TECHNICAL PAPER

Understanding the differences: FKM vs FFKM

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FKM and FFKM material types share many similarities. However, it is understanding the differences between the two material families which is the critical factor in determining the appropriate sealing solution for any given specific application.

Here we will cover some of the fundamentals of FKM and FFKM materials, investigating their respective strengths and weaknesses and the structural reasons for them, and the impact on their suitability for use in the most critical and challenging of sealing applications.

What is FKM?

FKM is the ASTM designation for a class of fluorinated, carbon-based synthetic rubber, commonly known as fluoroelastomer. FKM was originally developed in the late 1950s in response to demand for high performance seals in the aerospace industry. Development of FKMs continued through the 1980s, with advancements including greater thermal stability and improved solvent and compression resistance. Today, seals made from FKM materials can withstand temperatures greater than 200°C. FKM seals also exhibit strong resistance to high pressures, chemicals and other fluids, including several fuels.

FKM materials are commonly used to manufacture O-rings, gaskets and other custom seal profiles for many different high-performance applications in the automotive, aerospace, energy and semiconductor industries.

However, FKM materials do show poor resistance to ethers, ketones, esters, amines and hydraulic fluid-based phosphate esters. Special compounds are required to provide suitable resistance to hot water, steam and wet chlorine.

FKMs are not typically recommended for alkaline fluids and amines since a C-H bond next to a C-F bond in the polymer is highly acidic and would be attacked by alkaline species. The FKM polymer consists of long chains of carbon atoms with a combination of fluorine and hydrogen atoms attached.

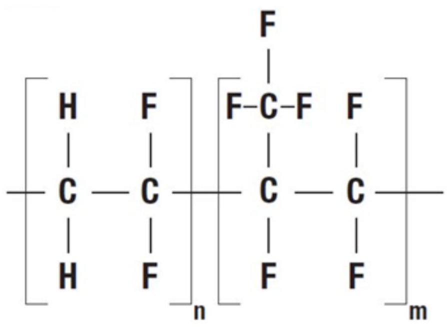

Figure 1 - FKM polymer structure

What is FFKM?

FFKM materials, commonly known as perfluoroelastomers, contain higher amounts of fluorine than standard FKM. The first commercially available FFKM seal was produced in the late 1960s, although widespread manufacturing of FFKM materials did not occur until the late 1980s. FFKM is used as a sealing material in environments where high temperatures and harsh chemicals are commonplace, for example, in semiconductor processing, oil and gas, life science industries and aerospace.

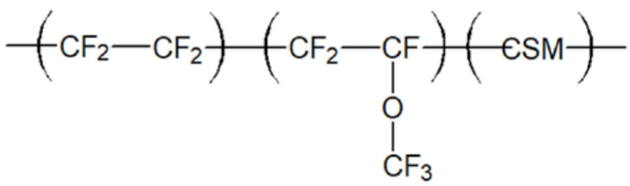

Figure 2 - FFKM polymer structure

In an FFKM material, the C-H bonds found in an FKM have been replaced with C-F bonds. These C-F bonds have higher bond dissociation energies, making FFKMs much more stable in high temperatures. FFKM materials have demonstrated sealing capability in temperatures in excess of 300°C. While thermal sealing ability is substantially increased, it is arguably in the chemical resistance of FFKM against FKM where the most significant improvements can be found. FFKM materials have nearly universal chemical compatibility, and when combined with their higher temperature resistance, it makes FFKM the leading candidate as a sealing material in applications where the consequences of a failed seal can be particularly costly, if not catastrophic.

From the extraction and processing of oil and gas, to semiconductor chip manufacturing, FFKM materials are emerging as the mainstream choice for high performance sealing systems. This is based on the proven performance benefits of FFKM across a range of factors, including mechanical strength, thermal and chemical resistance, and long-term reliability. FFKM polymer chains are engineered to be one of the most inert polymer structures available. The chemical resistance of FFKM polymers has enabled the material cleanliness and purity required to meet the stringent safety standards of food and pharmaceutical processing and production.

However, not all FFKM materials are the same. There are a number of different crosslink systems available for FFKM, which is one of the main reasons why FFKM materials have such significant variation in their temperature ratings. Some may be used up to 225°C, while others can be used up to 325°C. These crosslinks are not fully fluorinated and can therefore be prone to chemical attack. Typically, the high temperature, low compression set FFKM material grades do not have as broad a chemical resistance as grades with a lower service temperature and slightly higher compression set. It is necessary to understand these performance subtleties in line with the exact demands of the application, when selecting an elastomer in order to achieve optimum sealing performance.

In process industries, there are three main classes of sealing solutions:

- Chemically resistant general purpose FFKMs: these are typically peroxide cured FFKMs, and cover the majority of the overall volume
- High temperature FFKMs: these typically use nitrile cure system.
- Specialist FFKMs for life science applications: with food and pharma approvals such as FDA and USP Class VI accreditations.

Precision Polymer Engineering has developed several FFKM grades using different crosslinking technologies. To highlight the difference made through different crosslinking in FFKM materials, tests were conducted on three FFKM grades and an FKM in a series of aggressive conditions, and measurements of swelling and other physical property changes were taken.

In addition to the standard peroxide crosslinking technology (FFKM1), a special peroxide technology (FFKM2) was tested which delivers improved high temperature performance without losing chemical resistance. The FFKM2 bridges the gap on temperature performance between FFKM1 and nitrile-cured FFKM materials, also tested for comparison (FFKM3), which can seal at up to 327°C. Similar cure technologies to those tested here are also available in a white colour, suitable for life science applications and compliant with FDA and USP Class VI.

Figure 3 is a table which demonstrates the relative performance of FFKM1, FFKM2, FFKM3 and a peroxide FKM in high temperature steam, a 70% nitric acid solution, and ethylenediamine. Images of the respective samples after test completion give an impression of the extent of the seal damage.

We can see that in all test environments the FFKM outperforms the FKM material, but that between FFKM material grades there is also a marked difference in performance. This is most notable in the nitrile crosslinked material (FFKM3), where severe damage is observed under both the high temperature steam and ethylenediamine tests.

The results also illustrate the enhanced peroxide cross-linking technology, where FFKM2 has retained much the same chemical resistance properties as FFKM1 but with a higher upper temperature.

The test demonstrates that the performance capabilities between different FFKM technologies can be as apparent as the differences between FKMs and FFKMs, and as such, care should be taken against assuming the specification of an FFKM to be a catch-all solution in life science sealing applications.

	Crosslinking System	Upper Temperature	Steam	70% Nitric acid	Ethylenediamine
			168h at 250 ° C	168h at 80 ° C	168h at 100 ° C
FFKM1	Peroxide	260	1	1	1
FFKM2	HT Peroxide	290	1	1	2
FFKM3	Nitrile	327	4	1	3
FKM	Peroxide	225	4	2	4

1 = Excellent, little to no effect on physical properties

2 = Good, moderate (10-20%) swelling and change in physical properties

3 = Not Recommended, significant (>20%) swelling and noticeable change in physical properties

4 = Do Not Use, significant (>40%) swelling

Figure 3 - Table illustrating properties of FFKM with different cure technologies, under a range of test conditions

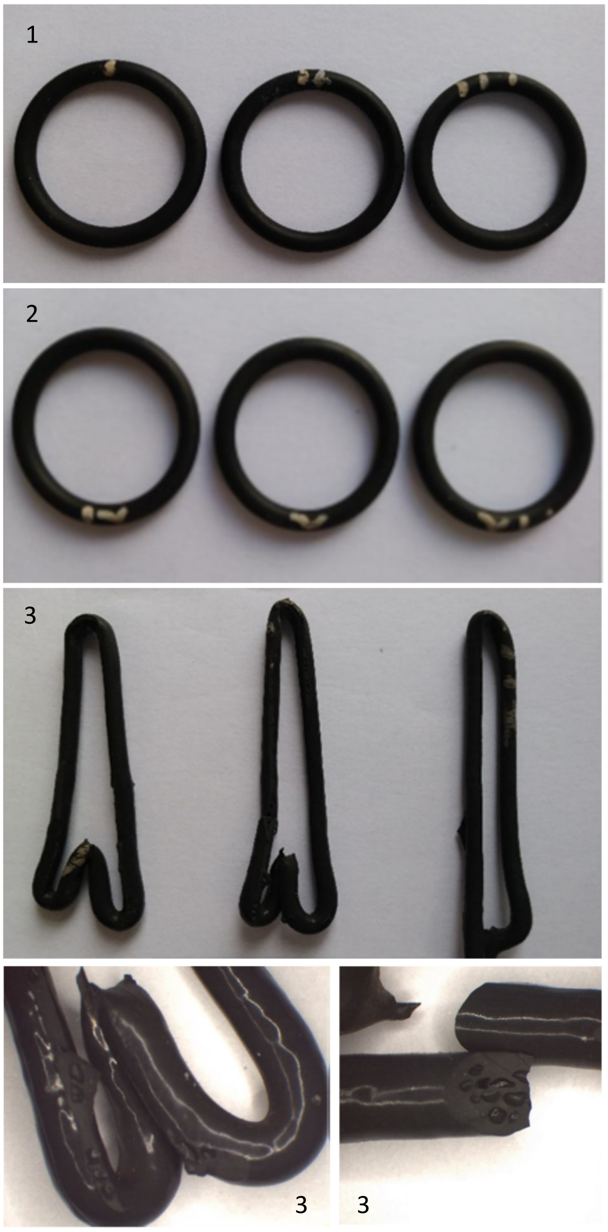

Figure 4 - Images of O-rings after steam exposure (168hr at 250°C), Top to Bottom: FFKM1, FFKM2, FFKM3, FFKM3

In the steam exposure test (*Figure 4*), the sample of FFKM3 has become porous, trapping water in the material, increasing its volume, and becoming very soft with a subsequent loss of mechanical strength.

In the nitric acid ageing test (*Figure 5*), there is very little visible damage to either of the FFKM test samples.

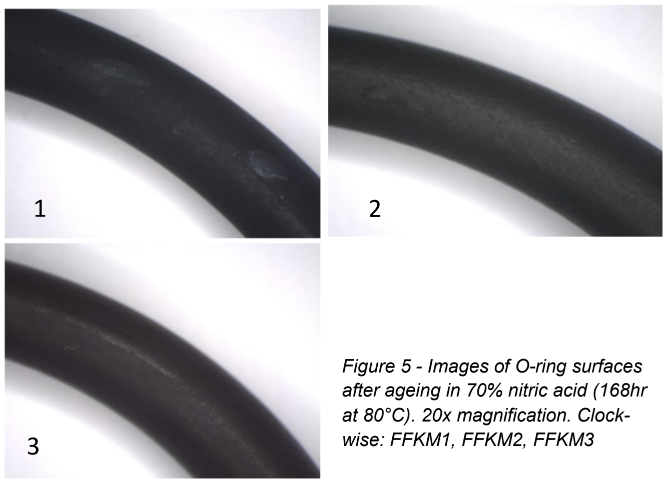

Figure 5 - Images of O-ring surfaces after ageing in 70% nitric acid (168hr at 80°C). 20x magnification. Clockwise: FFKM1, FFKM2, FFKM3

Figure 6 - Images of O-ring surfaces after ageing in ethylenediamine (168hr at 80°C), with severe damage to FFKM3. 20x magnification. Clockwise: FFKM1, FFKM2, FFKM3

In *Figure 6*, the corrosive damage due to amine attack on the nitrile-cured FFKM is clearly visible.

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Compressive Stress Relaxation (CSR)

Compressive Stress Relaxation (CSR) is a measure of the load force generated in a compressed material, and of how this force decreases with time as the material ages. Tests of CSR are a useful way for engineers to estimate the service life of an elastomeric seal over an extended time period. Once largely restricted to use in university research projects, a growing trend towards CSR tests in industrial applications has been observed in recent years. This is due in part to the introduction of CSR tests in product standards, such as sealing rings for pipes . While CSR testing is not a guarantee of material performance and reliability when sealing in real-world applications, it remains one of the best laboratory testing methods for comparing the suitability of sealing materials for long term use.

The process that is mainly responsible for CSR may be chemical or physical in nature, and under normal conditions both types of process will occur simulta-neously. However, at low or normal temperatures, and/or over a short time, stress relaxation is dominated by physical processes whilst over long time periods or high temperatures chemical processes are dominant. A key factor in achieving reliable, repeatable results while conducting the stress relaxation test is to keep the temperature and compression constant during all measurements.

Figure 7 shows a relaxation test report of three FFKM O-rings crosslinked with different curing systems (FFKM1, FFKM2, FFKM3) tested in parallel continuous CSR at 250°C in air.

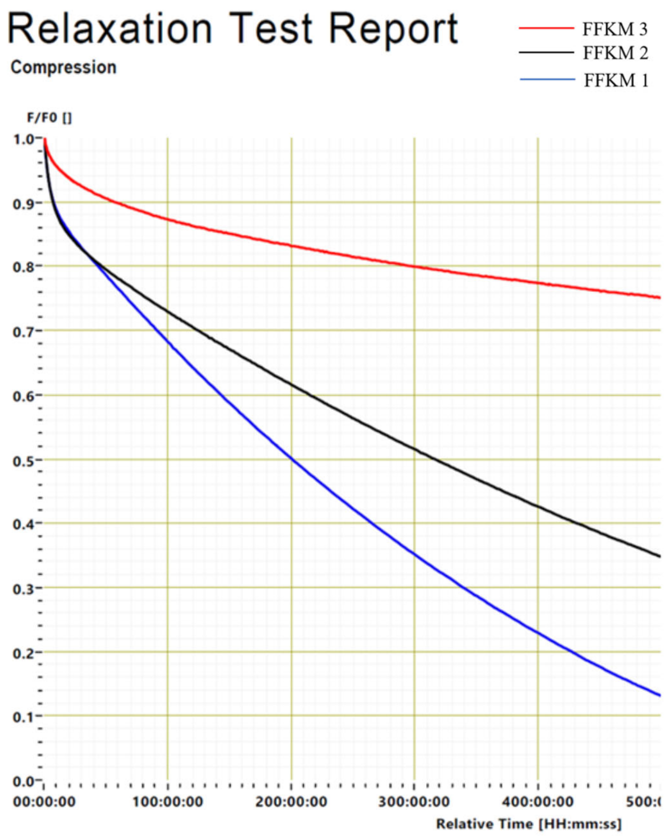

Figure 7 - Compressive Stress Relaxation (CSR) report of three FFKM O-rings, tested in parallel continuous CSR at 250°C in air.

The sample cured with a nitrile crosslinking system (FFKM3) demonstrates the best performance, retaining good sealing force even after 500 hours. Conversely, FFKM1 has lost most of its sealing force at this duration, whereas FFKM2 shows intermediate performance.

In both this CSR test and the submersion testing outlined earlier, the disparity in performance between different formulations of the same material is clear to see. There are so many variables within just FFKM material formulations in isolation, without even looking at other material families, that it is overly reductive to say an FKM performs like *x* and an FFKM performs like *y*. Identifying and specifying an optimal sealing material for any given application deserves a more considered approach.

Conclusion

In a general sense, an FFKM should outperform an FKM in most sealing environments – particularly for more critical applications and industries where seal failure could have catastrophic consequences. The question for engineers in these applications and industries then becomes *which* FFKM should be used. The answer here is entirely dependent on the industry type.

In semiconductor applications there is a demand for high temperature resistant sealing materials, plasma resistance, and exceptional material purity for the lowest possible trace metal contamination levels. In food and pharmaceutical processing applications, the focus is on finding a material sealing grade which delivers the best possible chemical resistance, for both resistance against process media but also highly aggressive CIP and SIP regimes, and conformity to all necessary safety accreditations and standards. For the chemical process industry, having good understanding of process media and operating temperature is key for selection of most appropriate FFKM.

It is therefore necessary to gain the deepest possible understanding of the demands to be placed on a sealing system, before the proper FFKM material can be correctly identified. Consultation with a specialist sealing engineer can be advantageous in this process.

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TP00119-20

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