

Developments in Testing

Since I first wrote a major review of progress in testing in 1972, the most striking point that has continued through subsequent reviews has been that development in apparatus has revolutionised testing but at the same time what we measure has changed very little. Consider one of the most common of tests – tensile stress strain properties. In 1950 and before we measured ultimate strength, elongation and “modulus” on mechanical pendulum type tensile machines with crude mechanical extensometers (or more often a piece of string). In 2001 we measure precisely the same properties with the same arbitrary test pieces but we do it on electronic tensile machines with computerised control and output.

It was suggested that developments in testing come about through the work of standards organisations, increasing fundamental knowledge of the behaviour of materials and advances in instrumentation. The main trends were seen as dynamic testing, non-destructive testing and automation with an overall trend to tests which are more related to service. In a 1984 review it was observed that additionally there was increased emphasis on measures of processability. In 1992 the scene was considered to be much the same but with the very significant addition of emphasis on reproducibility of tests.

For as long as can be remembered the most voiced criticism of existing test methods, particularly standard ones, has been that they are arbitrary and do not measure the fundamental properties needed for design purposes. For quality control purposes the existing standard methods are generally more acceptable but there is a continuing wish for quicker and cheaper tests.

As we move into the 21st century, what has happened? Advances in instrumentation, particularly automation, have made vast strides in improving efficiency, making tests easier and quicker to perform. Instrumentation, in combination with a drive towards more rigorous calibration, has also done much to improve the accuracy and reproducibility of results. It is only because of automated instruments that tests such as thermal analysis as a function of temperature and frequency have become viable.

The adoption of dynamic testing and NDT has not been as great as prophesied and there is still a dearth of tests yielding fundamental data. To devise a suitable fundamental test is generally difficult and expensive. Where suitable methods exist, such as for dynamic properties, they are only used by a minority with cost being the deterrent. The only plausible reason for insufficient improvement in this direction can be financial.

In fact, it is clear that commercial pressures have dominated. Instrument manufacturers wish to increase sales and have developed better and more efficient products, which have helped to satisfy the demands of users needing increased productivity and higher quality in their products. Also, as digital storage and communications have reduced costs, vast quantities of data can be collated and made accessible through databases.

The commercial pressures for fundamental design data do not seem to have so great an effect on productivity. However, despite the dominance of the traditional properties, there has been some increase in awareness and use of parameters such as stress relaxation, tearing energy and dynamic moduli, together with more demand for input data for finite element analysis. The demand for guaranteed quality has also led to a very significant increase in the amount of performance testing carried out on complete products, and the inclusion of such tests in product specifications.

The papers that follow demonstrate the importance of sophisticated apparatus in testing today and include examples of dynamic testing, obtaining lifetime prediction data which is useful for design and NDT. Where do we go next? There can be no doubt that there will be continued pressure for improved efficiency and we can expect more, and probably revolutionary, advances in instrumentation. Processing and accessing data will become more sophisticated and we will expect to view and even control our tests in real time remotely.

It would seem reasonable to suppose that the demand for data will not diminish because of the pressures to introduce new materials, more advanced designs and to ensure quality. However, it is widely suggested that practical testing will be increasingly replaced by computerised simulation – virtual testing. Logically, this is sensible but it raises interesting questions. The great majority of testing is done for control purposes but how does a simulated result predict the random mistakes of man or machine? If virtual testing is to advance for design data it requires an enormous effort to improve the understanding of material behaviour and to develop predictive models. Hitherto, there has been something of a lack of investment in better fundamental data, so where is the new funding coming from? The information will not be generated by virtual money.

Maybe it is just possible that after decades of taking second place more fundamental data will receive greater industry interest because of the relentless pressures to remain competitive. If this were so a future review may be able to report the demise of hardness testing – but I will not be putting any money on it.

Roger Brown
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Special on Testing

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Introduction

In December 1999 the Rubber Technology Group at the University of Twente acquired a RPA 2000 (Rubber Process Analyzer). This apparatus, a product of Alpha Technology, is specially designed for the measurement of dynamic rheological properties of rubbers and rubber compounds. Utilizing a wider range of frequencies and strains than common Dynamical Mechanical Rheological Testers, the RPA 2000 can characterize rubber before, during and after cure by varying frequency, strain and temperature on a single test sample. Materials tested include uncured rubber compounds; compounds cured in the RPA, raw elastomers and other thermoset materials. The RPA 2000 is based on a rotorless biconical die design comparable for the well-known Moving Die Rheometer used for cure testing of rubbers. A sealed and pressurized die cavity of 4,5 cm³ contains the sample during a test (see figure 1.)

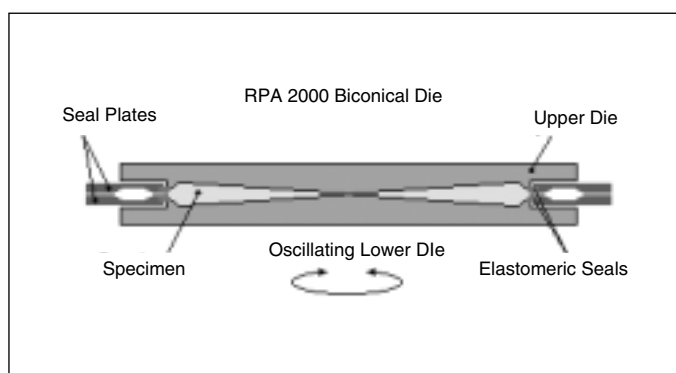


Figure 1. Die design

The lower die (driven by a digitally controlled motor) moves sinusoidally to programmed strains and frequencies at controlled temperatures, deforming the sample in shear. The upper die is connected to a torque transducer that measures the torque through the sample. This torque is the complex torque S^* , because it is not in phase with the applied strain. By applying a Fourier transform to the S^* signal, this is divided into an elastic component S' (in phase with the strain) and a viscous component S'' (90° out of phase with the strain). The accompanying software of the RPA 2000 now is able to calculate the phase shift $\tan \delta$ and can convert the torque into the shear modulus G .

The main advantage of the RPA 2000 is the possibility to vary multiple parameters, namely frequency, strain and temperature. The ranges of these test parameters are as follows:

Parameter	Range
Temperature (°C)	40 - 230
Oscillation strain (%)	± 0.7 - ± 1256
Oscillation frequency (Hz)	0.03 - 33

With the accompanying software different types of subtests are easily created. A complete test series consists of a combination of one or more of these subtests. During a subtest, typically a single parameter is varied, i.e. frequency, strain or temperature, keeping all others constant. Thus frequency, strain or temperature sweeps can be performed.

Additionally, cure versus time tests can be performed by keeping all parameters constant and measuring at selected time intervals. Finally,

stress relaxation experiments can be done by measuring torque relaxation after a strain step.

Example of application

At the Rubber Technology Group of Twente University, the RPA 2000 is mainly used to measure the dynamical rheological properties of typical silica filled tyre tread compounds (see issue 21 of "Natuurrubber"). The advantage of silica in comparison with carbon black as a filler is the low rolling resistance without losing a good wet or ice grip. The disadvantage of the hydrophilic silica is the poor dispersion in the hydrophobic rubber matrix due to the strong filler-filler interactions caused by the hydroxy groups at the silica surface. To enhance this dispersion a coupling agent is added which reacts with the hydroxy groups at the silica surface, leading to hydrophobation of the surface and a lower filler-filler interaction. This coupling agent is a bifunctional silane (Bis[triethoxysilylpropyl]tetrasulfide), that contains a tetrasulfidic group that during vulcanization reacts with the polymer matrix. Thus a chemical link between the filler particle and the rubber matrix is established.

To study the influence of the tetrasulfidic group of the bifunctional silane on the dynamical rheological properties, a sulphur containing silane was compared to a silane without sulphur. Two compounds were prepared consisting of the same basic recipe, with the silanes exchanged.

To study the filler-filler interactions of the uncured compounds (Payne effect), the G' (storage modulus), at small sample deformations, is studied. For this a strain sweep is performed with the RPA 2000 in which the G' is measured as a function of the strain (figure 2).

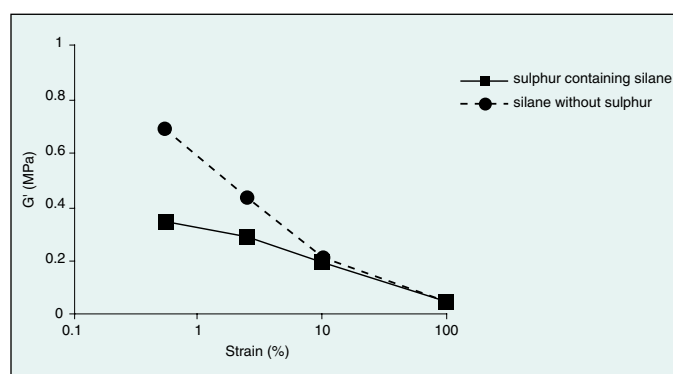


Figure 2. Strain Sweeps of the compounds without vulcanizing agents

The strain sweep shows that the compound with the sulphur containing silane has a lower G' at low strains. This shows that less filler-filler interactions occur in the compound, which indicates the silica is better dispersed in the rubber matrix. With increasing strain the filler network breaks down, leading to a decrease in G' .

Temperature sweeps are performed to study the reaction of the coupling agent with the rubber matrix. In this case G' is measured as a function of the temperature at a constant strain and frequency (figure 3).

From figure 3 it may be concluded that the sulphur containing silane reacts with the rubber matrix at 160°C, resulting in an increase of G' . On the other hand, when the silane without sulphur is applied no reaction with the rubber matrix can take place, resulting in a conventional temperature dependence of G' (figure 3).

Rheograms are performed to determine optimal vulcanization times (t_{90}), scorch times (t_{02}) and to compare crosslink densities (figure 4) after vulcanizing agents were added on a 2-roll mill.

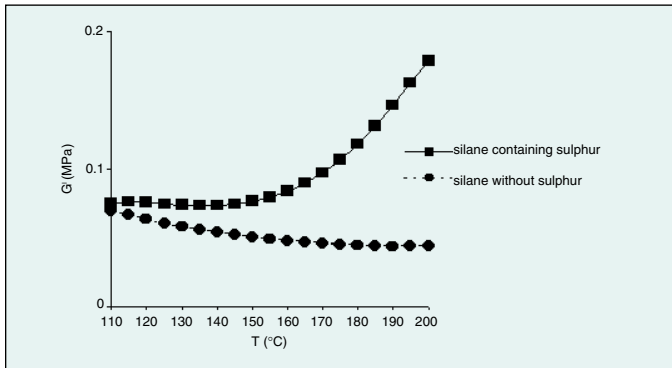


Figure 3. Temperature sweeps of the compounds without vulcanizing agents

When the optimal vulcanization time of the compounds is determined, frequency sweeps are performed to measure $\tan \delta$ at 60°C. For this a new uncured sample is vulcanized for the optimum vulcanization time. After optimum cure the sample is cooled down to 60° and $\tan \delta$ is measured at different frequencies (figure 5).

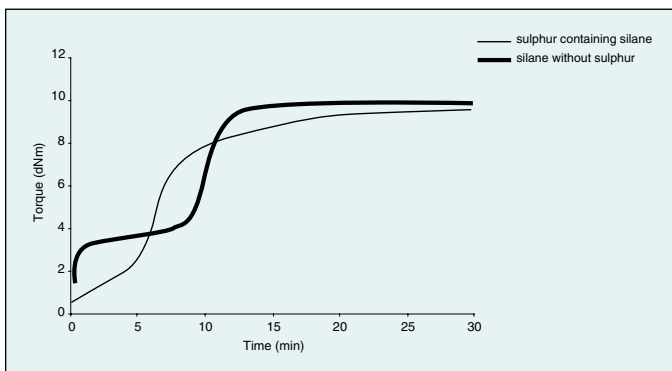


Figure 4. Rheograms of the compounds with vulcanizing agents

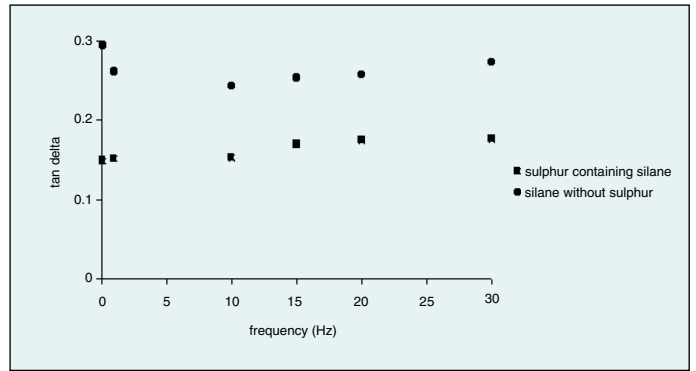


Figure 5. Frequency sweeps of the compounds with vulcanizing agents

The frequency sweeps of both compounds are showing that the sulphur containing silane has a lower $\tan \delta$ at 60°C over the whole frequency range and thus a lower rolling resistance.

Evaluation

As shown above, the RPA 2000 is very suitable to measure the dynamic rheological properties of especially rubber compounds in the cured and uncured stage. Frequency, temperature and strain are easily varied with the accompanying software to create subtests, which provides the user with the required dynamical rheological data at the preprogrammed settings.

One disadvantage of the RPA 2000 is the limited temperature range. Since it is air-cooled it cannot measure dynamical rheological data at a lower temperature than 40 °C. This means that properties like wet or ice grip, normally measured at 0 °C, can not be determined.

In perspective of the research that is performed within the Rubber Technology Group at Twente University, it can be concluded that the RPA 2000 provides a useful contribution to, for example, the study of silica tyre tread compounds.

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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 method 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 ISO (3). Another low temperature test is the Gehman test, which measures the stiffness (modulus) at a range of temperatures (4). A problem with 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. 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.

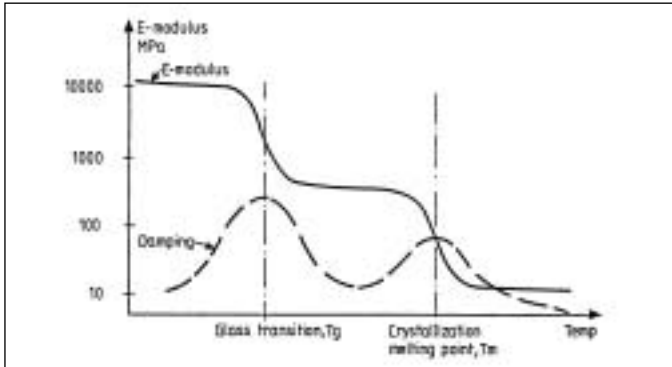


Figure 1

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:

• 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	–

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 $40\text{ mm} \times 6\text{ mm}$ 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.

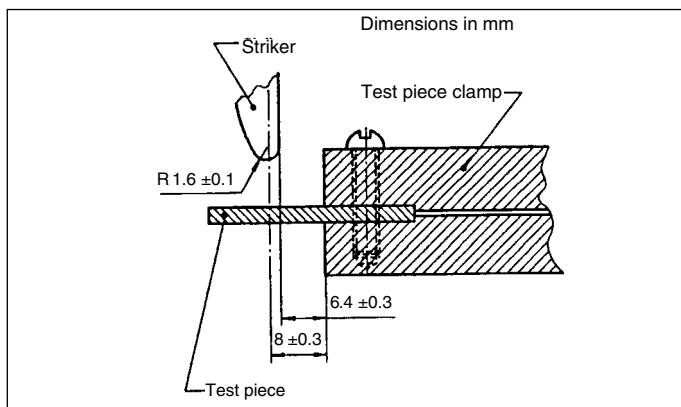


Figure 2

Compression set at low temperature: ISO 815

The test piece, normally a cylinder, 29 mm in diameter and 12.5 mm high, is compressed to 75% of its original height between two plates equipped with a quick release device. Immediately 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 10 and 1800 s. The compression set is then calculated in the normal way as the remaining deformation.

Determination of stiffness characteristics (Gehman test): ISO 1432

The Gehman test 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 $40\text{ mm} \times 3\text{ mm} \times 2\text{ mm}$ is connected in series with a torsion wire (figure 3).

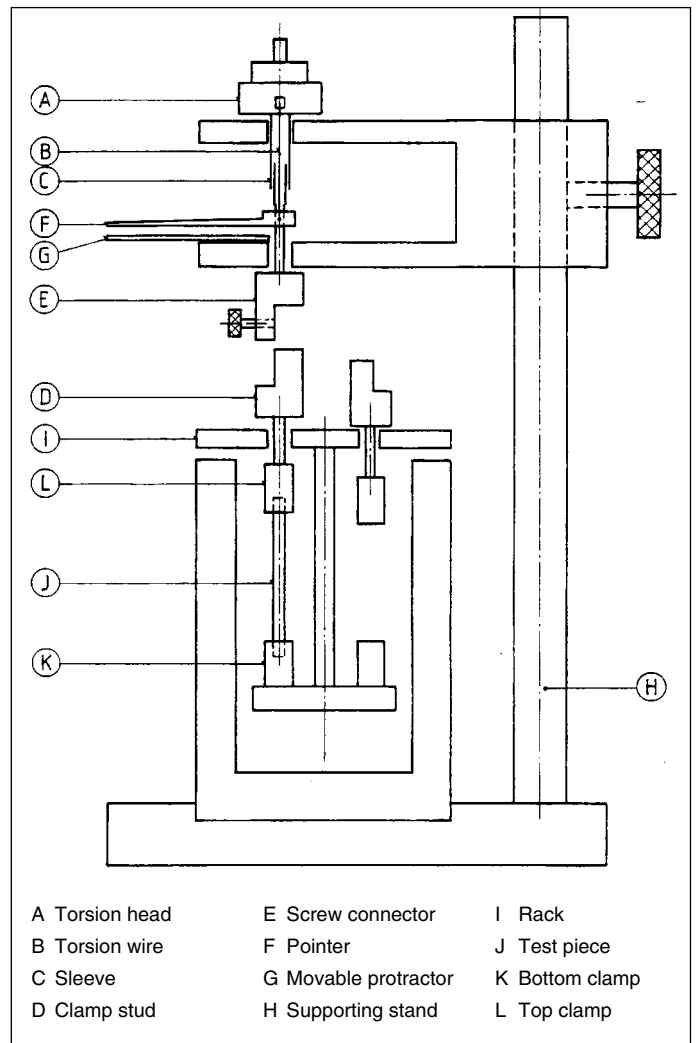


Figure 3. Apparatus for determination of stiffness characteristics

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 5 minutes. 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.

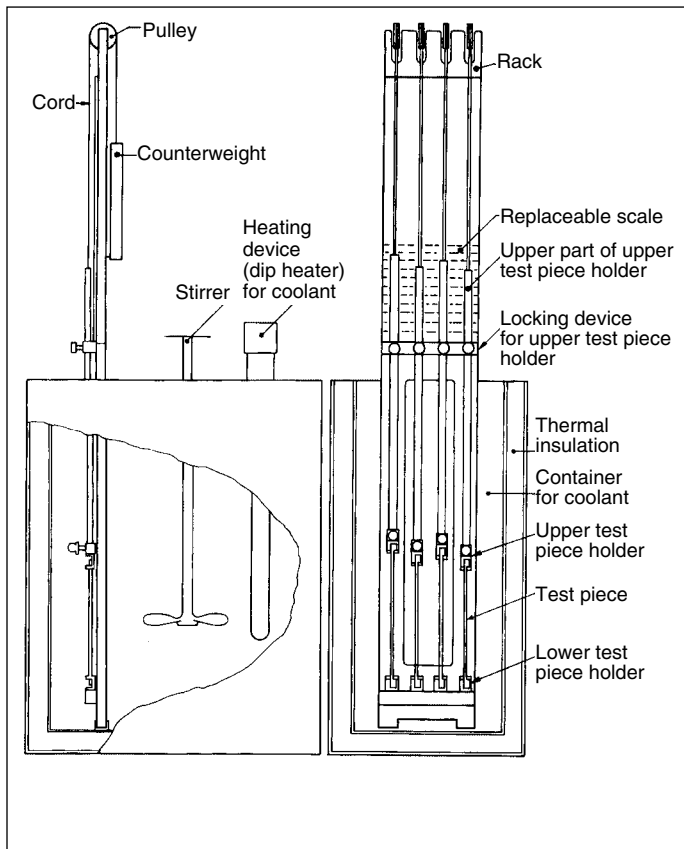


Figure 4. Retraction apparatus

Temperature retraction test (TR test): ISO 2921

The principle for this method is to elongate a rubber test piece, lock it and cool it to $-70\text{ }^{\circ}\text{C}$ in a cold liquid bath, for 10 min. After this time the test piece is released and the temperature is increased by $1\text{ }^{\circ}\text{C}$ (figure 4). 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: ISO 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.

Determination of crystallisation at low temperatures: ISO 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 5 shows the instrument.

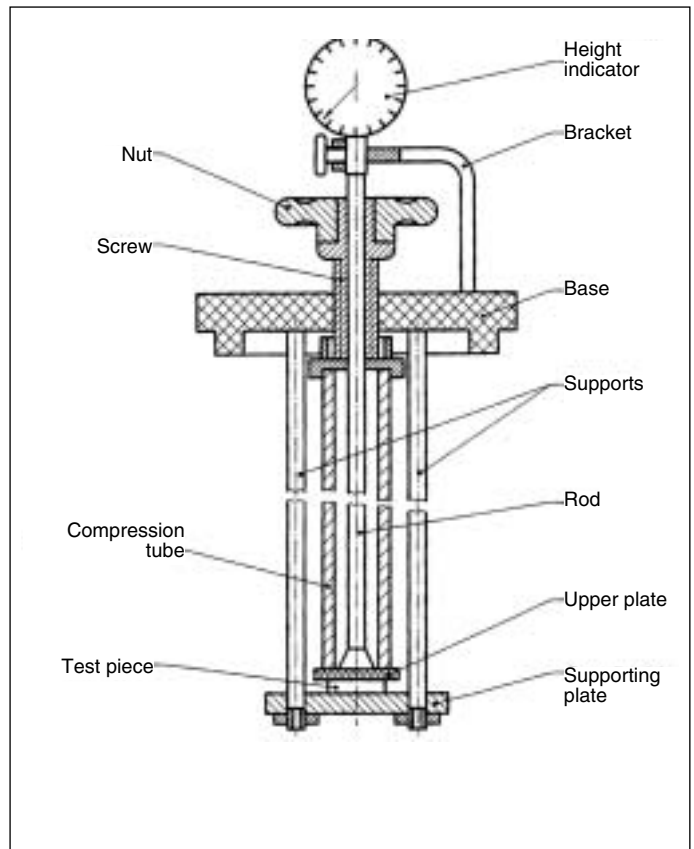


Figure 5. Apparatus for determination of crystallization under compression

Dynamic Mechanical Analysis

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 $1\text{ }^{\circ}\text{C}$ a minute. The test mode can be either tension, compression, bending or shear. The resulting graph is shown in figure 1.

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 $^{\circ}\text{C}$

	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

Twelve companies participated in the ITP (5) and the anticipated improvement between the 1985 and the 1987 ITP results did not occur, even after the instruments had been checked and adjusted. An explanation to the poor results in 1987 is that a 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 systematic 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.

Development of automated instruments

These ITP's show the need to improve the instruments and test methods. 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

For a traditional manual TR-tester, the operator has to manually set the temperature increase and for 1 to 2 hours watch and record the results. 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 are collected by a connected computer

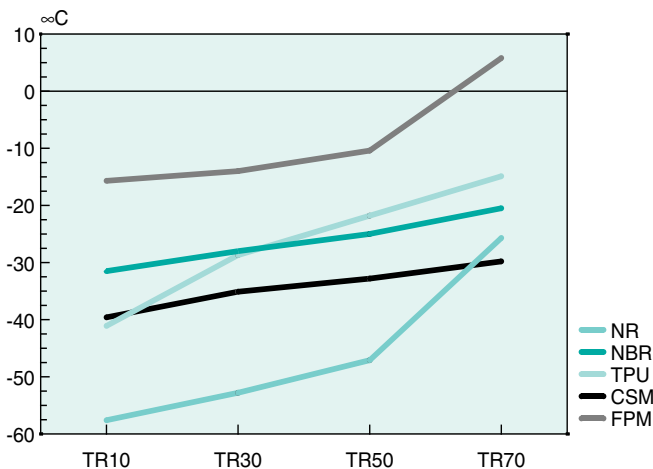


Figure 6. Rubber Materials

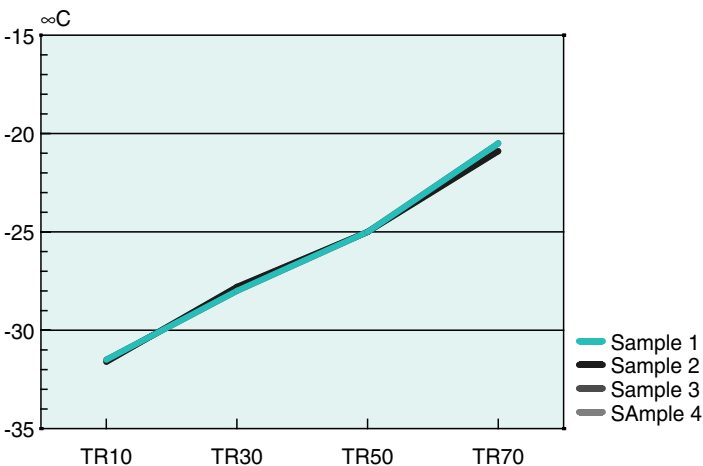


Figure 7. NBR Four samples in one test run

with Windows software. Figure 6 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.

The short term repeatability shows very good results for all materials, see figure 7. The long-term repeatability, however, shows some variations, especially for TR 70. 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 8 and 9. Crystallisation effects may cause this variation for NR, but this has to be further investigated.

Automatic Gehman tester

For a traditional manual Gehman tester, the operator has to manually control the temperature increase and switch between the test stations to perform the test at different temperatures. 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 pneumatic cylinders do the turning. Digital encoders measure the torsion angle of the test pieces. The temperature increase is controlled and all data collected by a connected PC-computer, with Windows software.

Figure 10 shows a printout with results. The results from three materials with two test pieces per material are shown. The results show good repeatability for each double test, but further precision tests will be done.

Summary

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

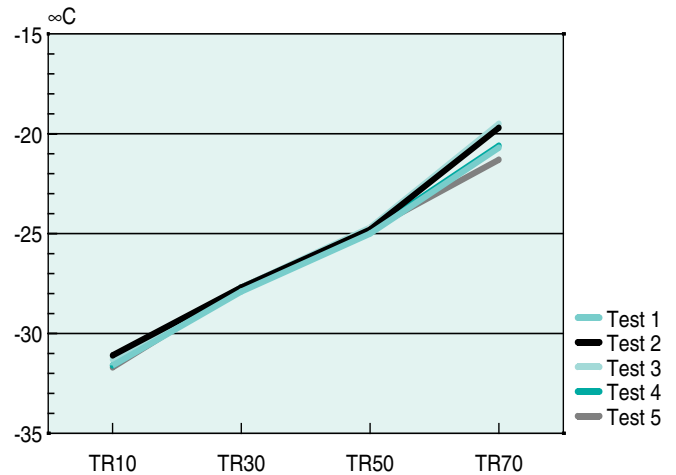


Figure 8. NBR Five test runs during 2 months

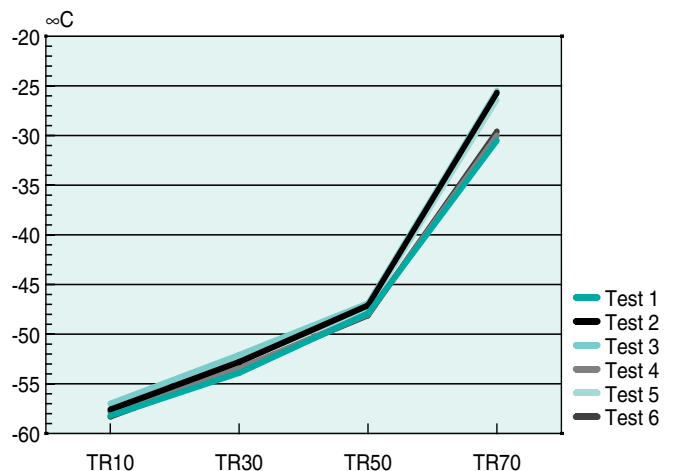


Figure 9. NR Six test runs during four months



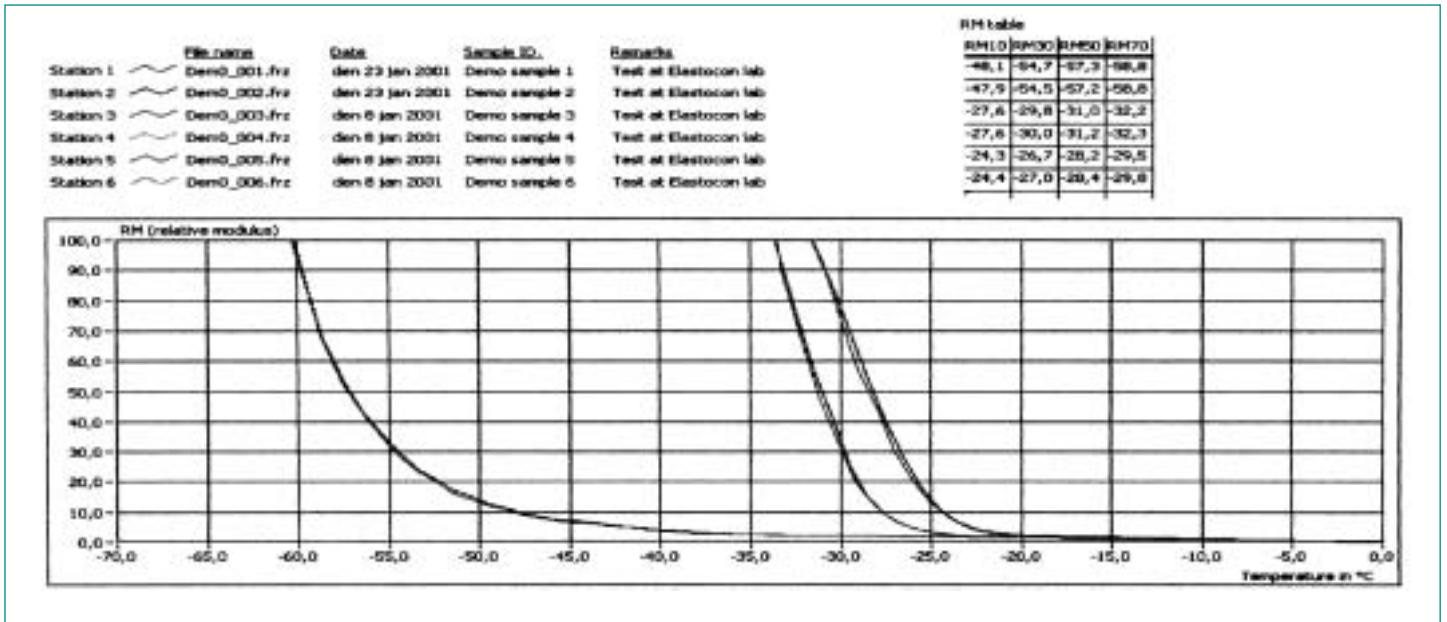


Figure 10. Gehman test report

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*) Elastocon AB, BORÅS, SWEDEN, www.elastocon.se

Scanning Electron Microscopy (SEM)

Jan Timmner * and Ben van Baarle

To prevent as well as to elucidate problems in the (natural) rubber practice a range of visual and microscopic techniques are available. For instance fractures and impurities can be shown, elements present in surface deposits can be analyzed and homogeneity of compounds as well as dispersion of ingredients can be determined. An example from daily practice by which Scanning Electron Microscopy is used to measure the dispersion of carbon black in uncured compounds is elaborated below.

SEM

SEM allows investigation of samples without extensive sample preparation. In general the sample has to be made conductive by sputtering a thin layer of gold in case high-magnified photographs have to be made or a thin layer of carbon when an element analysis has to be performed.

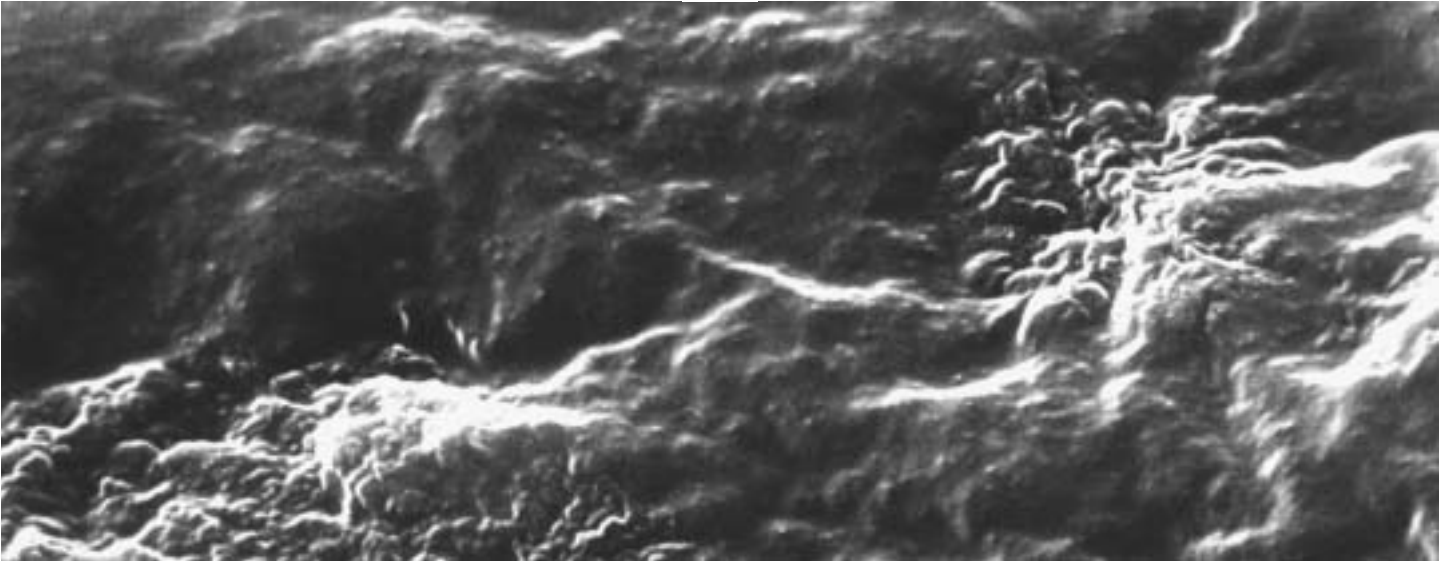
Combining SEM with the Röntgen Micro Analysis (RMA) technique makes it possible to carry out the element analysis. RMA determines elements from carbon and higher atom number simultaneously.

There are many very useful applications for SEM/RMA. Investigations into structure or morphology whether or not combined with (local) analysis of elements can be used to:

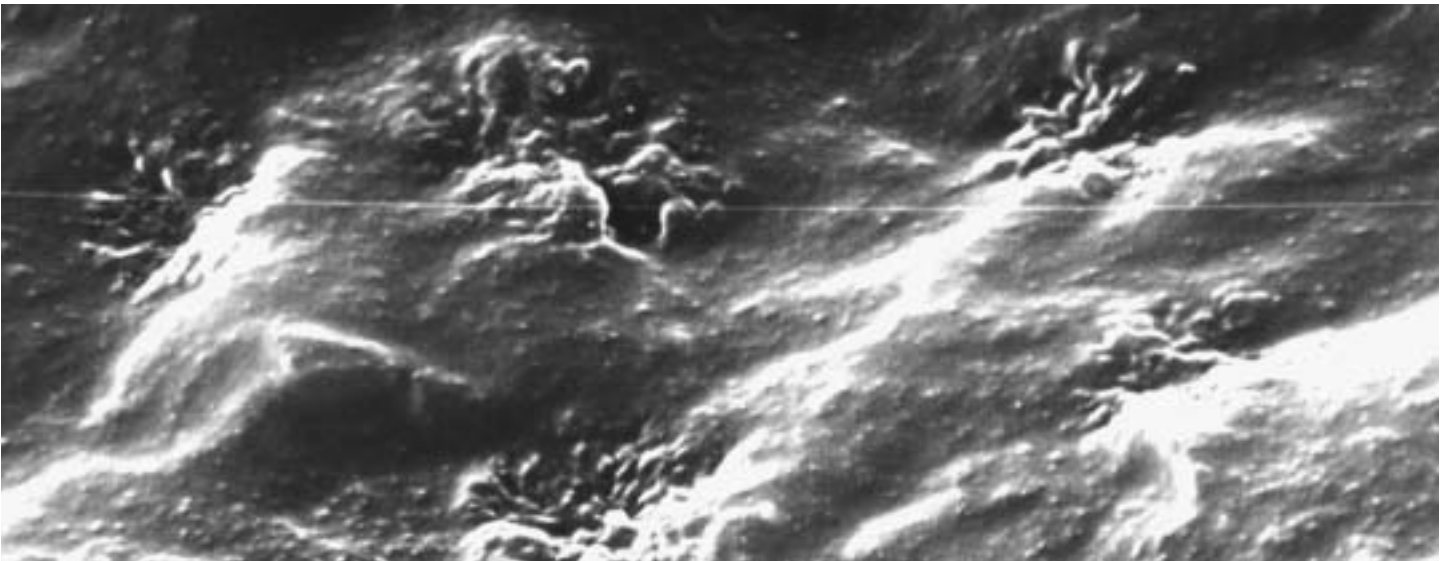
- study fractures;
- measure shape, size and distribution of additives;
- determine the dispersion of additives;
- analyse impurities and enclosures;
- characterise deposits on surfaces;
- get information on added (used) components;
- etc.

Technique	Enlargement	Resolution	Determination of*
Visual inspection			Color, shape
Loupe	7×		Ozone cracks
Light microscopy:			
Stereomicroscopy	5-100×	10 micrometer	Impurities
Polarization Light Microscopy (PLM)	30-1500×	1 micrometer	
Phase Contra Microscopy (PCM)	30-1500×	1 micrometer	
Scanning Electron Microscopy (SEM)	up to 50,000×	5-10 nanometer	Dispersion, homogeneity
Transmission Electron Microscopy (TEM)	up to 250,000×	1 nanometer	Dispersion, homogeneity

* For instance



Photograph 1. Compound 1, without dispersing agent



Photograph 2. Compound 2, dispersing agent A, 3 parts

Dispersion of carbon black

Vulcanisation and dispersing agents were mixed on a roller mill into a master batch of a standard tyre compound based on SBR/NR/BR, carbon black, aromatic oil and activators such as zinc oxide and stearic acid. The recipes are given in table 1.

Table 1

(parts)	Compound			
	1	2	3	4
Master batch	176	176	176	176
CBS	0.7	0.7	0.7	0.7
TMTD	0.3	0.3	0.3	0.3
Sulphur	1.5	1.5	1.5	1.5
Dispersing agent A	-	3.0	-	1.5
Dispersing agent B	-	-	3.0	1.5
Mooney Visc. 100°C	55	49	55	54

To measure the dispersion of the carbon black the uncured samples first were cold frozen in liquid nitrogen at a temperature of -180 °C and fractured. Next the surfaces of the fractured samples were sputtered with a very thin layer of gold and the now conductive samples were placed in the SEM at low vacuum.

Photographs 1 to 4 were taken at 3000× magnification.

Counting agglomerates per area and measuring the sizes of the agglomerates in micrometers establishes the dispersion of the carbon black. The results are summarised in table 2.

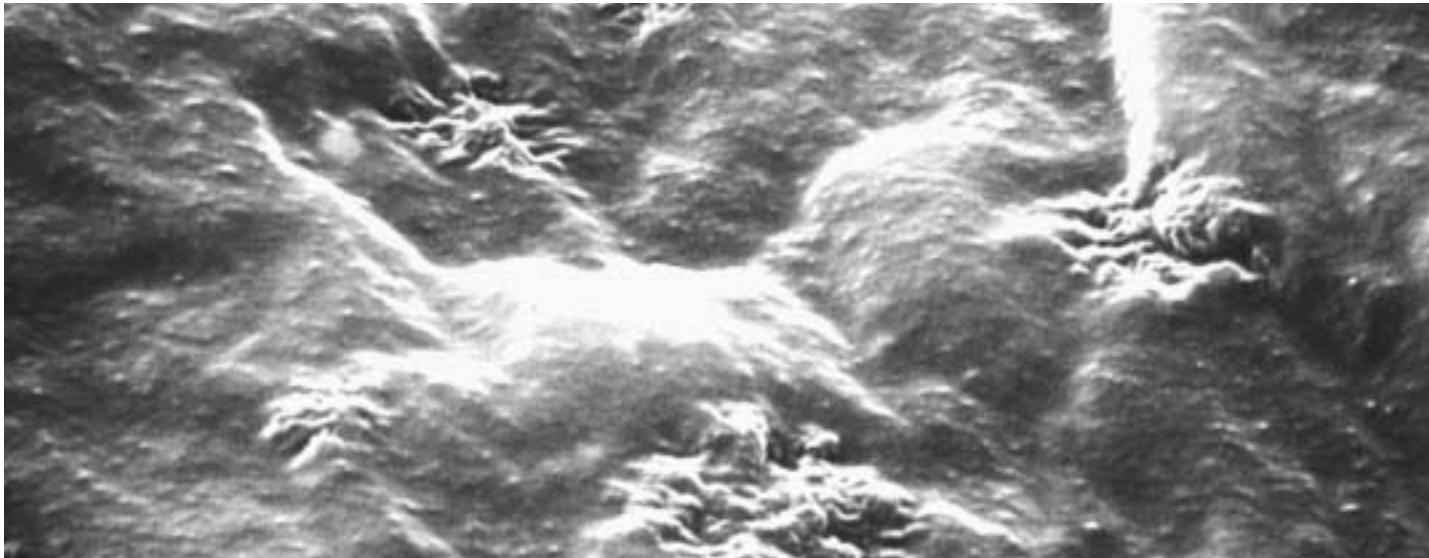
Table 2

	Agglomerates per area	Size of agglomerates in micrometer
Compound 1	2	10 - 20
Compound 2	6	5 - 10
Compound 3	9	2 - 8
Compound 4	16	0.5 - 3

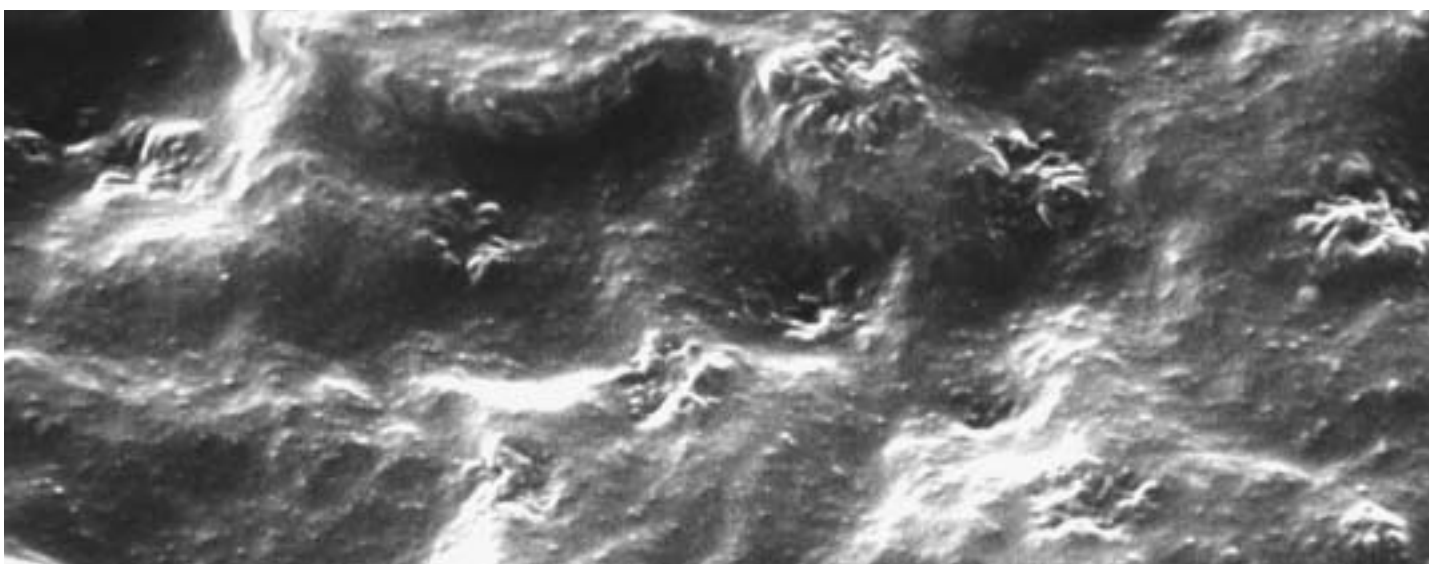
Photographs 1 to 4 as well as the results summarised in table 2 show an improvement of the dispersion of carbon black from compound 1 to compound 4. The combination of two dispersing agents in compound 4 gives the best result. However, the presences of agglomerates in all samples indicate that dispersion in none of the samples has reached an optimum.

* TNO-MEP, www.tno.nl





Photograph 3. Compound 3, dispersing agent B, 3 parts



Photograph 4. Compound 4, dispersing agent A, 1.5 parts and dispersing agent B, 1.5 parts

The Automated Analysis of NR using the ATAS Focus Sample Preparation Robot and Direct TD-GC/MS

R.B.H. Braakman*

Introduction

Natural rubber is formulated with numerous additives which all have their specific purposes, together giving the resulting product its final properties. Most components are stable; others however are less stable and are 'used up' or can migrate out of the material during use. So it is important to be able to identify and determine the levels of any substances that may be present in the rubber products.

Due to its chemical structure vulcanised rubber is difficult to analyse. Common methods involve using chromatographic analysis after a time-consuming extraction method. Using an organic solvent, components of interest are extracted from the rubber and the extract is injected in a chromatograph to be analysed. In the chromatograph the components are separated from each other and from the organic solvent. After separating they are detected and identified after which the quantities of the various components present in the rubber are calculated.

In this paper the analysis of natural rubber using direct thermal desorption (evaporation) as an alternative to a liquid extraction is discussed. This thermal desorption technique is suitable for volatile and semi-volatile components like accelerators, activators, antidegradants but also for residues of blowing and vulcanising agents. The thermal desorption is followed by gaschromatography (GC) as the separation technique.

With direct thermal desorption the raw sample is placed directly in the injection system of the GC. The injection unit rapidly heats up to a temperature where the compounds of interest desorb from the sample. As this process is fully automated the total analysis time is significantly reduced with several hours since almost no sample preparation and no solvent extraction is needed.

When for research purposes these components and other unknown components need to be identified a mass spectrometer (MS) is used as a detection technique for the GC. However, for quality control purposes



a much cheaper detector like a flame ionisation detector can be used. This detector is also much easier to operate.

Experimental

As an example, three rubber samples with different concentrations of additives are analysed. Approximately 5 mg of rubber, cut from the centre of a sheet of rubber, is weighed accurately and placed into a SepLiner™. This SepLiner™ (see info-box) is a glass tube which can be sealed and placed into a sample tray. A Focus sample preparation robot picks the SepLiner from the sample tray and inserts it into the injection system of the GC, then the analysis is started. Each component produces one or more peaks in the chromatogram, see figure 1. This chromatogram is automatically evaluated using a mass spectrometer. After identification measuring the area under every chromatographic peak quantifies the components.

In this example we focus on a common anti-degradant, N-Isopropyl-N'-phenyl-p-phenylenediamine (antidegr. 57, IPPD)¹. Other additives present in the material are detected and identified but have not been quantified due to the limited amount of time available.

The recipes are given in table 1. The system is calibrated with sample 1 and 2. After that sample 3 is analysed and the amount of IPPD is measured.

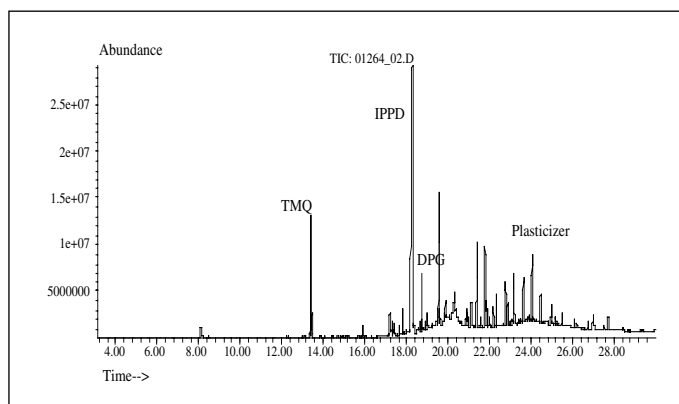


Figure 1. Chromatogram of a rubber sample analysed using Direct TD-MS



Figure 2.
The ATAS SepLiner™

An inlet liner often is a glass tube inserted in the injector of the gas chromatograph used to simplify cleaning of the injector and to minimize influence of contaminants on subsequent analysis. When dirty samples are analysed routinely, replaceable inlet liners are used which can be cleaned as soon as any loss in performance is noted.

The ATAS SepLiner™ (figure 2) can be seen as a sample probe that can hold various sample types, including solids or “dirty” liquids. The SepLiner™ is a glass tube with a medium porosity glass frit made from sintered deactivated glass placed at the optimum temperature zone of the injector. The liner is modified so that it can be sealed using a standard magnetic 11mm vial cap. This allows the liner to be transported using a sample preparation robot and to be reused easily. Automated insertion of the liner in the injector is achieved by mounting a DTD Head that opens and closes the injector automatically.

Each measurement is repeated three times. After each analysis the peak area of IPPD is calculated. To determine the reproducibility of the measurements the average areas and the corresponding relative standard deviations (RSD, standard deviation expressed in percents) are calculated for each rubber. The results are shown in table 2.

Due to the inhomogeneity of the sample (only milligrams!) and differences in sample shapes relative standard deviations around ten percent can be expected.

According to the recipe, rubber 1 contains 0.50 % IPPD, and rubber 2 contains 1.50 % IPPD. From the figures it can be seen that the linearity in average peak area between sample 1 and 2 is correct. The average area of the IPPD peak of rubber 1 is three times smaller compared to that of rubber 2.

The amount of IPPD found in rubber 3 is 1.4 %.

Table 1

Recipe	1	2	3
Rubber	100	100	100
Stearic Acid	2	2	2
TMQ	1.5	4.5	1.5
Akcera S	2	2	2
HAF carbon black	50	50	50
Arom. oil	5	5	5
IPPD	0.5	1.5	1.5
Sulfur	1.75	1.75	1.75
MBS	0.97	0.97	0.97
DPG	0.73	0.73	0.73
ZnO	3	3	3

Table 2

Rubber	% IPPD	Average peak area	RSD (%)
1	0.5*	14.4×10^6	1
2	1.5*	42.6×10^6	12
3	1.4	40.0×10^6	8

* sample used as calibration standard

Conclusion

The ATAS Focus DTD offers an alternative method for the quantification of additives in rubber. Minimal sample preparation is needed with thermal desorption, saving several hours of extraction time. The total analysis time is almost reduced to the time needed for a gas chromatographic analysis.

RSD values are around 10 %, which is acceptable because of the nature of the sample. Linearity appears to be good as a trend can be found between the different rubber samples. It is expected that RSD's can be improved when the shapes of the samples can be made more uniformly.

The system used consists of standard instrumentation, which makes the system cost saving compared with conventional thermal desorption and pyrolysis systems. Moreover, it is much more flexible, as it can be used for a number of standard analytical GC injection techniques.

References

- 1 Rubber Chemicals (Revised and enlarged edition), J. Van Alphen, C.M. van Turnhout, D. Reidel Publishing Company, 1973
- 2 GC Inlets – An Introduction, Matthew Klee, 1990, Hewlett Packard Company

*ATAS Benelux B.V., Zoetermeer, The Netherlands, www.atas.nl

Prediction of Life Time of (Natural) Rubber Products Jaap Havinga

Will this product last as long as I need it? Questions like this always have been the most difficult ones to answer, but especially nowadays engineers and constructors need the answers badly. This mostly is of course because they want to make products with a predefined lifetime and with a minimum of need for maintenance. At the same time, they are put under pressure by a society requesting more and more that environmental aspects are dealt with, making it sometimes impossible to use traditional, long-proven solutions. Means for predicting the lifetime of newly developed products as accurately as possible are therefore essential.

Reading books on rubber one could assume that this is easy for rubber products because increasing the temperature accelerates the ageing process. Moreover, they suggest that from results of tests carried out at a number of higher temperatures one can rather easily calculate the behaviour at a given service temperature. So, one only has to carry out a few tests at higher temperatures to be able to tell how long a product will last. Indeed, in principle this is possible but it is not as simple as it looks. For most products "ageing" is the result of many processes occurring in and to the rubber such as oxidation, ozone attack, fatigue, chemical degradation, swelling, permanent deformation, stress relaxation and so on. Except maybe for a full scale test under service conditions it is really impossible to design a single test that takes into account all possible effects acting on the rubber. And a full-scale test usually takes too much time or is sometimes even impossible...

So, what are we left with?

It is not that bad. On the moment one accepts that every prediction of lifetime of a rubber product has its limitations, there are almost always means to design a series of tests the results of which lead to a measured judgement about the lifetime that can be expected. However, this requires sufficient knowledge, both of the behaviour of rubber under different conditions as well as of the conditions the product will meet in service. One might be surprised to learn that the latter part often is the most difficult. Only think of the temperatures a simple O-ring in an aeroplane will experience: even on the ground, temperature may vary from maybe -40 °C when the plane stands over night in Alaska to +65 °C or more at daylight in the Sahara. When the plane flies, the temperatures can become much higher, up to for instance 140 °C, or, depending on where the O-ring is applied, lower, down to -70 °C. It is the problem of the engineer or constructor of the plane to supply the rubber technologist with reliable information about what will happen under service conditions. Often this appears to be the most difficult part of predicting (maybe better: estimating) the lifetime of a rubber product.

Each application will have its own set of factors having influence on the time a rubber product will retain its functionality. Therefore each application is unique. After the selection of a set of factors, for each one a realistic test has to be devised which gives insight in the durability of the rubber with respect to this particular factor.

In the end, the results of all tests have to be combined to deliver the answer one is looking for. This again is a difficult moment in the process of estimating the lifetime of a rubber product. This is because the combined effect of all factors influencing the behaviour of the rubber is not always simply their sum.

How to deal with the processes involved?

In most cases the **oxidation** process plays an important role. This process usually shows itself by stiffening of the rubber, causing for instance a decrease in tensile strength and elongation at break and an increase of hardness. Ultimately, thin rubber parts even may become brittle.

Oxidation is a chemical process that in principle can be described by an Arrhenius equation (see explanation frame). Increasing the temperature will cause acceleration of the oxidation process. By storing rubber parts in air at various elevated temperatures we can find the activation energy of the oxidation process for a given rubber compound. With that we are able to calculate the time to develop the same degree of ageing at another, usually lower temperature. Depending on the application a relevant measurable property or a number of properties to be followed can be chosen. In many cases hardness, tensile strength and elongation at break will give sufficient information. However, often the problem is to know what really will be the temperature during service. Usually during its functional lifetime a product will see a range of temperatures without clearly defined limits.

Chemical attack by for instance liquid or gases usually can be dealt with in a similar way. Rubber swells often considerably by the uptake of medium. Sometimes it can take up much more than its own volume. However, shrinkage is also possible, when the medium extracts and replaces substances like softeners from the rubber. In principle, ways to predict the lifetime of a product follow the same pattern as described before. Pieces of the rubber product then will be exposed to the medium at various temperatures and again the Arrhenius equation often can be used to judge the effects of the exposure on for instance hardness or compression set. Besides that, usually the volume swelling in contact with the medium is followed as a function of time and temperature.

To estimate in the laboratory the effect of long term exposure to (often only traces of) **ozone** is one of the most difficult items in estimating the lifetime of rubber products. The effect of attack by ozone is cracking of the surface of rubber. Sometimes, there are only a few, but very long and deep cracks, leading to failure of a product, but another time there are lots of short and shallow, but in fact harmless cracks. Ozone can only attack rubber when the (tensile) stresses in a stretched surface exceed a certain limit. Unfortunately, under service conditions most rubber products will be deformed in one way or another, because that's usually why rubber is used. Often, even during storage many rubber products will be deformed more or less, for instance already when lying at a site waiting to be mounted. Although most rubber products are used under compression, the outside surfaces of these products may show substantial tensile stresses as the result of ballooning of the sides. The most commonly used way to solve the problem of judging the resistance of a given rubber product to attack by ozone is by exposing stretched strips of rubber taken from the product to a higher concentration of ozone than the product is expected to meet in its life. When there is no cracking after a certain period the rubber is considered to be sufficiently resistant. The percentage of elongation of the strip, the ozone concentration and the exposure time can be chosen in relation to the expected working conditions but are often taken from specifications of other, more or less comparable products. It is known that cracks occur earlier at higher elongations or higher ozone concentrations but there is no well-established relationship between the results of laboratory tests and the number of years without cracking in practice.



Dynamically loaded rubbers are sensitive to **fatigue**. Here, the number of cycles as well as the way the rubber is stressed is important. Stresses caused by stretching the rubber are far more severe than those caused by compression. As was mentioned for ozone, one should keep in mind that in highly compressed products the rubber surfaces at the outside usually will show tensile stresses. For the engineer it is important to know that cycling from tensile stresses to compressive stresses is much more severe than cycling between two levels of either tensile or compressive stresses. Again, to be able to judge the resistance of the rubber product against dynamic loads, one should be sure that the operating conditions are known and that those are properly translated into a set of fatigue tests. Almost the only way to accelerate the fatigue process is by increasing the frequency during the test. However, this means that the rubber internally might heat up too much, causing another type of failure than will happen in real life.

Swelling is a physical phenomenon. The medium involved diffuses into the rubber matrix. Usually, some swelling is no problem as long as the product functionality is not influenced. The latter may happen for instance in the case of rubbers used in valves where a rather small increase in volume makes turning of the valve impossible due to the resulting high friction forces. One should be aware of the fact that swelling might continue over a very long period before an equilibrium stage is reached. By measuring the volume or weight increase at different temperatures as a function of time it is often possible to estimate the long-term effects at lower temperatures by using the Arrhenius equation.

Rubber is very often used for sealing purposes. To put it simply, the rubber fills a gap between two surfaces, preventing some medium to pass the gap. However, often such a gap can change in dimension, for instance because of thermal expansion of the surroundings. It is obvious that in case the rubber does not have the ability to follow such changes, even after a long period of service, this might lead to leakage. This is judged by measuring the resistance to **permanent deformation** of the rubber, either by tension set or compression set tests, at different temperatures as a function of time. In this way, it again is often possible to estimate the long-term effects at lower temperatures by using the Arrhenius equation.

For proper sealing, the stress exerted by the rubber on the sides of the gap must be high enough to prevent the medium to pass, even in the long run. At a given deformation, the stress in the rubber relaxes with time. Almost everybody will have observed that a rubber band around a package of letters loses most of its stress after being stored for a while. This phenomenon is called **stress relaxation**. Stress relaxation is measured by stretching rubber strips or compressing rubber cylinders and following the decrease of stress as a function of time. The stresses measured are usually plotted as a function of the logarithm of time. At higher temperatures, usually two phases can be discerned in such a plot.

- The first part of the curve is a straight line, where the decay of stress can be described as a percentage of the original stress per decade of time. This phenomenon commonly is called “physical stress relaxation”, a purely physical and reversible process.
- The second part of the plot shows a more rapid decay of stress. This is caused by irreversible changes in the rubber network by oxidative or thermal processes. This phenomenon is called “chemical stress relaxation”.

By measuring the stress relaxation at various temperatures, it is possible to estimate the behaviour at lower temperatures.

Microbiological attack in fact means digestion of the rubber by micro-organisms. Damage to rubber caused by rats, mouse or termites sometimes is called **biological attack**. Whether (micro)-biological attack will occur is hardly to predict. When there seems to be some risk it is possible to test whether the compound used is sensible for such attack but a prediction in terms of years before attack by micro organisms or for instance rats becomes a problem is impossible.

So far we have described the most important factors that may have influence on the lifetime of a rubber product. An example may help to give an idea how this lifetime can be estimated in a real situation.

An example: Water pipe sealing

Many water pipe systems consist of concrete pipes with a diameter of about 1 meter. These pipes are connected to each other using a male – female construction with an O-ring for sealing. The principle of such a joint is given in figure 1.

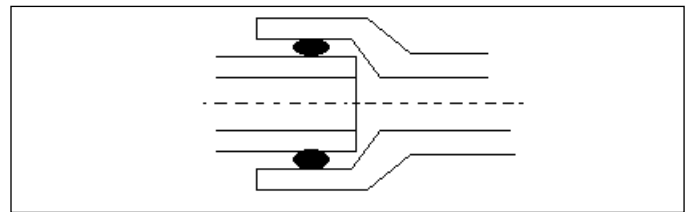


Figure 1. Principle of the seal

The service conditions of the rubber of the O-ring are mainly exposure to fresh water at the inside and ground water at the outside. The temperature range the rubber will be exposed to can be estimated to vary between 8 and 15 °C. Assuming that the O-rings are put into use rather shortly after production and that they are able to survive the storage period (especially with respect to attack by ozone) there are no other important influences. Of course substances that are harmful for rubbers might pollute the ground water but we assume that this is not the case here. Also, we leave out of consideration the possibility of attack by certain microbes.

Before we can start testing we need to agree on what should be considered as the end of the functional lifetime. Therefore we need to understand the functioning of the sealing ring. Roughly, the seal will function properly as long as the pressure the rubber is exerting on the concrete is higher than the water pressure. Furthermore, even when the pipe ends move a little bit with respect to each other, the rubber should be able to follow such movements quickly enough to prevent leakages. Such movements can be in the length direction of the pipes or can create a small angle between the pipe ends or both. Under all circumstances the rubber should not only be able to follow the movements but also to maintain sufficient sealing pressure.

For lifetime prediction we therefore need to take into consideration following processes:

- swelling, because of the contact with the water inside and outside,
- compression set, because of the possibility of the pipe ends moving slightly with respect to each other,
- stress relaxation, because a minimum of sealing force must be retained under all circumstances,
- oxidation, because the inside of the pipe contains fresh water and fresh water always contains oxygen.

So we choose to carry out the following tests:

- swelling in demineralized water, 23 °C (ISO 1817),
- stress relaxation at 60, 70 and 80 °C (ISO 6914),
- compression set at 55, 70 and 85 °C (ISO 815).



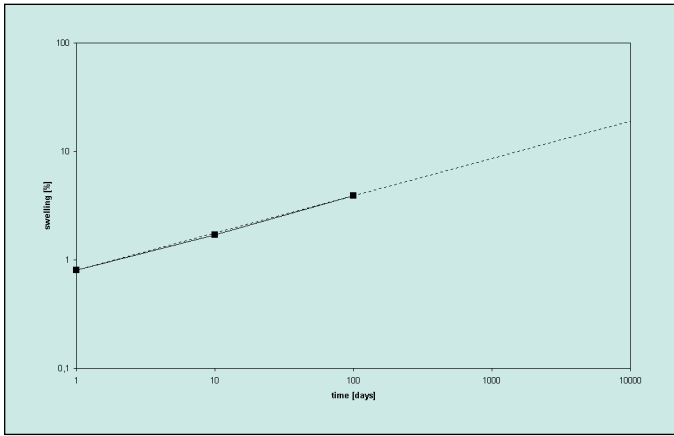


Figure 2. Results of the swelling tests

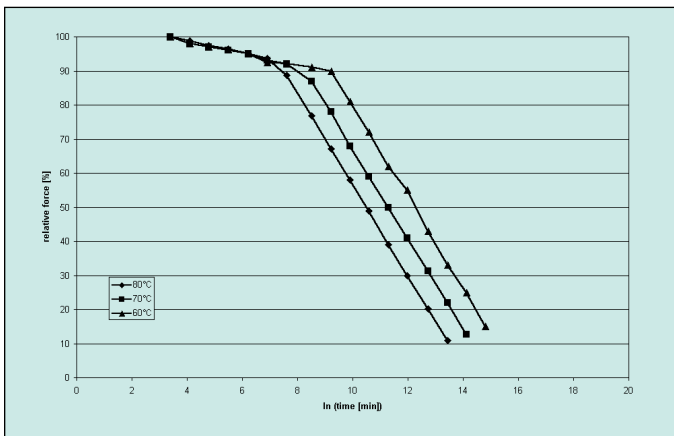


Figure 3. Results of the stress relaxation tests

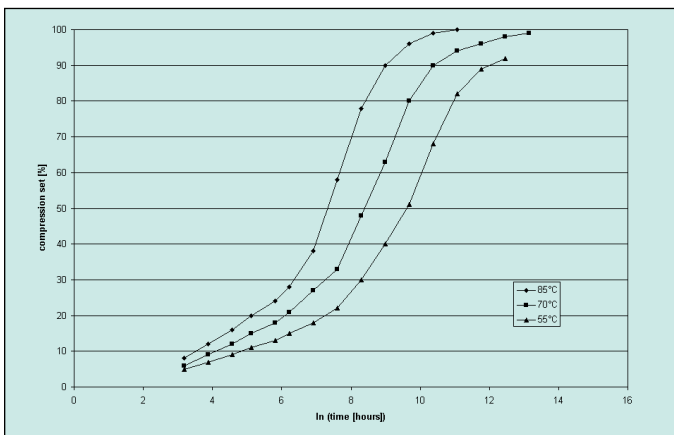


Figure 4. Results of the compression set tests

Suppose we get results as given in figures 2, 3 and 4, what does that mean for the lifetime of a sealing ring?

Considering the service conditions of the O-ring it will be clear that some swelling will be no problem. Excessive swelling should be avoided because then the mechanical properties of the rubber will change significantly. A long term swelling of 10 to 15 % generally is considered to be acceptable for this application. Swelling in water usually follows a straight line over a long period of time when plotted in a double logarithmic graph. Only after very long periods an equilibrium situation can be reached. For our purpose it therefore is safe to extrapolate the line forgetting about a possible equilibrium. We estimate that the swelling will become about 15 % after 25 years.

We assume that the O-ring start to show failure when the stress becomes lower than about 40 % of the original value as measured in a stress relaxation experiment. Plotting the times to 40 % of the original force for each temperature in a graph versus $1/T$, figure 5 is obtained. The line through the three data points can be extrapolated to a temperature of 15 °C. Then, we estimate that at 15 °C it will take about 95 years before the stress will be relaxed to 40 % of its original value. From the shape of the stress relaxation curves, it can be deduced that oxidation probably will play some role in the decay of stress as observed, but taking into account that the test pieces have a thickness of only 0.5 mm whereas the real O-ring is much thicker, oxidation is not expected to be a major factor. Mind you, here we assume that the tolerances of both the O-ring and the pipe are such that the original sealing force even under the most unfavourable conditions is such that 40 % of it is sufficient for proper sealing.

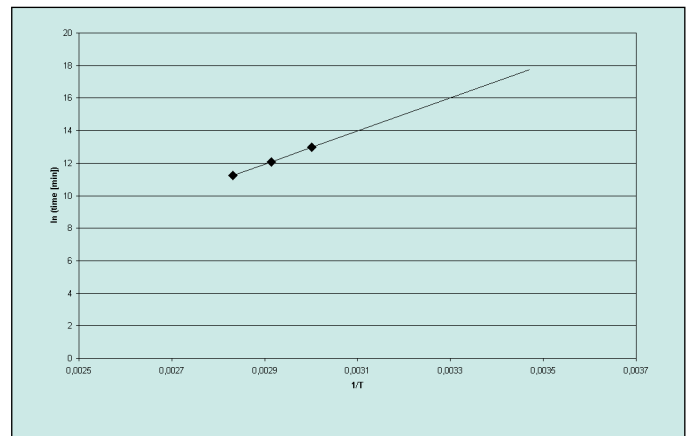


Figure 5. Arrhenius plot for the stress relaxation

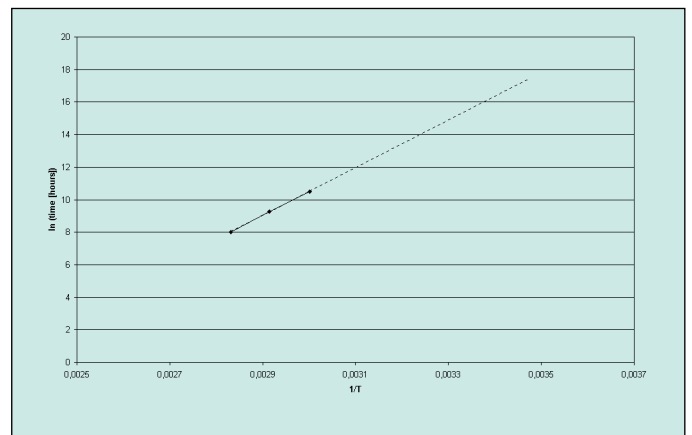


Figure 6. Arrhenius plot for the compression set

Similarly, for the compression set we assume that for O-rings in such an application the risk of failure becomes too high when the compression set as measured increases to a value of about 70 %. Plotting for each temperature the times to 70 % compression set in a graph against $1/T$ again results in a straight line (figure 6). By extrapolation it can be estimated that only after about 260 the compression set at 15 °C will become 70 %.

Combining all results it can be expected that an O-ring of the material we investigated will be able to function properly during at least 50 years. Of course one realises that we had to make several assumptions, that we had to accept that the influence of each factor had to be taken into account separately and that other factors like for instance biological attack, although well possible in this application, have not been considered at all. Even so, the results of a test program like this make clear

that it is reasonable to assume that this O-ring will perform satisfactorily over the period it is expected to do so.

This example, although relatively simple, gives an impression of how estimates of the lifetime to be expected of a rubber product can be made. With more complex rubber products and especially with more complex service conditions it is not always easy to set up a testing program that will deliver sufficient information to make a reliable estimate of the lifetime.

Very important for lifetime estimations is the “wall thickness” of a product. In fact, what is important is the area of rubber exposed to a medium compared to the total rubber volume. A good example of a product with a very favourable “wall thickness” is a bridge bearing: compared to its total volume only a relatively small area of the rubber is exposed to the open air. To put it simply, oxygen penetrates the rubber, oxidising a thin surface layer and from then on then this oxidised rubber layer protects the inner of the product for further oxidation. All over the world examples are known of natural rubber bridge bearings and other similar products the rubber of which shows only minor changes in functional properties even after almost a hundred years of service (see also Natural Rubber 13: Engineering Aspects of Natural Rubber – Part I. Properties and Applications by Dr Andrew Stevenson, MERL, UK). We ourselves have studied an one hundred years old ‘kolf’ ball (‘kolf’ is an old Dutch sport) made of natural rubber. After cutting the ball in half it was clearly visible that only the outer 3 to 4 mm was brittle by extreme stiffening of the rubber whereas the inside rubber was still elastic and in good condition. This means that in case of products with a large “wall thickness” testing with respect to the risk of oxidation hardly is required especially when such a product is used at (or below) ambient temperatures. On the other hand, for products with a thin wall like for instance gloves or condoms, oxidation can easily lead to total destruction of the rubber within a couple of weeks, even at ambient temperatures. This is especially true when the rubber does not contain proper antioxidants.

The same applies to natural rubber products in contact with fluids like hydrocarbons (oils and gasoline’s). The penetration rate fully depends on the viscosity of the medium. Therefore, although natural rubber is not really resistant to such fluids, products made of it can perform very well in applications where contact with higher viscosity oils cannot be prevented. Car engine mounting blocks are good examples: the surface

The Arrhenius equation describes the relationship between time and temperature of a first order chemical process.

$$t = A \times e^{\frac{E_a}{RT}}$$

with: t = the exposition time [s]

A = a constant

E_a = the apparent activation energy [J/mol]

R = the gas constant [8.314 J/(mol K)]

T = the absolute temperature during the ageing process [K]

Taking the natural logarithm

$$\ln(t) = \frac{E_a}{R} \times \frac{1}{T} + \ln(A)$$

makes clear that a straight line is to be expected in a 1/T versus ln(t) graph. By measuring the time for a given change of some property at three or more temperatures, this line can be drawn and the equivalent time at another, usually lower temperature can be read.

Care should be taken because such a relationship is only valid for a limited range of temperatures, namely those where the changes of a property are due to the same chemical processes, in other words where E_a is constant. Deviations may for instance occur at higher temperatures, when some components of a compound may evaporate or decompose which means that other processes also may cause changes of the chosen property.

area that might have contact with motor oils is only small compared to the total volume of rubber of such a block.

Hopefully this article gives you some insight in the complexity as well as the possibilities of predicting or better, estimating the lifetime of rubber products. It is good to know that there are almost always ways to estimate the influence of certain factors on the lifetime but one has to keep in mind that the results of investigations in this field in most cases only give a rough indication of what can be expected. Nevertheless, for many purposes this is quite sufficient for the engineers and constructors dealing with rubber products.

Shearography

Hielke Hoekstra & Hans Kayser *

Introduction

In the race for developing better products faster non-destructive testing methods have become important as a design tool. During the last decades, new testing systems became available for the tyre industry.

Vredestein sells about 4 million tyres a year. As a player in the niche market new product lines should be introduced on a regular base. The performance of these new tyres is more and more demanding. W-rated tyres require a speed rating over 270 km/h. Commercial tyres undergo very heavy loads at high speeds when mounted under delivery vans and light trucks. Although small separations do not always affect tyre performance, separations should not grow to inadmissible sizes before the tread has been worn-out. In order to design for protection and for production control Vredestein has bought the Steinbichler shearography testing equipment.

With holographic and shearographic testing equipment, it is possible to search for anomalies, blisters, separations, voids and cure problems, without damaging or preparing the tyre. Holographic testing machines monitor trapped air, built in between the layers.

In this paper the principles of shearography will be explained shortly. The method will be used for monitoring the crack growth in prepared tyres, which undergo a very heavy load in a so-called endurance test.

Shearography

In the shearography apparatus two adjacent laser beams reflecting from the object under study are superposed. The beams will interfere on an image plane sketched as in figure 1. The obtained image is registered by a video camera and stored into memory as the object’s original state.

After storing the image the object under study will be stressed and de-



formed. This is done by applying a little vacuum pressure in the tyre environment. Then the image of the tyre in the deformed state is subtracted from the stored image and the difference is displayed on the video monitor. In fact with this method the gradient of the deformation is determined. In case of scanning an object with a fault (e.g. a blister) a double series of rings reflecting the gradient of the fault will show up. The image acquired is sketched in figure 2.

The Steinbichler equipment is equipped with a rotating measuring device, which can scan the entire tyre in tangential direction, including both heels. For scanning the surface area 8 pictures are made with an angle of 45°. A picture of a build in blister is shown in figure 3. This blister has been made by including pieces of HDPE plastic between the different layers. It was found that blisters with a diameter of 2 mm could still be found.

Experiments

Figure 4 shows the construction of a radial tyre. The tyre gets its strength from the carcass. On top of the carcass other layers take care for thermal and dimensional stability, for cornering stiffness, for a proper mounting on the rim and of course for optimal skid, wear and rolling performance. Due to the complexity of the construction it is important that no air is trapped in between the layers during building and after curing the tyre. In order to study the ability of the machine to follow crack growth during service lifetime a tyre was prepared and tested indoors on a test drum. The tyre was built with air trapped under the surface area. Furthermore, it was made possible that the construction in combination with a very heavy load (more than 130 % of the permitted maximum load) at a speed of 110 km/h and at elevated temperatures will cause edge separation between the two belts (this is a crack running near the sidewalls and the cap ply at the edge of the belts running from one belt to the other).

Results and discussion

In figure 5 the results of the test are shown for different test distances on a drum indoors. In the horizontal direction three images are taken of the tyre, representing 135° circumferentially. From the first picture of figure 5 it becomes clear that air has been built in under the tread area. This is built in air trapped just between the surface layer and the cap ply. These pictures cover the tread area, including the full width of the belts but not the sidewalls and the heels. The picture was made before testing.

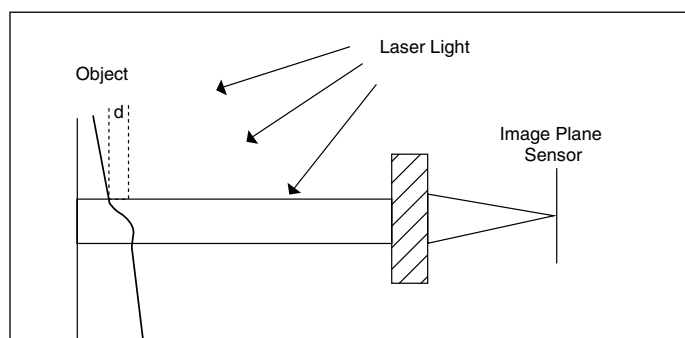


Figure 1. Principle of a holographic image

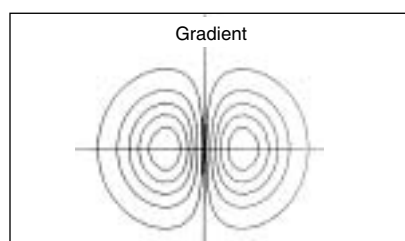


Figure 2. A schematic image of trapped air

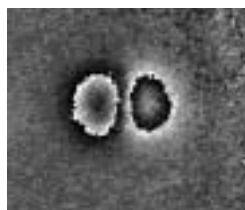


Figure 3. Picture of a build in blister

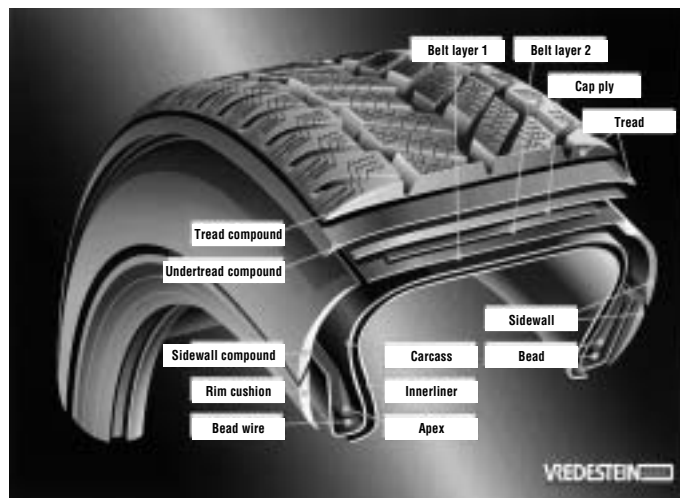


Figure 4. Construction of a tyre

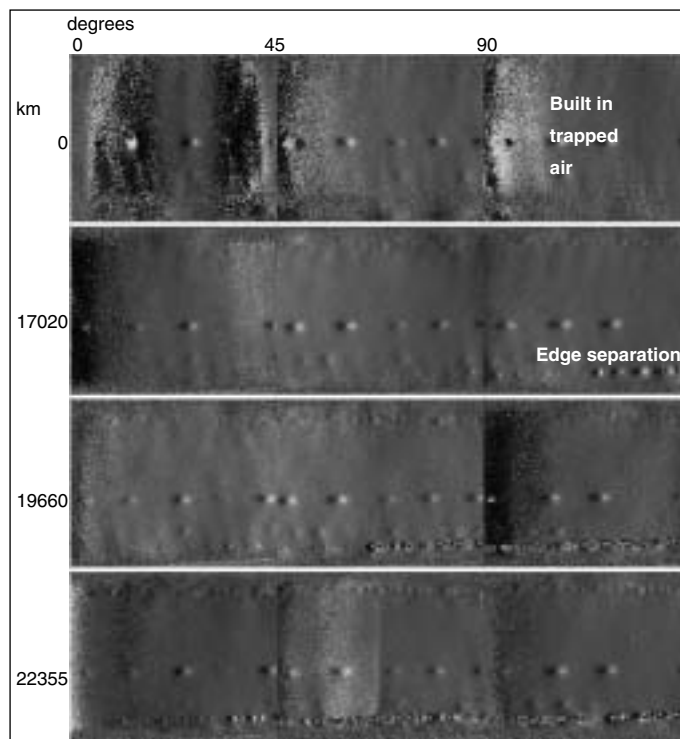


Figure 5. Sheorgraphy results of a tyre tested after different kilometers and at different places in the tyre under overload conditions

The second picture was made after running 17,020 km. The trapped air under the surface still exists, but no crack growth can be seen. However a small belt edge separation is visible on the lower side of the tyre. The crack becomes visible as a series of different faults. After 19,660 and 22,355 km's the separation grows in tangential direction. The intensity of the faults in the crack stays constant, which means that there is no growth of the crack in width directions. Even after very long test times the blisters in the tread area do not seem to change.

Conclusions

1. The sheorgraphy equipment is a valuable tool to analyse built in air in the tyre.
2. Crack growth can be followed with the sheorgraphy testing equipment. In this case cracks only seem to grow close to the edges of the belts, but not under the surface.

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Questions

Q.: "What about certification and (natural) rubber products?"

A.: "Certification helps preventing failures and, in case of unexpected failures, helps to remedy them."

In this special issue of Natural Rubber the emphasis is on tests and methods. However, nowadays testing is almost invariably connected in some way or another with certification, not in the least because today manufacturers as well as testing laboratories proudly show their certificates in all presentations to customers. Therefore, the question how certification and (natural) rubber products are related is well justified. To begin with, there is a variety of certificates: some certify that a production process is under control, others that a product meets a given set of properties, still others that a company works according to certain procedures and so on. In fact, the mere purpose of certification is to ensure that something really is as being claimed, whether it be the properties of a product or the way a banking company works.

Most certificates are based on ISO 9002 (which by the way is not a valid standard anymore as since 2000 there is only one ISO 9000 family). This type of ISO certificate tells a client that a company maintains certain working procedures and that the certifying body has verified that the company indeed works according to these procedures. ISO 9002 describes what, at minimum, should be dealt with in the procedures. Mind you, these procedures do not say anything about the quality or the functionality of the products leaving a factory. It only guarantees that their quality (good or poor) is constant within certain limits and that the production steps are traceable. So if one is satisfied with the performance of a given product then an ISO certificate may ascertain that other deliveries of the same products will have a similar level of quality. May be more important, the ISO certificate implies that in case of problems the company can trace back the production process, making it easier to discover what caused the problem.

Important for natural rubber are for instance certification systems like the SMR, SIR and STR schemes which certify that raw materials coded according to one of those schemes meet at least a set of specified minimum requirements. In these cases the governments of the countries involved

check on a regular base that the companies coding their products indeed work according to the rules set. The introduction of these schemes greatly improved the image of natural rubber as a raw material with respect to consistency of the quality. Even so, one should be aware that indeed only a number of minimum requirements need to be fulfilled and therefore variations between batches can still be significant.

Reacting on the problems caused by latex allergy, Malaysia has introduced a certification scheme for natural rubber gloves. The difference between this scheme and the SMR scheme is that in this case minimum limits are set with respect to certain functional properties of gloves. In the same category of certification fall for instance the CE marks for natural rubber condoms and medical gloves. Here, production control always is an integral part of the control system and minimum requirements on functional properties are set in such a way that a safe use is guaranteed.

Other types of certificates deal for instance with environmental aspects of a product. One should be aware that the scope of such certificates often is very limited. Mostly they only say something about the nature of the materials used for production or have to do with the limitation of pollution during the production process. Such certificates usually do not give any information or guarantee with respect to the functional aspects of products.

The same more or less applies to all kinds of trade markings like 'FDA approved', many 'CE' markings and so on. These 'certificates' only tell that the products in question meet minimum safety requirements, allowing them to be on the market. They do not give any information on the functional behaviour of the product, nor on the quality of the materials used or the consistency of the production process.

Concluding, certification can help improve the quality of products; also of those made of or containing natural rubber, by better control of items varying from management of factories, production processes, raw materials up to the final product people buy.

Jaap Havinga

Events 2001-2002

October 25 – November 1, K2001.

Düsseldorf, Germany. Tel. +49 211456001, fax +49 211 4560668.

November 5-9, The Future of Perennial Crops; Investment and sustainability in the humid tropics. Abidjan, Ivory Coast. E-mail cseri@bnetd.sita.net or nathalie.mercier@cirad.fr

November 6-7, 9th Brazilian Congress of Rubber Technology. Sao Paulo, Brasil. Tel. +11 253 3832, fax +11 253 3774. E-mail lcoml@francal.com.br

November 6-9, 4th International Rubber Technology, Machines and Articles Exhibition. Sao Paulo, Brasil. Tel. +11 7291 8188, fax +11 7291 0200. E-mail lcoml@francal.com.br

November 20-21, Rubber bonding 2001. Turin, Italy. Tel. +44 1939 250383, fax +44 1939 251118. E-mail conferences@rapra.net

December 4-5, Latex 2001 conference. Munich, Germany. Tel. +44 1939 250383, fax +44 1939 251118. E-mail conferences@rapra.net

December 6, VKRT: Rubber activities. Aachen, Germany. Tel. +31 73 6221833, fax +31 73 6238989. E-mail bvm@worldonline.nl

January 30, Health, safety and the environment II (BPRI). Brussels, Belgium. Tel. +32 9 282 8054, fax +32 9 282 4695.

February 4-8, Group meeting IRSG. Glasgow, UK. Tel. +44 208903 7727, fax +44 208903 2848. E-mail irsg@compuserve.com

February 20-22, Tire technology Expo 2002. Hamburg, Germany. Tel. +44 1306 743744, fax +44 1306 877411. E-mail m.fenner@ukintpress.com

March 19, BPRI-AGM (with ABIC) seminar. Brussels, Belgium. Tel. +32 9 282 8054, fax +32 9 282 4695.

The R-S Information Center for Natural Rubber

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The Information Center

- Provides **Information** by telephone about properties and processing of natural rubber and about products manufactured on the basis of this material. The first three hours spent on researching a question are without charge.
- Publishes the free **Newsletter** "Natuurrubber".
- Supplies **Technical Service**, via free company visits.

Editors "Natuurrubber"

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