Developments in Low Temperature Testing of Rubber Materials

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Introduction

The low temperature properties of rubber materials are important in colder climates, such as that encountered in Scandinavia. The requirements for these properties have since long been included in specifications, especially those of the automotive industry. There are a number of test methods in use (1), the most common methods in Scandinavia is the Temperature Retraction Procedure, also known as the TR-test (2). This test is now also included in the new material specifications that have been developed by the Swedish Standards Institute (3). Another low temperature test is the Gehman test which measures the stiffness (modulus) at a range of temperatures (4).

A problem with both these methods is that they are both very time consuming to perform however this is eliminated with automated instruments.

This paper will describe what happens in the rubber material at low temperatures and review the most common standardised test methods for low temperature properties. The new automated instruments used for testing and the improved precision that can be achieved will also be discussed.

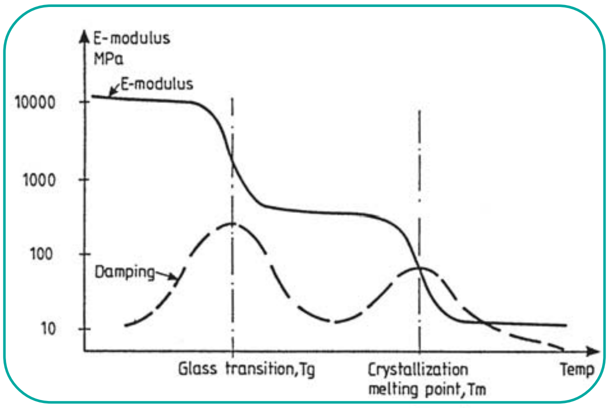
Effect of low temperatures

A high mobility of the molecular segments in a polymer is the condition for the rubbery state, i.e. high elastic elongation. In a rubber material this is combined with a light cross-linking of the molecular chains. With decreasing temperature the movements of the segments are reduced. At a certain temperature, movements of the molecular segments are completely frozen and the material becomes a stiff, brittle, plastic-like material with low elongation at break. This temperature is called the glass transition temperature, T_g.

The movements of the molecular segments can also be decreased by crystallisation, which means that part of the molecules are arranged in a regular structure. The crystalline, melting point, T_m, which gives the upper temperature limit for this transformation, is higher than the T_g. The crystallisation assumes a certain mobility of the segments and happens therefore with the highest speed at a temperature that lies between T_g and T_m (figure 1).

The condition for the rubbery state is consequently a low tendency for crystallisation and a low T_g. If a rubber material is cooled down , the T_g, point will be reached sooner or later and the material becomes stiff and eventually also brittle.

Figure 1



This means that the material is no longer useful as a rubber.

Changes in the viscoelastic properties of the rubber occur immediately upon the rubber being cooled down. Changes caused by crystallisation, however, need a certain time to develop and it can take a long time to reach equilibrium.

Most rubber materials have a lowest useful temperature in the region of -25 to -75 °C. Low-temperature properties can also be affected by the composition, and especially by type of softener used.

Brittleness point: ISO 812

By brittleness point is meant, the lowest temperature at which rubber materials do not exhibit brittle failure when impacted under specified conditions.

When testing, test pieces in the form of strips 40 mm x 6 mm and 2 mm thick are clamped as shown in Figure. 2 and then immersed for 5 min in a cold bath. After 5 min they are subjected to a single impact blow, then examined to see if they show any cracks. If they have failed, new test pieces are tested at a temperature 2 °C higher. The test is then repeated at higher temperatures until no failure is observed. This temperature is recorded as the temperature limit for brittleness.

Figure 3 Figure 3 shows a computer controlled instrument.

Review of low temperature test methods

The following test methods will be described and it must be noted that they may not give the same result or range the materials in the same order.

Table 1 Low temperature test methods

• Brittleness Point	ISO 812
• Low Temperature compression set	ISO 815
• Low Temperature stiffening, Gehman Test	ISO 1432
• Temperature Retraction, TR-test	ISO 2921
• Increase in Hardness	ISO 3387
• Determination of crystallisation	ISO 6471
• Dynamic Mechanic Analysis	ISO 4664-1

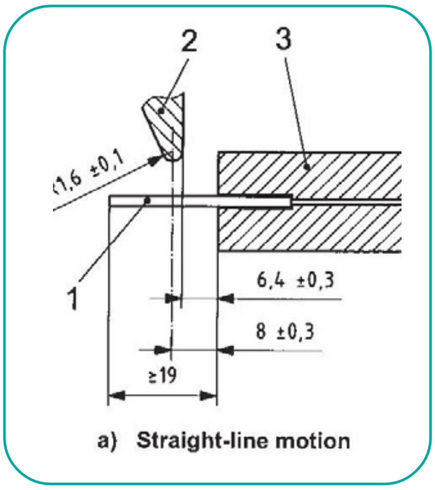


Figure 2

Compression set at low temperature: ISO 815-2

This test shows the ability of a rubber material to recover after being compressed at a low temperature.

The test piece, normally a cylinder, 13 mm in diameter and 6,3 mm high, is compressed to 75% of its original height between two plates equipped with a quick release device. Immeditely after compression the jig is placed in a low-temperature cabinet at the test temperature. After 24 or 72 h the test piece is released, still at the test temperature, and the height is measured, normally after 30 and 1800 s. The compression set is then calculated in the normal way as the remaining deformation.

Determination of stiffness characteristics (Gehman test): IS0 1432

The Gehman tests determines the relative stiffness of a material over a temperature range from room temperature down to - 150 °C. The test can be used both for vulcanized and thermoplastic rubber.

The principle for this test is that a rubber strip 40 mm x 3 mm x 2 mm is connected in series with a torsion wire (figure 4).

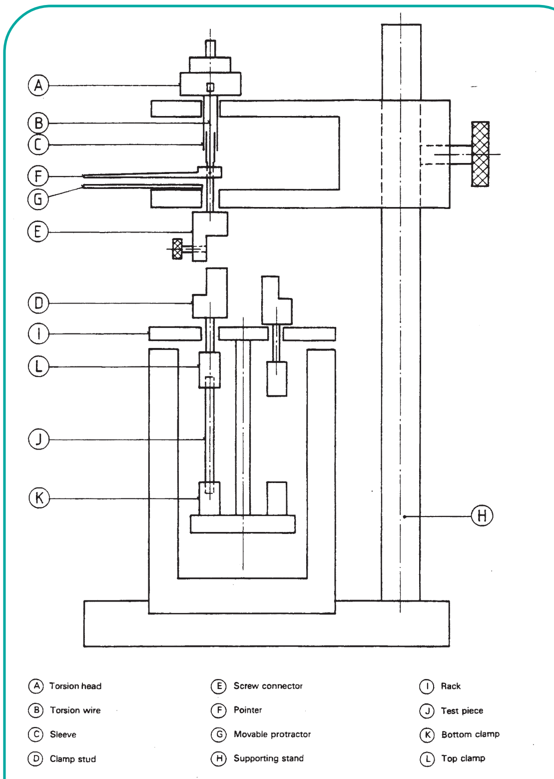


Figure 1 – Apparatus for determination of stiffness characteristics

Figure 4

The rubber strip is placed in a cold liquid bath. When one end of this combination of torsion wire and rubber strip is twisted to a certain angle, the torsion will be divided between the rubber strip and the wire in inverse proportion to their torsion stiffness.

The stiffness of the material is first determined at room temperature. The bath is then cooled down to the lowest temperature desired. The temperature of the bath is increased by 1 °C/min and the stiffness is measured every minute. The result can be shown in a graph as the relative modulus against temperature between the stiffness at each temperature and 23 °C. The temperatures at which the relative modulus is 2, 5, 10 and 100, are determined from the curve.

Temperature retraction test (TR test): IS0 2921

This method shows the elastic retraction of a rubber material at different temperatures.

The principle for the method is to elongate a rubber test piece, lock it and cool it to -70 ºC in a cold liquid bath, for 10 min. After this time the test piece is released and the temperature is increased by 1 ºC (figure 5).

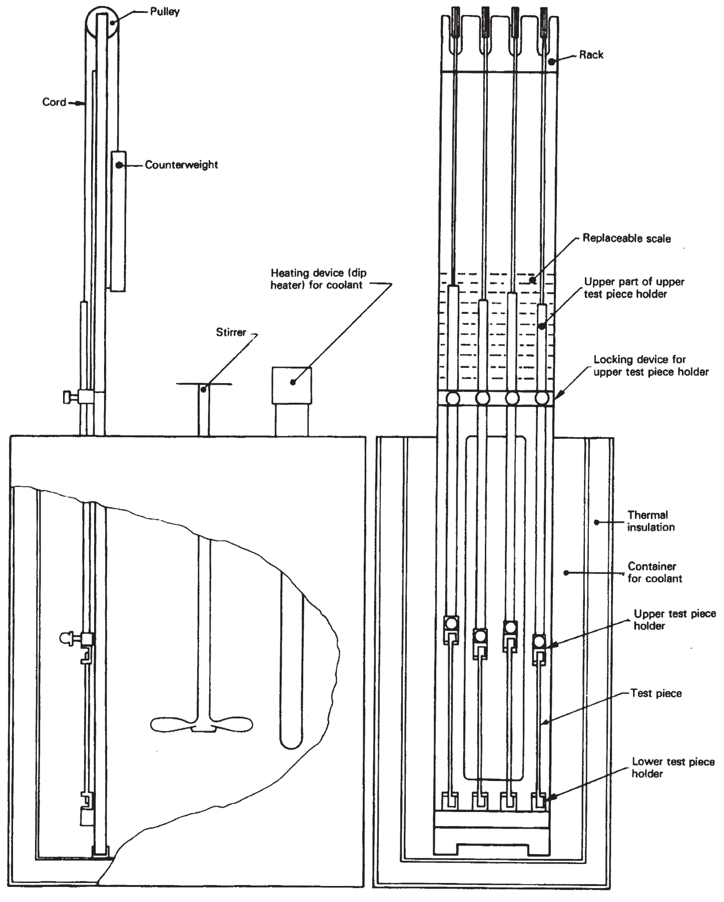


Figure 2 – Retraction apparatus

Figure 5

The temperatures at which specified retractions occur are then calculated. The specified retractions are normally, 10 %, 30 %, 50% and 70%, and are called TR_{10}, TR_{30}, TR_{50} and TR_{70} respectively. This method is not suitable for TPE-materials, as they can experience high tension set.

Increase in hardness: IS0 3387

This method describes a test based on hardness measurements for determining the progressive stiffening of rubber with time, caused by crystallisation. The method is applicable to both raw and vulcanised rubbers. It is mainly of interest for rubber with a marked crystallisation tendency at temperatures experienced in cold climates such as, for instance, chloroprene and natural rubber.

The test pieces are placed in a cold chamber at the test temperature and the first hardness measurement is done after 15 min conditioning time. The hardness measurements are then repeated after 24 and 168 h storage. If a curve is to be plotted, measurements can be made at intermediate times.

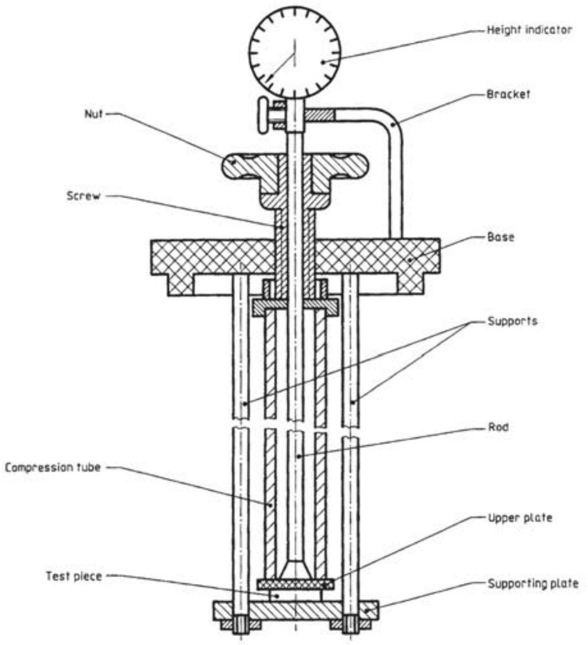


Figure 1 — **Apparatus for determination of crystallization under compression**

Figure 6

Determination of crystallisation at low temperatures: IS0 6471

This method describes the determination of the tendency of vulcanised rubber to crystallise, and the time dependence of crystallisation, by measurement of the recovery of compressed test pieces. Crystallisation, which occurs more rapidly under high compression, reduces the elastic recovery of the rubber.

The test pieces are first compressed with low deformation and the recovery is determined without crystallisation. The test pieces are then compressed with high deformation and the recovery is determined after crystallisation. Normal holding times are 30 or 60 min, but if the time dependence is to be studied the results after different times are plotted on a graph. From this curve the half-time to crystallisation can be determined. Figure 6 shows the instrument.

Photo PerkinElmer

Figure 7

Dynamic Mechanical Analysis : ISO 4664-1

In a dynamic mechanical instrument the modulus of the test piece is determined continuously, while making a temperature sweep from a low to a high temperature. Often used conditions are a frequency of 1 Hz and a temperature increase of 1 ºC a minute. The test mode can be either tension, compression, bending or shear. The resulting graph is shown in fig 1 and an instrument is shown in figure 7.

Precision

As the TR-test is an important test in Sweden, two interlaboratory test programmes (ITP:s) were conducted in 1985 and 1987 . The results are shown in table 2.

Table 2 Reproducibility R, in °C

	1985	1987
TR_{10}	6,2	5,9
TR_{30}	7,2	7,8
TR_{50}	6,3	11,2
TR_{70}	7,1	12,6

12 companies participated in the ITP (5) and the anticipated improvement between the 1985 and the 1987 ITP results did not occur, even if the instruments had been checked and adjusted. An explanation to the poor results in 1987 is that an NR material was one of the four materials used and this material showed extreme variations, probably due to crystallisation effects, especially as 250 % elongation was used. The results from the participating laboratories also showed clear systematical errors.

Further investigations of the TR-test were carried out early in the 1990's, within a project of Improving Testing Precision, organised by the Swedish Plastic and Rubber Institute.

The experiences gained from these projects showed that the following factors are important to get good repeatability and reproducibility.

- **Accurate temperature measurement;**
- **Good agitation of the cold bath to avoid laminations;**
- **Accurate speed of temperature ramp;**
- **Accurate measurement of retraction;**
- **Automated test sequence to avoid operator influence.**

An ITP was organised within ISO 1986 for Compression set with the following results:

Table 3 Reproducibility R, in % at – 25 °C

Test piece	Ave	R
A, 10 s	61	44
B, 10 s	55	48
A, 800 s	39	55
B, 1800 s	34	56

The results shows that the reproducibility is extremely bad.

No ITP:s have been carried out for the other test methods.

Development of automated instruments

These ITP:s shows the need to improve the instruments and test methods and the use of automated instruments, to get rid of the operator influence, is the best way to improve the accuracy. The automation, which means an instrument controlled by a computer also improves the test capacity and the calculation, presentation and storage of test results.

Automatic TR-tester

Figure 8 shows a traditional manual TR-tester, where the operator has to manually set the temperature increase and for 1 to 2 hours watch and record the results.

Figure 8

The automatic TR-tester consists of a bath for the low- temperature liquid and a test rig where the samples are attached. Agitation in the test bath is carried out by a pump system that moves the cold liquid from the bottom to the top of the bath. The heating element used to control the temperature in the bath also covers the bottom of the tank to avoid excessively low temperatures in the bottom as a result of stratification. Bath cooling can either be achieved manually with, for instance dry ice, or automatically with an attached cryogenic bottle with liquid nitrogen.

The test rig is raised by a pneumatic cylinder for ease of use and the retraction of the test pieces is measured by a digital device. Release after the pre-cooling period, the temperature increase and the retraction are all controlled and all data collected by a connected computer, with a Windows software.

Figure 9 shows the automatic TR-tester.

Figure 10 shows the TR results from five different rubber materials. From these it can be seen that there are quite pronounced differences between the different materials.

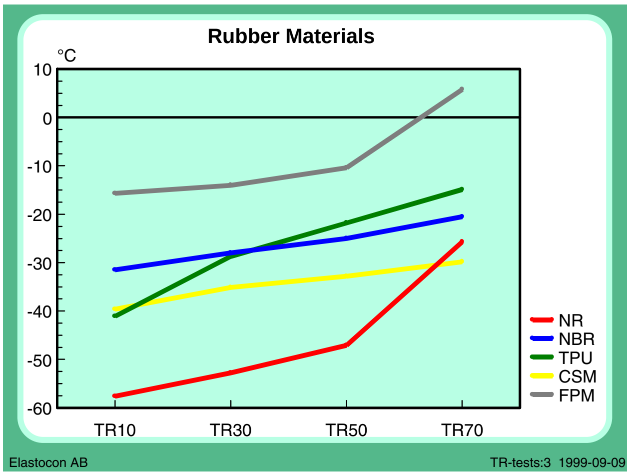
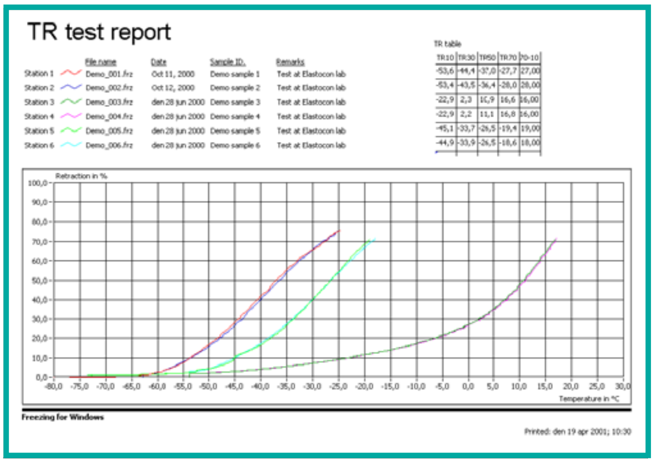


Figure 10

Figure 9



TR test report

	File name	Date	Sample ID.	Remarks
Station 1	Demo_001.frz	Oct 11, 2000	Demo sample 1	Test at Elastocon lab
Station 2	Demo_002.frz	Oct 12, 2000	Demo sample 2	Test at Elastocon lab
Station 3	Demo_003.frz	den 28 jun 2000	Demo sample 3	Test at Elastocon lab
Station 4	Demo_004.frz	den 28 jun 2000	Demo sample 4	Test at Elastocon lab
Station 5	Demo_005.frz	den 28 jun 2000	Demo sample 5	Test at Elastocon lab
Station 6	Demo_006.frz	den 28 jun 2000	Demo sample 6	Test at Elastocon lab

TR table

TR10	TR30	TR50	TR70	70-10
-53,6	-44,4	-37,0	-27,7	27,00
-53,4	-43,5	-36,4	-28,0	28,00
-22,9	2,3	10,9	16,6	16,00
-22,9	2,2	11,1	16,8	16,00
-45,1	-33,7	-26,5	-19,4	19,00
-44,9	-33,9	-26,5	-18,6	18,00

Freezing for Windows

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Figure 11 shows the good repeatability of 3 rubber materials tested with two test pieces per material

The short term repeatability shows very good results for all materials, see figure 12. The long-term repeatability, however, shows some variations, especially for TR$_{70}$.

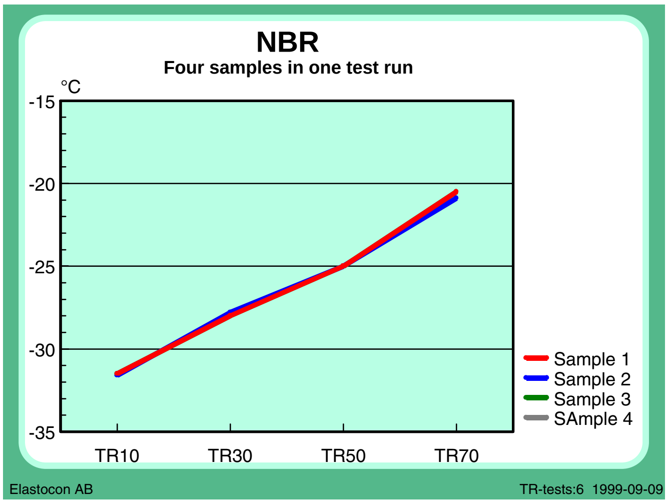


Figure 12

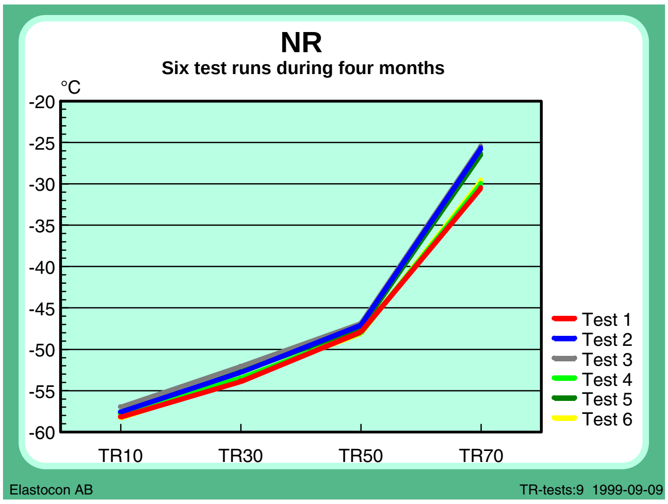


Figure 14

Automatic Gehman tester

A traditional manual Gehman tester is shown i figure 15 where the operator has to manually control the temperature increase and switch between the test stations to perform the test at different temperatures.

Figure 15

The NBR material shows a fully acceptable variation of ± 0,9 °C for TR$_{70}$ but the NR material shows a variation of ± 2,5 °C for TR$_{70}$, see figures 13 and 14. This variation for NR may be caused by crystallisation effects, but this has to be further investigated.

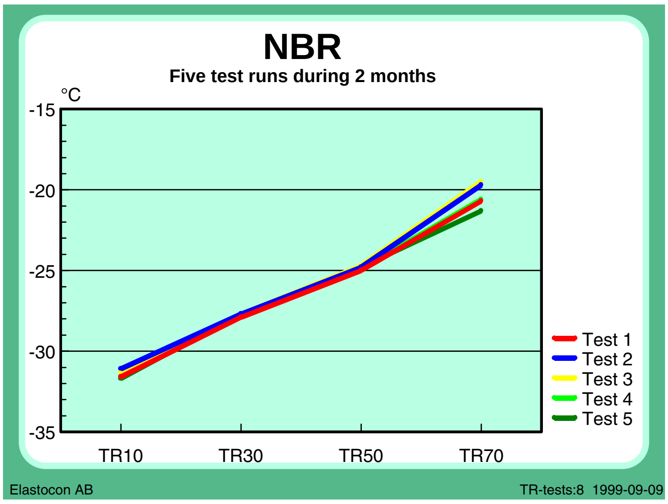
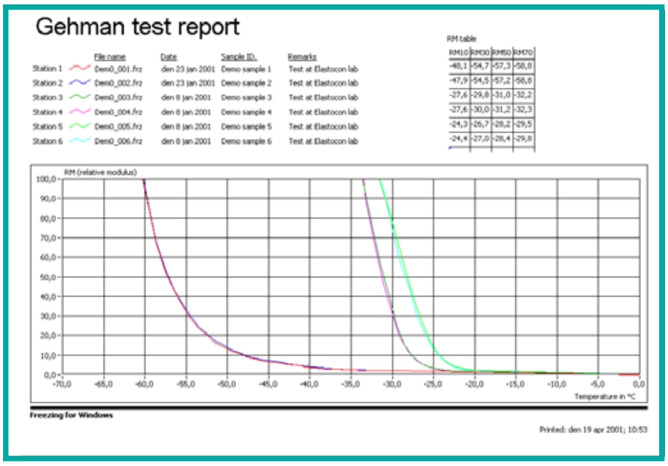


Figure 13

Figure 16

An automated Gehman tester, has recently been developed based on the TR-tester, where the test rig on the TR-tester is changed to a Gehman rig. The test rig is raised and the turning is done by pneumatic cylinders. The torsion angle of the test pieces is measured by digital encoders. The temperature increase are controlled and all data collected by a connected computer, with a Windows software. Figure 16 shows the automatic Gehman-tester.



Gehman test report

	File name	Date	Sample ID.	Remarks
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Station 2	Dem0_002.frz	den 23 jan 2001	Demo sample 2	Test at Elastocon lab
Station 3	Dem0_003.frz	den 8 jan 2001	Demo sample 3	Test at Elastocon lab
Station 4	Dem0_004.frz	den 8 jan 2001	Demo sample 4	Test at Elastocon lab
Station 5	Dem0_005.frz	den 8 jan 2001	Demo sample 5	Test at Elastocon lab
Station 6	Dem0_006.frz	den 8 jan 2001	Demo sample 6	Test at Elastocon lab

RM table

RM10	RM30	RM50	RM70
-48,1	-54,7	-57,3	-58,8
-47,9	-54,5	-57,2	-58,8
-27,6	-29,8	-31,0	-32,2
-27,6	-30,0	-31,2	-32,3
-24,3	-26,7	-28,2	-29,5
-24,4	-27,0	-28,4	-29,8

Freezing for Windows

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Figure 17 shows a printout with results. The results from three materials with two test pieces per material is shown. The results shows good repeatability for each double test.

Summary

The results and experiences with the automated low temperature-testers shows a much improved accuracy, together with a good reduction of operator time needed to perform the tests.

Additional information in the second edition

Figure 18

Automatic Brittleness Tester

Elastocon has now also developed an automatic Brittleness tester. This instrument is built on the same base unit as the Elastocon TR- and Gehman testers.

The instrument is using a falling weight to achieve the specified speed of 2 m /s and the speed is measured after impact to show that the energy in the strike was sufficient to keep the specified speed of 2 m/s +/ - 0,2 m/s. The software controls the strike and records the temperature at impact. The number of failed test pieces is noted in the software and a test report cn be printed.

Automatic Low Temperature Compression Set tester, LTCS

Low temperature compression set has always given big spread in the test results both within a laboratory and between laboratories. In an ISO project a revised method for this test has been developed where all measurements are done without touching the test piece.

Figure 19, Automatic Low Temperature Compression Set tester

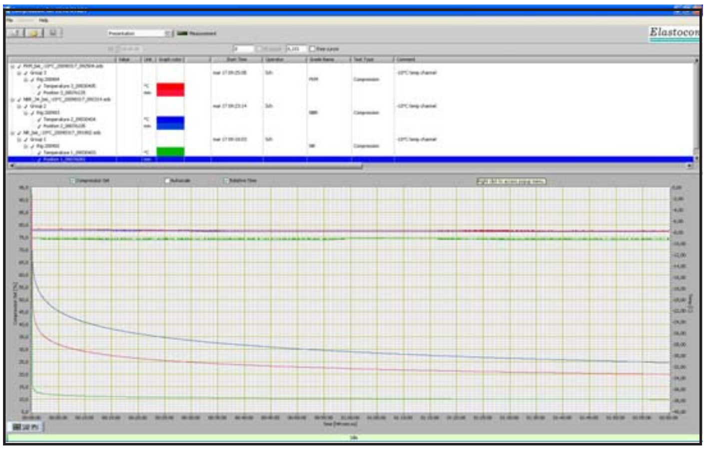

Figure 20, LTCS curve

The Elastocon instrument consists of a test rig and a modified laboratory Freezer, se fig 19 The test piece is compressed in the rig and the rig is placed in the freezer for 24 h or 72 h conditioning at low temperature. After this time the compression is released and the test piece can recover. The instrument measures the recovery and the software plots a curve of the compression set against time, see figure 20

References:

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2. ISO 2921Rubber, vulcanised - Determination of low-temperature characteristics- Temperature-retraction procedure (TR-Test).
3. SS162010,Vulcanized Rubber - Material specifications.
4. ISO 1432, Rubber vulcanized or thermoplastic - Determination of low temperature stiffening (Gehman test)
5. Comparative Testing - Rubber Materials, Part 10, Determination of Temperature Retraction, according to SIS 16 22 21 (ISO 2921), retest. Lars-Åke Henriksson and Göran Spetz, Swedish National Testing Institute, report 1988:29

Key Words: Rubber, Temperature retraction, TR-test, Gehman test, low temperature elasticity, low temperature stiffening.