Chemical Attack and Swelling
Destruction of Network Structure by Contact Medium

1. Classification and Frequency of Failure

Out of the four main failure mechanisms an incorrect media exposure is classified into the first group of the main groups mentioned beneath:

1. Media
2. Temperature / Ageing
3. Mechanical / Physical Damages
4. Manufacturing Errors

According to the analysis of more than 2000 processed failures, a chemical attack or an incorrect swelling can be matched in a little more than 10% of all sealing failures as cause of failure.
2. Professional Background Knowledge about Damage Symptoms

Since the mid-18th century, when the first rubber samples arrived for examination from South America, the new material was especially of interest for chemistry.\(^1\) Whereas at the beginning the point was to find a suitable solvent for rubber to make it processable, later the chemical resistance became more and more the focus of interest. By now, due to the wide range of synthetic rubbers, cross-linking systems and compound ingredients which improve the chemical resistance, the “tailor-made” elastomer compound for almost any contact medium is available to the practitioner.

Again and again there are sealing failures because of chemical attack and swelling despite the very comprehensive and detailed knowledge about chemical resistance.\(^2\) This is due to the fact that in this area we often deal with complex processes involving several interactions which cannot be overviewed at the starting point of an application.

The following compound ingredients have influence on the resistance to chemical attack and swelling:\(^3\)

1. Base polymer (e.g. EPDM, NBR or FKM)
2. Polymer architecture (e.g. diene concentration in EPDM, acrylonitrile concentration in NBR, used initial monomers in FKM, e.g. co- or terpolymers)
3. Cross-linking system (e.g. bisphenolic or peroxide in FKM respectively triazine or peroxide in FFKM)
4. Fillers (e.g. carbon blacks can present a problem in highly oxidising media)
5. Other compound ingredients (e.g. acid acceptor system in FKM (for example magnesium oxide), anti-ageing agent in NBR or EPDM, plasticiser)

At this point swelling and chemical attack should be differentiated before taking a closer look at the points mentioned above:

An excessive swelling is a largely reversible process. If, for example, an NBR swells in fuel, the swelling can be reversed by re-drying, an evaporation of the solvent. In most cases a residue of the solvent remains in the elastomer. In specific cases even shrinkage can occur,

\(^1\) Cf. concerning this: DE LA CONDAMINE; Ch. M.: Mémoire sur une résine élastique nouvellement découverte à Cayenne par M. Fresneau, Mémoires de l'Académie des sciences de Paris, 1751 (among others the dissolution of rubber through warm nut oil) http://gallica.bnf.fr/ark:/12148/bpt6k3549p/f545.pdf (access to web page on 25th May 2017)

\(^2\) Examples of specialist literature and information about the chemical resistance of elastomers:
- NAGDI, Khairi: Gummi-Werkstoffe - Ein Ratgeber für Anwender, Dr. Gupta Verlag, Ratingen, ²2002, Kap. 17, S.345-358 (clear presentation in short form)
- Gummiquellungen - Einfluß organischer Flüssigkeiten auf Vulkanisate, SIS-Handbuch 131, Gentner-Verlag, Stuttgart, 1979
Examples of web pages which are subject to registration (access to web pages on 25th May 2017):
- https://dupont.secure.force.com/CRG_Signin

\(^3\) Cf. NAGDI, Khairi: Gummi-Werkstoffe - Ein Ratgeber für Anwender, Dr. Gupta Verlag, Ratingen, ²2002, Kap. 17, p. 345 and

for example if the solvent dissolves the plasticiser out of the elastomer. In cases of extreme swelling (e.g. polar solvent in polar elastomer) irreversible damage of the elastomer matrix and the seal can arise. Due to excessive swelling the component can massively lose strength which can result in material breakout and shearing within the application. For dynamic seals even moderate swelling rates (over 10%) can lead to a significant shortening of durability. With statically applied seals clearly more swelling can be allowed. If the fitting area permits it, swelling rates in oils up to 30% and swelling rates in solvents up to 50-60% are no criterion for exclusion.

Concerning chemical attack we deal with an irreversible process. At first the medium attacks the contact surface of the seal. After that it spreads – driven by the diffusion of the medium - to the inner parts of the seal. In the course of this an interaction with the network structure of the material consisting of the polymer and cross cross links takes place which leads to post curing and/or the destruction of cross links and/or the segmentation of the long polymer chains. The implications of this are loss of sealing force (relaxation) and decrease of strength, measurably faster than this would occur through temperature and exposure to atmospheric oxygen.

The base polymer is of crucial importance for the chemical resistance of an elastomer. As first orientation for swelling behaviour the Latin rule „Similia similibus solvuntur“(= Like is dissolved in like) known from alchemy can be of help. Thus a rubber blend of a polar FKM-rubber for example is not resistant against polar solvents like acetone (swelling > 100%). However, it is resistant against nonpolar solvents like oil and fuels. By contrast a nonpolar rubber like EPDM swells massively in nonpolar mineral oils (> 100%).

Polymer architecture is defined as the structure of the polymer which is generated by specific process engineering during production. In the case of EPDM for example special attention has to be directed to diene and ethylene concentration. If it is high, i.e. > 6%, this usually leads to a poorer ageing resistance and a poorer long-term compression set of the elastomer components which are made from it. A high ethylene concentration, i.e. a value between 60 and 65%, ensures high tensile strength, good tear strength, but also the decline of low temperature flexibility. Further examples of the influence of polymer architecture can be found in U. Blobners and B.Richters publication „Prüfmethoden zu Sondereigenschaften der wichtigsten Dichtungswerkstoffe“(Testing Methods for Special Properties of the most important Sealing Materials). 4

Moreover the vulcanisation system has to be included in the resistance analysis. Due to the limited hot water resistance of a bisphenolic cross linking system for example FKM-materials which are cross linked in this way should not be applied permanently in water over 100°C. By contrast peroxide cross linked FKM-materials have a significantly wider area of application and can be applied in water up to 200°C if the compound design is optimal.

In highly oxidising media it can make sense, not to use carbon blacks as fillers.

In the case of FKM-materials acid acceptor systems also play a prominent role. They may be the explanation why one highly fluorinated FKM-recipe in concentrated hydrochloric acid at 60°C after 3 weeks shows a volume swelling of over 200% whereas another highly

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fluorinated FKM-recipe only swells 7% under equal conditions. In the case of a slight swelling effect of the medium (e.g. brake fluid in EPDM) the presence of plasticisers can also lead to extraction and thereby to shrinkage. Especially in the case of plasticiser amounts of over 10% in a recipe this alone can cause the failure of the seal.

From this one can infer that it is not sufficient to choose a material by means of a media resistance table alone, even if this constitutes an important prerequisite. Concerning the selection of material it is also important to have a compound design which is suitable for the application. Besides these two points operation temperature and period of application are of vital importance for a chemical attack.

The reaction-velocity-temperature-rule (also known as van’t Hoff’s rule) says that a chemical reaction proceeds with double or triple speed if the temperature is increased by 10 Kelvin. In today’s elastomer applications, however, the enhanced Arrhenius-equation is used.

In practice this means that e.g. an elastomer in a specific fluid at ambient temperature was not attacked after one week of storage and apparently counts as resistant whereas it can be destroyed at 70°C within the same time frame. For this reason resistance tests take place at preferably high temperatures and over long periods to reproduce a preferably long application period.

3. Failure Symptoms

3.1 Description of Failure Symptoms and Problematical Areas

A chemical attack can, but need not leave traces on the surface in the contact area. It can also ‘just’ lead to a high compression set, especially if it only came to an attack on the cross-links.

3.1.1 Failure Type ‘Chemical Attack’

The following points are evidence that a chemical attack has happened (see Figure 1-5):

- Cracks towards the medium which are visible to the naked eye or only under the microscope and in stretched condition. These can already occur before the material loses its elasticity.
- Strong setting behaviour of the seal
- Sticky surface and strong softening (polymer degradation), to some extent also sooty surface
- Hardening and loss of elasticity, i.e. breaking of the seal after light bending or tensile stress
Figure 1: EPDM seal destroyed by disinfectant

Figure 2: Chemical attack on FKM-material by an inorganic acid
Figure 3: Chemical attack and swelling with blistering

Figure 4: Hydrolysis (= chemical attack by water) of a polyurethane seal
3.1.2 Failure Type ‘Swelling’

The following points are evidence that swelling as cause of failure has taken place (see Figure 6 and 7):

- The seal still behaves typically elastic.
- Material disruptions or one- or two-sided extrusion flash
- Significant increase of volume which usually leads to decrease of density and hardness and increase of the cross sectional area
- A comparison with a new (unused) seal in a thermogravimetric analysis (TGA) reveals a significantly higher amount of vaporisable respectively extractable components
3.2 Effects of Failure

Through chemical attack polymer degradation and thus softening can occur. Thereby the risk of gap extrusion increases and the resilience of the seal decreases significantly. Or the attack leads to a hardening and finally to the rupture of the seal which causes a failure of the sealing system. Frequently the compression set is a side effect of a chemical attack which in the end leads to leakage.

3.3 Differentiation from similar Failure Types

The Damage symptoms of ageing through heat and oxygen (= thermal overload), see Figure 8, are very similar to the damage symptoms of chemical attack for ultimately the actual failure mechanism is the same, namely post curing and chain scission, only now caused by atmospheric oxygen.
The two different failure mechanisms can be distinguished by the fact that a chemical attack damages the seal on the contact side towards the medium whereas ageing through heat and oxygen occurs on the air side or in the contact area with the housing.

The damage symptoms of swelling can look similar to the damage symptoms of a groove overfilling due to a groove which is too narrow or a seal which is too large. Yet, in this case the typical side effects of swelling, see above, cannot be found.

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<tr>
<th>Occurred Failure Parameter</th>
<th>Chemical Attack</th>
<th>Thermal Overload</th>
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| Cracks                     | Usually on the product side in the contact area with the medium | **Long-term-overheating:** occur especially in the case of bending on the air side of the seal or on the contact surface of the seal (heat transfer)  
**Strong short-term-overheating:** deep, fine cracks which become only visible when the seal is stretched |
| Elasticity/Embrittlement   | Seal is often still elastic, but breaks in the case of strong bending or tearing. | **Long-term-overheating:**  
Seal is usually embrittled (like after extreme accelerated ageing)  
**Strong short-term-overheating:**  
Seal is usually not yet visibly embrittled |
| Surface                    | In the case of polymer degradation sticky surfaces can occur. Typical is a surface which has changed its gloss and is now rather dull than shiny. | EPDM: sooty surface, black abrasion  
NBR: shiny surface |

Table 1: Distinctive features between chemical attack and thermal overload by reference to various failure parameters
Today various analytical detection procedures are available for the user to be able to clearly differentiate a chemical attack from other damage symptoms and to determine the attacking medium:

Concerning this the GC-MS analysis should be mentioned first. By a thermodesorption volatiles are desorbed from the polymer. Then they are separated by a gas chromatograph and afterwards identified by a mass spectrometer. The FTIR-analysis can also serve well in this case. The damaged seal is extracted and the extracts are analysed. However, this method has a significantly lower resolution. A comparison with the not yet swollen, new seal is highly recommended. It should be noted that the detection of matter which diffused into the polymer is no compelling evidence that this matter has also caused the chemical attack or the swelling. This can be accomplished as part of a plausibility check, for example by means of media resistance tables or by resistance tests.

4. Preventive Measures

The following questions can help the practitioner to prevent failure:

- Are indeed all media known which the component comes in contact with?
- Are there maybe upstream or downstream processing, cleaning or fitting steps where the elastomer might come in contact with critical media?
- Are the actual temperature loads and the contact period with critical media of the respective application known?
- Is there a good state of the art of the sealing material? (e.g. in comparison to ISO 3601-5), see below
- Are there recipe specific test results of the seal supplier? If not, it has to be checked (risk estimation) whether compatibility tests have to be performed, see below.

5. Practical Tips (Testing Possibilities / Standard Recommendations)

As a first step media resistance tables can give valuable assistance for the clarification of the resistance of an elastomer. Then it is important that a recipe according to the state of the art from the recommended polymer group is chosen. The new ISO 3601-5 for example gives a good overview which requirements a good compound should meet. Especially when using oils it is not just the compatibility with the base oil that matters but also the compatibility with the additives of the oil. This uncertainty can generally only be removed by adequate resistance tests, e.g. according to ISO 1817. Special attention is in order when it comes to the use of FKM-materials in acids as well as the use in hot water and steam because the potential which is immanent in these materials can only be maxed out by using special recipes.

Last but not least, it is always good to make use of the assistance of an expert, be it the assistance of a seal supplier, a polymer manufacturer or a specialised service provider like the O-ring test laboratory.
6. Miscellaneous

An abstract of this article was published in German in the magazine “DICHT!” , issue 03/2017. A longer German version of this article was published in the magazine “Industriearmaturen & Dichtungstechnik”, issue 4/2017.

These are often recurring errors which lead to failures due to chemical attack:

- Standard FKM-materials (bisphenolic cross linked with magnesium oxide / calcium hydroxide as acid acceptor system) used with hot water or hot water mixtures over 100°C
- FKM in applications used in sterile process technology where it is common to work with alkaline detergents and disinfectants
- EPDM-materials used in hospital operations which come in contact with highly concentrated heavily oxidising disinfectants
- Polyurethane materials based on polyester which are used in aqueous media or in hydrophilic fluids
- Bisphenolic cross linked FKM-materials which are used in gear oils, highly enriched with additives
- Silicone (VMQ) in flue gas