

# **EXPERT KNOWLEDGE** **FAILURE ANALYSIS** **OF ELASTOMER COMPONENTS**

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Information as of 06/2017

## **Chemical Erosion and Swelling** **Destruction of Network Structure by Contact Medium**

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### **1. Classification and Frequency of Failure**

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

- **1. Media**
- 2. Temperature / Aging
- 3. Mechanical / Physical Damages
- 4. Manufacturing Errors

According to the analysis of more than 2000 processed failures, a chemical erosion 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 mid-eighteenth century, when the first rubber samples arrived for examination from South America, the new material was especially of interest for chemistry.<sup>1</sup> Whereas at the beginning, the point was to find a suitable solvent for rubber to make it processable. Later, however, the chemical resistance became progressively more of the focus of interest.

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.

Over and over there are sealing failures because of chemical erosion and swelling despite the very comprehensive and detailed knowledge about chemical resistance.<sup>2</sup> 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 erosion and swelling:<sup>3</sup>

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 oxidizing media)
5. Other compound ingredients (e.g. acid acceptor system in FKM (for example magnesium oxide), anti-aging agent in NBR or EPDM, plasticizer)

<sup>1</sup> 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 25<sup>th</sup> May 2017)

<sup>2</sup> Examples of specialist literature and information about the chemical resistance of elastomers:

- NAGDI, Khairi: Gummi-Werkstoffe - Ein Ratgeber für Anwender, Dr. Gupta Verlag, Ratingen, 2002, Kap. 17, S.345-358 (clear presentation in short form)
- PRUETT, Kenneth: Chemical Resistance Guide for Elastomers IV, Compass Publications, 2015 (extensive standard reference)
- Gummiquellen - 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 25<sup>th</sup> May 2017):

- [https://www.tss.trelleborg.com/global/en/service/desing\\_support/chemicalcompatibility\\_1/chemical-compatibility.html](https://www.tss.trelleborg.com/global/en/service/desing_support/chemicalcompatibility_1/chemical-compatibility.html)
- [https://dupont.secure.force.com/CRG\\_Signin](https://dupont.secure.force.com/CRG_Signin)

<sup>3</sup> Cf. NAGDI, Khairi: Gummi-Werkstoffe - Ein Ratgeber für Anwender, Dr. Gupta Verlag, Ratingen, 2002, Kap. 17, p. 345 and RÖTHEMEYER, F. und SOMMER, F.: Kautschuktechnologie, Hanser-Verlag, München, 2001, p.38f.

At this point *swelling* and *chemical erosion* 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 or evaporation of the solvent. In most cases a residue of the solvent remains in the elastomer. In specific cases even shrinkage can occur, for example, if the solvent dissolves the plasticizer 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 erosion, we deal with an irreversible process. At first the medium erodes 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 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 aging 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. Blobner and B. Richters publication “*Prüfmethoden zu Sondereigenschaften der wichtigsten Dichtungswerkstoffe*” (Testing Methods for Special Properties of the Most Important Sealing Materials).<sup>4</sup>

Moreover, the vulcanization 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.

<sup>4</sup> BLOBNER, U. and RICHTER, B.: Prüfmethoden zu Sondereigenschaften der wichtigsten Dichtungswerkstoffe, online publication, as of: February 2015:

[http://www.o-ring-prueflabor.de/files/bersicht\\_pr\\_fmethoden\\_sondereigenschaften\\_02\\_2015\\_1.pdf](http://www.o-ring-prueflabor.de/files/bersicht_pr_fmethoden_sondereigenschaften_02_2015_1.pdf)

In highly oxidizing 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 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 plasticizers can also lead to extraction and thereby to shrinkage. Especially in the case of plasticizer 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 erosion.

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 eroded 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

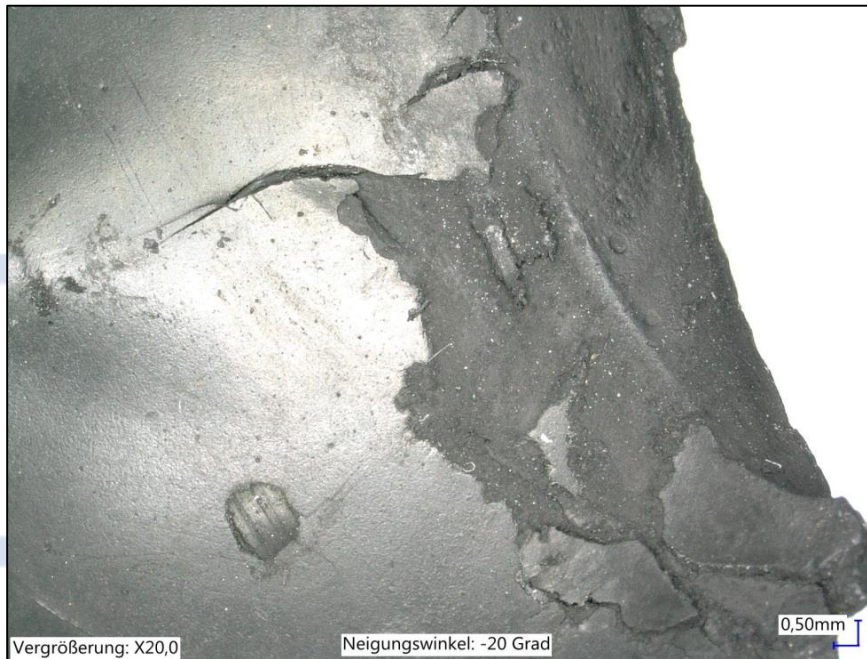
A chemical erosion can but doesn't necessarily leave traces on the surface in the contact area. It can also 'just' lead to a high compression set, especially if it only came to an erosion on the cross-links.

##### 3.1.1 Failure Type 'Chemical Erosion'

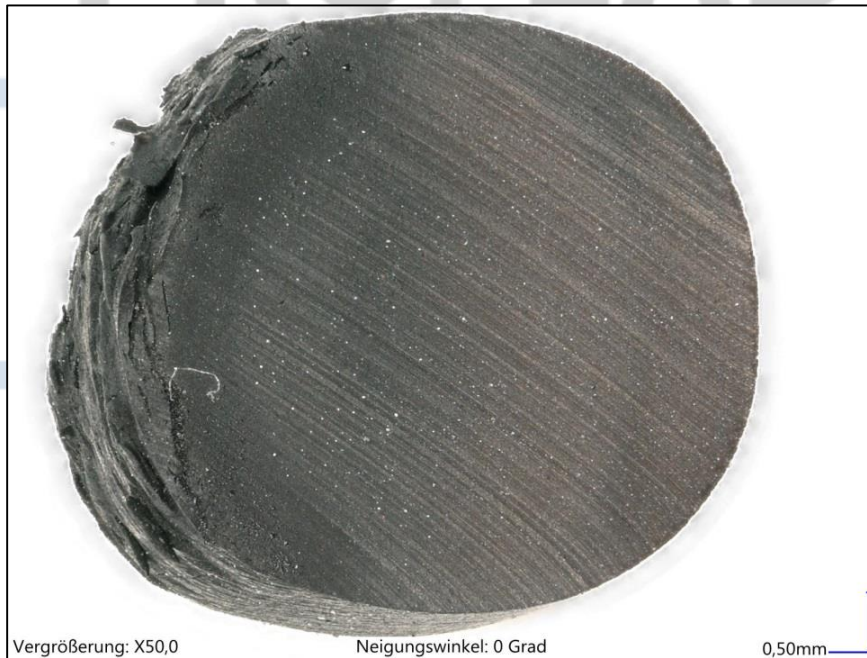
The following points are evidence that a chemical erosion has happened (see **Figures 1-5**):

- Cracks towards the medium, which are visible to the naked eye or only under the microscope in a stretched condition. These can already occur before the material loses its elasticity.
- Strong setting behavior 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

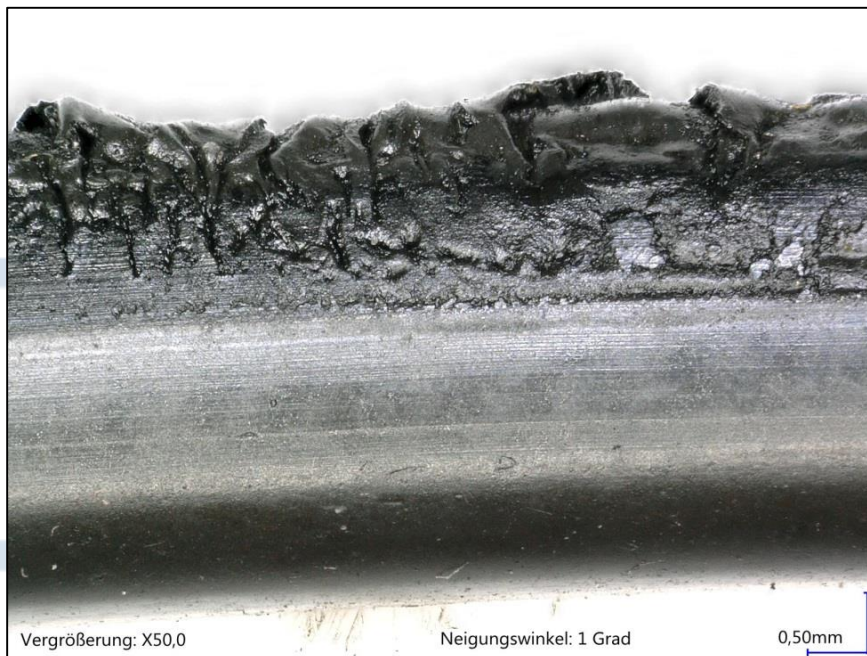


**Figure 1:** EPDM-seal destroyed by disinfectant



**Figure 2:** Chemical erosion on FKM-material by an inorganic acid

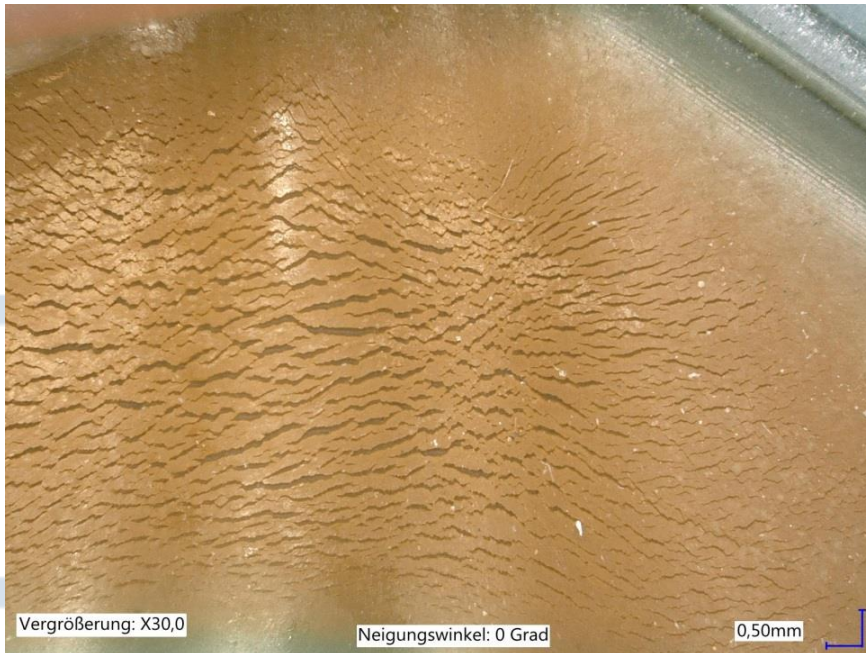




**Figure 3:** Chemical erosion and swelling with blistering



**Figure 4:** Hydrolysis (= chemical erosion by water) of a polyurethane seal



**Figure 5:** Chemical erosion on FVMQ-membrane probably by blow-by-gas in engine oil

### 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



**Figure 6:** Strong swelling which resulted in shear



**Figure 7:** Strongly swelled EPDM-seal after dynamic stress of a lip seal

### 3.2 Effects of Failure

Through chemical erosion, 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 erosion which in the end leads to leakage.

### 3.3 Differentiation from Similar Failure Types

The damage symptoms of aging through heat and oxygen (= thermal overload), see **Figure 8**, are very similar to the damage symptoms of chemical erosion. The actual failure mechanism is the same, namely post curing and chain scission, only now caused by atmospheric oxygen.





**Figure 8:** Cracks on the contact surface of an O-ring due to aging through heat and oxygen, made visible through slightly stretched condition

The two different failure mechanisms can be distinguished by the fact that chemical erosion damages the seal on the contact side towards the medium whereas aging 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.

Occurred Failure Parameter	Chemical Erosion	Thermal Overload
Cracks	Usually on the product side in the contact area with the medium	<p><i>Long-Term Overheating:</i> Occur especially in the case of bending on the air side of the seal or on the contact surface of the seal (heat transfer)</p> <p><i>Strong Short-Term Overheating:</i> Deep, fine cracks which become only visible when the seal is stretched</p>
Elasticity/ Embrittlement	Seal is often still elastic, but breaks in the case of strong bending or tearing.	<p><i>Long-Term Overheating:</i> Seal is usually embrittled (like after extreme accelerated aging)</p> <p><i>Strong Short-Term Overheating:</i> Seal is usually not yet visibly embrittled</p>

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
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**Table 1:** Distinctive features between chemical erosion 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 erosion 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 and 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 erosion 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 all media, which the component comes in contact with, known?
- Might there be 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 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 of 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 specialized service provider like the O-Ring Prüflabor Richter.

## 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 erosion:

- 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 oxidizing 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