ISSN: 1863-4699

DICHT!

Special issue O-Ring Prüflabor Richter

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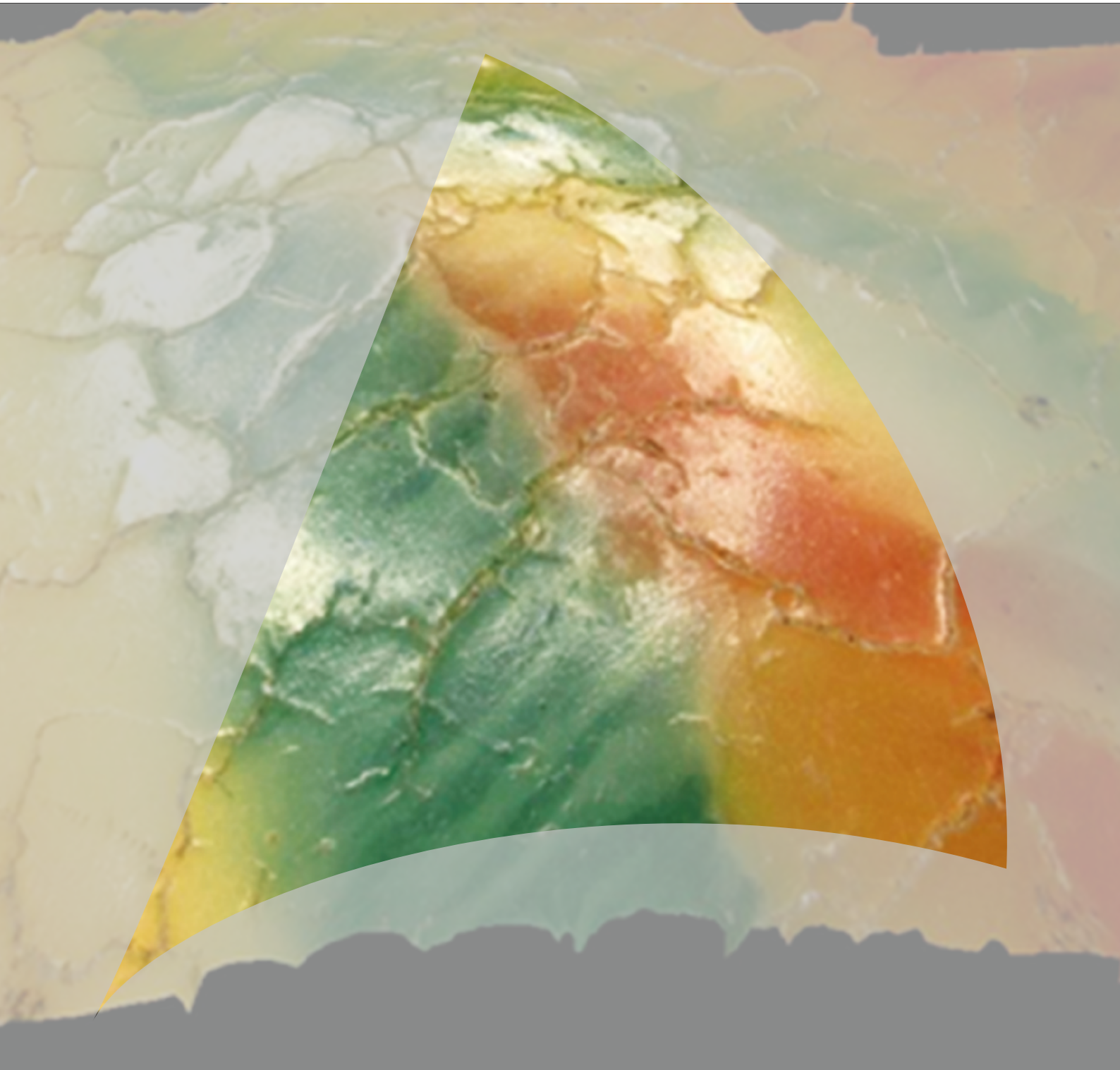

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- Conformity tests according to DIN EN ISO 9539

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Perhaps you or one of your colleagues have already made such a statement about the purpose of examinations. Yes, the testing of elastomer materials and seals is a very large field that is difficult for a newcomer to enter, but even a more experienced seal user can quickly lose himself in it.

This special edition includes all nine episodes of a series of articles written by us which appeared in the magazine "DICHT!" over a period of almost three years.

The range of test methods presented here does not claim to be exhaustive, nor does it claim to include a comprehensive „in-depth approach" to the respective test procedures. Rather, this copy should give the practitioner a quick and easily understandable insight into important test methods and create interest for more. In the digital version of this compilation you will also find further links to our website. In the case of specific problems, you can find further in-depth information on many different subjects.

With these relatively short articles we have tried to compromise scientifically correct reproduction and user-relevant reduction with the essential. In addition to constantly improving the reproducibility of our tests and therefore the reliability of the test results, it is just as important to us to support our customers in solving problems, advising them and making our test results transparent and explainable. Our extensive seminar and publication activities also reflect this.

„I've commissioned an expensive investigation, but how does all this data help me with my problem?"

This series of articles start with the most frequently discussed testing method of rubber materials, the hardness measurement, followed by the compression set/tensile set test and the tensile test. Furthermore, the heat aging of elastomers is introduced, and the series ends with the increasingly important physical and chemical analytical test methods for elastomers, such as FTIR or TG analysis.

It is now up to you to evaluate whether we have succeeded in presenting these articles in a compact and informative way. We hope you enjoy reading them and have many „Aha" experiences. We would be pleased to further discuss this with you in order to be at your disposal as your elastomer specialist.

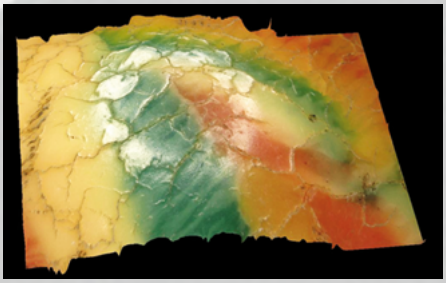
Sincerely

Bernhard Richter

Founder and Managing Director,
O-Ring Prüflabor Richter GmbH,
Großbottwar , Germany

More Information about
Bernhard Richter

Background to cover picture:
A lot started with this: A rubber ball from my youth that I had found again decades later after outdoor weathering - a prime example of aging.



(Picture: O-Ring Prüflabor Richter GmbH)

Limitations and Possibilities of Test Methods

The Hardness Test – Important, but often overrated

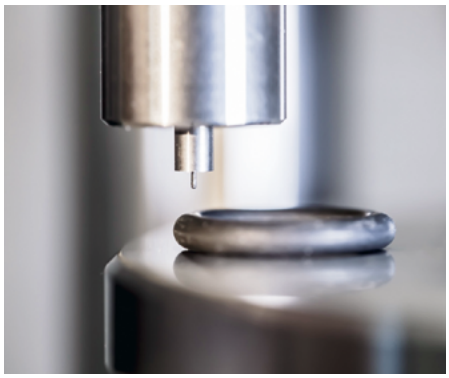
from DICHT! 4.2014

MEASUREMENT AND TESTING TECHNOLOGY – To ensure the function of a seal, it is subjected to various measuring and testing procedures along with the respective seal materials. But what can be achieved by the individual methods and what are the limits? This series provides designers, purchasers and quality managers with an overview of the usual procedures and practical tips for classifying outcomes.

Hardness is defined as the resistance that a body sets against a harder penetrating body. The force of the indenter is usually determined in advance. In the case of metals, the hardness is assessed after removal of the indenter on the basis of the permanent plastic deformation. In the case of elastomers, most of which exhibit elastic behavior, the indentation depth of the indenter is measured during the test [1].

Test Methods

The most common method for testing vulcanized elastomer compounds and articles is Shore A hardness (» 1). This test method was developed in 1915 by the American Albert L. Shore. This test is carried out with a truncated cone as indenter and is actually only permitted for tests on test plates. If certain requirements are met – which will be discussed in the following article – ShA hardness tests can also be carried out on finished parts. The test force is generated by a spring and depends on the penetration depth of the truncated cone. The Shore hardness results from the penetration resistance. Due to this technical condition it was possible to build handy pocket measuring instruments, which were among other things a reason for the large acceptance of this test method in practice.



»1 Hardness test (method IRHD-CM) on an O-ring
(Picture: O-Ring Prüflabor Richter GmbH)

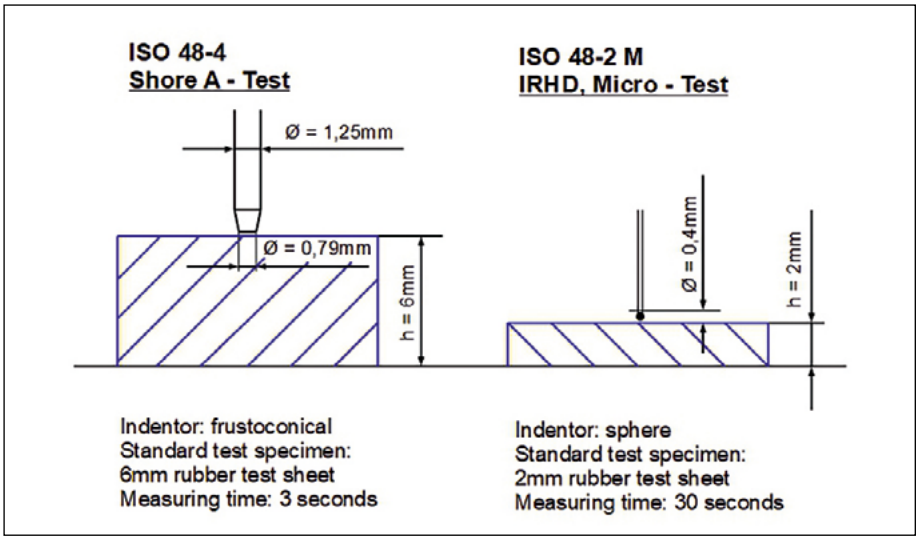
Better for finished products is usually a measurement of the micro-hardness in IRHD-M »1, since a much smaller indenter (ball) is used. The indenter is loaded with a constant force (total force applied to the ball is 153.3 ±1 mN). The ratio between penetration depth and degree of hardness is not linear.

»2 compares the two different test methods Shore A and IRHD, Micro. Test results from the two different test methods mentioned above should not be compared and cannot be converted to each other by a formula, for example. Therefore, in practice, the desired degree of hardness with ± 5 hardness points are chosen very generously, so that the ShoreA hardness on the test plate as well as the Micro IRHD measurement (=IRHD-M) on finished parts are still within this wide hardness range (± 5). Due to this large tolerance, the hardness test method is only suitable to a limited extent for describing the consistency of a compound or the quality of an O-ring or seal.

Practical Relevance

For many users, hardness is the only material test at all that is carried out, which is why deviations from the target value are often evaluated too highly. For this reason, the following article will clarify why and when hardness testing is important and in which areas it does not help:

- The hardness gives a reference value for the deformation behavior of the material. A hard material (90 ShoreA / IRHD-M) has a higher resistance to gap extrusion at high pressures (> 70 bar), and also offers greater protection against assembly damage. A soft material (50 ShoreA / IRHD-M or less) deforms more easily and can better seal surface defects, e.g. a partition line in a plastic molded part. Therefore, the choice of the nominal hardness determines to a certain extent the functionality of a gasket.
- „Hardness cannot be assumed to be a close measure of stiffness. It is true that hardness and stiffness are both stress-strain relationships but the relationships are established for two entirely different kinds of deformation. Hardness measurements derive from small deformations of the entire mass. Because of this difference, hardness is not a reliable measure of stiffness. Even if hardness and stiffness did have a better correlation, the irreducible five-point variation in durometer readings would be equivalent to a 15 to 20% variation in stiffness as measured by a compression-deflection test. Hardness measurements would not, therefore, be sufficiciently accurate for design purposes." [2] The hardness values on O-rings, for example, provide only a rough indication of the resistance to gap extrusion; further valuable indications of resistance can be derived from a tensile test using stress values and strength values.
- Hardness can only be regarded as a material parameter if tests are carried out in accordance with standards, which means on test plates.
- For finished part tests, deviations from the standard hardness may occur due to the geometry. For molded parts, it must be decided at which point the measurement will be carried out. Technical literature also contains formulas for calculating the „true hardness". However, these can only be used in practice to a limited extent or with the respective specialized knowledge. In practice, it is particularly important to ensure that the test specimen has plane-parallel spots. If necessary, profile cuts can be made from finished parts. If the prere-



»2 Comparison of the Shore A and Micro-IRHD test methods in the same ratio. This shows the sensitivity of the test device for Micro-IRHD testing. For instance, special care must be taken that the test ball does not break off, as this only leads to slightly altered test results and is therefore often detected too late. (Picture: O-Ring Prüflabor Richter GmbH)

quisites for reproducible measurements are fulfilled on certain finished parts, the hardness testing method is a simple and effective method of material testing.

- As a finished part test, hardness offers a simple way of compound identification if it is evaluated together with other tests (e.g. density).
- Hardness measurements only give a very rough indication of possible undercure. Therefore, hardness is not an effective measure to ensure a sufficient degree of vulcanization. This is often mistakenly assumed.
- The hardness test is clearly worse than other measuring methods with regard to the measuring equipment capability. Therefore, a deviation from the nominal value does not necessarily represent a significant reduction in quality. This can only be reliably assessed in combination with other tests (e.g. by the compression set or the tensile set). Detailed information can be found in the appendices to the respective standards.

Conclusion

Hardness is a valuable test feature but should always be combined with other tests during quality testing, for example with density and/or compression set. In practice, the significance of the hardness value is often significantly overestimated.

Literature
[1] Cf. Röthemeyer, F. und Sommer, F., Kautschuktechnologie, Hanser-Verlag, München, Wien, 2001, pg. 490
[2] Smith, L.P.: The Language of Rubber, Butterworth-Heinemann, Oxford, 1993, pg.12 f.
Test standards used
ISO 48-2, Method M (Edition 2018-08),
DIN ISO 48 (Edition 2016-09),
ISO 48-4 (Shore A) (Edition 2018-08),
DIN ISO 7619-1 (Edition 2012-02),
DIN EN ISO 868 (Edition 2003-10),
ASTM D1415 (Edition 2006, reapproved 2012),
ASTM D 2240 (Edition 2015)

DICHT!digital: Expert Knowledge Testing methods – Hardness

DICHT!digital: Identity tests Hardness and density

DICHT!digital: 100 years Shore A

The Compression Set Test – Simple and Significant

from DICHT! 1.2015 und 3.2015

Elastomers are not ideally elastic materials. For example, if a seal is deformed for a long-time span, it will not return completely to its original shape after the applied deformation is removed. If this deformation takes place with applied heat this effect is particularly distinct even if the temperature limit – typical for the given polymer – is not exceeded. In the standard test of compression set, an elastomer test piece with exactly defined dimensions is compressed to a predetermined percentage (usually 25%) in a special device and placed in the stressed state for a certain time (often 24 hours) to a laboratory oven. After the stress is removed (= release of the deforming force), the remaining height is measured, and the compression set in percent is calculated. This article deals with the testing of compression set only at elevated temperatures, with the discussion and evaluation of results as well as their meaning for practical applications. The test standards used are ISO 815-1 (edition 2019-11) and ASTM D395 (edition 2018). Compression set test is a relatively simple but also a diagnostically conclusive testing method that is performed for various purposes.

Base polymer		NBR				HNBR		FKM				VMQ	EPDM				ACM	Test method
Curing system		Cured with sulfur		Cured with peroxide									Cured with sulfur		Cured with peroxide			
Hardness IRHD	°, CM	70	90	75	90	75	90	70	75	80	90	70	70	80	70	80	70	ISO 48 CM
Max. CS 24(+0/-2)h	%	35	35	30	30	40	50	25	25	25	30	35	30	35	30	30	40	ISO 815-1, method A
Testing temperature	°C	100	100	100	100	150	150	200	200	200	200	175	100	100	150	150	150	

»3 **Excerpt from ISO 3601-5 (published 2015-04-01) [4]** (Picture: O-Ring Prüflabor Richter GmbH)

Comparative Evaluation of a Formulation

The compression set should permit a comparative evaluation of a formulation (recipe), which means that the compression set value represents as a measurable material characteristic the performance potential of the formulation in data sheets. For this purpose, the testing times 22+2 h or 70+2 h according to ASTM D395B are often used. The test for this is performed on standard test pieces (usually the test piece B of the ISO 815 with the dimension approximately Ø13x6 mm). In many cases the found value of compression set may indirectly give the answer as to what cross-linking system was used..

Testing of Finished Parts

The greatest practical importance of the testing of compression set pertains to the testing of finished products, in particular with O-rings. It is not only about determining the formulation-specific characteristic value as shown in material data sheets but being able to provide a clear statement about the state of cure of the finished part. However, the compression set gives barely sufficient statement about viscoelastic properties of the material. If the compression set value is not 10 to 30% higher than the formulation-specific characteristic value for 24-2 h (testing temperature = permissible 1,000 h-continuous temperature), it can be assumed that the state of cure is acceptable. Orientation values for a finished part (common industrial standard or good state-of-the-art) are shown in »3 .

Verification of the Suitability for Application Technology

The testing of compression set should furnish the proof of the suitability of a material for the application technology. If the service life-temperature collective of the application is known, it is possible to determine the isothermal substitute service conditions (= chronologically shortened thermal service conditions at a constant temperature). This involves the use of simplified Arrhenius multiplicators (rule of thumb: 10 degrees Kelvin temperature increase = doubling of the reaction rate of aging). Then, when the finished part is tested using the isothermal substitute service conditions (time/temperature) it is possible to represent the application fairly close to reality by a laboratory test.

Determination of Information Regarding Long-Term Behavior

At first glance, it may seem that test times for compression set measurements between 6 and 18 weeks cannot provide any information about the long-term behavior of seals over the entire service life of a product, required to fulfill its sealing effect for years and sometimes even decades. However, if the long-term compression set behavior of the finished part is known for at least two, ideally three different temperatures, and if the highest test temperature still permits unrestricted aging, that is not delayed by geometric effects, – e.g. by the large cord thickness of an O-ring, which continues in a detailed explanation in the following chapter – then service life straight lines can be determined [1]. This article deals only with the compression set in hot air. In some cases, however, a more detailed prediction for practical application can be obtained by additionally determining a compression set in a liquid test medium (e.g. engine oil, gear oil, etc.) [2]. This is a trend in newer specifications, especially among vehicle manufacturers.

Important, Currently Valid International Testing Standards for Compression Set Testing

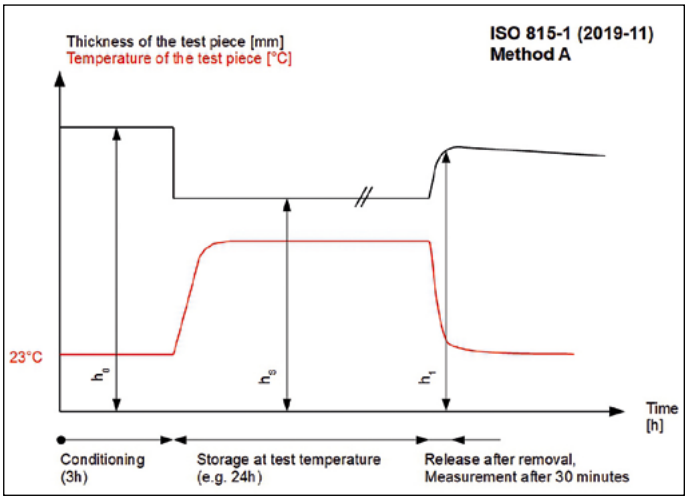
There are various international testing standards for determining compression sets. The two most frequently used standards are ISO 815 and ASTM D395. As with other material standards, the primary objective is to determine a specific material characteristic to describe the property of a given formulation. For this purpose, certain standard specimen is required. However, the great practical significance of these standards is that the degree of cross-linking of finished parts can be tested and the vulcanization process of the finished parts can be evaluated. Both standards, however, only describe the compression set test on standardized test specimens, but not on real seals such as O-rings. The latter can also be subjected to a compression test, but the results can only be compared with the values determined on standard specimens for short-term tests (24 h) as long as the test temperature does not exceed the permissible maximum 1,000 h continuous temperature load limit of the material. This can be confirmed by numerous laboratory results. For instance, in the case of longer-lasting compression set tests on O-rings (from 70 h), an influence of the seal geometry is noticeable.

ISO 815-1 in its currently valid version of November 2019 deals with compression set testing at elevated temperatures, while Part 2 of this standard describes compression set measurement at low temperatures. The recommended compression of specimens depends on their hardness. For elastomer specimens in the hardness range from 10 to 80 IRHD, a compression of 25 ± 2% is prescribed, for 80 to 89 IRHD 15 ± 2% and for 90-95 IRHD 10 ± 1%. There are two different types of specimens:

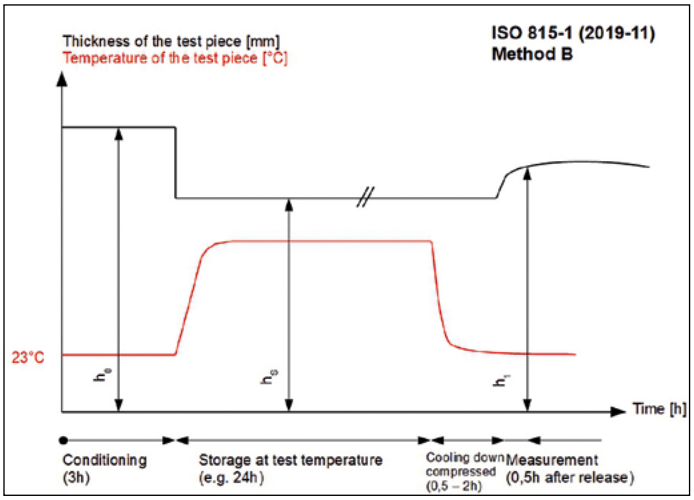
- Type A (Ø = 29 mm ± 0.5 mm x h = 12.5 mm ± 0.5 mm)
- Type B (Ø = 13 mm ± 0.5 mm x h = 6.3 mm ± 0.3 mm)

If no test plates with the required heights are available, layering of a maximum of three layers is permitted. „The larger size [of disc test pieces] is preferred for low set materials because of the greater accuracy." [3] However, this means that the ratio of free surface to mass is no longer comparable with typical finished parts such as O-rings. In the case of large specimens, relatively little mass comes into contact with the ambient air, which allows only limited aging at high temperatures. There is then the danger that the results obtained will be much better in aging and relaxation resistance of elastomer materials than what they actually are on real seals.

The specimens are compressed at room temperature (23°C). The standard also provides precise information on test duration, test temperatures, sample pretreatment and requirements for the laboratory oven. Particular attention must be paid to the end of the test. A distinction is made between three methods:



»4 ISO 815-1, Method A: Return measurement 30 min after relaxation
(Picture: O-Ring Prüflabor Richter GmbH)



»5 ISO 815-1, Method B: Cool down to room temperature in the tense state, return measurement 30 min after relaxation, the method with the highest demands on the material (Picture: O-Ring Prüflabor Richter GmbH)

- Method A requires the test fixture to be opened immediately after removal which practically means it's still at test temperature. The specimens are then placed on a wooden base.
- Method B requires cooling to room temperature between 30 and 120 min. after the mold is opened. After another 30 ± 3 min. the height is measured.
- Method C requires that at the end of the test period the test fixture in the oven is opened and the specimens remain in the oven for another 30 ± 3 min. at test temperature for relaxation. Then the specimens are removed and after further 30 ± 3 min. cooling at room temperature, the height is measured.

The best (meaning the lowest) compression set values are obtained with method C. The high temperature at relaxation causes a higher mobility of the molecular network and thus an easier return towards the original shape. The worst, meaning the highest compression set values are obtained with method B, because the specimens are cooled down to room temperature and only then relaxed.

Method B, with some minor modifications, is preferably used in the automotive industry. However, method B also sometimes leads to discussions due to widely differing values. This has to do especially with the method of cool-down. Good repeatability can only be achieved here if cooling is supported by a fan and the cooling time is determined so that - irrespective of the test temperature and the mass of the compression set plates - the laboratory temperature of 23 °C ± 2 °C is always reached before the specimens are relaxed. There are particularly many discussions with customers in our testing laboratory when the set values are no longer reached. But even a relaxation temperature of the test specimens increased by 5 °C compared to the laboratory temperature can improve the result by more than 10%. **»4 and 5** illustrate the different cooling and relaxation procedures of ISO 815-1 (procedures A and B). According to ISO 815-1, the compression set is calculated as follows:

$$CS = \frac{h_0 - h_1}{h_0 - h_s} \times 100$$

h_0 = Original height of the specimen [mm]
h_1 = Height of test specimen after relaxation [mm]
h_S = Height of the spacer between the test plates = compressed height [mm]
CS = Compression set [%]

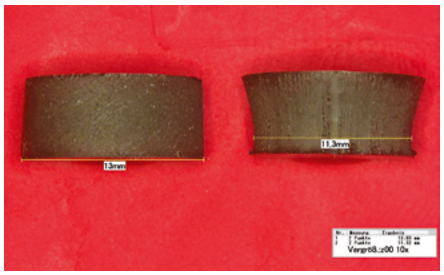
The formula illustrates that an ideal elastic material would have a compression set of 0%, which means that the material springs back completely to its initial height. A purely plastic material would have a compression set of 100% (at test temperature). In practical application this would be the worst case, whereby the seal stays in its deformed position and therefore has no residual sealing force. In some cases, this can even result in a value of over 100%, because the sample still cools down after relaxation and therefore shrinks before the reference value h_1 is determined (Method A). In long-term compression sets, shrinkage can also be caused by plasticizer losses.

ASTM D395 (Edition 2016) deals with the determination of compression set only at elevated temperatures. Part A deals with the determination of the compression set under constant force. Since this method is not very common in Europe, it will not be discussed here.

Part B of ASTM D395 deals with deformation testing under constant compression. The required test specimen 1A is identical in its dimensions to the test specimen type A of ISO 815-1, there are small differences only in the height of the test specimen 2B. However, these differences are considered irrelevant to the result. It is more important for a resilient result that the compression is comparable, e.g. 25%. At first glance, there seems to be a difference in the test durations. While the ASTM requires a test time of 22 h, the ISO standard requires a test time of 24 h. Since the storage times cannot be kept to the minute in day-to-day laboratory practice, a tolerance is necessary. This tolerance is +2 h for ASTM and -2 h for ISO, so that there is again comparability between the two standards. The ASTM only provides one relaxation and cooling procedure that corresponds to method A of ISO 815-1. Concluding, it can be observed that the results obtained using these two standards can be compared if the same test parameters (time, temperature, compression and relaxation method) are used.

Test Device to Determine the Compression Set

Both test standards mentioned above also give precise instructions on the condition of the test device. Strong and rigid metal plates are required, which are screwed to the desired height using spacers. Especially during compression set testing of silicones (VMQ) in the temperature range of 150 °C or higher, and of fluororubbers (> 200 °C), if the speci-



»6 **On the right, the punched specimen is visible, on the left the cut specimen. In this case, the smallest diameter of the punched specimen (11.3 mm) deviates up to 13% from the nominal value (13 mm).** (Picture: O-Ring Prüflabor Richter GmbH)

Test conditions	NBR 70 IRHD,M [100 °C] cured with sulfur	NBR 90 IRHD,M [100 °C] cured with sulfur	NBR 75 IRHD,M [100 °C] cured with peroxide	NBR 90 IRHD,M [100 °C] cured with peroxide	HNBR 75 IRHD,M [125 °C]	HNBR 90 IRHD,M [125 °C]	Test method
max. CS [%], 72(+0/-2) h	40	40	40	40	40	45	ISO 815-1:2019-11, Method A
max. CS [%], 336(+0/-2)h	60	70	50	60	60	70	ISO 815-1:2019-11, Method A

Test conditions	FKM 70, 75, 80 IRHD,M [175 °C]	FKM 90 IRHD,M [175 °C]	VMQ 70 IRHD,M [175 °C]	EPDM 70 IRHD,M [100 °C] cured with sulfur	EPDM 80 IRHD,M [100 °C] cured with sulfur	EPDM 70, 80 IRHD,M [125 °C] cured with peroxide	ACM 70 IRHD,M [150 °C]	Test method
max. CS [%], 72(+0/-2) h	25	30	35	30	35	25	40	ISO 815-1: 2019-11, Method A
max. CS [%], 336(+0/-2)h	40	45	55	60	60	40	50	ISO 815-1: 2019-11, Method A

»7 **The compression set values are specifications for formulations determined on type B test specimens (Ø 13 mm x 6 mm). These specimens are cut or punched from test plates [4]** (Picture: O-Ring Prüflabor Richter GmbH)

mens are poorly tempered, the specimens may adhere to the test tool. When the tool is opened, the specimens are raised slightly and the results are falsified positively. In order to prevent the specimens sticking to the mold, the use of lubricants is required in the standards. Another effect of the lubricants is to allow transverse deformation of the specimen. If this transverse deformation is hindered, the stress state in the specimen changes, which can also influence the results indirectly.

Special attention should also be paid to the production of the test specimens. Typically, the specimens are punched according to ISO 815-1 Type B (Ø = 13 mm) from 6 mm thick test plates. Depending on hardness and type of material, there is usually no right-angle cutting edge to the contact surface. For this reason, it has been decided to cut the test specimens with a turning knife »6.

Performance Range of Important Elastomers According to ISO 3601-5

ISO 3601 Part 5 was developed under German project management. It replaces ISO 3601 from 2002. ISO 3601 consists of five parts and deals with O-rings for sealing fluids in mechanical engineering. It defines, among other aspects, diameters, tolerances, installation conditions, quality criteria, support rings and finally material specifications for O-rings in general industrial applications and the compounds used for them. The latter compound specifications will be discussed in the following: Requirements for the finished O-ring product have already been cited. In the ISO requirements for the materials, the influence of the hardness and the cross-linking system on the compression set are also taken into account. If these target values are achieved, the practitioner can be sure that a material will be obtained according to a good state-of-the-art. »7 [4] provides an extract.

Using the example of sulphur cross-linked NBR, the differences due to different hardness become visible in the long-term compression sets (336 h). A material with a high hardness usually results in an increase, which means worse compression set value, since hard elastomer compounds have a higher filler content. As a result, the polymer matrix, which is responsible for springback due to its cross-linking, has a lower proportion in the compound.

With EPDM, you can clearly see the variations generated by a different cross-linking system. Although the peroxide crosslinked EPDM is tested at higher temperatures than the sulfur crosslinked EPDM, it can achieve better compression set values.

As important as individual material properties such as compression set may be, when evaluating this property, it should always also be considered which additional properties of the compound or finished part are of importance for the application. If, in certain applications, the compression set is actually the essential criterion for a reliable sealing function – which is the case for many O-rings – it should also be understood on which influences a good or low compression set value.

Influences of the Compression Set or the Degree of Cross-Linking Material Properties

As mentioned above, the compression set is an indirect measure of the cross-linking density of a material. The cross-linking density has a major influence on various important properties of a seal.

Influences on the Compression Set Test Result

The result of the compression set value can be influenced positively or negatively by many factors. Understanding the factors influencing the compression set results is important in order to obtain consistent and reproducible measurements. This knowledge is particularly helpful if the measurement results are at the limit of a specification requirement.

Influences of the Specimen Geometry

In »8 it becomes apparent that the O-ring with the lowest cord thickness (d2 = 1.78 mm) has the worst compression set values. The critical compression set value of 90% is reached after 205 h already. The best results are obtained with the O-ring with a cord thickness of 6.99 mm. The critical compression set value of 90% is only reached after 1,300 h. This O-ring can best be compared with the dimensions of the type B specimen (Ø 13 mm x 6.3 mm) according to ISO 815-1. With this background it becomes clear that compression set values determined on standard specimens cannot be com-

pared with O-ring values and are generally better than the values measured on real seals.

How can the results found above be explained theoretically? The speed of chemical reactions increases exponentially with temperature (Arrhenius equation), which means for aging by heat and oxygen that an O-ring only ages without restriction if it has sufficient contact with oxygen. If the ratio of free surface to mass is determined by the geometry (= cord thickness), then the supply of oxygen is limited depending on the geometry. Compression set long-term tests on NBRO rings have shown that this geometric influence at 80 °C is not yet of any significance, but that a considerable influence is already discernible at 100 °C (approx. four times the oxygen requirement compared to 80 °C) and that the influence at 125 °C is severe (approx. 25 times the oxygen requirement compared to 80 °C).

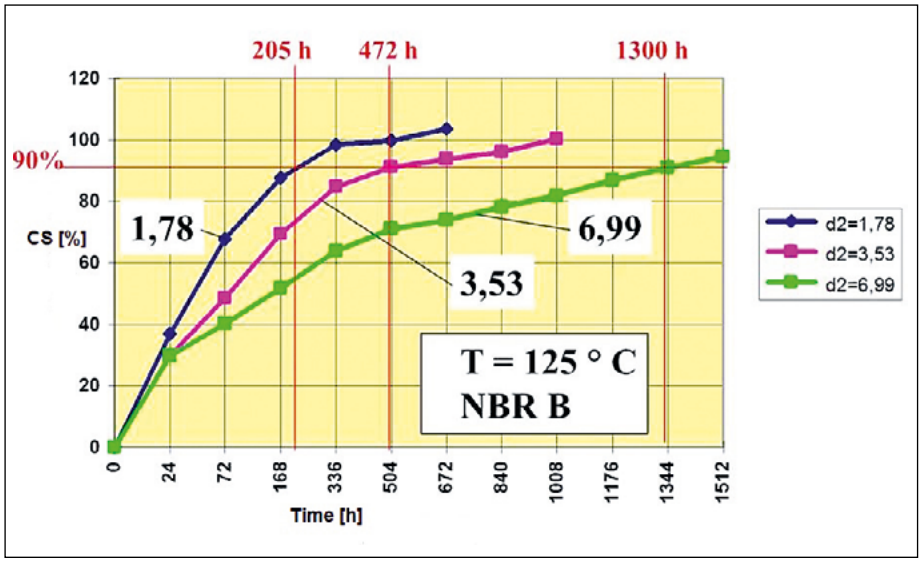
However, Arrhenius' law only applies if there are always enough reaction partners available. Since the Arrhenius law shows that at 100 °C the aging reaction takes place four times faster than at 80 °C, this will only happen if four times as much oxygen is available at 100 °C as at 80 °C.

At temperatures of approx. 20 °C to 25 °C below the permissible continuous temperatures (1,000 h criterion) of O-ring materials, the influence of the cord thickness is very slight. For NBR these are temperatures up to approx. 80 °C, for peroxide cross-linked EPDM up to approx. 125 °C, for FKM up to approx. 175 °C and for VMQ up to 150 °C.

What do these findings mean in practice? In critical applications, an O-ring with a larger cord thickness is to be preferred - if the installation conditions allow it. In addition, compression sets measured on standard test specimens must be critically questioned with regard to their transferability to O-rings, if these compression set values were determined at higher temperatures than those specified above.

Influence of the Percentage of Compression

As already indicated in the presentation of the ISO 815-1 test standard, the compression of 25% ± 2% is the most common standard for determining the compression set. For harder materials, the compression is reduced accordingly. However, there are also specifications from various users of O-rings that also require higher compressions, such as 30%, 40% or 50% (cf. VW specification PV3330).



»8 Influence of cross section on compression set of NBR at 125°C (long-term compression set measurements) (Picture: O-Ring Prüflabor Richter GmbH)

Generally, it can be said that the compression set results can improve with increasing compression (up to approx. 35 to 40%) and that on O-rings considerably worse results are achieved with compressions below 10% than with 25%. Therefore, the installation spaces for O-rings should also ensure that a minimum deformation of 10% is maintained. If the compression is too high, there is a risk of internal stress cracking at high temperatures. This danger increases with increasing cord thickness. Therefore, critical deformations are significantly lower with thick cord thicknesses than with thin cord thicknesses. For O-rings with a maximum cord thickness of 6.99 mm, experience has shown that with normal hardness values (max. 90 ShoreA) and a compression of 25%, the risk of bursting due to internal stress cracks is low, as long as the permissible continuous temperatures are not exceeded.

Influence of the Relaxation Temperature of the Test Specimen

As shown in »4 und 5, ISO 815-1 allows three different relaxation methods (Section 7.5.2 in the standard: Methods A, B, C): In method A, the test specimens are relaxed immediately after removal from the oven, whereas in method B, after removal from the furnace, the test specimens are cooled down to room temperature for 30 to 120 min. in the tense state. The latter method is the most demanding for an elastomer compound and usually provides the worst results. Materials that have a low elasticity at room temperature (e.g. fluorine and acrylate rubber compounds) show large differences in the measured values between methods A and B. These materials spring back relatively faster in the warm state than at room temperature [5].

For practical application, this means that materials with low elasticity at room temperature, or low temperatures, can only be used to a limited extent in dynamic systems with large temperature fluctuations. At permanent high temperatures, their use is less problematic.

Influence of the Test Medium

Compression set tests in mediums often result in better compression set values than in pure ambient air contact. This has to do with the fact that the corresponding contact medium protects the seal against oxygen and rapid aging. In exceptional cases, however, there are also contact mediums that are more corrosive than air, in which case the opposite is true. For practical application, this means in many cases that a seal which is submerged by a medium has a longer service life [6].

Influence of Specific Sealing Shapes on the Reproducibility of the Measurement

In order to obtain reproducible test results, exact test methods should be specified for more complex sealing geometries (meaning no O-rings), such as flange seals. It is advisable here to precisely record the conditions, at which point the section to be tested is cut out of the gasket in the test plan and also to record the often-difficult positioning of the specimen in the fixture, for the incoming goods inspection. Either a special fixture must be procured for holding the piece to be tested, or a crossing point of three or four seal arms must be cut out, e.g. for flange gaskets, so that the specimen can stand securely and independently in the compression set

(Picture: © tatomm – stock.adobe.com)

test fixture. Of course, sections from flange gaskets can also be tested lying flat, but problems often arise here due to holding studs, the concave shape, weld lines and the low height, which limits accuracy and reproducibility. In general, it is recommended to develop such specific test plans in cooperation with the seal manufacturer. This will make communication easier when problems arise.

Influence of Processing

The properties of elastomer products are permanently influenced by the modular network. On the one hand, a characteristic network structure is created and on the other hand, the network density is also important, including the number of network bridges and their length [7].

This modular network is decisively dependent on two factors - formulation quality on the one hand and processing quality on the other. These two properties combined are a measure of the service life quality of a gasket, which can be determined using the compression set.

Lifetime Quality (Compression Set) = Formulation Quality x Processing Quality

The multiplicative connection means that a high formulation quality, that is a good compound, has no effect if an elastomer seal is not vulcanized under the right conditions during production. In contrast to optimally vulcanized specimens from test plates, seals are often vulcanized within a fraction of the time. For this reason, data sheet information only provides information about the formulation quality, but not about the quality of the finished products.

Today, many compounds are already completely vulcanized in the mold. However, the high cost pressure that exists everywhere causes the cycle time and consequently the vulcanization time to be shortened, cutting costs at the wrong end with sometimes fatal consequences. There are also compounds with longer vulcanization times, which cannot be achieved economically during the injection molding process. These seals are left in the mold until dimensional stability is achieved and then post-cured in special tempering ovens. Since this additional process cannot be automated as easily as an injection molding process, there is a risk that it will either be forgotten or not carried out correctly. If this step is missing, the seal will most likely fail in practical use. With the help of the compression set test, this defect can usually be easily detected and traced, but hardly ever by means of a hardness test, as this is too inaccurate to indicate under-vulcanization.

Influence of Typical Variations on Test Results of Different Measurements

In practice, variations in the range of ± 2% on standard specimens and ± 3% on finished parts (O-rings) are still within the measurement uncertainty. It is common (but not standard) to specify compression set values with one decimal place. However, it is not advisable to overestimate the significance of this decimal place. For example, if a specification allows a maximum compression set value of 30% and a material is offered with a compression set value of 29% and another material with a compression set value of 25%, it is recommended to choose the latter, even though both meet the specification at first sight. This way, with the better compression set, there is a greater certainty that the specification requirements will also be met in the future.

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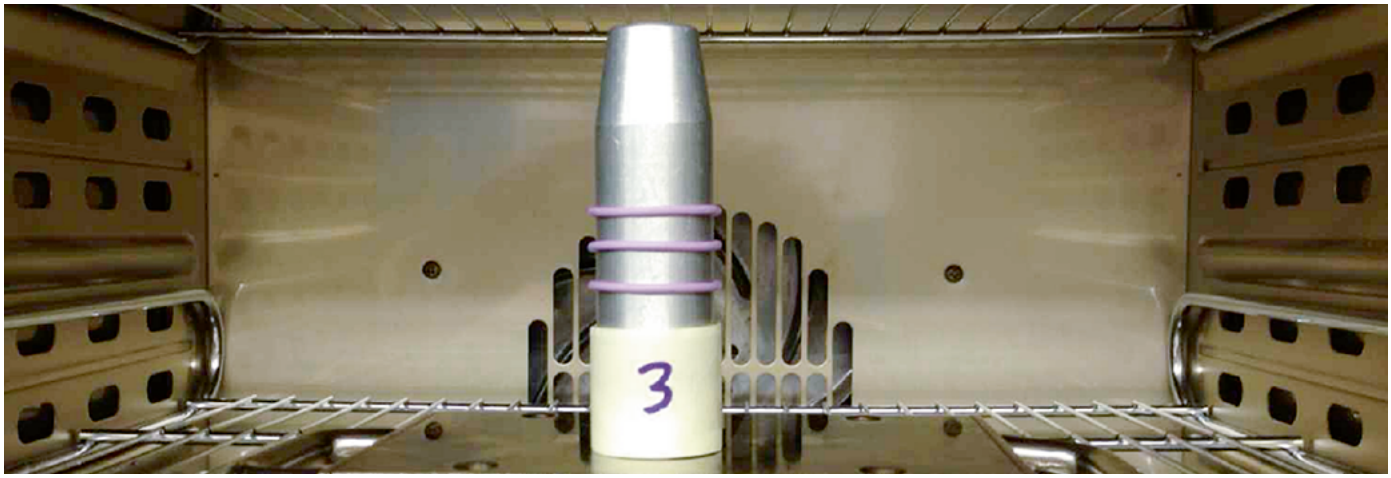
DICHT!digital:Long version of the article

Tension Set Test – Insider Tip for Finished Part Testing

from DICHT! 4.2015



»9 **Test mandrel with O-rings during tensile set testing** (Picture: O-Ring Prüflabor Richter GmbH)

The tension set test, like the compression set test, is a way of obtaining information about the relaxation behavior and the crosslinking state of a specimen after a defined temperature load. In special applications and with special sealing geometries, it is a helpful supplement to the compression set test, which was presented in detail in the last two DICHT! issues.

The Tension Set Testing Procedure and Important Testing Standards

In the tensile set test, the specimen is stretched. In most cases this is a constant strain. The specimen is either a strip specimen, a strip specimen with widened ends (similar to a tensile test rod), or a ring. It is either a pure elongation in length (of the elastomer strip or shoulder rod) or a radial elongation, see »9 with elongated O-rings. The elongation is usually 25% or 50% and according to a defined

- Temperature stress (e.g. 24 h/150 °C) and
- Cooling procedure (Here there are differences to the compression set in the cooling procedure of method B.)

the specimen is relaxed again. The permanent elongation or expansion is set in relation to the absolute elongation or expansion. The standard does not specify a standard length for the longitudinally expanded specimens. Usually, however, 50 mm [1] are used as the measuring length. The advantage of tension set specimens is that no additional holding clamps are required, since the specimen with widened ends can easily be suspended in the fixture. The length to be measured is then the distance between the clamping plates. For other specimens, such as dumbbell bars, the measuring length must then be marked with marking pens [2] in the initial state.

Since relatively short strip specimens usually are used and because in many cases no very large strains are measured back during tension set, accurate and exact measuring devices are absolutely necessary [1]. The change in length is measured with an accuracy of 0.1 mm [3]. The result of the tension set correlates approximately with that of the compression set test. The tensile set E4 in percent is calculated according to DIN ISO 2285 as follows:

E4 = 100 x (L5-L1)/(L2-L1)

Defined as:
E4 = Tensile set (%)
L1 = Unstretched initial measuring length (mm)
L2 = Stretched measuring length (mm)
L5 = Measuring length after the recovery phase (mm)

The permanent deformation after the tensile set test is caused by similar effects as with the compression set. The tensile set is usually performed much less often than the compression set.

Advantages and Disadvantages of Tensile Set Testing Compared to Compression Set Testing

The tensile set test is applied almost exclusively with finished parts. For O-rings with very small cord thicknesses, the measurement uncertainty is lower here than with the compression set test method. On many rod and piston seals as well as on radial shaft seals (on the sealing lip which is cut out) the tensile set test is the only way to measure the degree of cross-linking.

The procedure is simpler than compression set testing, a mandrel is easier to produce than plane-parallel plates and spacers. The method is therefore suitable for recurring dimensions if the right mandrel is already available.

The accuracy of tensile set tests is not always as high as compression set tests when non-contact measuring machines for O-rings are not available.

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DICHT!digital: Long version of the article

Tensile Test –Reflection of the Cross-Linking Network

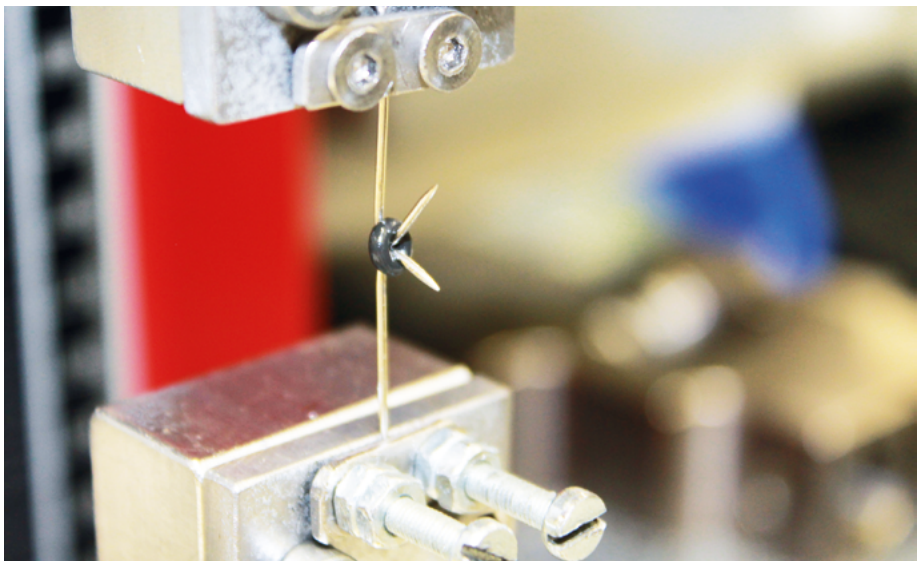
from DICHT! 1.2016 und 2.2016

During the tensile test, standardized test specimens (in most cases „dumbbell bars“) are clamped in a tensile testing machine and stretched at a constant feed rate until they tear. During this process, the course of the required force and elongation is recorded and a tensile elongation diagram is generated. Important individual parameters are tensile strength and elongation. The tensile test can also be carried out on many finished parts »10.

The Purpose of Tensile Testing

The tensile test provides practical benefits for the user under various aspects:

- Conclusions on mechanical strength - The results of the tensile test are in many cases of less interest to the designer at first glance, as elastomers are rarely subjected to permanent tensile strain. However, it should not be overlooked that during the assembly process large expansions (> 100%) can occur. Also, a high elongation at break with highly compressed seals results in greater protection against stress cracking. It prevents the gasket from bursting inside due to the high deformation.
- Conclusions about the mixing and processing quality of a material - According to Dick [1], the tensile test provides the quality assurance engineer with information as to whether the compound has been thoroughly mixed and dispersed, whether there are impurities due to foreign particles such as dirt or paper, whether the material has been over- or under-cured or whether there are porosities. It is not always easy to identify whether problems are caused by poor compound quality or poor processing quality (e.g. injection molding). Sometimes the tensile test is not conclusive enough. Finally, it is important for the practitioner to understand that test plate compounds normally have better tensile strengths than production-scale compounds because the test plates are more thoroughly dispersed.
- Conclusions about the service life, mechanical and chemical resistance/load limits of materials (aging) - In order to obtain conclusions about the service life of materials, aged test specimens are compared with new ones. Aging takes place either by air or specific test mediums (e.g. oils, fuels, hot water etc.) at elevated temperatures. Of primary interest here are the percentage changes in the test parameters tensile strength and elongation at break, which provide information about the network. The percentage changes indicate the extent to which the three-dimensional network is damaged. Long testing durations can also be used to simulate lifetime loads.
- Material characteristics for numerical calculations - In contrast to many other materials, the calculation of elastomers is a very complex field, since the thermoviscoelasticity of rubber materials and other important properties of a compound strongly depend on the recipe and application temperature and are not easy to calculate and define. In order to obtain the material model of a compound, a determination of the respective material characteristics is necessary, depending on the application and the specific objective. The tensile test – in some cases with temperature chamber – is also one of several important test methods [2, 3].
- Conclusions on polymer-filler correlations – The non-linear stress/strain curve, often with an inflection point, also shows the effect of the reinforcing fillers. While in the first, more strongly inclining part of the curve polymer chains are stretched and in the flattening part the partial detachment of the polymer from the filler can be seen.



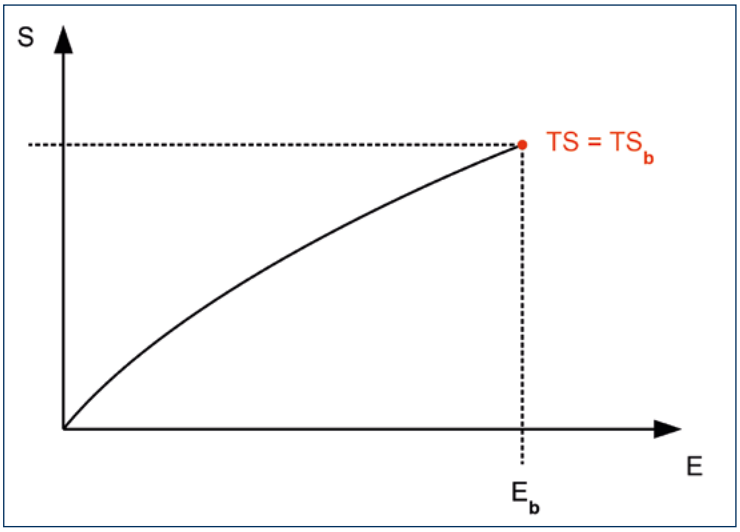
»10 Tensile test on a micro O-ring with self-developed brackets
(Picture: O-Ring Prüflabor Richter GmbH)

Important Test Standards for Tensile Tests

In Germany, the most commonly used standards are ISO 37 (11-2017) and DIN 53504 (03-2017), which define testing on standard specimens.

For standardized test specimens, dumbbell-shaped test pieces (shoulder bars) are most frequently used. These are usually punched out of vulcanized elastomer test plates. ISO 37 defines five different test pieces, whereby types 2 and 3 are most frequently used. The „Type 2“ is identical with the „S2 dumb-bell“ in DIN 53504 and „Type 3“ with the „S3A dumb-bell“.

Both ISO 37 and DIN 53504 also define each two rectangular rings for tensile testing. However, these rings are almost completely replaced by the dumb-bell test pieces in today‘s testing routine. DIN 53504 also provides information on the testing of O-rings, but only for O-rings with an inner diameter of 34.8 mm or more. ASTM D1414, on the other hand, describes in great detail the testing of even smaller O-rings and is also used in the O-ring material standard ISO 3601-5.
The test speed specified in ISO 37 is 200 mm/



»11 Tensile strain curve of an elastomer: The maximum force F_{max} (= TS) is equal to the force F_R (TS_b) occurring during tearing [6].
E = elongation (%), Eb = elongation at break (%), S = stress,
TS = tensile strength (N/mm²),
TS_b = tensile strength at break (N/mm²)
(Picture: O-Ring Prüflabor Richter GmbH)

»12 Dumb-bell test piece shortly before tearing. The extensometers are in contact with the test piece and measure its elongation.
(Picture: O-Ring Prüflabor Richter GmbH)

min (for Type 3 and 4 rod test specimens) and 500 mm/min (for Type 1, 1A and 2 rod test specimens). DIN 53504 requires a feed rate of 200 mm/min for the dumbbell rods S2, S3 and S3A and 500 mm/min for the larger rods S1 and S1A.

Important Characteristics from The Tensile Test and Its Significance for Practice [4]

The tensile strength σ_R is the force at the moment of tearing F_R of the specimen, relatived to the initial cross section A_0. It is given in N/mm² or MPa. Low strength elastomers have values of < 5 N/mm² (or MPa) and high strength elastomers have values of > 15 N/mm². Values above 30 N/mm² are possible for HNBR elastomers. A related material characteristic is the tensile strength σ_{max} This is the quotient of the maximum force F_{max} and the initial cross section A0. For most elastomers, however, the maximum force is identical to the force at the moment of tearing.

It should be noted that the terms tear strength and tensile strength are often used synonymously because: „...in the case of elastomers (...) the force F_R occurring during tearing is generally also the maximum force F_{max} if the tensile test is carried out at room temperature (...) [5] »11.

In the case of elastomers, the elongation during the tensile test results in a strong reduction of the original cross-section. If one were to calculate the stress with the cross-section at the moment of tearing, one would sometimes obtain result values up to ten times as large [7] »12.

With elastomers, there is only a very small range in which Hooke's law applies. Rubber materials are almost always used in a range for which no single modulus of elasticity can be specified. Ecker [8] refers here to the „differential modulus of elasticity E'". In the tensile test it is therefore usual to specify the stress values at e.g. 100% or 200% elongation. According to DIN 53504, the stress value σi is the quotient of the tensile force Fi at a certain elongation and the initial cross section A_0 [9]. Sometimes the earlier common term „module value" (e.g. M100 for the stress value at 100% elongation) can still be found, which is, however, incorrect for the reasons mentioned above.

One way of using the tensile test can be to determine the optimum degree of cross-linking of a material. On the other hand, it is also important to know which external influencing factors can significantly change or even falsify test results from the tensile test.

Influence of Specimen Production

Attention must be paid to the production of the test specimen. Dumb-bell test pieces are punched out of 2 mm thick test plates. During punching, the test plate is compressed before and during shearing, resulting in a concave geometry after relaxation. This effect particularly occurs with blunt punching tools. If such a test piece is examined in cross-section, it becomes apparent that a tip has formed at the beginning or end of the concave cutting edge. At this point, premature tearing usually occurs, which in our experience can worsen the test results by up to 10% »13.

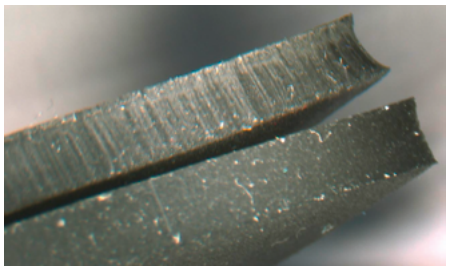
Influence of Elevated Temperature

Generally, the tensile strength and elongation at break of elastomers decrease with increasing temperature. At high temperatures, the physical load limits of an elastomer material decrease.

Such tests provide indications of the load limits of a material in real use, which usually takes place at elevated temperatures. In the case of compounds with a high filler content, the temperature influence is lower. »14 gives an overview of how tensile strength and elongation at break can change with increasing hardness and temperature [10]. The sharp drop in both properties begins already at only slightly higher temperatures – still far from the real operating temperatures.

Influence of Changed Deformation Rate

In ISO 37 the test speed is specified at 100, 200 and 500 mm/min. According to BROWN [11], a deviation of ± 10% from the test speeds required by the standards generally has a negligible effect on tensile strength.



»13 **Comparison of the cut surfaces on an S2 test piece: The upper dumb-bell was punched with a classic punching tool, the lower with a punching knife** (Picture: O-Ring Prüflabor Richter GmbH)

	Test temp.	FKM 55 ShA	FKM 60 ShA	FKM 75 ShA
Tensile strength [N/mm²]	23 °C	8,5	11,1	10,4
	70 °C	3,0	4,6	5,4
	120 °C	2,1	2,6	3,7
	150 °C	1,8	2,2	3,3
Elongation at break [%]	23 °C	282	236	231
	70 °C	170	143	140
	120 °C	116	99	84
	150 °C	90	81	72

»14 **Influence of temperature and different hardness values on tensile strength and elongation at break of bisphenolic cured FKM compounds** (Picture: O-Ring Prüflabor Richter GmbH)

Influence of the Specimen Cross-Section or Volume

As early as 1948, HIGUCHI [12] and employees were able to demonstrate the correlation between tensile strength and volume in tensile tests on various elastomer compounds (NR, SBR, etc.), while stress values and elongation at break are hardly influenced by this. NAGDI [13] describes the influence of specimen geometry on tensile strength as follows: „In general, the following rule applies: the larger the initial cross section or the larger the volume of the test specimen, the lower the tensile strength at break. This dependence can be explained by the number of flaws in the specimen. The smaller the volume of the specimen, the lower the probability that flaws are present."

Iman NAZENI [14] presented an interesting study on the influence of the thickness of the test pieces on the tensile test result at a lecture conference of the German Rubber Society in Berlin in 1960: He proceeded from the assumption that the same skin from the roller was used for test plates of different thicknesses. During the further processing of this skin and the production of thin test plates, it is compressed more at certain points than on others. Due to the higher pressure, microcracks from the manufacturing process can most likely be closed on the roller. The pattern of the cracks is then probably no longer statistically irregular, but depends on the thickness of the test specimen. This is shown by the higher strength values of thin test rods compared to thicker ones.

Influence of the Compound Composition

Especially when formulations with mineral, hydrophilic fillers are used, it is known that they show a significant decrease in strength after a short storage period (a few days) at room temperature due to humidity. This can be reversed by drying the samples (e.g. 4 h/150 °C). For this reason, this is required in some test specifications. Especially on colored compounds, this can explain considerable differences in results depending on how much time has passed since vulcanization or after the last drying of the specimen.

Testing After Pre-Load: Mullins Effect

Normally, almost all tensile tests are carried out on unloaded specimens that have aged to a maximum in advance. In practice, however, a seal is not considered to be unloaded shortly after its first use. And as a pre-loaded seal, it spends most of its service life.

In our case of the tensile test, it is about the influence of elongations of the material before the actual tensile test, meaning a preload of the material. If an elastomer specimen from a filled compound is pre-stretched, the stiffness decreases in the subsequent tensile test. This phenomenon was first discovered in 1903 by BOUASSE and CARRIERE and was extensively investigated and described by MULLINS in 1947. The reasons that lead to the Mullins effect can be both reversible and irreversible processes that cause changes in the polymer filler and cross-linking structure. In practice, knowledge of the Mullins effect is particularly important in the design and construction of shock-absorbing elements that are subject to constant preloading (e.g. engine mounts). The material characteristic of the elastomer component can be changed by the preload via the Mullins effect [15]. When determining the spring stiffness of prefabricated components, it is recommended to run several load cycles in order to be able to measure reproducibly. This prehistory must of course be recorded in the test documentation [16].

Usual Accuracies for Tensile Tests

Towards the end of DIN 53504 there is a chapter dealing with the precision of the process.

The results of interlaboratory comparisons, in which the O-Ring Prüflabor Richter regularly participates, show that there can be significant differences between the tensile tests carried out. Some of the results showed differences in tensile strength of ± 10%. Typical variations in tensile tests are between 2 and 10% (standard deviation/average value) and can still be regarded as typical for rubber.

The largest variance is usually obtained with the elongation values at break, the smallest variance is with small modulus values (e.g. 100%). Hard materials (> 85 ShoreA) usually show significantly worse results than softer materials (50 to 70 ShoreA). If the variances exceed 15%, it is a clear indication of a manufacturing defect in the samples.

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DICHT!digital: Long version of the article

DICHT!digital: Further information on the tensile test on rings

Heat Aging of Elastomers – Life Insurance for the Seal User

from DICHT! 1.2017 und 2.2017

In the case of elastomers, the term „aging" describes a number of processes that lead to the chemical and physical conversion and degradation of vulcanized test specimens or finished parts. Several aging test methods have been developed, which attempt to reproduce these damage mechanisms from the everyday use of sealing materials in the laboratory in a kind of „time-lapse". The damage processes during aging are irreversible causing the material to become unusable after a certain time and temperature load. The scientific assessment and evaluation of these aging processes are intended, among other things, to ensure that these estimated time- and temperature-limits of materials are not exceeded during the application. Aging can be triggered by various processes:

- Aging by radiation – UV radiation, light, radioactive radiation
- Aging due to mechanical stress – static or dynamic load
- Aging due to contact mediums – external influences (e.g. copper), due to liquid mediums (e.g. oils, fuels, acids, water, etc.) or present in the material structure (e.g. impurities, inhomogeneities)
- Aging through biological processes
- Aging by gases – ambient air (in particular by oxygen), ozone, other gases (e.g. blowby gases from the engine crankcase)
- Aging by temperature – without gas or air supply, meaning in an inert or closed atmosphere (e.g. in autoclaves), or with fresh air supply (a combination of aging by gases (O_2) and temperature)

Heat aging is a method that combines the last two points, which is a standardized aging test using heated ambient air. A standardized test specimen is exposed to hot ambient air at a pre-defined constant temperature for a predefined period of time. This is done either for several samples in a type of circulating air oven with fresh air supply »15 or in cell ovens separated by samples »16. The evaluation of the heat-aged materials is carried out by comparing physical values (e.g. hardness, tensile strength, elongation at break, etc.) before and after aging.

Heat aging causes most elastomers to harden, and physical properties such as tensile strength and elongation at break decrease dramatically. The properties of an elastomer material change exponentially with temperature (Arrhenius function) and more linearly with exposure time. Therefore, it is important to know the limit operating temperature range of the elastomer (which in turn depends on the loading time) as small temperature increases can already have a significant effect.

Results from Pressureless Heat Aging

Oxidation

The process of oxidation is undesirable in practical applications as it destroys the polymer. Heat aging is an attempt to carry out this process of oxidation under defined and reproducible conditions, or at least a process similar to reality. A test temperature as high as possible is decisive for effective artificial aging since the oxidation per 10K temperature-increase multiplies by a factor of 2 to 4 and a diffusion of the oxygen into the specimen as evenly as possible is desired. In practice, however, only heterogeneous oxidation is usually possible, which means that the marginal areas of the specimen age more than the inner areas. Oxidative aging consists mainly of two factors:

- Breakage of molecular chains (degradation of the molecular structure)
- Post-crosslinking (construction of the molecular structure).

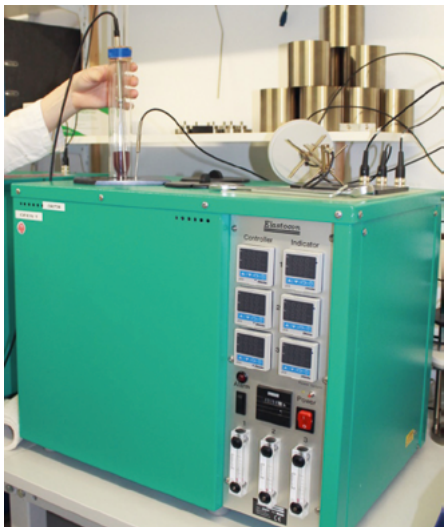
Evaporation of Volatile Components

The heat causes the volatile components (e.g. plasticizers) to gas out at the surface of the test specimen and are then transported away by the air flow in the classic oven. This effect must be avoided or kept to a minimum, as it is undesirable.

Cross-Contamination Between Different Samples

If specimens of different elastomer compounds are stored in the same oven, an exchange of volatile components may occur,

»15 Heating oven with opened door and grids, on which the test specimen holders are placed (Picture: O-Ring Prüflabor Richter GmbH)



»16 Inserting of the cell (= borosilicate glass tube) into the cell oven (Picture: O-Ring Prüflabor Richter GmbH)

e.g. volatilize from mixture A and then diffuse into mixture B. This is an undesirable side effect that should be avoided.

Other Undesirable Effects

It must also be ensured that the air in the ovens does not contain any rubber poisons. These heavy metal compounds accelerate the aging of elastomers. Copper, manganese and combinations thereof should be mentioned in particular.

Practical Benefits of this Procedure

Conclusions on the Heat Resistance of a Material

When an elastomer is exposed to hot air, its physical properties change. The elongation at break and tensile strength of a rubber material are particularly sensitive to oxidation. During heat aging, a component is exposed to a predetermined temperature limit. To evaluate the results, important material parameters after heat aging are compared with unaged specimens (e.g. hardness, volume, tensile strength, elongation at break, etc.). The determined changes provide information about the network damage. However, heat aging only illuminates the aspect of oxidation. In many practical applications, however, additional mediums such as fuels, highly additive oils or aggressive acids are added.

Predictions about the Service Life of a Material

In the practice of sealing applications, questions frequently arose as to the service life of a component and the maximum temperature that a particular elastomer compound can withstand. No definitive answers can be given here. The service life and maximum temperature resistance of a material can always only be specified in a combination of permanent maximum load temperature and time. As a general rule, the shorter the required service life, the higher the maximum limit temperature of a given or tested material can be. In practice, however, a single continuous temperature rarely occurs over the entire period of use. Most of them were temperature collectives. Mathematical – physical operations can be used to determine isothermal equivalent stresses.

Conclusions on the Mixing and Processing Quality of a Material

Heat aging only provides information about a certain range of compound quality, e.g. the heat stability of the compound (e.g. admixture of antioxidants, use of certain crosslinking systems, etc.). If the determination of the compression set – which takes place using a hot-air oven – is also regarded as a subtest method of heat aging, this method can provide useful information, especially about the processing quality.

Test standards for hot-air ageing

Test standards for heat aging in everyday testing in German laboratories are found in ISO 188 as the most frequently used standard. DIN 53508, ASTM 573 and D865 also are relevant in this context.

ISO 188 [1]

This standard distinguishes between two methods:

- „Method A" – Aging in a cellular oven or in a heating cabinet with slow flow velocity with at least 3 to 10 air changes per hour.
- „Method B" – Heating cabinet with forced ventilation, at 3 to 10 air changes per hour.

This standard also places requirements on the ovens. The classic oven is very similar to a convection oven, the cell oven is a glass tube, similar to oversized test tubes, which are placed in a good thermal conductor. Exhaust air from one cell should not flow into other cells. For ovens with forced ventilation, a distinction is made between „Type 1" (laminar flow) and „Type 2" (turbulent flow). Most aging tests are carried out in a „Method B, Type 1" heating cabinet (forced ventilation with laminar flow).

With regard to the requirements for test specimens, ISO 188 recommends aging tests only on standardized test specimens, but not on finished parts. Furthermore, only specimens with similar dimensions should be compared. In practice, however, finished part tests **»17** are still carried out, but they are only conditionally suitable for determining formulation-specific material properties. However, these tests best reflect the application.

The duration of the aging test should be dimensioned in such a way that physical tests of the specimens are still possible after its end. The elastomer specimen must not be damaged to such an extent that, for example, it cannot be clamped in a tensile testing machine anymore. The aging temperature should be as high as possible, but if the temperature is too high, the damage mechanisms are different from those in practice. The storage temperatures should be kept as constant as possible, since a deviation of only 1 °C corresponds to a difference of 10% in the aging time (with an Arrhenius factor of approx. 2).

ASTM D865 – 11 [2]

ASTM D865 deals exclusively with heat aging in cell ovens. The „cells" consist of borosilicate glass tubes **»18 und 19**. The cells must be 300 mm long and 38 mm in diameter. Important specifications for the test procedure are:

- No more than three specimens per cell
- Only specimens from the same compound should be tested per cell
- The specimens should hang freely, so they do not touch each other, nor the cell wall
- The test tube-shaped cell is closed with a stopper in which two glass tubes are located, which serve as inlet and outlet for the ambient air
- No air exchange rates or flow velocities are specified
- After the test, the cells must be thoroughly cleaned to remove volatile trace elements from the aging test which have condensed on the glass walls

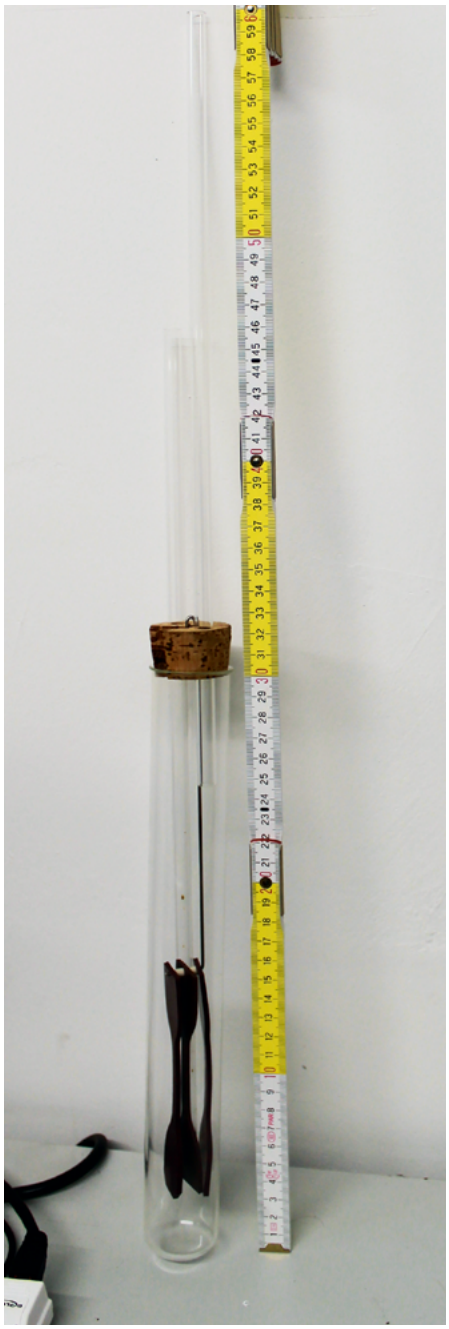
Evaluation of Test Results

If test conditions and therefore aging effects on the elastomer are to be created that reflect the practical application as well as possible, it is necessary to know important influencing factors on aging and to control them.

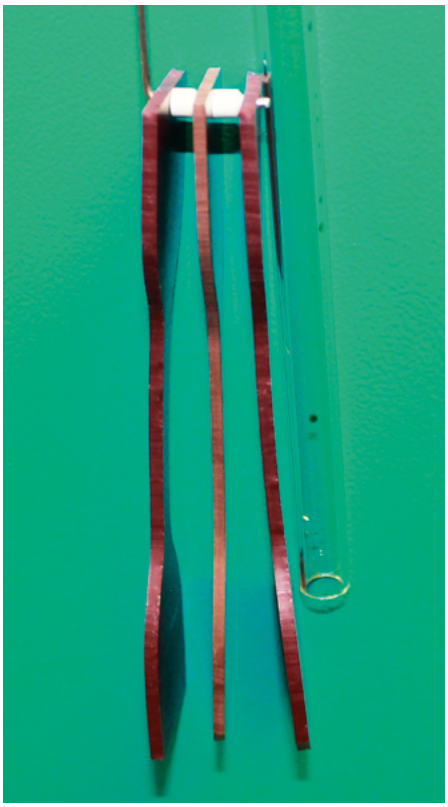
Influence of the Temperature Stability

Temperature has the greatest and most important influence on the test results. A distinction is made between temperature constancy over the entire test period and temperature constancy at various points within the

»17 **Heat aging on O-rings: The isolated suspension prevents contact migration of constituents between the rings. The bent wires on the O-rings are used to distinguish between them** (Picture: O-Ring Prüflabor Richter GmbH)



»18 **Cell (= borosilicate glass tube) equipped with three ASTM test samples „C" according to ASTM D865** (Picture: O-Ring Prüflabor Richter GmbH)



»19 **The white ceramic rings serve as spacers to prevent migration of constituents**
(Picture: O-Ring Prüflabor Richter GmbH)

oven. With modern electronic temperature control, a maximum deviation of values below 0.5 K can be maintained. Generally, the deviation from the set oven temperature must not be greater than the tolerances described in the standard at any point in the oven where test specimens are located (ISO 188: Storage temperatures ≤ 100 °C → ± 1 °C and at T ≥ 125 °C → ±2 °C).

Influence of the Inflow or Air Speed

ISO 188 describes that high air velocities improve temperature homogeneity in the furnace. At a slow air velocity, degassed compound components and degradation products accumulate in the oven. Oxygen removal may also occur. ISO now specifies air velocities and distinguishes between laminar and turbulent flow [3].

Due to the heat aging in the cell oven with an air velocity nearing zero, the surface of the test specimens age much less than in heat cabinets. Microhardness mainly measures surface effects. This also explains why the change in hardness reacts more sensitively to the air velocity than parameters from the tensile test [4].

Influence of Specimen Geometry

In addition, the surface/volume ratio of the test specimens plays an important role. It has a significant influence on aging. If the ratio is favorable (small surface area with large volume), delayed aging occurs because relatively little oxygen can penetrate the material and fewer antioxidants can be emitted or consumed.

Literature
[1] Cf. International Standard ISO 188: Rubber, vulcanized or thermoplastic — Accelerated ageing and heat resistance tests, Fifth Edition: 2011-10-01
[2] Cf. ASTM – International: Designation: D865-11: Standard Test Method for Rubber – Deterioration by Heating in Air (Test Tube Enclosure), Approved 2011
[3] Cf. International Standard ISO 188: Rubber, vulcanized or thermoplastic — Accelerated ageing and heat resistance tests, Fifth Edition: 2011-10-01, pg. 2, chapters 4.1.1 und 4.1.3
[4] Cf. Spetz, Göran: Recent Developments in Heat Ageing Tests and Equipment in: Polymer Testing, Vol. 15, issue 4, 1996, pg. 388

DICHT!digital: Further Information on hot air aging

DICHT!digital: 100 years hot air aging according to W.C.Geer

Physical Analytical Test Methods – Character Testing on Elastomers

from DICHT! 3.2017

Thermogravimetric Analysis (TGA)

This method is suitable for the description of formulation compositions and for the rapid detection of formulation consistency. Rubber compounds and elastomer finished parts are multi-component mixtures of processing additives, plasticizers, polymers, carbon blacks and fillers. They all influence the performance properties. Even though it is extremely difficult to determine the original formulation from a vulcanized article, approximate methods have been established with which, for example, the proportions of the main components can be measured quickly and reproducibly.

In the TGA, a material sample (approx. 10 mg) is continuously heated up to max. 1,000 °C and the relative weight loss is measured as a function of temperature. The evaluation allows the quantitative determination of the compound components in vaporizable or volatile components (predominantly plasticizers), pyrolysable components (predominantly polymers), oxidizable components (predominantly carbon black) and non-oxidizable components (fillers, primarily metal oxides), also referred to as ash residue.

Unfortunately, there is no universal TGA method to suit the diverse world of elastomers. There are various test specifications in use as well as many factory or laboratory standards:

- VDA 675 135 (May 2016) – The old edition described an effective, simple method with a constant heating rate, the new edition of the 2016 standard has come closer to ISO 9924.
- ISO 9924-2 (August 2016) – It is suitable for polar and halogen-containing samples with long measurement times and has the advantage that the carbon black produced during polymer pyrolysis is (usually) detected separately and not added to the carbon black quantity.
- DIN EN ISO 11358 (October 2014) – It is a general description for the performance of a thermogravimetric analysis, the heating-up program is not defined.

»20 shows an example of the results of a TGA. The green curve shows the weight decrease as a function of temperature (initial weight at RT = 100%), the blue curve the first derivative of the relative weight as a function of temperature. The latter is used to differentiate more precisely between the curves and the events. The method according to ISO 9924-2 shows 11.8% volatile components, 49.1% pyrolysable components and 2.1% pyrolysis carbon black. The high ash residue of 36.8% and the low oxidizable components of 0.2% are typical for a colored mixture without carbon black as filler.

Differential Scanning Calorimetry (DSC)

This DSC method (Differential Scanning Calorimetry) measures changes in the specific heat capacity of samples as a function of temperature. The specific heat capacity indicates how much thermal energy a substance can accumulate. The most common and well-known application of this method in the elastomer range is the determination of the glass transition. This is determined by the infection point of the heat flow over the temperature. The test method most frequently used in laboratories for this purpose is ISO 11357-2, which alternatively determines the glass transition point using either the first derivative (Ti,g) or half the height of the tangents (T1/2,g) »21. Further test standards for the DSC are VDA 675116, ASTM D3418 and ASTM D7426. However, the glass transition temperature determined according to a calorimetric measuring principle does not always correspond to the thermomechanical glass transition temperature.

This means that the temperatures determined are not always reliable low-temperature limits for seal applications, as crystalline sequences in the polymer in particular can impede resetting. This can occur particularly with EPDM and HNBR materials. Therefore, for EPDM and HNBR materials, another method is recommended to determine the low temperature limit (TR 10 according to ISO 2921, compression set at low temperatures according to ISO 815-2 or dynamic in DMA). Furthermore, DSC analysis offers the possibility to detect and quantify endo- and exothermic reactions during heating and subsequent cooling. This can be helpful, for example, to detect residual amounts of crosslinking in the elastomer.

Dynamic Mechanical Analysis (DMA)

DMA is an increasingly important test method, which can be used to determine characteristic values for numerical simulation. In recent years, this method has become more and more important and is no longer reserved for pure materials research. Elastomers are viscoelastic materials and combine viscous and elastic properties. These properties can be ideally measured in dynamic tests using DMA. It measures quantitatively and qualitatively (at different deformations and frequencies):

- Viscoelastic behavior and shock-absorbing properties, loss and storage modulus
- Flow and relaxation characteristics as a function of temperature (-100 °C to 600 °C).

In contrast to older dynamic test methods, which usually require precisely standardized specimens, the DMA can easily analyze sections of finished parts, test plates or damaged parts. As standard, the usual tensile specimens (S3A, S3 etc.), which are shortened in the clamping range, are used in tensile mode. The compression and bending modes require plane-parallel specimens from test plates or finished parts.

The most common test modes are:

- Cantilever (clamped bend, single or double)
- Tensile mode
- Compression mode

The tests are carried out according to defined standards, such as ISO 6721-1, or user specifications. In contrast to the limited measurement possibilities with TGA and DSC, many possibilities are available with DMA:

- Distance, different amplitudes
- Frequencies
- Force, static or dynamic
- Storage and loss module
- Loss angle (tan δ)
- Glass transition (frequency-dependent)

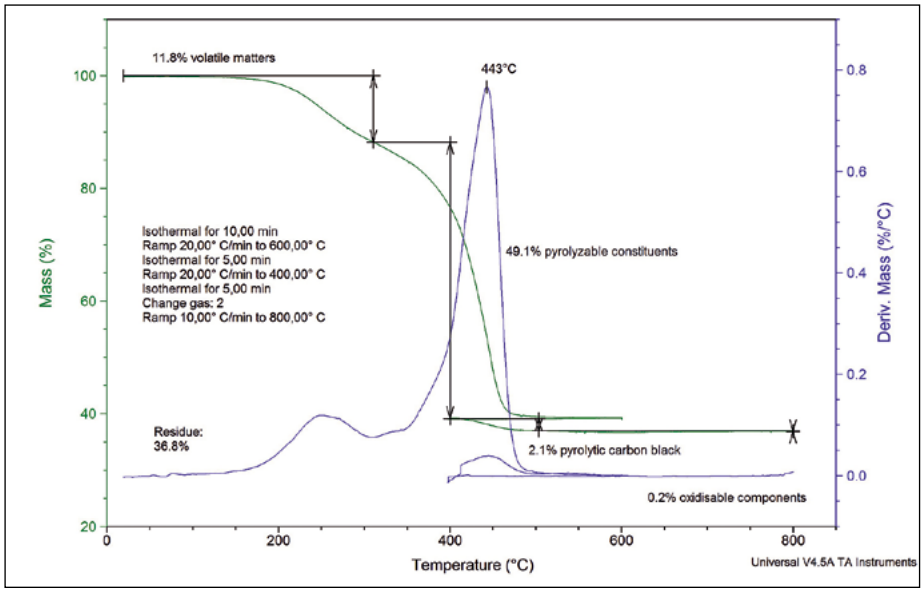
All values are measured within a very small tolerance range (dependent on equipment):

- Force max. 18 N (resolution: 10^{-5} N)
- Distance resolution 1 nm
- Frequency (sinusoidal) up to max. 200 Hz
- The usual temperature range for elastomers from -100 °C to above the decomposition temperature of the polymer

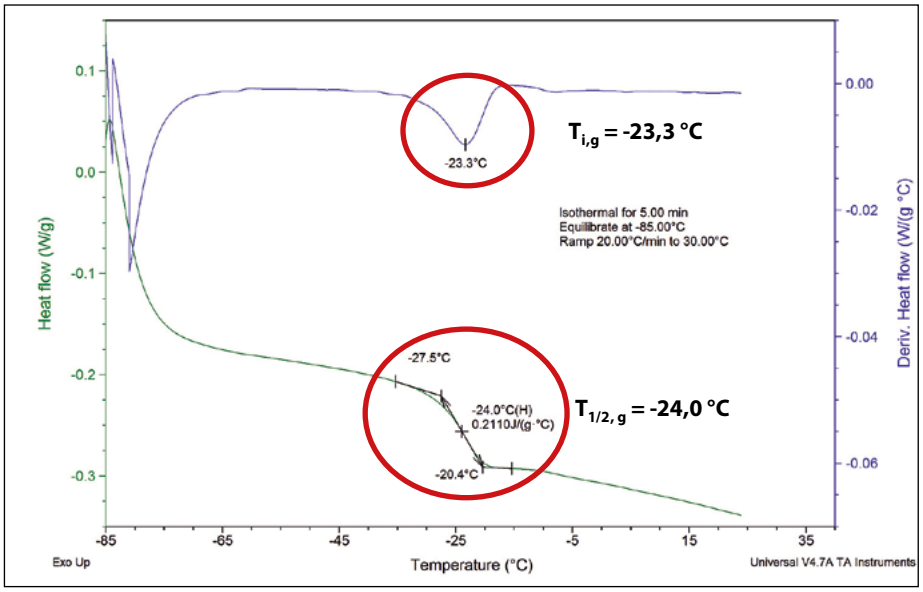
The measuring periods per test are usually longer than with the TGA or DSC. The DMA has a larger sample chamber volume and a poor heat transfer into the sample, therefore low cooling and heating rates are applied. Basically, two operating modes of the DMA can be distinguished:

1. Dynamic measurements at different frequencies, amplitudes or temperatures,
2. Creep tests under constant load or constant deformation at constant or linearly decreasing or increasing temperatures. The resulting deformations are then measured under a constant load or the changing force required under a constant deformation.

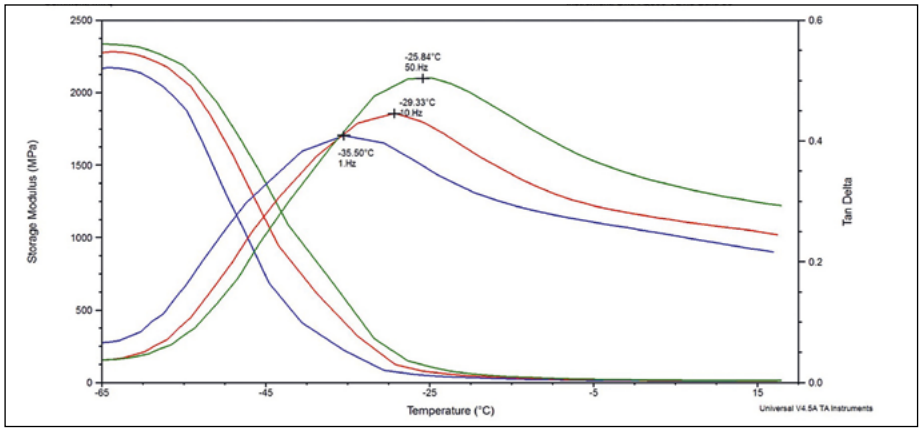
»22 shows the DMA test of an EPDM material at different frequencies in the tensile stress test mode (blue: 1 Hz, red: 10 Hz, green: 50 Hz). The declining curves on the left of the diagram show the storage modulus. The higher the frequency, the faster it increases with decreasing temperatures. The curves in the middle show the tan δ (maximum = glass transition point). This increases with a higher frequency (-35 °C at 1 Hz, -26 °C at 50 Hz). DMA can be used to determine a large number of material properties, but a great deal of expertise and experience is required in order to be able to interpret and use the results for the user in a practice-oriented manner.



»20 **Result curves of a TGA test** (Picture: O-Ring Prüflabor Richter GmbH)



»21 **Result curves of a DSC test for determining the glass transition s**
(Picture: O-Ring Prüflabor Richter GmbH)



»22 **Result curves of a DMA test at three different frequencies (memory module and tan δ)**
(Picture: O-Ring Prüflabor Richter GmbH)

DICHT!digital: Long version of the article

Chemical-Analytical Test Methods – Finding the Material DNA

from DICHT! 4.2017

IR: Simple and Fast Method for Polymer Determination

Infrared spectroscopy (IR) uses invisible infrared radiation with a wavelength between visible light and microwaves. The infrared waves can only interact with polarizable bonds and trigger them to oscillate, resulting in radiation absorptions that stimulate different groups of molecules depending on the wavelength. The evaluation of these groups provides information about the contents of an elastomer. However, IR does not provide trace analysis (detection limit 2 to 5%).

Whereas previously dispersive IR was used in the elastomer field, now only Fourier Transform Infrared Spectroscopy (FTIR) is used. With the help of the Fourier transformation of the measured values, the desired spectrum is obtained. This results in relatively short measurement periods with stronger signals. Elastomer spectra contain complex mixtures, so that separation is not always possible. However, the significance can be increased by coupling different methods. Since most elastomers are black and therefore not transparent to light and infrared, pyrolysis FTIR or FTIR with ATR (attenuated total reflection) can help here.

In the case of pyrolysis FTIR, the condensed vapor of a thermally decomposed elastomer sample is analyzed, while in the case of the ATR technique IR radiation passes through a special crystal (e.g. made of germanium), which is placed on the elastomer sample and penetrates it only for a few µm. The reflected radiation passes again through the ATR crystal and then hits the detector..

Simplified, elastomers consist of the following four groups of substances: polymer, fillers, plasticizers/processing aids and carbon black. The first three groups can be found in the ATR spectrum, the pyrolysis spectrum can only detect the polymer and the plasticizers/processing aids.

The wave numbers of important peaks (triggered by characteristic functional groups, e.g. C≡N nitrile group in NBR at a wave number of 2,235 cm^{-1}) of the common polymers are known via databases, with which fast base polymer identification is possible. »23 shows an example for an FTIR polymer analysis of an NBR-O-ring. The Y-axis shows the intensity of the absorption, while the X-axis shows the wavenumber (= reciprocal value of the wavelength) for display reasons.

The analysis of extracts is also of great practical importance. Hot extraction using a solvent mixture can be used to separate many important compound ingredients from the rubber and thereby analyze the compound constituents more precisely than in ATR analysis or pyrolysis. This process is frequently used in quality assurance to compare different batches of a compound. »24 shows a comparison of two batches of an NBR-70 formulation with large differences. In a failure analysis, the extract comparison of a failed seal with a new seal reveals which organic substances have diffused into the seal.

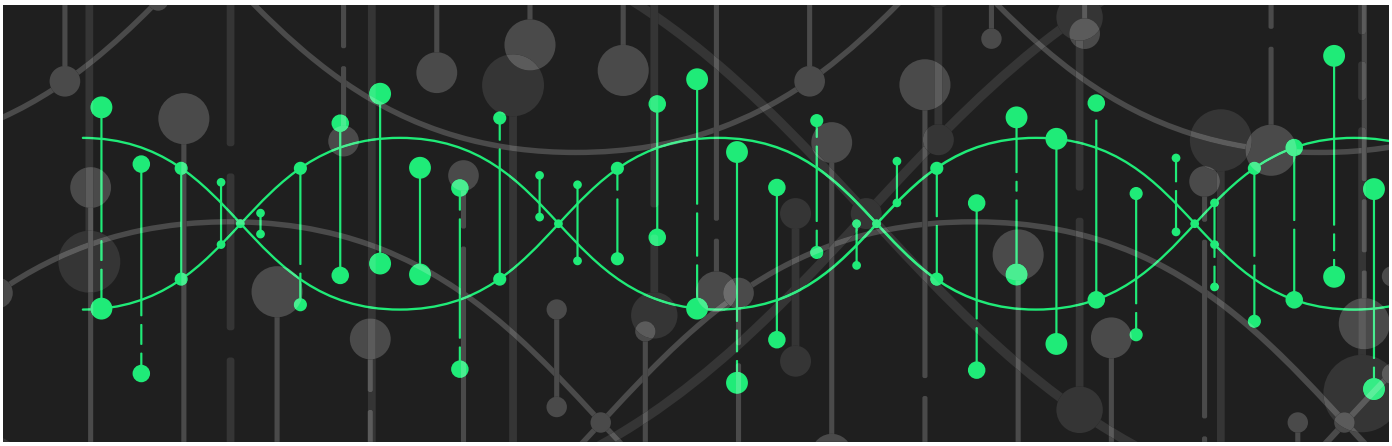
FTIR analysis using ATR technology is also of practical importance in the chemical characterization of coatings. It can be determined, for example, whether the O-rings sampled by the supplier are coated with the correct bonded coating (e.g. based on PTFE or VMQ).

Overall, FTIR analysis is a frequently used analysis method in elastomer technology. For simple QA tasks, basic chemical knowledge for the application is sufficient with the aid of good software. For more complex testing tasks (e.g. compound development, production or damage analysis), the operator should have a solid basic chemical understanding.

GC-MS: For a Deeper Insight into the Elastomer Composition

Pyrolysis gas chromatography with mass spectrometry coupling (GC-MS) is used for this purpose. A gas chromatograph (GC) uses pyrolysis or thermal desorption to separate the components of a rubber compound. For this purpose, the sample is heated which, depending on the temperature, leads to outgassing of the volatile components or to decomposition (pyrolysis). The individual components travel through a long, thin, coated column - depending on their chemical nature - with an inert gas stream (helium, nitrogen or hydrogen) at different speeds and therefore arrive at the end of the column at different times. There, the individual molecules - still in the gas phase - are ionized and accelerated differently in an electric field according to their mass and charge. At the end they meet an analyzer (in the mass spectrometer MS). The signals can be compared with a database and the individual components identified.

The detection limit of 10^{-10}g is extremely low. Especially in failure analysis it can be very beneficial that even the smallest sample quanti-



(Picture: © Egor – stock.adobe.com)

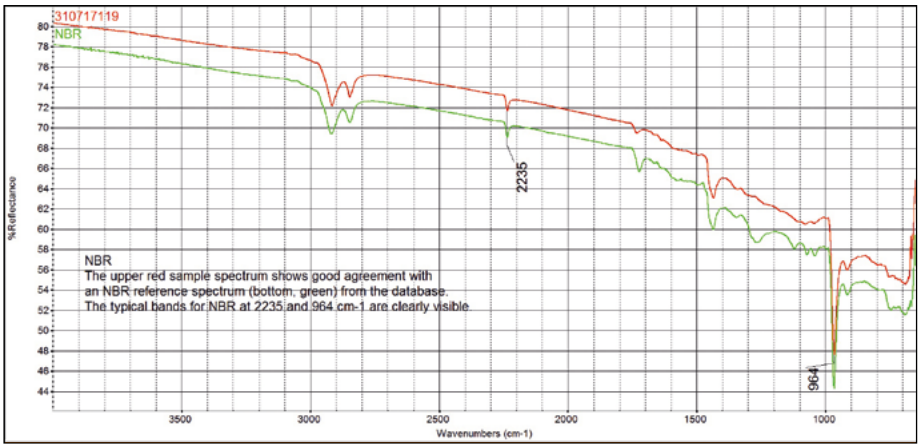
ties of approx. 0.3 mg are sufficient for an analysis. Due to the low detection limit, the application area of GC-MS analysis in elastomer technology begins where FTIR analysis ends.

Compared to the FTIR analysis, the evaluation and interpretation is much more complex and requires a profound chemical education. The acquisition costs are also considerably higher than for an FTIR analyzer. As an instrument for quality assurance, this high-resolution analysis method is still rarely used in elastomer technology. In critical applications or in cases of failure that are difficult to explain, the GC-MS can be the decisive factor in problem identification, as it can reveal even the smallest differences in formulation that can result, for example, from the use of comparable mixing chemicals from different suppliers. However, the procedure can also eliminate the last uncertainties regarding batch fluctuations in suspected cases. »25 shows a batch comparison of an FKM material with high correspondence. Each individual signal can be assigned to a chemical using a mass spectrometer.

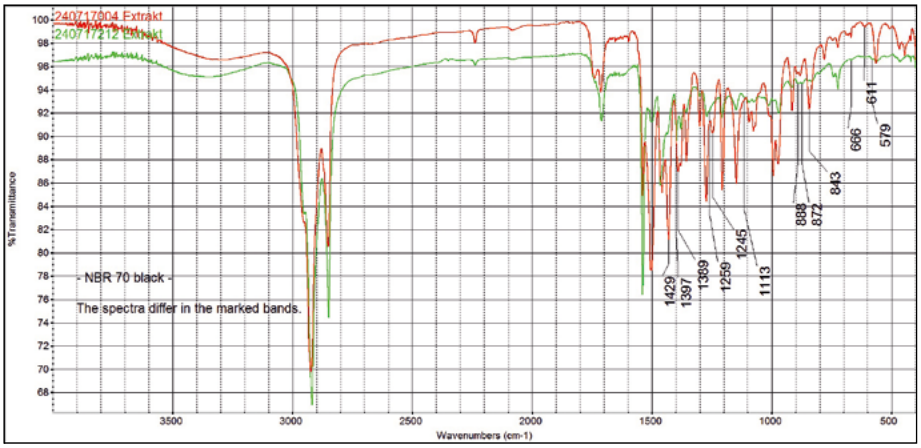
In the O-Ring Prüflabor Richter, GC-MS analysis is mainly used in failure analysis. It usually helps identifying which substances have diffused into the seal and therefore it can indicate the cause of the failure. Micro parts in particular react sensitively to plasticizers extracted from hoses or other rubber parts during operation. Impurities carried in can be identified. On swollen seals, the cause can be identified much more precisely than with the FTIR analysis. Sometimes it is also very helpful to prove that there has been no external contamination of the material and that therefore it has not caused the damage. The advantages of the GC-MS analysis are therefore the higher accuracy and resolution compared to the FTIR analysis, and also a quantitative analysis that can be carried out if required.

DICHT!digital: Further Information on infrared spectroscopy

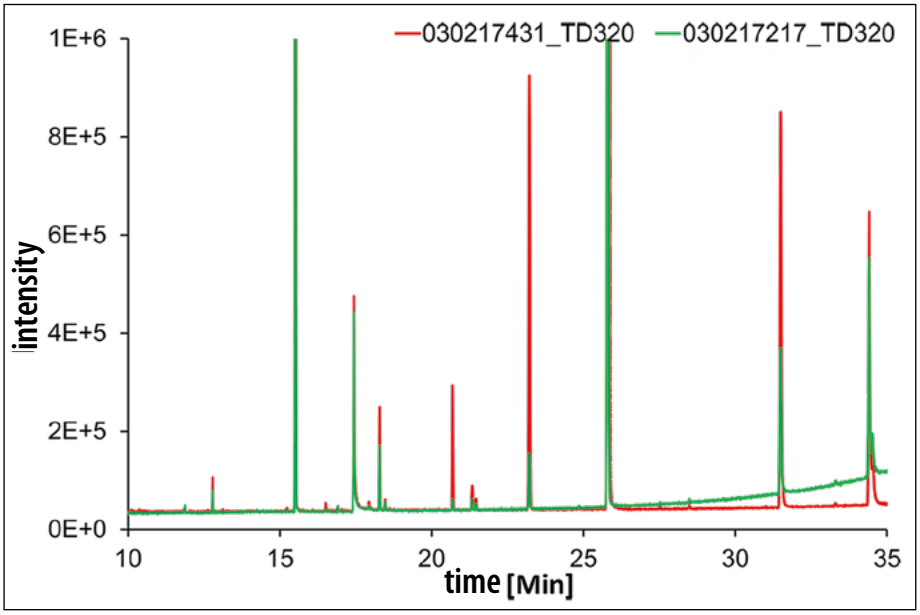
DICHT!digital: Further Information about pyrolysis GC-MS



» 23 **FTIR polymer determination using the ATR method** (Picture: O-Ring Prüflabor Richter GmbH)



»24 **Extract comparison of two batches of an NBR compound** (Picture: O-Ring Prüflabor Richter GmbH)



»25 **Chromatogram of two batches of an FKM material** (Picture: O-Ring Prüflabor Richter GmbH)

Small NBR Materials Science for Users

Differences that matter

Some sealing materials have special properties in the polymer or in the mixture that are unique to them. Usually there are then two or more variations of this parameter and therefore resulting special properties of the material. In practice, these small variations in particular can decide whether a seal functions reliably or whether it fails altogether. If this in-depth knowledge is lacking, one can have bought the „right material", but still fail with it.

The standard tests, such as hardness, tensile test, compression set etc. can be carried out on standard test specimens from test plates of all elastomeric seal materials. In many cases, however, special test methods are necessary in order to track down the special properties.

The Classic – NBR

Acrylonitrile-butadiene- (NBR)- rubbers are among the oldest synthetic rubbers with good oil and fuel resistance. Despite increased temperature and medium loads, this type of polymer can still be used in modern mechanical engineering and application technology.

One of the most important features of an NBR compound is its ACN (acrylonitrile) content, which is matched to the application. If its content in the polymer is high, the elastomer product has good oil and hydrocarbon resistance. In addition, a high ACN content (max. 50%) results in low cold flexibility, which is less desirable in most applications.

An NBR with a low ACN content (min. 18%), on the other hand, has good low-temperature flexibility, but poorer oil and hydrocarbon resistance. Especially this example clearly shows a common dilemma of elastomer sealing materials: „Nothing works without a good compromise".

In practical testing technology, the ACN content of an NBR mixture is not determined directly, but test methods are used with which an indirect conclusion can be drawn about the ACN content. With the help of Differential Scanning Calorimetry, better known as DSC, the glass transition temperature can be determined and a prediction can be made about the cold flexibility of the material. The latter can also be investigated using the TR 10 test »26, which is standardized in ASTM D1329 and ISO 2921. Although this test originated in the USA, it is becoming more and more popular in Europe due to its very helpful conclusions for users in practice. Lastly, the resistance to oil and hydrocarbons can be determined by immersion tests.

However, there are also small tricks in compounding to improve the low-temperature flexibility of an NBR. This can be achieved by using plasticizers. In addition, the plasticizer portion reduces the polymer portion that swells in oils. This can result in lower oil swelling. However, it should be investigated in the elastomer test whether the plasticizer will not be extracted too quickly from the compound in the application. Depending on the application, heat aging and/or immersion tests in extracting paraffin oils (e.g. IRM 901) are recommended.

»26 TR10 testing in the O-Ring Prüflabor Richter
(Picture: O-Ring Prüflabor Richter GmbH)

»27 Equipment of an ozone test chamber in the O-Ring Prüflabor Richter
(Picture: O-Ring Prüflabor Richter GmbH)

Another interesting feature of NBR is the possibility to mix it with PVC thermoplastic. This results in so-called NBR/PVC blends. The main advantage of this is that the NBR material, which is inherently susceptible to ozone cracking, can therefore be very effectively protected against ozone attack (with sufficient PVC content). However, the PVC content worsens the low-temperature flexibility and the long-term sealing effect (higher permanent deformation).

Thermogravimetric analysis (TGA) can be used to quantitatively determine the most important components of a formulation. This method is also used for the detection of PVC (chlorine separation). The compression set test provides information on the behavior under long-term and/or high-temperature loading. The investigation of NBR/PVC blends in immersion tests with strongly swelling mediums (e.g. IRM 903) is finally carried out in order to investigate the hydrocarbon resistance, and with the aid of an ozone test »27, the effectiveness of the ozone protection can be demonstrated.

The analysis of failure cases often shows that it is the details that are important in new or special applications. For many other elastomer types there are other special properties which can be studied in more detail in technical literature. A user who is aware of the various parameters and their effects will be able to address a seal manufacturer much more effectively and will also be able to ask for meaningful test results more directly. This will help to avoid errors, especially in product development, and to achieve sealing systems that work for the long term at an early stage.

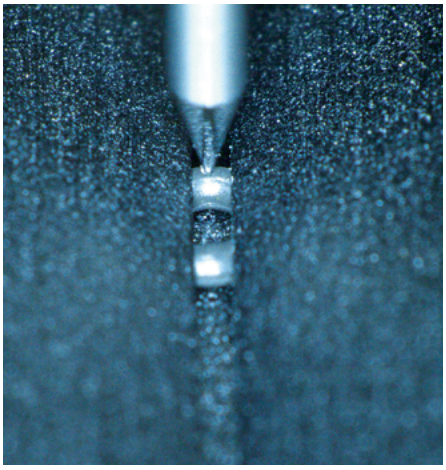
New Test Method

IRHD and Shore A Hardness-Measuring on microparts

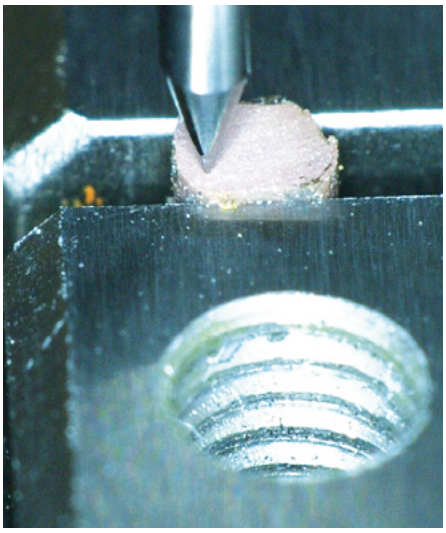
Since December 2019, the O-Ring Prüflabor Richter has been offering a high-resolution microindenter for the analysis of parameters on polymer materials »28, 29. "The LNP® nano touch is a compact, infinitely variable force-position sensor with frictionless bearing and dynamic force generation up to 1.4 N. This guarantees a precise force generation without friction or guiding losses. Combined with an optical incremental position sensor with a high-resolution of up to 10 nm, a damage-free, high-precision geometrical and physical measurement is achieved, as is the determination of material properties." [1] The LNP® nano touch is a device whose physical principles have been known for decades, but which has only become possible through a combination of the latest high-precision measuring technology in combination with an intelligent and scientifically based software.

Together with different microindenters, the smallest with a radius of 0,02 mm, hardness tests corresponding to IRHD, M can be performed on small-cross-sections up to 0,3 mm. In the field of sealing failure analyses hardness measurements on profile cuts can indicate hardened zones of the seal and therefore they can help to identify the failure cause.

Literature
[1] Ludwig Nano Präzision GmbH (Ed.): LNP® nano touch Micor-indenter for the analysis of elastomer parameters The Measurementsystem (English company brochure), March 2018, pg. 4, Weblink: https://lnp-northeim.de/wp-content/uploads/2018/07/Nanotouch032018_eng.pdf (Website accessed on 1st May 2020)



»28 Hardness measurement with the LNP® Nano touch on an O-ring with a cross-section of 0,65 mm with an indentor radius of 0,041 mm and a load of 22 mN (Picture: O-Ring Prüflabor Richter GmbH)



»29 Hardness measurement on the cross section of a cut O-ring – to understand the proportions, the O-ring has a cross-section of 1,5 mm (Picture: O-Ring Prüflabor Richter GmbH)

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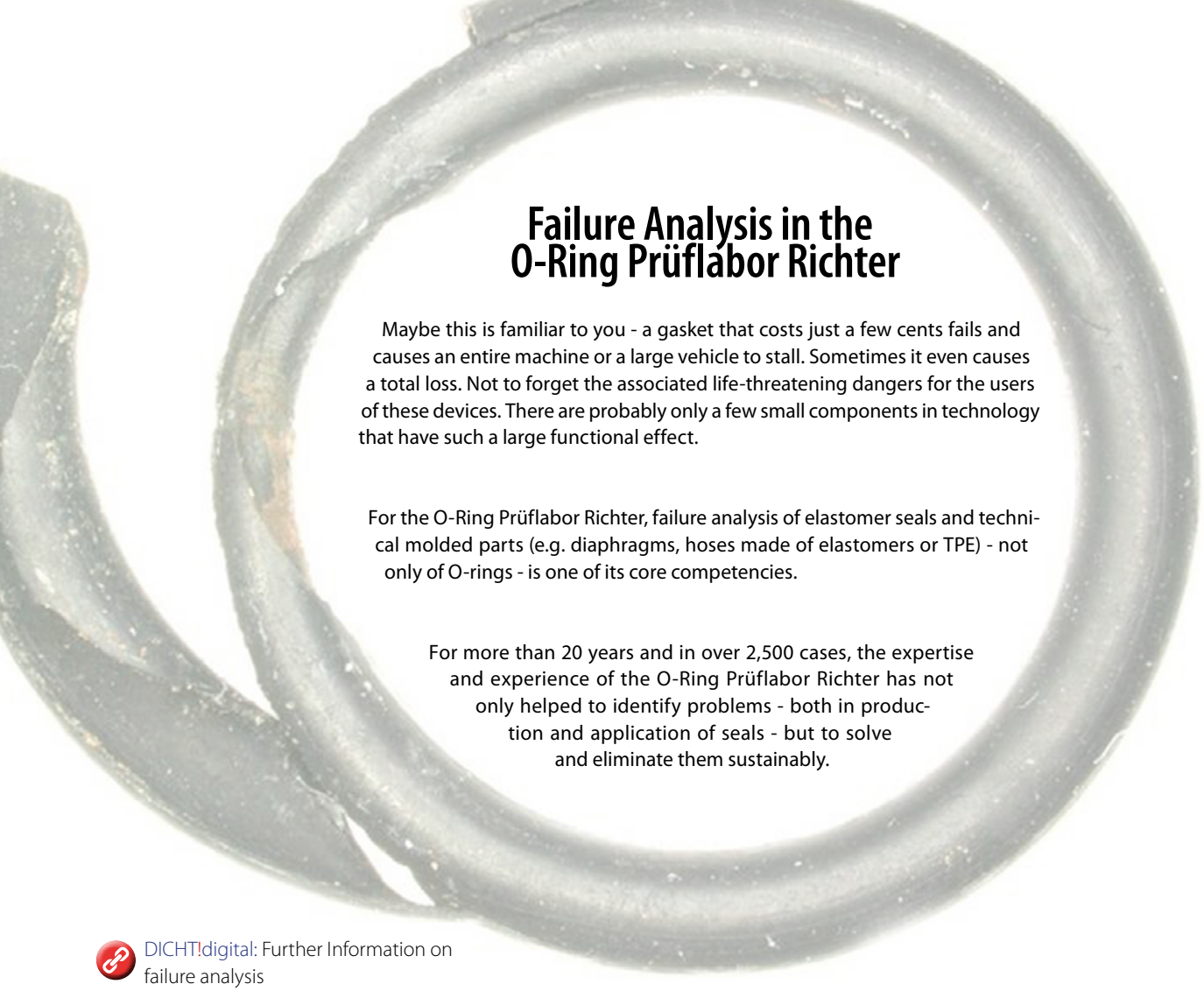
Further Information

This special issue can also be downloaded as PDF under the following link:
https://www.o-ring-prueflabor.de/files/expert_knowledge_special_issue_dicht.pdf

You can also use the QR code for mobile devices.



Failure Analysis in the O-Ring Prüflabor Richter

Maybe this is familiar to you - a gasket that costs just a few cents fails and causes an entire machine or a large vehicle to stall. Sometimes it even causes a total loss. Not to forget the associated life-threatening dangers for the users of these devices. There are probably only a few small components in technology that have such a large functional effect.

For the O-Ring Prüflabor Richter, failure analysis of elastomer seals and technical molded parts (e.g. diaphragms, hoses made of elastomers or TPE) - not only of O-rings - is one of its core competencies.

For more than 20 years and in over 2,500 cases, the expertise and experience of the O-Ring Prüflabor Richter has not only helped to identify problems - both in production and application of seals - but to solve and eliminate them sustainably.

DICHT!digital: Further Information on failure analysis

Seminars of the O-Ring Prüflabor Richter

For many years, the O-Ring Prüflabor Richter has been offering seminars on the topics of elastomer sealing technology and materials science. These seminars incorporate more than 20 years of expertise in materials testing, customer consulting and failure analysis. Today, nine open seminars and approximately 20 in-house seminars are held annually. Particularly in-house seminars are precisely tailored to customer requests and needs. The open seminars provide expert insight on the following topics:

- Elastomer materials and seals
- O-ring seals – dimensioning, operational limits and applications
- Failure analysis of elastomer seals
- Testing of elastomer seals – seminar and workshop
- Quality of elastomer products – from the mixture to the finished part

In 2017, an advanced seminar was offered for the first time (Senior Expert Training - in-depth seminar on elastomers & seals), which gained great interest.

DICHT!digital: More info about seminars

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