

Testing and Prediction of Material Compatibility of Biofuel Candidates with Elastomeric Materials

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ABSTRACT

In this paper compatibility studies of biofuel candidates and similar liquids with the elastomeric materials nitrile butadiene rubber and fluoroelastomer are presented. The results gained with defined reference elastomers are compared to results gained with the materials used in the technical application. For this purpose test specimens are prepared from fuel hoses and the material used for shaft seals of fuel pumps. The experimental results are subsequently used to evaluate prediction approaches based on the HSP- and QSPR-method. Finally a comparison of these two approaches is given.

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INTRODUCTION

Tailor-Made Fuels from Biomass

Since crude oil is a limited resource the need to develop future energy and mobility concepts has become a topic of increasing attention. At RWTH Aachen University the cluster of excellence "Tailor-Made Fuels from Biomass" (TMFB) seeks to find novel fuels and production pathways based on a biomass feedstock. To address this complex task an interdisciplinary approach has been chosen and therefore the cluster consist of researchers from multiple disciplines such as chemistry, biology and various divisions of mechanical engineering. The Institute of Fluid Power Drives and Controls (IFAS) is part of the latter group. The biofuel related research at IFAS can be divided into three main fields: The rheological fluid properties at high pressures and temperatures [1], their tribological characteristics [2] [3] [4] and the interactions of the biofuel candidates with common engine related materials and components, such as elastomeric seals [5].

This paper will focus on the research regarding the compatibility of developed biofuel candidates with common seal materials. Particularly the possibility to predict the interactions of elastomer materials and fluids will be presented and discussed. Besides the great importance sufficient compatibility has for a successful introduction of any future fuel to the consumer market, this topic is also highly relevant to ensure a safe and reliable handling of the biofuel candidates within the research in the cluster itself.

Material Compatibility

Due to the nature of the cluster's research the list of potential biofuels and reference fluids that is investigated includes a variety of linear, branched and cyclic molecules. Among these are alcohols, aldehydes, alkanes, ethers, furans and ketones. In [Figure 1](#) 1-octanol (a),

2-methyltetrahydrofuran (b), di-n-butylether (c) and butyl levulinate (d), which are some of the most popular biofuel candidates derived from the research within the cluster of excellence, are shown.

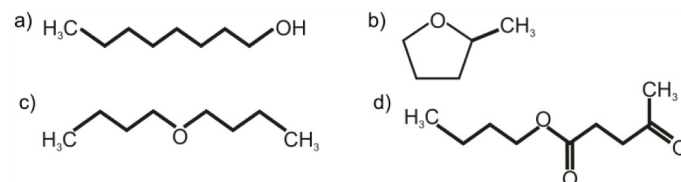


Figure 1. Selected biofuel candidates

These molecules differ from those that are present in conventional diesel and gasoline. Hence, the interactions of the new fluids with the materials in combustion engines have to be investigated.

The main focus in this research field lies on the compatibility with seal materials. In [Figure 2](#) the principle structure of elastomers is depicted.

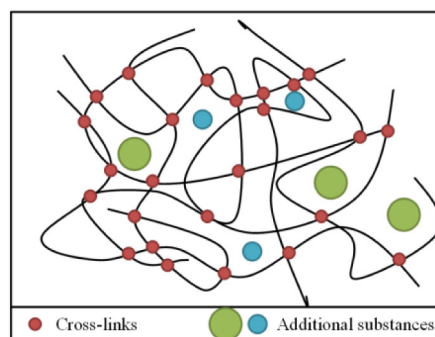


Figure 2. Structure of elastomer materials

As shown, the backbone of the elastomer is made up by long chained molecules which are balled in a broad-meshed matrix and connected via crosslinks by the process of vulcanisation. The properties of the elastomers can be tailored through the amount of crosslinks. The space between the carbon chains can be filled with additional substances like plasticizers, fillers and curing agents [6]. For elastomers significant changes can result from the exposure to liquids [5]. Such an insufficient compatibility of the seal material and sealed fluid can lead to swelling, loss of hardness and mass. All of these changes can result in the failure of the seal leading in turn to the failure of other components of the engine, or even leakage of the fuel into the environment. A detailed description of the physical and chemical reactions, which cause the changes of the seal can be found in [7].

EXPERIMENTAL INVESTIGATION OF COMPATIBILITY

Test Procedure

A test procedure for evaluating compatibility of a fluid with a material is described in DIN ISO 1817. This norm describes how elastomeric samples have to be immersed into a test liquid.

Nevertheless, the test parameters of the immersion test described in this paper differ slightly from the norm. To cope with the limited fluid amount due to exotic nature of some TMFB candidates, the elastomer specimens are reduced in size and they are submerged in 30 ml of fluid. Despite the fact that the temperature of the fluid in the injection system can reach 120°C [8], due to the basic nature of this study and the high volatility of some fluids, the temperature of the tests is set to 40°C. The test duration is fixed to a maximum of 28 days. Consequently, due to the short term testing no reliable conclusions on long term effects can be drawn.

Unlike the recommendations of the norm the three tests for one pair of elastomer and fluid are not conducted the same way. To detect on the one hand the property change of the elastomer over time and on the other hand the influence of multiple extraction during the test on the result, only one sample is extracted three times after one, seven and 28 days. The second and third sample are just extracted once at the end of the test after 28 days. Only minor variations regarding the result were detected in previous studies [5]. Volume and hardness are measured at each extraction of the elastomer. After 28 days of immersion the specimens are dried for three days at 40°C and their mass is recorded via a laboratory balance.

With respect to the injection system such immersion tests should be performed with specimen made from the material used for the technical applications. This has the advantage that the test is more representative to the technical application. The drawback is that the precise composition of such materials is often kept secret and can be very different for a specific type of elastomer. This hinders the analysis and interpretation of the experimental results. For a fundamental research it is often appropriate to avoid these problems by conducting tests with so called standard-reference-elastomers (SRE). The composition and properties of these materials are standardised, see [9]. In this paper both approaches are presented, see

Figure 3. The focus lies on the two most common elastomers in injection systems, namely nitrile butadiene rubber (NBR) and fluoroelastomer (FKM) [10]. Both materials were purchased from the Federal Institute for Materials Research and Testing (BAM). In Table 1 the standardized composition of these elastomers is given.

Table 1. Composition of the SRE specimens

ISO 13226 SRE-NBR 28/SX		ISO 13226 SRE-FKM/2X	
	Parts by mass		Parts by mass
NBR with 28 % by mass of acrylonitrile	100.0	Vinylidene fluoride-hexafluoropropylene copolymer	100.0
Antidegradant TMQ	2.0	Calcium hydroxide	2.0
Zinc oxide	5.0	Magnesium oxide	3.0
Stearic acid	1.0	Carbon black N 990	25.0
Carbon black N 550	65.0	Organic phosphonium salt	1.45
Accelerator TMTD	2.5	Bisphenol AF	2.76
Accelerator CBS	1.5		
Sulphur	0.2		

First, for basic studies experiments with SRE are conducted for NBR as well as for FKM. Afterwards the material of NBR-and FKM-hoses and the elastomeric FKM-material used for radial shaft seals of injection pumps are tested. The specimens of the SRE and the radial shaft-seal-material have the same size and shape. The specimen made from the material of the hoses exhibit a different shape, but similar size.

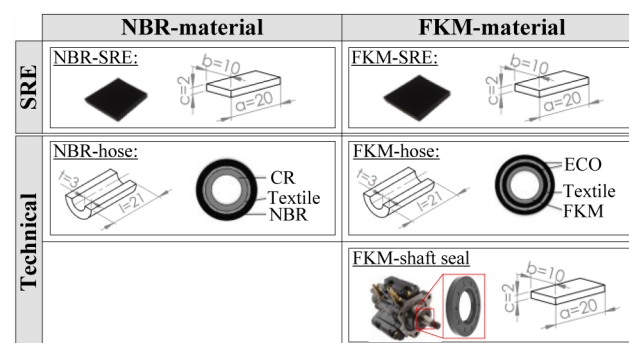


Figure 3. Investigated materials

The geometrical dimensions of all specimens before and after submersion were taken with a precision gauge. Each specimen's hardness, including those derived from the hoses, were determined with a *Bareiss digi test* according to the IRHD M standard [11]. The hardness of the SRE are limited to a range of 76 - 81 IRHD for the NBR material and 67 - 73 IRHD in case of the FKM [9]. No deviations from these values were found among the investigated specimens.

Reference Materials

Figure 4 shows the results for NBR-SRE, which is, due to the nitrile group, a polymer with a polar molecular structure. These and all following results are also given the tables in the appendix of this paper. It can therefore be assumed, that polar fluids are able to be absorbed by NBR. The swelling behaviour of most NBR specimens confirms this postulation. It is affected by functional groups of the solvent. In general, ketones and aldehydes cause high swelling rates while alcohols and alkanes cause lower swelling rates. Furthermore, especially solvents with a cyclic molecular structure, for instance γ -valerolactone, 2-chlorophenol and 1-methyl-naphthalene, seem to cause a higher swelling rate than solvents with a linear molecular structure.

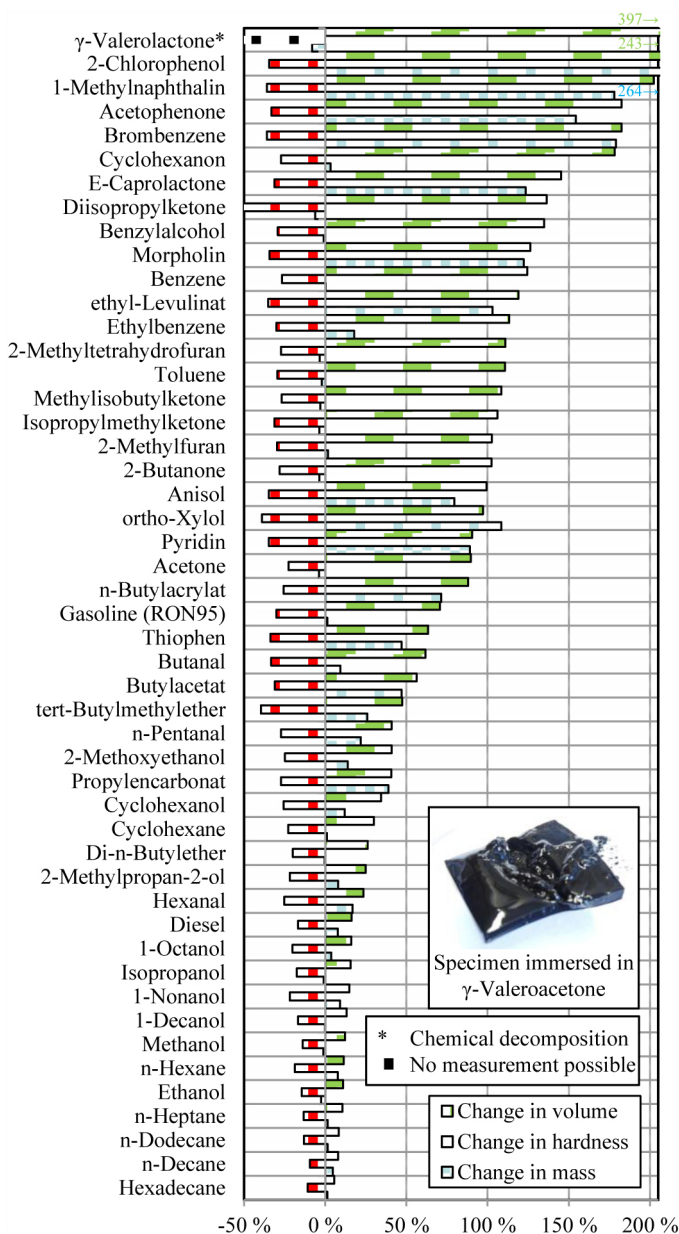


Figure 4. Property changes of NBR-SRE after 28 days

Due to a chemical decomposition the swelling rate of γ -valerolactone has to be judged critical and no hardness value can be determined after immersion.

In Figure 5 the results for FKM-SRE specimens in several solvents are shown. The basic molecular structure of FKM is polar as well. Therefore it can also be assumed, that the swelling behaviour is dependent on the polarity of the solvents. As Figure 5 shows, polar solvents cause higher swelling rates than nonpolar solvents, like heptane. Regarding the functional groups of the solvents, ketones and aldehydes cause high swelling rates, while linear alcohols alkanes and ethers causes low swelling rates.

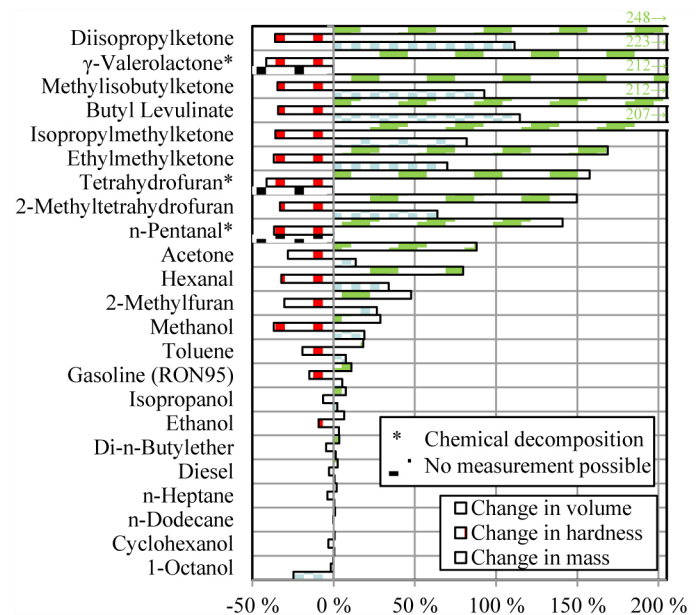


Figure 5. Property changes of FKM-SRE after 28 days

In addition to γ -valerolactone, chemical decomposition occurs for tetrahydrofuran and pentanal.

Besides the change of properties after the total testing time of 28 days, the change over time is of special interest, because this gives a hint towards the ongoing phenomena. This is investigated by the multiple extractions of one specimen of each combination. Regarding the basic course of the property change, there are at least three different types of course, see Figure 6.

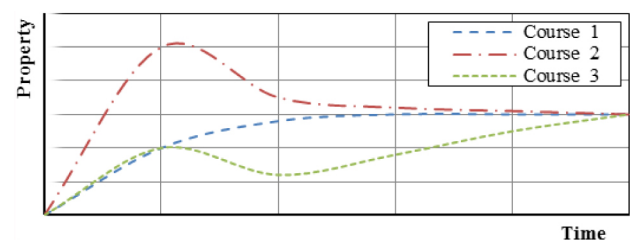


Figure 6. Characteristic courses over time

The first type is characterized by an asymptotic increase towards a stationary value after 28 days. It represents a typical saturation process, as for instance the absorption of fluid by the elastomer. This course is the most common among the investigated fluids. The second type of course is characterized by an increase at the beginning of immersion followed by an asymptotic decrease towards a stationary value. This shape is an indicator for at least two competing phenomena, for instance absorption of fluid by the elastomer as well as an extraction of components. The third kind of characteristic is distinguished by a local extreme as well as no visible asymptotic behaviour towards the end of the test. Hence, even if the changes after 28 days are similar, completely different courses due to different ongoing phenomena can lead to the results after 28 days. In Table 2 fluid-elastomer-combinations are listed, whose swelling characteristics over time differ from the first type of course.

Table 2. Fluid-elastomer-pairs with a swelling characteristic over time comparable to the second and third type of course

NBR	FKM
n-Heptan, ethanol, methanol, pentanal, ethylbenzene, p-xylol, butylacetat, butanal, n-butylacrylat, acetone, pyridin, anisol, 2-methyltetrahydrofuran, γ -valeroacetone	Gasoline, hexanal, pentanal, ethylmethylketone, methylisobutylketone, isopropylmethylketon, diisopropylketone

Technical Materials

The ingredients of SRE and the technical elastomers differ most likely. In general technical elastomers contain several additives and fillers for performance enhancement [6]. Due to the different composition the results of the immersion tests are expected to vary. For ten fluids immersion tests are conducted with technical elastomeric materials. Since the dimensions of the specimens of the FKM-sealing-material are identical to the specimens of the SRE, the test procedure is completely comparable to the test procedure of the SRE. Because the specimens for the material of hoses are cut out of hoses, the shapes of the specimens differ, see Figure 3. For calculating the volume of this specimen the length, the thickness as well as the diameter is necessary. Since a measurement of the diameter of deformed specimens is not possible in an accurate way, just dimensional changes in two directions are considered for this specimen.

The results for the elastomeric material of the FKM rotary shaft seals are shown in Figure 7. Results regarding the property changes of the NBR- and FKM-hose-material are given in Figure 8 and Figure 9, respectively.

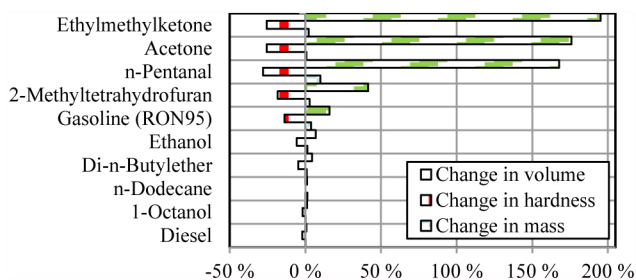


Figure 7. Property changes of FKM-shaft-seal-material

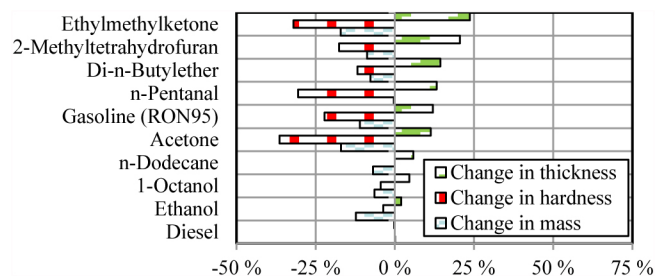


Figure 8. Property changes of NBR-hose-material

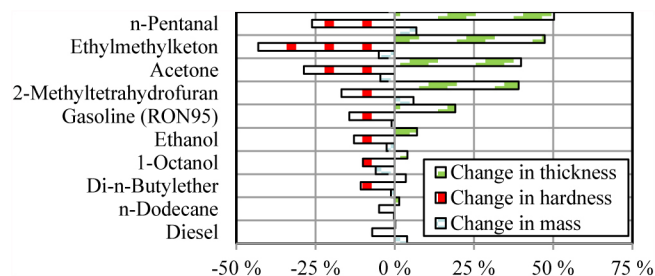


Figure 9. Property changes of FKM-hose-material

In comparison to the SRE no chemical decomposition occurs for the tested fluid-elastomer-combinations. For instance pentanal leads to a decomposition of the FKM-SRE, but not to the FKM-shaft-seal- and hose-material.

Correlation between Reference and Technical Materials

It is of special interest, if there is some kind of correlation between the results of the SRE and the technical elastomers. To address this, correlation studies are presented in the following.

First, the results of FKM-shaft-seal-material and the FKM-SRE are compared. A correlation is visible between the changes in volume, see Figure 10, as well as in hardness, see Figure 11. Furthermore, the scale of both changes is comparable. With 2-methyltetrahydrofuran there is one distinct outlier that leads to considerable less swelling of the technical material (42 %) than of the SRE (150 %).

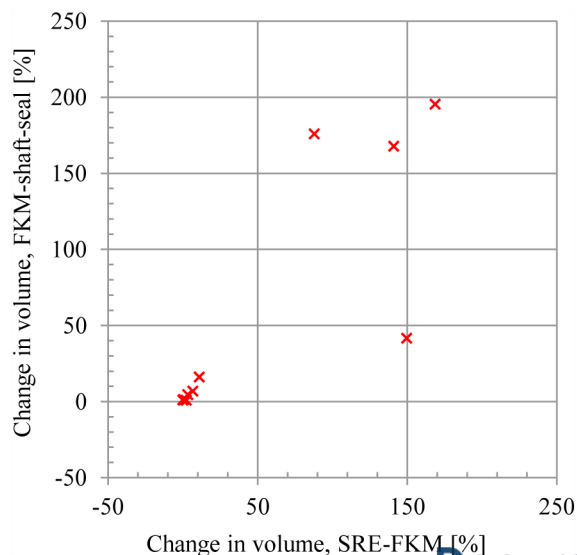


Figure 10. Volume changes of FKM-SRE and technical FKM-shaft-seal-material