Title
Influencing factors for static immersion tests of compatibility between elastomeric materials and lubricants

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Abstract
The material compatibility is an important factor to consider during the development of new lubricants and sealing materials. Static immersion tests provide a first idea about the compatibility between elastomeric materials and lubricants. For the same material combination, significant deviations among the test results of different laboratories have been reported. In order to identify the relevant factors affecting the results, a systematic investigation was carried out. Reproducibility tests show that the estimation of the compatibility is compromised due to the deviations, which appear for the change of the mechanical properties of the considered reference elastomers. The influence of the closure of the test apparatus and of the volume ratio, as well as the development of the aging process were investigated. The results showed that in order to differentiate between elastomer-lubricant material combinations, standard test durations of approximately 1008 hours are to be preferred. Volume ratios 64 and 80 and small variations of the vessel closure did not lead to significant deviations of the results. In contrast, tests with open and closed vessels showed significant deviations for the hardness and mechanical properties of the elastomeric materials.

Keywords
Chemical, Oils, Elastomer, Compatibility

## 1. Introduction

In order to ensure the correct functioning of machine elements made of elastomeric materials and to reduce maintenance costs, it is important to consider the interactions, which occur between the elastomeric parts and the surrounding medium in service. More than 500 failure analyses for O-rings show for example that approximately 41% of the failure causes can be grouped under the classes Media and Temperature/Aging [1]. Elastomeric materials have a three-dimensional network structure composed of polymer chains, which degrees of freedom are restricted by crosslinks and chain entanglements. This network structure grants elastomeric materials a high elongation capacity. The properties of elastomeric materials are strongly affected by UV radiation, heat, oxygen and chemicals, which can cause a progressive deterioration of the material with time. There is a distinction of the form of aging in the literature. The physical aging refers to a change of the physical structure of the material e.g. crystallization, stress relaxation, alignment, whereas during the chemical aging there is a non-reversible change in the chemical structure e.g. molecule cleavage, increase of the crosslink density. In reality both forms of aging take place at the same time with effects which are sometimes opposed to each other [8], [9].

Regarding the compatibility of elastomeric materials with different fluids, several influencing factors are mentioned in the literature. The polarity is known to influence the swelling behavior. Polar fluids are likely to diffuse into polar elastomers and similarly non-polar fluids are likely to diffuse into non-polar elastomers. The molar volume of the fluid and the percentage of bound acrylonitrile in nitrile rubbers (NBR) are also known to have an effect on the swelling behavior. According to Starmer [10] the relation between the volume change of the elastomer after the immersion in a fluid and the percentage of bound acrylonitrile in the elastomer can be approximated with a Gaussian curve. The percentage of bound acrylonitrile for the maximum increase of volume depends on the polarity index of the fluid. Furthermore acid-base interactions play also an important role [10]. NBR is

considered to be a hard base and a soft acid, which is likely to interact with hard acids and soft bases. According to ASTM D 471 the aniline point of an oil is also determining for the swelling behavior. In general applies, the lower the aniline point, the stronger the swelling effect of the oil.

Static immersion tests provide a first idea about the compatibility between elastomeric materials and lubricants. In the test, specimens of elastomeric materials are immersed in a recipient with lubricant. The specimens remain immersed under controlled conditions of temperature and for a determined duration. Although these screening tests do not reproduce the tribological conditions present in reality, they allow a first assessment of the material compatibility with simple laboratory equipment. The test procedure has been standardized in several specifications. The standard ASTM D 471 [2] has the highest acceptance in America, while in Europe the standard ISO 1817 [3]/ISO 6072 [4] is the most recognized.
Like many other products lubricants must comply with several tests before they get the approval for a specific market e.g. DIN 51524: minimum requirements for hydraulic oils [5] and DIN 51517: minimum requirements for lubricating oils [6]. The test of compatibility with elastomers is among the requirements that lubricants must fulfill. Unfortunately, the current standards do not define clearly the test apparatus and test conditions. The specification of a loose closure of the recipient has for example led to different interpretations. Some test laboratories use for example aluminum foils, other use ground glass, etc. This has led to the definition of several company-specific standards, which at the end affects lubricant and elastomer producers, who have to fulfill several tests of elastomer compatibility as a consequence. Additionally, the definition of reference elastomeric materials in different standards with the same name convention has led to confusion [7].
In order to identify the relevant influencing factors of the test apparatus and to determine the influence of the test conditions on the test results a systematic investigation was carried out.

## 2. Methods

In order to test the compatibility of elastomeric materials with different fluids different standards have been developed in the past. The present study was mainly carried out taking the standard ISO 1817 / ISO 6072 as reference for the tests. ISO 6072 applies specifically for the test of hydraulic fluids and is based on the more general standard ISO 1817, in which the test procedure is described in detail. A few tests were performed according to ASTM D 471. For this reason, a brief comparison of the standards ISO 6072 / 1817 and ASTM D 471 is provided in Table 1.

| | ASTM D 471 | ISO 6072 / ISO 1817 |
|---|---|---|
| Reference elastomers | Not defined | NBR1, NBR 2, FKM 2, EPDM 1, HNBR 1 |
| Reference oils | IRM 901, IRM 902, IRM 903, IRM 905 | IRM 901, IRM 902, IRM 903 |
| Test vessel | Glass test tube, L: 300 mm x D: 38 mm | Not defined |
| Volume of the test fluid | 100 ml (Volume change), 150 ml (Hardness change, change of tensile strength and elongation at break) | The volume of the test fluid must be at least 15 times the volume of the test specimens in the test vessel |
| Form of the test specimens | Rectangular 25 x 50 x 2 mm (Volume change), Dumbbell specimens type C according to ASTM D 412 | Dumbbell specimens type 2 according to ISO 37, circular specimens, rectangular specimens |

Table 1. Comparison of the test standards ISO 6072 / ISO 1817 and ASTM D 471

## 2.1 Test materials

The standard ISO 6072 defines reference elastomeric materials for the tests with hydraulic fluids. It includes specifications for the production of NBR (acrylonitrile butadiene rubber) elastomers with different acrylonitrile content, with different types of crosslink (sulfur, peroxide), as well as for the production of FKM (Fluoroelastomer) elastomers, among other materials. Besides ISO 6072, the standard ISO 13326 [11] also defines reference elastomers, which are quite similar to those defined in ISO 6072. Table 2 shows the reference elastomers, which were tested in this study.

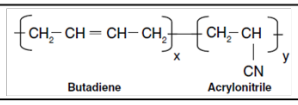
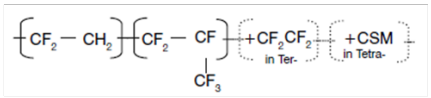
| Standard for the production of the Elastomer | Designation | Acrylonitrile mass fraction in % | Crosslink type | Chemical structure | Others |
|---|---|---|---|---|---|
| ISO 13226 | NBR 28/PX | 28 | Peroxide |   | Polar, unsaturated |
| ISO 13226 | NBR 28/SX | 28 | Sulfur | | |
| ISO 6072 | NBR 1 | 28 | Peroxide | | |
| ISO 13226 | FKM 2X | - | Bisphenol |   | Neutral |

Table 2. Reference elastomeric materials for the immersion tests

Similarly, reference oils were selected for the tests. Table 3 shows the FVA (Forschungsvereinigung Antriebstechnik e.V.) reference oils, which were tested.

| | **Mineral Oil: FVA 3A** | **Polyglycol: FVA PG 3A** |
|---|---|---|
| Kinematic Viscosity | At 40°C: 90 $mm^2/s$<br>At 100°C: 10,5 $mm^2/s$ | At 40°C: 247,4 $mm^2/s$<br>At 100°C: 41,7 $mm^2/s$ |
| Additives | 4% Anglamol 99 (Sulfur EP/AW additive) | 4% LP 1655 (Corrosion inhibitor, AW additive) |
| Others | Unpolar | Polar |

Table 3. Reference oils for the immersion tests

## 2.2 Test apparatus

Figure 1 shows the test apparatus used in this study to perform the immersion tests according to ISO 1817/6072. It consists of a glass vessel with ground lid. The glass has a height of 153 mm and a diameter of 85 mm. A support made of stainless steel wire was used to hold the test specimens in place. For a test with 430 ml oil and 5 specimens type 2 (ISO 37) results a volume ratio (Volume of oil relative to the volume of the specimens in the glass) of 64. The volume of air in the closed vessel is approximately 78.3 ml.

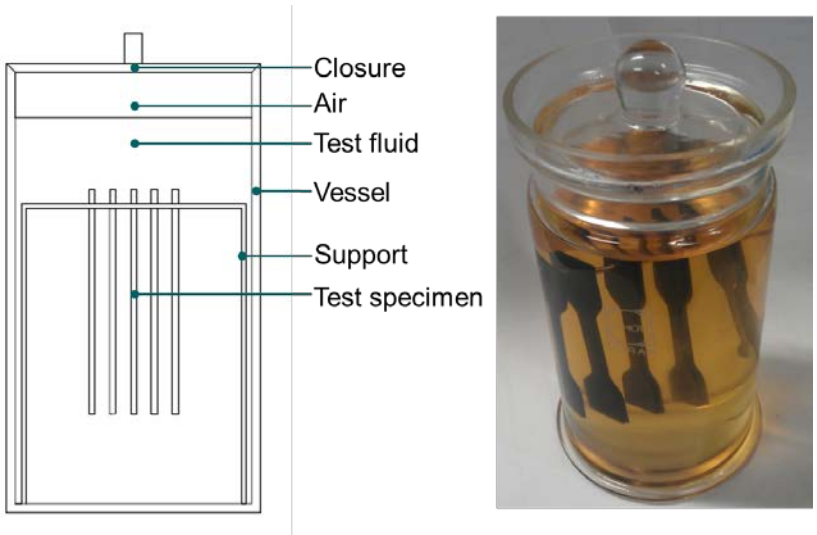


Figure 1. Test apparatus. Glass with ground lid. Diameter: 85mm, Height: 153 mm.

### 2.3 Determination of the elastomer compatibility index

The Elastomer Compatibility Index (ECI) is a measure of how strong the elastomeric material is affected after the immersion. It is defined in ISO 6072 as the change of the properties hardness, volume, tensile strength and elongation at break of the elastomeric test specimen after the immersion test. The change of hardness was measured with a Micro-IRHD hardness tester. The change in volume was determined based on the mass of the specimen in air, distilled water and in fresh test oil. The measurements were done with an analytical balance with 1 mg readability. In order to determine the tensile strength and elongation at break, tensile tests according to ISO 37 were performed using a tensile testing machine MTS Criterion Model C42.503 with a 1 kN load cell (class 0.5 1-100%) equipped with an extensometer with a resolution of 0,004 mm.

## 3. Results and discussion

Before considering the variation of parameters of the test, the reproducibility of the results with the test apparatus described in 2.2 and the test equipment described in 2.3 was estimated. For this purpose, immersion tests were repeated up to six times with the same materials and test conditions.

The deviations for the change of hardness and change of volume shown in Figure 2 are acceptable in comparison to common limit values of compatibility (+/- 8 IRHD, -4% to 15% Volume change after 168 hours [12]).

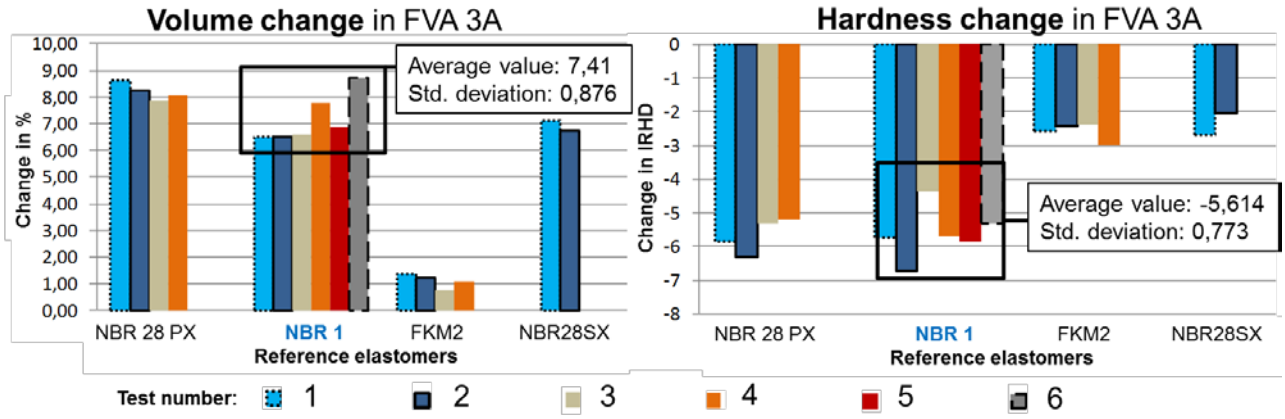



Figure 2. Reproducibility of the volume and hardness change in mineral oil FVA 3A. Test duration: 168 hours, T=100°C, each bar shows the result of a test with five specimens.

Considering again common limit values of compatibility as a reference (maximum tensile strength change of -20% and maximum elongation change of -20% after 168 hours [12]), Figure 3 shows a significant dispersion for the change of the tensile strength and for the change of elongation at break. In case of the change of elongation at break, the deviation of the test results is comparable to the limit value of -20% according to the guideline provided in the earlier ISO 6072 2002 [12] (The guideline appears no longer in the ISO 6072 2011), which renders any evaluation of compatibility based on the test results for the change of elongation at break inappropriate. The tensile tests with the specimens before the immersion show already significant deviations mostly for the elongation at break. The comparison of the dispersion before and after the immersion does not indicate a systematic improvement or deterioration of the dispersion as a consequence of the immersion. In comparison with metals, elastomeric materials show higher deviations in their mechanical properties. This is mainly due to their network structure and to its susceptibility to the manufacturing process.

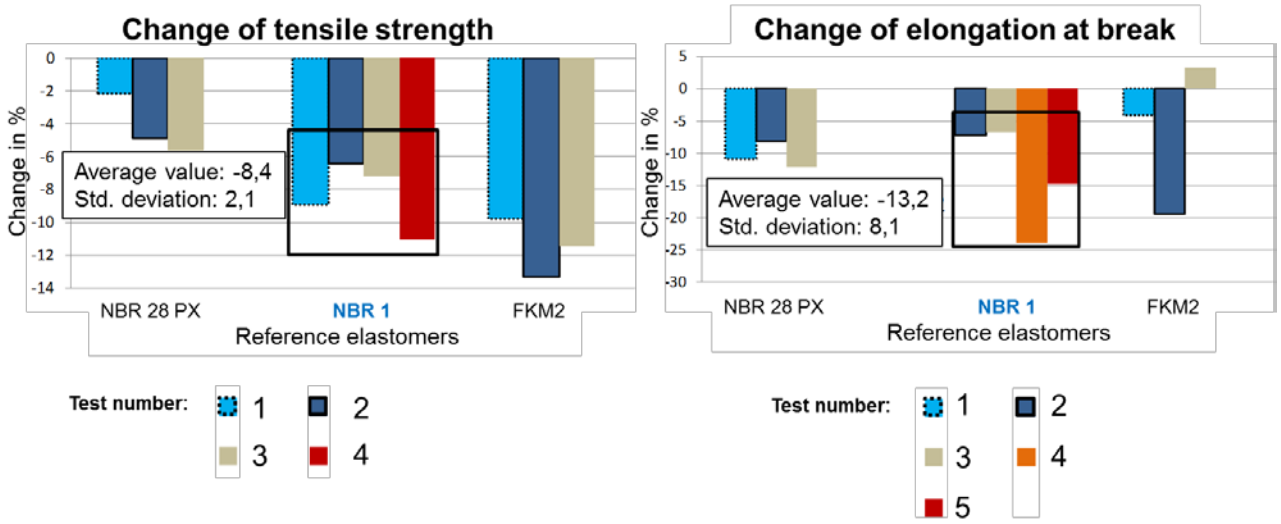



Figure 3. Reproducibility of the change of tensile strength and change of elongation at break in mineral oil FVA 3A. Test duration: 168 hours, T=100°C, each bar shows the result of a test with five specimens.

Table 4 summarizes the dispersion of the four parameters of the ECI, which results in average for the four test materials of section 2.1.

| **Parameter** | **Dispersion (approx.)** | **Applicability for the evaluation of the compatibility between elastomers and lubricants** |
|---|---|---|
| Change of hardness | 1.5 IRHD | - Suitable |
| Change of volume | 1.5 percentage points | - Suitable |
| Change of tensile strength | 5 percentage points | - Bigger deviations and higher susceptibility<br>- Differentiation between compatibility levels not clear |
| Change of elongation at break | 20 percentage points | - Biggest deviations and highest susceptibility<br>- Should not be used to evaluate the compatibility without considering the other parameters |

Table 4. Dispersion of the test parameters.

The physical (crystalline regions, chain alignment) and chemical structure (chemical bounds) are mostly determined during the processing of the elastomeric material. A guideline for the processing of reference elastomers is included in the standards ISO 6072 and ISO 13226 among with control tests. The manufacturing process involves a mixing procedure, cooling on a flat metal surface followed by curing of the elastomeric sheets. Process parameters like temperature and time, along with the mechanical shearing of the mixture are determining for the structure and final properties of the elastomeric material.

The determination of the tensile strength and elongation at break of elastomeric materials is standardized in ISO 37 and ASTM D 412. Test specimens type 2 are usually chosen for the immersion tests due to its favorable size. Despite the limited potential to reduce the dispersion of the test results during testing, given that the final properties of the elastomer are mainly determined during the manufacturing process, the choice of specimens with a more homogeneous stress distribution, like for example the specimens type 1A (see ISO 37), could improve the reproducibility of the test results.

### 3.1 Test duration

In ISO 1817 the standard test durations are given in multiples of 168 hours. Tests with a total duration of 1008 hours were carried out with measurements of hardness and volume performed every 168 hours without replacing the oil. After 1008 hours the specimens were subjected to the tensile test. The periodic measurements of hardness and volume show the progression of the aging process. Figure 4 shows the hardness change relative to the hardness before the immersion as a function of time for the tests with NBR in mineral oil FVA 3A and in Polyglycol FVA PG 3A. In mineral oil the hardness of NBR increases with time, whereas in Polyglycol the hardness decreases. For the combinations of NBR elastomers with FVA 3A, the results show after 168 hours a decrease of the hardness, which is most likely caused by physical mechanisms like the diffusion of oil in the elastomer (chemical mechanisms take place at the same time). From 168 hours to 1008 hours the hardness increases as a consequence of a mix of physical and chemical processes such as the thermal-oxidative aging. The results show that individual measurements performed after a specific period of time, like usually done in the industry, provide only an instantaneous picture of the aging process. Performing periodical measurements to record the aging process is however costly. During the first 168 hours, when the physical effects seem to dominate, all considered material combinations show a similar behavior making difficult a distinction. In the case of NBR and mineral oil FVA 3A a clear differentiation between the six elastomer-lubricant combinations can be seen after 1008 hours.

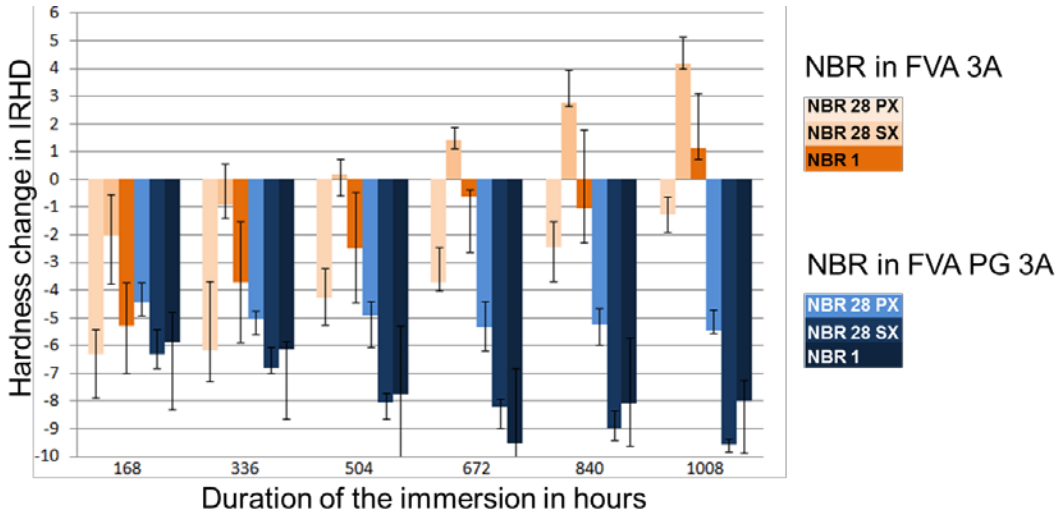



Figure 4. Hardness progression. NBR in FVA 3A and FVA PG 3A, T=100°C

### 3.2 Vessel closure

According to ISO 1817 the oxygen entering the test vessel should be kept as low as possible. The closure is nevertheless not clearly specified in the standard. In order to clarify the effect of oxygen and of using different types of closures on the results of the immersion tests, several tests with open and closed vessels and with different closures were carried out.

The tests with open glass show that the influence of oxygen depends highly on the elastomer-oil combination. The effect of oxygen was particularly strong for the combination NBR 28 SX and mineral oil. For this combination results a continuous hardness increase with time. The comparison between the tests with closed glass, with and without grease shows no significant influence of applying grease to the ground lid on the hardness change (see Figure 5).

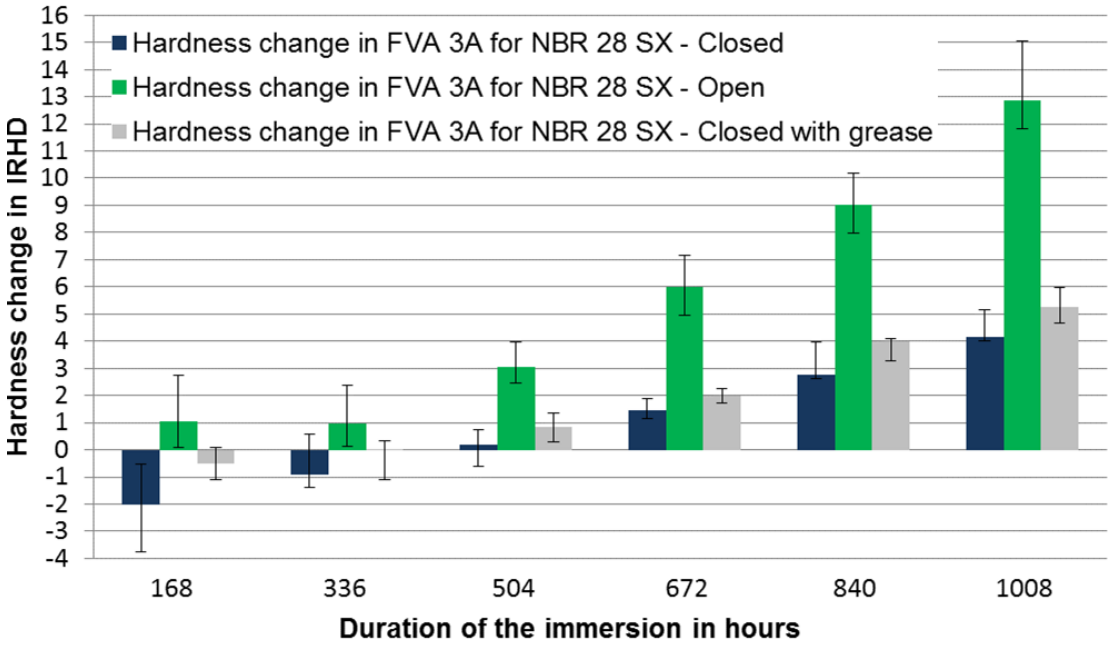



Figure 5. Hardness change in FVA 3A for NBR 28 SX. Open glass, closed and closed with grease, T=100°C

Furthermore, the stress-strain curves of Figure 6 show an embrittlement of the NBR elastomeric material with increasing immersion duration. Regarding the effect of the vessel closure, the curves show a stronger embrittlement for the tests with open glass.

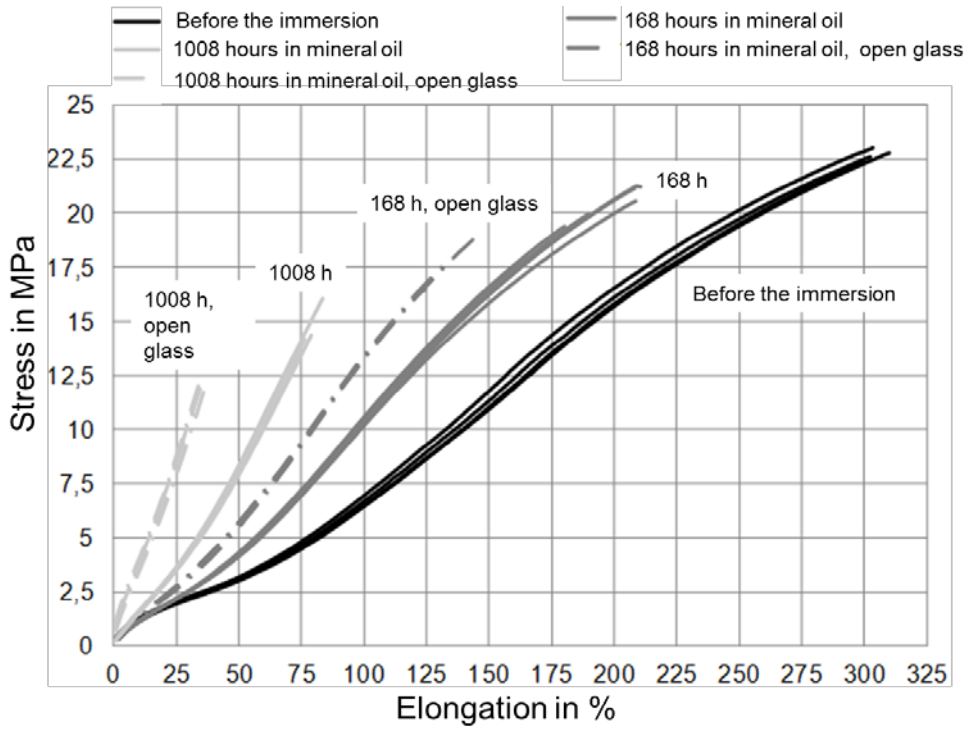



Figure 6. Stress-strain curve for NBR 28 SX in FVA 3A. Before the test and after 168 and 1008 hours immersion time. Open and closed vessel, T=100°C

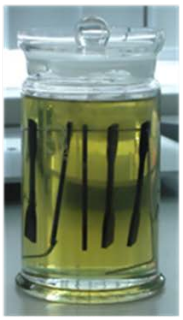
The embrittlement and hardness increase of the NBR 28 SX specimens are mainly a consequence of the thermal-oxidative aging of the elastomeric materials. This process is triggered by high temperatures and the presence of oxygen with several mechanisms taking place at the same time [8]. An increase of the crosslink density and cleavage of the macromolecules are characteristic of this aging process, which showed a stronger embrittlement for sulfur-linked NBR in comparison

with peroxide-linked NBR. The impact on sulfur-linked elastomeric materials has been reported for example in [9].

In contrast to the hardness and mechanical properties, the volume of the specimens was not significantly affected by the oxygen availability.

In order to determine how much the results can deviate by using different glasses, selected elastomer-lubricant combinations were tested using closures with ground glass, with screw cap and with a sealed cap (see Figure 7).

Preserving jar



Glass with ground lid

Marmelade glass

| Glass | Volume ratio with 5 specimens |
|---|---|
| Preserving jar | 124 |
| Glass with ground lid | 64 |
| Marmelade glass | 60 |

Figure 7. Immersion tests with different glasses, duration: 168 hours, T=100°C

The results did not show significant deviations for the different closures. Figure 8 shows the results of the volume change in FVA 3A after 168 hours for selected reference elastomers.

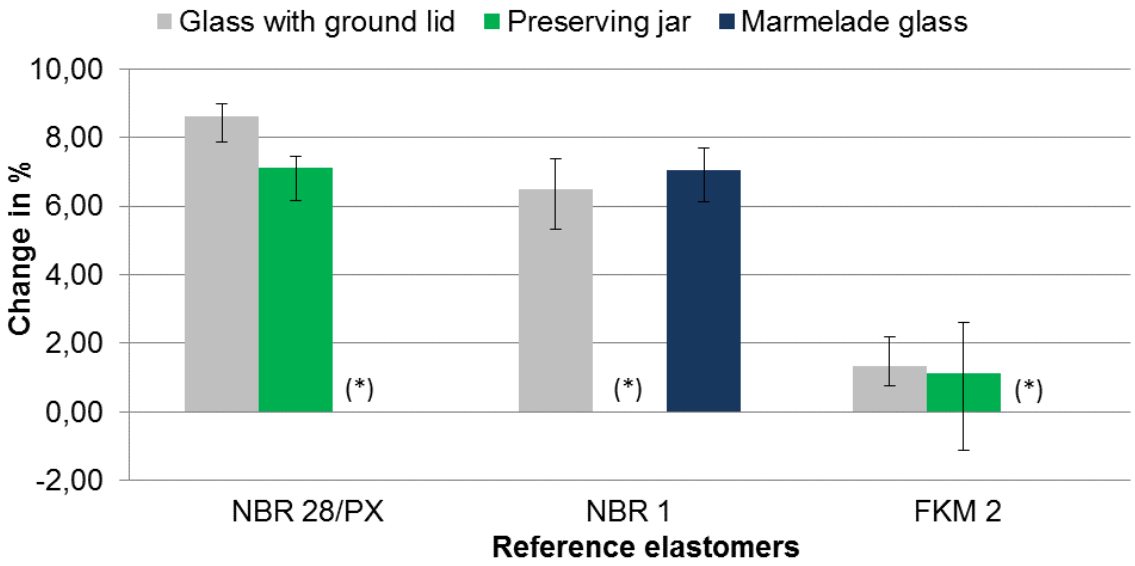



Figure 8. Volume change in FVA 3A for selected reference elastomers, duration: 168 hours, T=100°C, (*) missing values

### 3.3 Volume ratio (volume of oil relative to the volume of the specimens in the glass)

According to the standard ISO 1817 the volume of oil relative to the volume of the specimens in the glass must be at least 15. An upper limit is not specified in the standard. In order to investigate the influence of the volume ratio keeping the volume of air inside the glass nearly constant, the number of specimens was varied. Thus, with 4 and 5 specimens, volume ratios of 80 and 64 were respectively tested. The results did not show any significant influence of the volume ratio. Figure 9 shows the change of hardness for the tests with volume ratio 64 and 80.

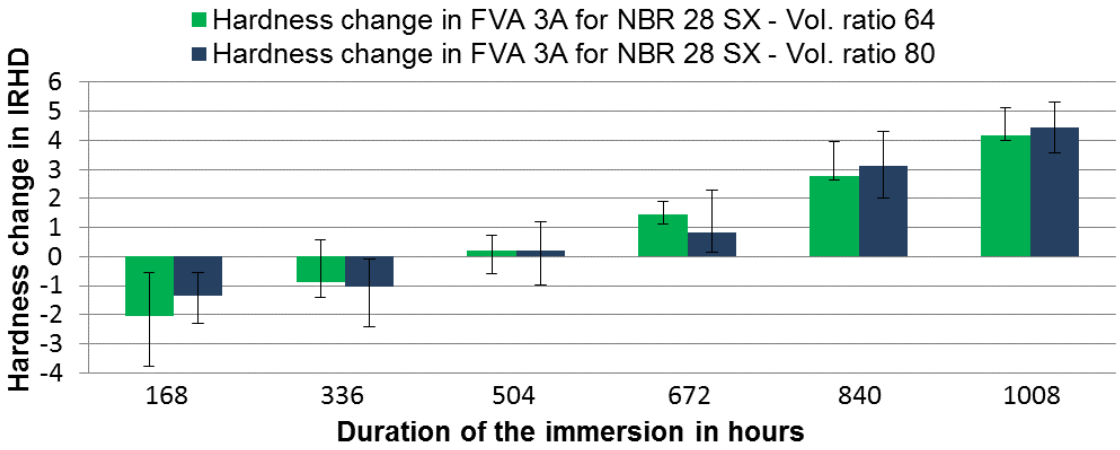


Figure 9. Hardness change in FVA 3A for NBR 28 SX. Volume ratio 64 and 80, T=100°C

### 3.4 Oil analyses

The changes resulting in the oil during the immersion tests were investigated with different methods like Infrared Spectroscopy (IR), Nuclear Magnetic Resonance (NMR), Elemental Analysis (ICP) and Gas Cromatography (GC-MS). The color change of the oil after the immersion allows a first differentiation of the different oil-elastomer interactions occurring during the test. Figure 10 shows the oil for different oil-elastomer combinations after the immersion test according to ASTM D 471. A darker oil resulted for the combination Polyglycol and sulfur crosslinked NBR elastomer suggesting a stronger level of interaction in comparison to the case between Polyglycol and the peroxide crosslinked NBR. In contrast, no significant tendencies regarding the color change for mineral oil were observed.

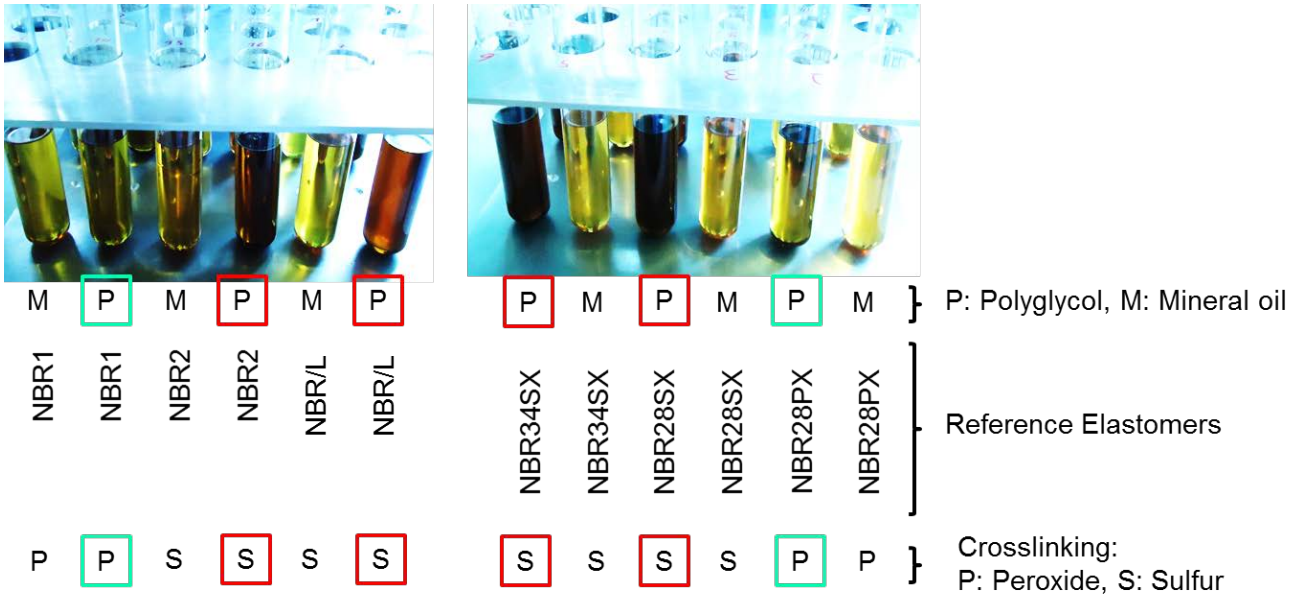


Figure 10. Visual evaluation after immersion tests according to ASTM D 471. Duration: 168 hours, T=100°C

Furthermore, the elemental analyses show an increase of the zinc content in the oil after the immersion test (see Figure 11). The increase was higher for the immersion tests with the sulfur crosslinked elastomer NBR 28 SX in comparison to the peroxide crosslinked NBR 28 PX. Additionally, the results show that the increase was higher in mineral oil FVA 3A compared to polyglycol FVA PG 3A. Zinc oxide acts as an accelerator during the vulcanization process. The hardness, tensile strength and elongation at break of the elastomer are not affected by the decrease of zinc according to [13].

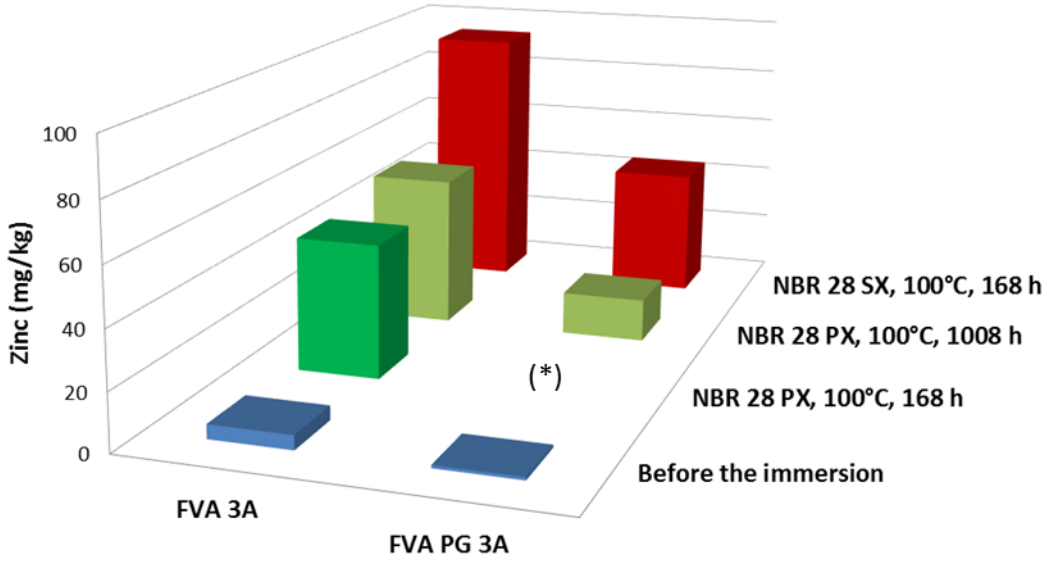



Figure 11. Zinc content before and after the immersion test, (*) missing value

NMR and Gas Chromatography (GC-MS) analyses were performed after the 1008 hours immersion of NBR 28 SX and FKM 2 in FVA 3A. Regarding the effect of the test conditions (e.g. Vessel closure) on the oil degradation, no significant influences were identified.

## 4. Conclusions

A systematic investigation was carried out to identify relevant influencing factors on the compatibility immersion tests and to quantify their effects. For this purpose, the factors volume ratio (fluid volume relative to the volume of the test specimens) and vessel closure, which are not clearly defined in the current standards were considered. First of all, the reproducibility of the test results with the same material combination and test conditions was determined. The results of the hardness and volume change present acceptable deviations in comparison with common limit values. Despite the tests being performed with reference elastomers, significant deviations appear for the tensile strength and elongation at break. Therefore, a comparison between different material combinations should not be performed exclusively on the basis of these two parameters.

The impact of the vessel closure on the test results was highly dependent on the material combination. In case of the NBR elastomers, the type of crosslinking (peroxide, sulfur), which largely determines the mechanical properties of the specimens, seems to play an important role for the material compatibility as well.

The immersion tests performed with volume ratios 64 and 80, which are typical values for tests performed according to ISO 1817, revealed no significant deviations of the test results with the selected reference materials.

Regarding the influence of the closure, significant deviations between the results of the tests with open and closed vessel appear. During the tests with open vessel, the higher availability of oxygen resulted in a stronger hardness increase in comparison to the tests with closed vessel. Furthermore, the tensile strength and elongation at break showed a stronger decrease for the tests performed with open vessel. The deterioration of these properties was mainly caused by the thermal oxidative aging of the elastomers, which was promoted by high temperature and the interaction with oxygen. The tests with typical closures like ground glass, screw cap and sealed cap, which present comparatively minor variations of the oxygen availability, did not result in significant deviations.

The tests up to 1008 hours with measurements in intervals of 168 hours show that individual measurements, like specified in some standards, provide only an instantaneous picture of the aging process. In addition, short duration tests can lead to a wrong judgment of the material compatibility. Regular measurements show the development of the aging process but are costly. An individual measurement after 1008 hours, which is a common duration for long tests, allows a differentiation of the material combinations and provides therefore a better assessment of the material compatibility.

## 5. Acknowledgements

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