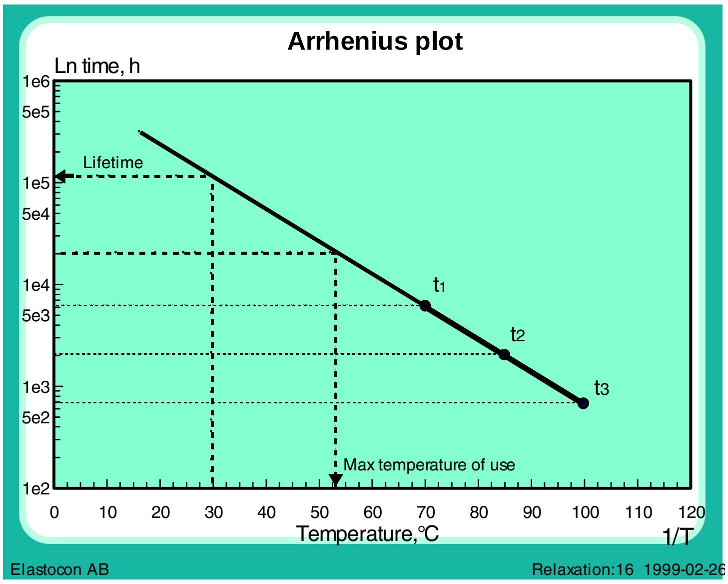

Figure 10 *Arrhenius plot*

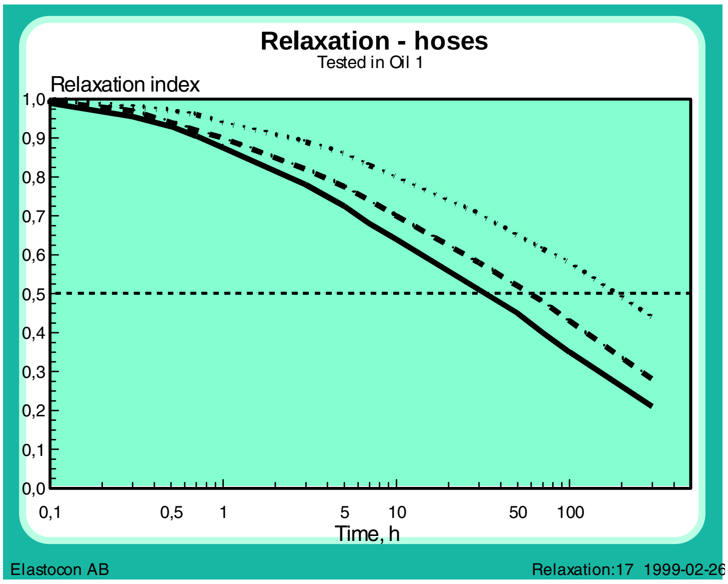

Figure 11 *Stress relaxation test on hydraulic hoses*

Test results from different materials

Figure 12 to 15 shows results from testing in tension and figure 16 to 19 results from testing in compression.

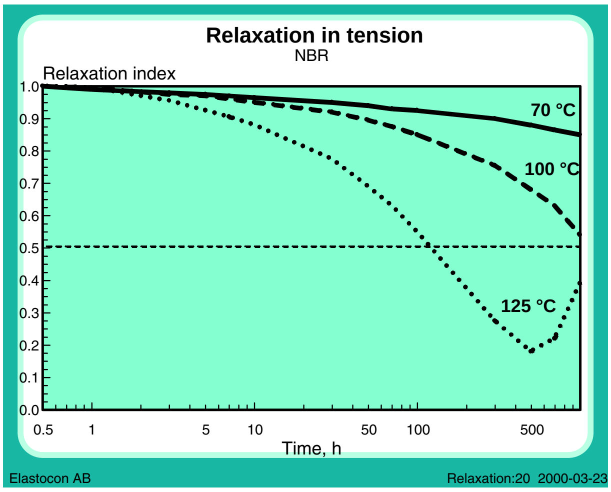

Figure 12

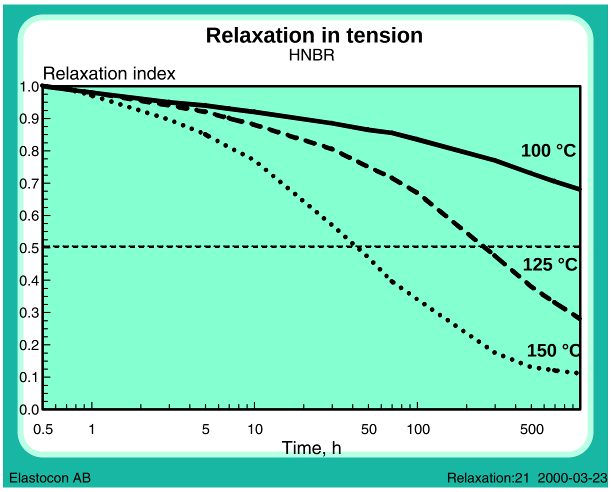

Figure 13

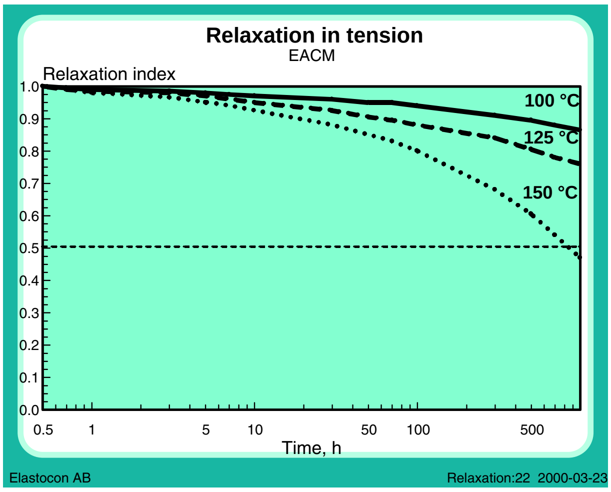

Figure 14

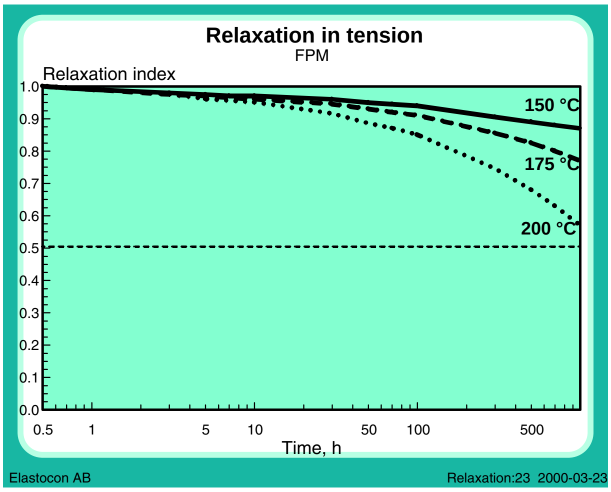

Figure 15

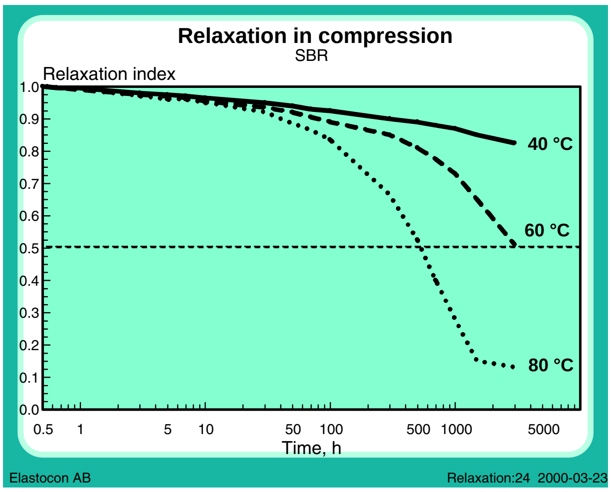

Figure 16

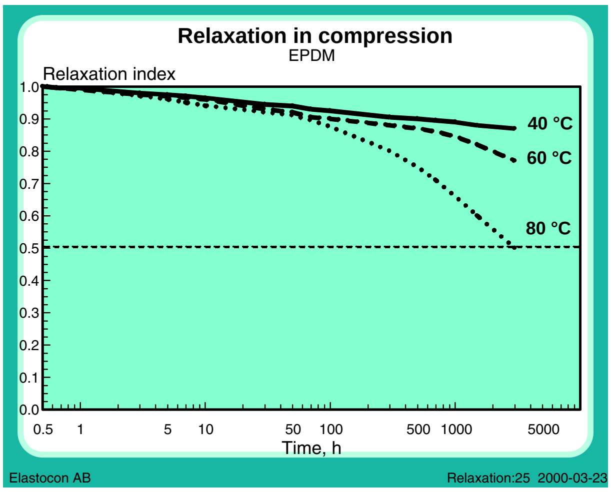

Figure 17

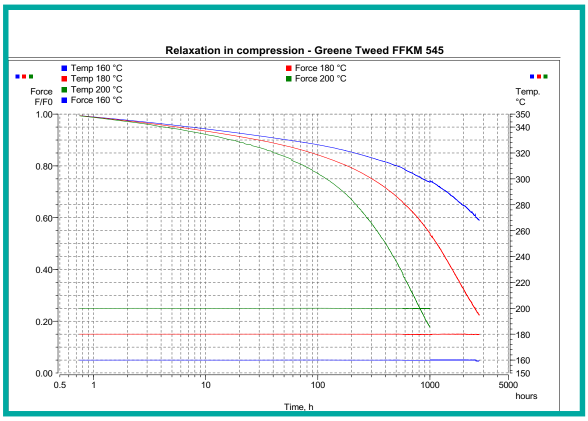

Figure 18
Relaxation test of a perfluoro rubber at three temperatures

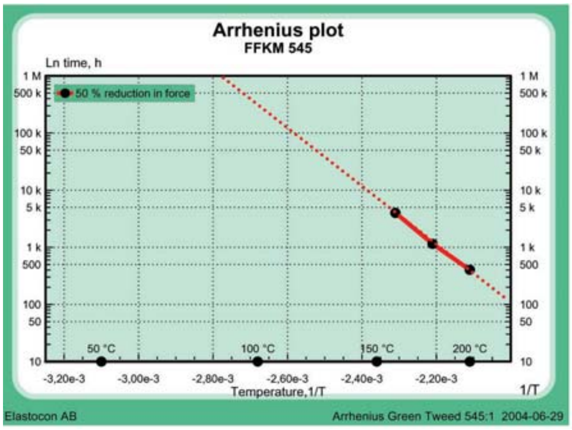

Figure 19
Arrhenius plot of the test in figure 18

References:

1. EN 681-1: Elastomeric seals - Materials requirements for pipe joint seals used in water and drainage applications - Part 1 : Vulcanized rubber

2. ISO 3384: Rubber, vulcanized or thermoplastic - Determination of stress relaxation in compression at ambient and at elevated temperatures (revision of ISO 3384:1991)

3. ISO 6914: Rubber vulcanized or thermoplastic - Determination of ageing characteristics by measurement of stress relaxation in tension.

4. Stress Relaxation in compression of Rubber, Peter Henricsson, Daniel Marcus, Borås University College, Institution for technology.

5. ISO 11346: Rubber, vulcanized and thermoplastic - Estimation of lifetime and maximum temperature of use.

Key Words: Stress relaxation, ageing, rubber, lifetime

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