FKM Sealings for Alternative Fuel Mixtures

Swelling and Mechanical Properties with Flex Fuels

The addition of varying amounts of bioethanol to gasoline in order to create so-called flex fuels changes the properties of the fuel. Consequently, all sealing components that come in contact with the fuel – such as valve stem seals, radial shaft seals (Simmer rings), and O-rings – must be resistant to ethanol. The flex fuels' aggressive combustion products and blow-by products must also be taken into consideration. Freudenberg Dichtungs- und Schwingungstechnik has developed and successfully tested special fluororubber (FKM) compounds for flex fuel seals. These sealing elastomers have been optimized in such a way that they neither swell significantly nor do their mechanical properties, like elongation at break and tensile strength, change when they come in contact with E 22, E 85, and E 100. These sealing materials meet the automobile industry's requirements for use in flex fuel vehicles.

1 Introduction

In response to the automotive industry's self-imposed pledge to reduce the amount of CO_2 emitted by their vehicles, Freudenberg, the car industry, and fuel manufacturers have been working together for over ten years to determine and improve the compatibility of elastomer sealing materials with all available alternative fuels. The focus of these development efforts has been on developing materials

- that swell minimally and
- whose mechanical properties undergo only minimal changes in contact with the relevant medium.

The optimization of these parameters is the starting point for ensuring a permanent sealing function because ageing processes and volume changes caused by swelling and shrinkage have a decisive influence on the strength of the elastomer and, consequently, on the performance of the sealing technology component. Moreover, it is essential when selecting an appropriate material for flex fuel seals that the material has good low-temperature flexibility in order to ensure that the component functions properly in cold weather.

The fact that flex fuels are available with varying concentrations of bioethanol – between 10 and 85 % and right up to pure bioethanol (E 100) – has a direct impact on all seals that come in contact with the flex fuel. Although ethanol does not chemically attack the elastomer, the addition of oxygen-containing components to conventional gasolines influences a series of fuel characteristics, which can in turn affect the seals. The following factors are particularly relevant in this regard:

- phase separation of the fuel mixture can occur at low temperatures (< 10 °C) and in the case of water content levels of over 0.5 % of the volume.
- high water content in the blow-by-gas, which can go as high as 50 %, can damage FKM seals;
- the alcohol and water content increases the risk of metal corrosion.
- a high acid content in the flex fuel mixtures may necessitate the addition of neutralizing agents, which can in turn result in increased deposits in engine components.
- The amount of ethanol that blends with the engine oil is much higher in flex fuels than it is in conventional gasoline. This impairs the lubricating properties of the engine oil and can even result in its degradation.

2 Investigations with Selected FKM Compounds

Freudenberg recently tested the resistance of selected FKM compounds to E 22, E 85, and E 100 at 23 °C and 60 °C. The test medium was a mixture of the test fuel FAM A and the corresponding percentage of ethanol.

For this test, standardized test specimens made of the relevant elastomer were stored in the appropriate flex fuel at the appropriate temperature for a period of 168 h. At the end of this period, standardized measurement procedures were used to determine the mechanical parameters (hardness, elongation at break, and tensile strength) and the change in volume of the elastomer test specimens.

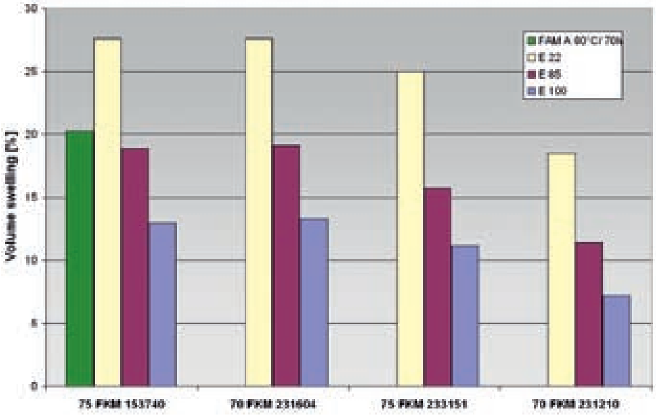

Figure 1: Comparison of volume swelling of selected FKM compounds in the fuels E 22, E 85, and E 100 at 60 °C over 168 h compared with the pure test fuel FAM A (60 °C over 70 h)

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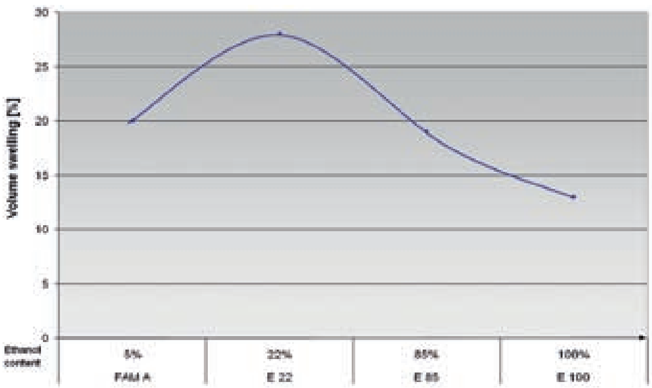

Figure 2: As the proportion of ethanol in the fuel increases, volume swelling in 75 FKM 153740 peaks in E 22

Tests showed that the volume of the specially developed FKM materials changed only slightly as a result of contact with the investigated flex fuel mixtures and that this change did not impair the performance of the sealing component. For example, the FKM compounds used in the test swelled by less than 20 % in E 85 at 60 °C, **Figure 1**. FKM terpolymers with a high fluorine content such as 70 FKM 231210 demonstrated the lowest levels of swelling, namely approximately 11 % in E 85. Generally speaking, the greater the fluorine content, the greater the chemical resistance of fluororubbers and the lower their low-temperature flexibility. The FKM material 75 FKM 153740, which is used in a wide variety of fuel applications, demonstrated low swelling behavior in E 85 and good low-temperature flexibility. As a rule, volume swelling of up to a maximum 30 % for O-rings and approximately 10 % for rotary shaft seals is acceptable and does not impair the sealing function.

One of the most important findings of these tests was the discovery that volume swelling in elastomer does not increase continuously with the level of ethanol in the flex fuel, but peaks in flex fuels with an ethanol level of between 20 and 50 %, **Figure 2**. The following can be said regarding changes in the materials' mechanical properties: the higher the level of ethanol in the fuel mixture, the less marked the changes in elongation at break, **Figure 3**, and tensile strength, **Figure 4**. This means that both a high proportion of alcohol and a very low proportion of alcohol in the fuel, as is the case in FAM A, have the least effect on the properties of the elastomer. Consequently, from the point of view of the seal manufacturer, fuels containing a low (< 15 %) or very high proportion of ethanol (for example E 85) are recommendable.

The special demands made on sealing elastomers by the flex fuels with which they come in contact are particularly relevant for valve stem seals, radial shaft seals, and O-rings. Seals made of a variety of FKM materials are already being used in series. The sealing material 70 FKM 231210 has proven ideal for use in applications where the seal comes in direct contact with flex fuels. In all tests, this material underwent the most minor changes of all. Both in terms of swelling and in terms of the changes in mechanical properties, this material comes up trumps.

3 Influence of Combustion and Blow-by Products

Although there are as yet no harmonized definitions of the ethanol fuel mixtures that will be used in future and no reliable data about their combustion and blow-by products, years of experience in this field lead to the assumption that these gas mixtures will be more aggressive than existing combustion by-products. Because of the changes in temperature, these products constitute a particular challenge for seals. In order to be able to offer reliable seals for these vaguely defined marginal conditions, Freudenberg uses modern sealing materials made of FKM terpolymers. These contain a high level of fluorine, which means that even aggressive combustion products cannot damage seals made of this material.

In order to simulate the effects of blow-by gases from flex fuels, a cycle test was conducted. To this end, selected FKM materials were exposed to the following substances and the following conditions one after the other:

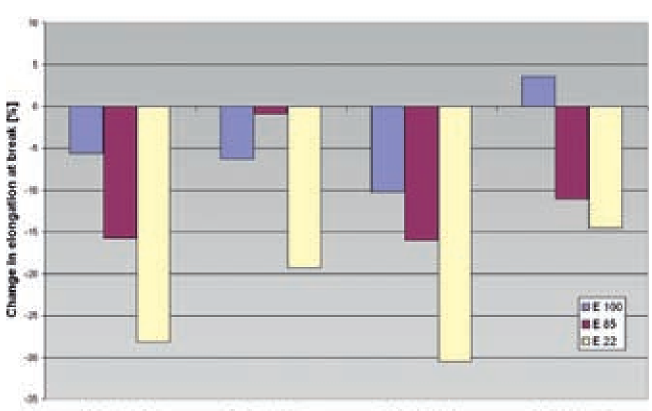

Figure 3: Change in elongation at break of FKM compounds in E 22, E 85, and E 100 at 60 °C over 168 h

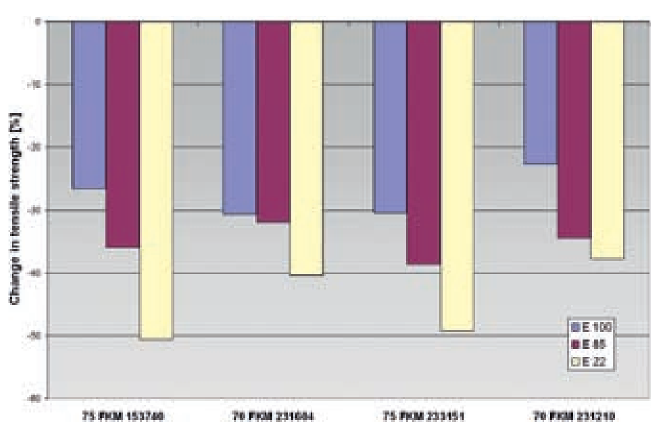

Figure 4: Change in tensile strength of FKM compounds in E 22, E 85, and E 100 at 60 °C over 168

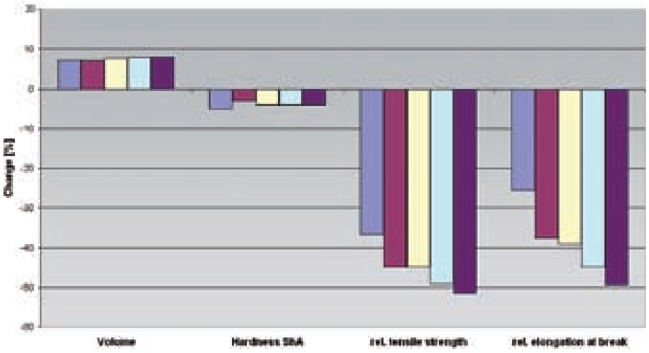

Figure 5: Changes in the volume and mechanical properties of 75 FKM 153740 over the course of five test cycles; each test cycle included storage in 1-mol nitric acid for 5 h at 60 °C, in engine oil for 22 h at 150 °C, and in E 22 for 22 h at 23 °C

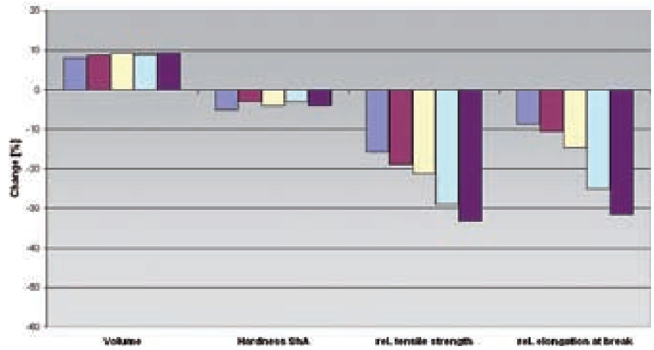

Figure 6: Changes in the volume and mechanical properties of 70 FKM 231604 over the course of five test cycles; each test cycle included storage in 1-mol nitric acid for 5 h at 60 °C, in engine oil for 22 h at 150 °C, and in E 22 for 22 h at 23 °C

– acid for 5 h at 60 °C
– engine oil for 22 h at 150 °C
– E 22 for 22 h at 23 °C.

Subsequently, the influence of these media on the mechanical properties of the materials was analyzed.

At the end of every cycle, the mechanical properties and the changes in the materials' volume and hardness were measured. At the end of five cycles, both the standard material 75 FKM 153740 and the special materials 70 FKM 231604 and 70 FKM 231210 demonstrated only minor volume changes of less than 10 %. The mechanical properties such as tensile strength and elongation at break diminished with every cycle. It became evident that the sealing performance of the standard material 75 FKM 153740 was not impaired even after five cycles, **Figure 5**. The special material 70 FKM 231604 proved very resistant to these aggressive media. After five cycles, tear strength had diminished by only 32 %, **Figure 6**.

4 Effects of Engine Oil Degradation

Flex fuels contain more water and acid than conventional fuels. The entry of fuel into the engine oil is critical, particularly in short driving cycles such as stop-and-go applications or taxi journeys.

After extended periods of driving, the engine oil heats up and a large proportion of the blended fuel evaporates. Nevertheless, non-volatile constituents accumulate in the engine oil. Because of the fact that more flex fuel enters the engine oil, the amount of water and acid in the engine oil increases, which naturally has an effect on the properties of the oil. For example, alkaline additives, which are used for protection against wear, corrosion, and aging, and to improve viscosity, are neutralized by the high acid content.

In order to estimate the influence of the acid content in the engine oil on elastomers, Freudenberg tested a variety of sealing materials. To this end, defined amounts of different acids were used to simulate different operating conditions for the engine oil. A standard FKM compound, HNBR, and an ACM mixture were tested in conjunction with a TBN2 (Total Base Number) engine oil and an over-acidified TBN3 engine oil.

The tests showed that the elastomers were generally more resistant to old engine oil (TBN2) than to fresh engine oil. The additives, most of which are amines, were neutralized in the old oil, which means that they could no longer do any damage to the FKM. The mechanical properties of the elastomers were more heavily influenced by contact with the over-acidified oil (TBN3). However, resistance was still better than in the case of fresh engine oil.

It is to be expected that because flex fuels add increased levels of acid and water to the oil, new engine oils with larger amounts of additives will be developed for flex fuel vehicles in order to extend the life of the oil. In this case, the resistance of the seals to these new oil mixtures will have to be tested.

5 Summary

Freudenberg is already in a position to provide both static and dynamic seals made of suitable elastomer materials not only for all flex fuels, but also for biodiesel, CNG/LPG, BTLs, sun and syn fuels, as well as for fuel cells. When using the various sealing materials in conjunction with different flex fuel mixtures, it is important to take into consideration that changing between different ethanol fuel mixtures can result in different swelling behavior.

In order to ensure that all seals perform properly when using different flex fuels, specially developed fluororubbers are necessary. The composition and the influence of the blow-by gases on elastomers must be analyzed. It is not yet possible to say with any accuracy the impact that ethanol will have on engine oil. Moreover, it is likely that new oil generations with even more additives will be used in the future. This means that more tests will have to be conducted in conjunction with car manufacturers and fuel manufacturers in order to ensure that seals are optimized and can meet the demands of flex fuel applications. ■