EXPERT KNOWLEDGE FAILURE ANALYSIS OF ELASTOMER COMPONENTS

An offer of

O RING PRÜFLABOR RICHTER

TESTING CONSULTING DEVELOPING

Source: www.o-ring-prueflabor.de
Information as of 07/2019

High Permanent Deformation –

If the Gasket is "Stuck"

Authors:
Dipl.-Ing. Bernhard Richter,
Dipl.-Ing. (FH) Ulrich Blobner

1. Classification and Frequency of the Damage Pattern

Of the four main damage mechanisms, the high permanent deformation is predominantly attributed to the second main group:

1. Mediums
► **2. Temperature / Aging**
3. Mechanical / Physical Effects
4. Manufacturing Defects

The second main group can be divided into four subgroups: overheating, incorrect material, aging, poor mixture. The high permanent deformation is a special case as it can be caused by any of these subgroups. In addition, a poor degree of vulcanization, which is a manufacturing defect, or a poor installation space (incorrect groove depth / excessive diameter play) can also cause this damage pattern. The high permanent deformation represents a special case as it cannot be assigned to only one main group of damage mechanisms.

In approx. 3% of the more than 2000 damage cases analyzed in the O-Ring Prüflabor Richter, a high permanent deformation was the reason for the failure. In addition, however, there are almost daily procedures in the daily routine of the testing laboratory in which an unexpectedly high permanent deformation of a material or seal is found. This is therefore a topic with which seal users are frequently confronted with.

2. Technical Background Knowledge on the Damage Pattern

A high permanent deformation is the cause of failure if a seal fails significantly before its age-related service life limit or considerably before the user's service life expectancy due to a lack of elastic re-deformation. The damage pattern is represented by a flattening of the seal on both sides, whereby it is often the case that the seal still has an elastic effect, which means it still behaves typically rubber-elastic.

There are the following ***mechanisms*** which can lead to a high permanent deformation of elastomer components:

- Modification of the network structure (premature aging due to temperature, mediums including chain breaking and re-crosslinking in a deformed state) ► most common mechanism (irreversible)
- High crystallization tendency or unfavorable glass transition area of the polymer (partially reversible deformation, see 2.2)
- Seal shrinkage due to loss of plasticizer (irreversible deformation, see 2.3)
- Creep of elastomers (irreversible, damage mechanism in elastomer building / bridge bearings, not relevant in classical sealing applications).

Depending on the mechanism, one or more of the following ***causes*** must be readjusted:

2.1 Manufacturing Defects or Insufficient Vulcanization

Elastomers only become elastic during shaping through chemical conversion into the cross-linked state. This requires a precise process control of temperature and time during vulcanization in the mold and post-tempering.
This error is caused either by a shortened post-crosslinking time in the injection mold or in the tempering furnace or by forgetting the post-tempering step, with fatal consequences for the sealing application. Therefore, a regular quality control, e.g. an ASTM D395 (compression set) test, on the finished seals is recommended. If an inadequate degree of cross-linking is then found, the defects can either be corrected by additional post-tempering (e.g. with peroxidically or bisphenolically cross-linked FKM, VMQ, Sulphur-cross-linked NBR) or the goods must be declared as rejects because post-tempering outside the injection mold is not possible due to the material type (e.g. peroxidically cross-linked EPDM or HNBR).
Typical for this cause of damage is a permanent deformation without a significant increase in hardness. The obvious conclusion, of course, is that the seal is of poor quality. This is the case,

for example, if the seal has been insufficiently vulcanized due to the possible faults described above. A high permanent deformation of the seal then occurs without the typical material limits of the elastomer having been reached. On new seals, this can be seen well in compression deformation tests on finished parts. On seals that have already been used, it is only possible to a limited extent afterwards. This is because the heat from the application of the seal can lead to post-vulcanization. However, if the compression set is actually measured on the failed seal (after thermal conditioning, see 2.2 for reasons for this) and there are high, therefore poor compression set results, one can be fairly certain that the cause was insufficient vulcanization. If, on the other hand, low, therefore good, compression set results are found, no clear conclusion can be drawn. The good compression set results can also come from the new cross-linking in the compressed state at elevated operating temperature and it is therefore no longer possible to say whether the seal was well or insufficiently cross-linked in the installed state.

2.2 Poor Polymer Properties (Glass Transition Temperature, Crystallization Tendency)

Typical for this cause of damage is also a permanent deformation without a significant increase in hardness.
The viscoelastic behavior of elastomers means that the chain mobility is temperature-dependent and can already be considerably restricted at room temperature. The decisive factor here is how close the elastomer material is to its glass transition area when cooled down. If this is relatively high, as for example the case with FEPM, FFKM or FKM polymers, this limited chain mobility is no longer sufficient for sufficient resetting once the deformed seal has been heated and the polymer chains have reoriented or relaxed as a result of thermal activation and then cooled in the new orientation. This means that when the polymer chains are heated, they are reoriented, which can lead to considerable permanent deformation when they are subsequently cooled to room temperature, even without aging.
If an elastomer has crystalline areas, such as EPDM, similar effects to those described above may also occur, even if the elastomer has a relatively low glass transition area. In EPDM polymers, the ethylene content can vary between 40 and approx. 85% depending on the polymer architecture. If it is very high, this can lead to crystalline sequences. Only at elevated temperatures (>100°C) can this effect be compensated by the increased chain mobility. If a component or test specimen is then deformed and used at elevated temperatures, the significantly lower viscosity or the increased chain mobility leads to a reorientation of the polymer chains according to the deformation stresses. If cooling to room temperature then takes place, the crystalline sequences result in the component only partially recovering after relief, although the temperature is still considerably above the glass transition temperature of the EPDM polymer (< - 40°C) and no significant destruction of the network has taken place due to aging.
The high setting performance of FKM, HNBR and EPDM seals and many TPE materials is in some cases not due to poor vulcanization or Sulfur crosslinking, but to the polymer properties.

If residual compression set values according to ISO 815-1[1] are found in data sheets, these almost always refer to method A, meaning that the specimens are relaxed again at test

[1] ISO 815-1: 2014-09: Rubber, vulcanized or thermoplastic - Determination of compression set – Part 1: At

temperature. However, this type of test does not reflect the practical application, where the seals cool down to room temperature or below in the deformed state. In order to identify this as a possible cause of failure, a compression set test over 24 hours at 100 to 150°C is sufficient if the test is carried out according to method B (relaxation of the specimen only after reaching room temperature). This value according to method B can hardly be found in data sheets because it is considerably worse than the value according to method A, even though all major German automobile manufacturers require this value for material qualification.
It is therefore advisable to thermally condition seals with noticeably permanently deformed seals after measurement, e.g. 1 h 100°C, so that the seal can regress again if the permanent deformation is caused by the reversible effects described above and not by aging caused by heat and oxygen or by chemical degradation which leads to irreversible permanent deformation.

2.3 Poor Mixture Formulation

Typical for this damage mechanism is a permanent deformation with a significant increase in hardness and a loss of volume. However, the seal still behaves typically rubber-elastic, which means that it does not break through a bending test.
Sealing materials that are not used in the high temperature range (like FKM) usually contain plasticizers in their formulations. They have a wide range of functions, from improving process ability, low-temperature flexibility, filler distribution and elasticity to price reduction of the compound (stretching of a mixture). If large amounts of plasticizer are washed/extracted from a seal by ambient fluids or outgassed, it can lead to high permanent deformation. In addition to the settling behavior caused by aging, this results in additional volume shrinkage. As soon as this volume shrinkage can no longer be compensated by the elastic recovery behavior, leakage occurs.
This cause of damage is most common in EPDM materials because they can be most easily stretched with mineral oils as plasticizers. The polymer industry already uses oil-stretched polymer types that contain up to 50% plasticizers. NBR materials can contain up to 20% plasticizers.
The type and quantity of filler in an elastomer compound also have an influence on the setting behavior of a seal. With elastomer compounds that are comparable in formulation and differ only in hardness, the softer compounds usually show less permanent deformation than the harder ones. The hardness of a rubber material is adjusted, among other things, by the type and proportion of filler. However, the elastic springback of a seal is achieved by the three-dimensionally cross-linked polymer. The smaller its quantity, the greater the risk of premature high permanent deformation of the seal.
A significant factor influencing the permanent deformation of a material is the cross-linking system. In Sulphur crosslinking, a distinction is made between conventional crosslinking systems, which form longer Sulphur bridges, and Sulphur-reduced systems (e.g. EV systems, "efficient vulcanization"). "The permanent deformation after a deformation stress becomes more favorable with decreasing index x in C-Sx-C bridges, meaning that the values become

ambient or elevated temperatures

lower. This is particularly true for stress at higher temperatures.” [2] The reason for this is that cross-linking bridges with short chains have an increased binding energy.
Peroxide crosslinking systems provide vulcanizate with improved heat resistance and lower compression set than Sulfur crosslinking. Peroxide crosslinked elastomers are thermally more stable than Sulfur crosslinked elastomers. Some rubbers can be crosslinked both with Sulfur and peroxide (e.g. NR, NBR, HNBR, EPDM). If low permanent deformation is a major requirement for the end product, peroxide crosslinking is generally preferable.

2.4 Inappropriate Installation Situation

Typical for this cause of damage is a permanent deformation without a significant increase in hardness.
A high permanent deformation means that the seal takes on the dimensions of the installation space and no longer has any reset reserves to bridge the gap. This can be substantially facilitated by the installation space if the degree of deformation of the seal is too low as a result of a too large groove depth or an incorrect seal design. With small deformations of e.g. 2-5% of the cross-section, the restoring forces generated by the deformation can be significantly reduced even without aging. This can be explained by the wide-meshed cross-linking, whereby this effect increases even more at elevated temperatures. This means that in the case of slightly deformed seals, the relative proportion of deformation force or restoring force lost due to physical relaxation is relatively high. This effect is further intensified by heating and subsequent cooling, see also 2.2. If, on the other hand, the degree of deformation of the seal is increased, chain mobility is restricted. For example, ISO 3601-2[3] for O-rings with a cord thickness of 1.78 mm requires a deformation between 14 and 35%.
If elastomer seals are used in a main force connection, the probability increases that they will fail prematurely due to a high permanent deformation. This sealing principle places great demands on the rubber material. In order to achieve a good sealing effect, high compression forces are required which are reduced by a relatively early onset of stress relaxation. As a result, only lower pressures than, for example, O-rings in the force shunt, can be sealed.
In most cases, the high permanent deformation is caused by a faster aging of the material than expected. A seal can only age without restriction if it comes into contact with sufficient oxygen. With regard to aging, O-rings with large cord thicknesses have a more favorable ratio of free surface to mass than thin cord thicknesses and therefore have better compression set properties.

2.5 Impermissible Thermal or Chemical Effects

In addition to the permanent deformation, a significant increase in hardness is often typical for this damage mechanism, and the seal also breaks at a slight bending stress or shows crack formation. This is a sign that the formulation-specific material stress limit for heat and chemical resistance has been reached.

[2] Translated from SEEBERGER, D.: Kautschukchemikalien in: HOFMANN, W. und GUPTA, H.: Handbuch der Kautschuk-Technologie, Dr. Gupta-Verlag, Ratingen, 2001, Kap. 7, S.13
[3] ISO 3601-2:2016-07: Fluid power systems - O-rings – Part 2: Housing dimensions for general applications

If this failure occurs at a fraction of the desired service life, this is a sure sign that the material is not suitable for the application. The question remains how the wrong material was chosen. There can be various reasons for this:

- The application temperatures are higher than assumed. Already 10K more can lead to a halving of the life span, 20K more to a quarter of the life span. In addition, self-heating of the seal due to vibrations or additional heat input - e.g. due to compression heat in the case of cyclic pressure increases for gases - can lead to premature failure. If there are only short-term strong temperature overshoots, this can lead to local flattening and cracking occurring only in the area of the heat input, see **Fig. 1**.
- The existence of heavy metals can lead to premature failure due to autoxidation. In the case of EPDM materials, this can lead not only to permanent deformation but also to softening and complete degradation of the polymer into carbon black. Heavy metals can be detected by SEM-EDX analysis.
- The seal is exposed to substances that lead to chemical degradation. These can be aggressive cleaning or sterilization substances in process engineering or highly additive oils or other aggressive fluids. If this suspicion is obvious, the seal can be examined for traces by means of a GC-MS analysis.
- A lack of knowledge about the long-term performance leads to an incorrect material selection. The common term "permissible continuous temperature" is misleading because the permissible continuous temperature of elastomers is always determined together with the designed application time. In the polymer industry, a time span of 1000h (= 6 weeks) has become established as the "continuous temperature" without the seal manufacturer explicitly pointing this out again. A temperature increase of 10K in the application leads to a halving of the service life, while a temperature reduction of 10K results in a doubling of the service life. If a sealing material is not tested according to this rule of thumb with regard to the desired service life, this can lead to an incorrect choice of material. For example, in a heating application (60° C in hot water) no NBR is selected as the gasket material, although its permissible "continuous temperature" (=1000h) is 100°C, because the user wants to use this gasket for at least 30 years. Instead, a good, peroxide cross-linked EPDM material is used.
- Misleading data pretend a non-existent heat resistance. The compression set is usually determined in data sheets using measured values on cylindrical specimens with a diameter of 13 mm (specimen B) or even 29 mm (specimen A). Long-term tests in the O-Ring Prüflabor Richter have shown that a considerable influence of the wall thickness or the geometry is already present at the permissible continuous temperature according to the 1000h criterion (DLO effect, "Diffusion Limited Oxidation"). Results from short-term tests (24h) on standard specimens and O-rings are still roughly comparable. If the test time is extended, the O-rings show worse test results than standard specimens due to their poorer surface to mass ratio. Increased temperatures (e.g. at NBR 125°C or at HNBR 175°C) lead to a complete distortion of the possibilities for O-rings. Only long-term compression deformation residual values of cylindrical specimens A and B, 20K below the permissible 1000h continuous temperature (at NBR 80°C) can also be achieved on O-rings with thin cord thicknesses.

3. Damage Pattern

3.1 Description of the Damage Pattern and Problematic Areas

It is normal for an elastomer seal to deform permanently under the influence of temperature and substances. For this reason, a damage analysis must assess whether the permanent deformation found can be the cause of a leak. For this reason, the installation space must be known. If the remaining seal height is significantly higher than the groove depth, the permanent deformation is ruled out as the cause of the leakage, provided that the seal has not regressed to a considerable extent after removal.
Other important characteristics of a damage pattern to be investigated are whether it still behaves typically rubber-elastic, whether the hardness (**Fig. 4**) has changed significantly and/or whether the volume of the seal has decreased considerably. This then allows an evaluation of the damage pattern. Residual compression deformation measurements can further confirm the assumptions made.

Fig. 1: Cross-section of a damaged O-ring: Short-term overheating leads to local flattening in the area of heat exposure

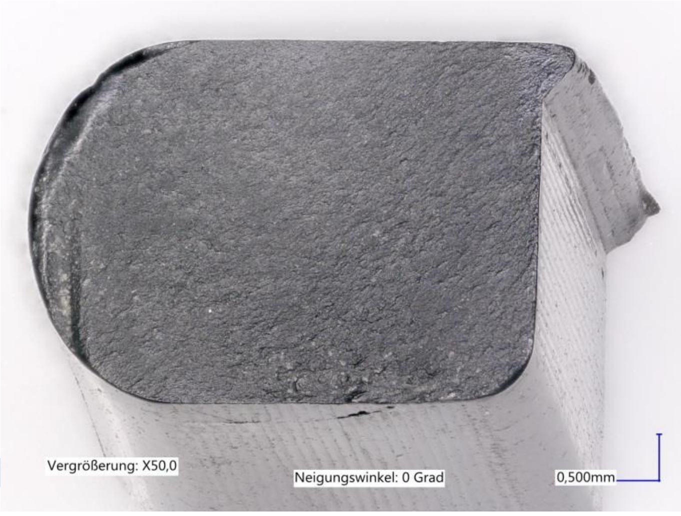

Fig. 2: Cross-section of a damage O-ring: In addition to the permanent deformation, a typical impermissible thermal stress is a complete embrittlement, which is indicated here in the structure of the sectional surface.

Fig. 3: Permanent deformation due to chemical degradation - the stronger degree of deformation in the left area can be clearly seen (medium side)

Fig. 4: In addition to permanent deformation, a typical impermissible thermal stress is complete embrittlement, which is shown here in crack formation after slight bending stress in the contact area of the seal.

It is sometimes difficult to distinguish the damage pattern of permanent deformation due to insufficient vulcanization from the damage pattern of short-term overheating, especially with FKM seals.

3.2 Consequences of the Damage

This damage shows symptoms similar to those of a seal failure at the end of its lifespan, but at a much earlier point in time. It leads to leakage and can lead to total failure of the sealing system.

3.3 Differentiation from Similar Types of Damage

At first glance, the cross-section of an O-ring that has failed due to excessive abrasion can be confused with a high permanent deformation. When comparing the cross-sectional area of an abraded O-ring with that of a new O-ring, however, it quickly becomes clear that the cross-sectional area of an O-ring damaged by abrasion is missing. Since rubber materials can initially be regarded as incompressible, no significant surface change occurs with a high permanent deformation, but only a rearrangement of surfaces. In addition, the abraded ring often shows grinding marks, see **Figs. 5 and 6.**

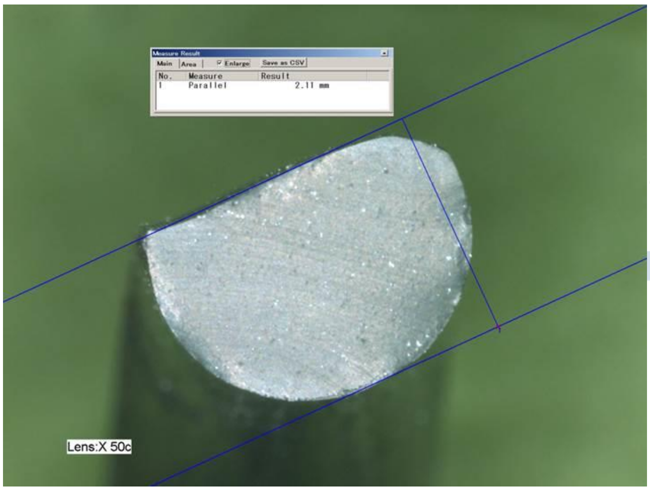

Fig. 5: Abrasive O-ring (EPDM, 70 ShA) out of "static" sealing with too large pressure-conditioned axial stroke

Fig. 6: Plan view of the outer diameter of the damaged O-ring from Fig. 5 with clear marks from the abrasion process.

4. Preventative Actions

To avoid this damage, in most cases it is sufficient to deal with four points when designing a gasket: temperature stress on the gasket, degree of deformation, material and processing quality.
In addition to the maximum peak temperatures, time-temperature collectives over the service life must also be estimated and taken into account in the selection of materials. When designing the installation space, it must be ensured that certain minimum degrees of deformation are ensured. For O-rings, for example, this means a compression of at least 10%. The selection of the right material is a very complex field. This is why most seal users depend on a competent supplier. In addition to the classic requirements, such as a good and open customer-supplier relationship, on which both sides must work, the user can also make a major contribution to ensuring a well-functioning sealing system. On the one hand, a detailed requirement specification is a great decision-making aid; on the other hand, a designer with the appropriate rubber expertise can ask more specifically for critical points, in this case, e.g. for cross-linking systems or the crystallinity of the polymer. In addition, the specifications for formulation properties in ISO 3601-5[4] can help to maintain an appropriate state of the art.

5. Practical Tips (Testing Possibilities / Standard Recommendations)

The compression set test (ISO 815-1) is very easy to perform and provides good information as to whether a material has a tendency to high permanent deformation or not. In addition, limit values for compression set measurements on finished parts should always be defined, both according to method A and method B.

[4] ISO 3601-5:2015-04: Fluid power systems - O-rings - Part 5: Specification of elastomeric materials for industrial applications

A good processing quality should be ensured by two pillars: on the one hand, by the already mentioned customer-supplier relationship and on the other hand, by regular and meaningful quality controls of the finished seals. If the company does not have sufficient rubber competence in-house, these tests can also be carried out by external accredited testing laboratories, such as the O-Ring Prüflabor Richter. The costs remain manageable through appropriate framework agreements and therefore there are no delays in production.
However, every gasket user should be able to check a minimum of parameters (hardness, density, dimensions) in-house in order to avoid material mix-ups during assembly in case of doubt.
Thermogravimetric analysis (TGA) is very suitable for the examination of mixture formulations. It can be used to find out how much plasticizer a mixture contains. In the case of seal shrinkage by outgassing or extraction of plasticizers, the comparison of unused and failed seals provides clear evidence of the cause of the damage.

6. Other

This article is published in a short version in the journal DICHT!, issue 03/2019.
Link to the digital editions of this journal (German):
https://dichtdigital.isgatec.com/de/profiles/1d1042c9c353/editions