Gummi Fasern Kunststoffe, 66, No. 11, 2013, pp. 760–763

Evaluation of stability tests for elastomeric materials and seals

B. Richter

O-Ring Prüflabor Richter GmbH, Großbottwar

Selected from International Polymer Science and Technology, 40, No. 12, 2013, reference GK 13/11/760; transl. serial no. 17103

Translated by M. Grange

Methodology and interpretation of stability tests as commonly applied when testing elastomers are described. Traditional compatibility screening does not adequately reproduce the operating conditions of many elastomeric seals, such as O-rings for instance. For this reason, compression set testing of mass-produced parts in contact with the operating media is presented here as an effective test procedure. Several examples from real life have made it possible to demonstrate that, even after short testing periods, conclusive indications regarding the selection of materials can be obtained.

INTRODUCTION

The issue of adequate stability or resistance is one that is repeatedly faced by users of seals, whether qualifying a new formulation or supplier or for a new application with different temperature requirements, with new oils containing different additives or with other new operating fluids, such as fuels or coolants. At the same time, constant cuts are being made to new product development times, putting severe constraints on comprehensive testing. Moreover, the typical user is not an elastomer specialist and is therefore looking for simple criteria on which to base decisions. This paper is therefore aimed specifically at this group of users, who are already finding it difficult to cope with the wide range of stability criteria. It begins by presenting the classic method of evaluating stability tests and explains the different objectives of these tests. It then goes on to present simple procedures for qualifying seals for different media or temperature ranges.

WHAT DOES "RESISTANT" ACTUALLY MEAN?

Although the question sounds straightforward, it is difficult to give a general answer that is valid for all seal applications. Three approaches are listed below:

- Application-based approach

  The seal must withstand the effects of all surrounding media for a predetermined time/temperature combination without causing a leak.

- Ideal material-based approach

  The surrounding media must not significantly shorten the lifespan of the seal relative to its lifespan in air. Typical examples can be seen in **Figure 1**. Gear oils 2 and 3 produce considerably greater changes in the post-immersion properties of the seal material compared with air, while gear oils 1, 4 and 5 create no major changes.

- Specification-based approach

  If a predetermined limit is reached, the material is considered to be resistant to the particular medium. This is current practice, so numerous relevant technical specifications exist. In practice, the following two questions are often asked: "Is the specification too weak or too strict?" and: "How do I deal with deviations?"

To summarize, when the topic of stability is being discussed, the risk of misunderstandings is high. Ultimately, all stability tests should serve the purpose of ensuring that the first of these approach criteria is met as effectively as possible, i.e. with the lowest possible outlay in terms of time and testing technology, while providing a high level of reliability.

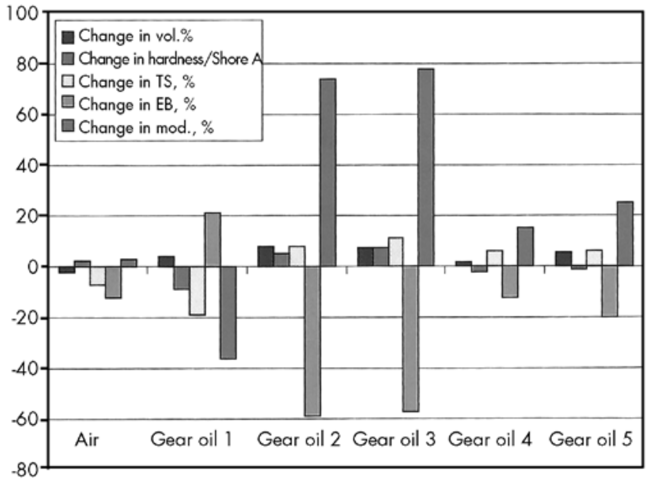

Figure 1. *Changes in properties of an ACM 70 material after 168 h/150°C in five different gear oils and air*

THE CLASSIC PROOFS OF STABILITY

The challenge for the materials specialist is to define a test that can reproduce the demands of the application in a simple way. The classic immersion tests [1, 2] offer a number of different possibilities, with immersion tests according to ISO 1817 forming the usual basis for compatibility screening. The test conditions and limiting criteria depend on the particular aims in each case, which are characterised briefly in the sections below [4].

Simple swelling tests

The simple swelling tests are only used to determine the swelling/extraction behaviour. The aim of these tests is merely to ascertain whether the material/oil pair being investigated is suitable in principle for the particular application or whether, for example, there have been any changes in behaviour compared with other material or oil batches. Tests over 72 or 168 h at 100°C are adequate for this purpose. Only changes in volume and hardness are taken into account. For elastomer seals, up to 25% swelling is considered non-critical for static applications and about 10% for dynamic applications. Any volume reduction should always be avoided if possible and in no circumstances should it exceed 10% shrinkage.

Short-term orientation tests

These tests run over 72 to 168 h at the upper continuous temperature limit of the seal material (at least 100°C) or the maximum continuous use limit of the fluid (generally 150°C) and include changes in tensile strength, elongation at break and 100% modulus. In many cases, these investigations are sufficient to highlight any chemical incompatibilities that exist by virtue of the fact that the changes are considerably greater than in a corresponding test in air. These tests are therefore widely used as proof of a defined stability within the framework of specifications. They are also suitable as a comparative test between different oil or material formulations. Changes of 25-30% are generally specified as typical limiting criteria for the relative change in elongation at break, which is considered to be the most sensitive indicator of a chemical attack.

Proof of long-term stability

Long-term stability tests take place over at least 500 h and almost always over 1000 h and are carried out at the upper continuous temperature limit of the seal material (at least 100°C) or the maximum continuous use limit of the oil or fluid. If, after these long periods of immersion, there are no detectable changes exceeding those after a corresponding period of storage in air, particularly in terms of tensile strength, elongation at break and modulus, then adequate chemical resistance is assumed. Proof of stability of this type is often found in automotive industry specifications. Permissible relative changes in elongation at break here are up to 50-60%.

Proof of compatibility over the lifespan

If the chemical resistance of a seal throughout its life is to be ensured by means of testing, a substitute temperature must first be determined for the set of temperatures that can be assumed over its entire operating life, which should be the highest permissible continuous temperature of the seal material or oil in order to minimise testing times. Since the Arrhenius equation can be applied to the relationship between temperature and rate of reaction for chemical reactions, this means that the higher temperatures should be given significantly more weighting than the lower ones. It is generally assumed that the rate of a chemical reaction doubles with a temperature increase of 10-15°C, which has been confirmed for many ageing processes in elastomeric materials. Thus, for example, an isothermal stress of 6000 h at 80°C can be approximately equated to a temperature stress of 3000 h/90°C or 1500 h/100°C or 750 h/110°C. However, this assumed relationship refers exclusively to a chemical reaction between the oil and the seal material being investigated. As soon as the oil changes chemically as a result of thermal ageing, these assumptions no longer apply. As limiting criteria here, relative changes in the elongation at break up to max. 60-70% are still classed as acceptable, provided that the absolute value of the elongation at break does not fall below 50%.

DIFFERENCES BETWEEN IMMERSION TESTS AND APPLICATION CONDITIONS

It is already clear from the above that the term "stability" can be defined in a number of ways in the form of material tests and that relatively long test periods are needed in some cases. Despite long test periods, however, these tests are not always able to provide an adequate estimate of the behaviour of O-rings in these media. This is ultimately down to the fact that these test conditions do not adequately reproduce the application in terms of the state of stress and the geometry, for example, but also the degree of vulcanisation of the specimens. However, any one individual influence can represent the crucial difference compared with the application, especially when the ageing and compression set tests in air are also included (**Table 1**).

The differences relating to constant and intermittent or cyclic temperature will be perceived as an accelerating effect, which is in fact desirable; likewise the exposure of all sides of the specimens to the test medium or air in the test. The different geometric ratios will also be perceived as an accelerating effect in immersion tests with dumbbell test specimens from a cross-section of about 2.62 mm (standardised cross-section) upwards. With smaller cross-sections (1.78 mm), however, this will be reversed. On the other hand, a very marked delaying effect is found with compression set measurements on 13 mm × 6 mm test discs compared with O-rings. Only a cross-section of 6.99 mm is ultimately comparable with a 13 mm × 6 mm disc – any thinner cross-section has a greater ratio of free surface area to volume or mass than the standard 13 mm × 6 mm test specimen. At the continuous temperature of a rubber material (1000 h criterion) this already has a significant influence on the result, which is greater at higher temperatures, but this is only considered here in passing [5]. However, particular attention will be paid to the differences in the state of stress of the samples, which deviates considerably from the immersion tests in the case of O-rings and most other elastomeric seals, and the degree of vulcanisation of the samples.

STABILITY TESTS ON O-RINGS – EXAMPLES OF DIFFERENT AREAS OF APPLICATION

To accommodate the definition of stability given above under the application-based approach, stability testing should as far as possible be carried out on O-rings with original dimensions, vulcanised under mass production conditions and deformed under conditions that simulate the application (25% compression). How this can be achieved in practice is shown on the basis of a few examples which, with acceptable outlay, have led to a clear decision-making criterion – something that has not always been possible with the stress-free immersion tests.

Steam generator application

For the application in a steam generator, two different solutions were proposed by two suppliers. One supplier recommended an EPDM material and the other an FKM material, referring to good results from immersion tests. Comparative tests were then performed in our testing laboratory. The data obtained can be seen in **Table 2**. Result of the investigation: the FKM O-ring does not display good stability in water at elevated temperatures, cf. high compression set value. This had not been indicated by the stress-free immersion tests.

Petrol application

High degrees of deformation of O-rings from field returns that had been used in a petrol application meant that the material or O-ring supplier had to be changed, and tests were performed to prove the effectiveness of this

Table 1. Test conditions in stability and ageing tests compared with application conditions for O-rings [3]

Comparison criterion	Test method: Stability according to ISO 1817 / accelerated ageing according to ISO 188 / compression set according to DIN ISO 815-1	Application condition: typical use of O-ring
Temperature	Constant	Cyclic/intermittent
Exposure to test fluid/air	On all sides	Partial
State of stress	Stress-free	Triaxial stress – influencing factors – temperature degree of deformation/cross-section time swelling rate
Geometry	Specimen surface/volume ratio: S_2/rod: 1.5 mm^{-1} 13 x 6 disc: 0.47 mm^{-1}	Specimen surface/volume ratio: d_2 = 1.0:4.0 mm^{-1} d_2 = 6.99:0.57 mm^{-1}
Degree of vulcanisation of specimens	Optimum (e.g. 20 min/177°C + 4 h/160°C post cure)	Variable (e.g. 3 min/180°C + 4 h/160°C post cure)

Table 2. Seal for steam generator – stability comparison of EPDM 70 and FKM 70 [6]

O-Rings with d_2 = 2.0 mm	EPDM 70 (perox.)	FKM 70
Water 336 h/150°C (ISO 1817)		
Volume change / %	7.9	10.6
Hardness change / IRHD	-6	9
Tensile strength change / %	-42	-28
Elongation at break change / %	-20	+10
Compression set 336 h/150°C (DIN ISO 815-1)		
In air / %	62.8	14.7
In water / %	24.0	94.4

measure, as demonstrated here by the example of one of a number of fuel mixtures that were tested (FAM B – DIN 51604) (**Table 3**).

While the evaluation of the stress-free immersion test indicates significant differences in the swelling rate, it does not show up any chemical attack (cf. values after redrying). The increase in strength with the old O-ring can probably be explained by a post-vulcanisation (the compression set value in air shows that the O-rings had not been optimally vulcanised). On the one hand, the tests explain the high remaining deformations of the O-rings that were found from field returns and on the other hand, after a test time of just a week, they also prove the significantly better behaviour of the new O-rings.

Fuel application at a higher temperature

On the same subject as in the section above, i.e. FKM O-rings in fuels, proof was requested that these are also suitable for use with fuel at higher temperatures (160°C). Again, this was provided by carrying out a compression set test in FAM B test fuel. As is standard practice for FKM O-rings, the stability was tested by immersion in FAM B at room temperature. In parallel, the O-ring was tested for adequate long-term stability when exposed to heat by means of compression set measurements at 180°C. The results are compiled in **Table 4**. They show that the FKM O-ring being tested is in fact unsuitable for use in methanol-containing petrol up to 160°C if both sides of the O-ring are exposed to the test fuel at 160°C, but this is not actually the case in a typical O-ring application. An accelerating effect is therefore being produced here, which is desirable in principle but must be taken into account when evaluating the results for the particular application.

Cylinder liner application

The fourth example again concerns aqueous media, specifically a 1:1 mixture of water and Glysantin G48,

Table 3. FKM O-rings for petrol – stability comparison of new FKM and old FKM in FAM B

O-Rings with d_2 = 1.78 mm	FKM new	FKM old
FAM B 168 h/130°C		
Volume change / %	22.8	37.7
Hardness change / IRHD	-15	-22
Tensile strength change / %	-53	-45
Elongation at break change / %	-16	-7
Subsequent redrying 22 h/125°C		
Volume change / %	0	-1.3
Hardness change / IRHD	-1	-1
Tensile strength change / %	-9	33
Elongation at break change / %	5	7
Compression set 168 h/130°C (DIN ISO 815-1)		
In air / %	9	19
In FAM B / %	14	72

Table 4. FKM O-ring for petrol at higher temperature – long-term compression set behaviour

O-Rings with d_2 = 2.0 mm	FKM 70
FAM B 168 h/23°C	
Volume change / %	29.8
Hardness change / IRHD	-11
Tensile strength change / %	-54
Elongation at break change / %	-30
Subsequent redrying 22 h/85°C	
Volume change / %	1.6
Hardness change / IRHD	-1
Tensile strength change / %	-9
Elongation at break change / %	2
Compression set (DIN ISO 815)	
In air, 1008 h / 180°C, %	49
In FAM B, 504 h / 160°C, %	>100

which is intended to represent a typical coolant mixture as used in motor vehicles. FKM O-rings are used there for sealing cylinder liners against coolants and engine oil. Ideally, these are hot-water-stabilised formulations, since standard FKM formulations do not achieve the service life required for this application by users and there is therefore the risk that the operating life of a diesel engine could be limited by unsuitable FKM O-rings. Relevant OEM specifications therefore require long-term qualification over at least 1000 h for this demanding application, usually on standard test specimens. However, our testing laboratory is constantly receiving enquiries about a suitability test for O-rings for this application. In this case too, therefore, the approach taken was to carry out compression set tests in the coolant at elevated temperatures (150°C). **Table 5** provides an overview of the compression set values that were measured. The

Table 5. Comparative measurements on FKM O-rings for wet cylinder liners

O-Rings with d_2 = 3.7 mm	FKM 1	FKM 2	FKM 3	FKM 4	FKM 5
Colour	Green	Black	Black	Green	Black
DVR 24 h/200°C in air / %	29	20	25	20	25
DVR 168 h/200°C in air / %	67	48	59	50	59
DVR 168 h/150°C in KW / %	99	77	37	88	38
Change in hardness after 168 h/150°C in KW* / Shore A	+17	+5	-7	+8	-7
DVR = compression set; KW = coolant, water:Glysantin G48 1:1 **Measurement on O-ring sections from DVR test in KW and subsequent conditioning 2 h/150°*					

results enable a clear distinction to be made after just one week, as O-rings 3 and 5 showed by far the best performance.

CONCLUSIONS

This paper describes the methodology/evaluation of stability testing as commonly applied in elastomer technology, and how it has proved its usefulness in numerous cases, particularly in oil compatibility testing. In addition, it is shown that the usual stability tests fail to provide an adequate reproduction of the application conditions of many elastomeric seals, such as O-rings. The compression set test with exposure to chemicals, using mass-produced finished parts, is presented here as an effective method. Four examples were used to illustrate how, even after a comparatively short test period, this method can be used to provide crucial indicators for material selection and for comparing different formulations.

REFERENCES

1. VDA 675301 – December 1992 – Elastomerbauteile in Kraftfahrzeugen, Prüfverfahren zur Beständigkeitsprüfung, Einwirkung von Prüfölen.
2. ISO 1817:2005-10, Rubber, vulcanized, Determination of the effects of liquids.
3. ISO 188:2007-06, Rubber, vulcanized or thermoplastic, Accelerated ageing and heat resistance tests.
4. B. Richter, Bewertung von Beständigkeitstests von Elastomeren Werkstoffen mit Getriebe- und Motorölen bezüglich des Funktionsverhaltens von Radialwellendichtringen, paper presented at the VII. Hamburger Dichtungstechnischen Kolloquium 24-25.9.2009, Hamburg.
5. B. Richter, Lebensdauer von O-Ringen, proceedings of the 11th International Sealing Conference 3-4 May 1999, pages 489-499.
6. DIN ISO 815-1:2010-9, Bestimmung des Druckverformungsrestes bei Umgebungs- oder erhöhten Temperaturen