Compatibility of sealing materials with biofuels, biodiesel-heating oil blends and premium grade fuel at different temperatures

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Summary

Biofuels including ethanol and biodiesel (fatty acid methyl ester) represent an important renewable fuel alternative to petroleum-derived transport fuels. Increasing biofuel use would bring some benefits, such as a reduction in oil demands and greenhouse gas emissions, and an improvement in air quality.
Materials compatibility is a major concern whenever the fuel composition is changed in a fuel system. The question arises of whether sealing materials are resistant to fuels with bioethanol and biodiesel (rapeseed oil fatty acid methyl ester).
The aim of this work is to study the interaction between sealing materials such as FKM (fluorocarbon rubber), EPDM (ethylene-propylene-diene rubber), CR (chloroprene rubber), CSM (chlorosulfonated polyethylene), NBR (acrylonitrile-butadiene rubber), IIR (butyl rubber), VMQ (methyl-vinyl-silicone rubber), FVMQ (methyl-fluorosilicone rubber) and PA (polyamide) and biofuels such as biodiesel (FAME, non-aged and 2 years aged), E85 (fuel with 85% ethanol) and B10 (heating oil with 10% biodiesel, non-aged and one year aged) compared with premium-grade fuel at 20 °C, 40 °C and 70 °C for 84 days. Exposure experiments were conducted with specimens of these elastomers to document the changes in the mass and tensile properties of these sealing materials. Visual examination of some test specimens clearly showed a great volume increase until breakage or partial dissolution.
The sealing materials FVMQ, VMQ and PA were evaluated as resistant in E85 at 20 °C and 40 °C with a reduction of tensile properties limited to 15%. None of the examined materials was evaluated as resistant at 70 °C with even fluorocarbon rubber losing 20% of its tensile strength in E85.
When exposed to biodiesel, elastomers were affected in two ways: firstly, by absorption of liquid by the elastomers and, secondly, by dissolution of soluble components from the elastomers into the liquid medium. Swelling was the result of the high absorption by the elastomers CR, CSM, EPDM, IIR and NBR in comparison to their dissolution in non-aged and two years aged biodiesel. FKM, VMQ and PA were evaluated as resistant sealing materials in non-aged biodiesel at 40 °C. FKM was still resistant in aged biodiesel at 40 °C but only to a limited degree at 70 °C.
The sealing materials CR, CSM, EPDM, IIR, NBR and VMQ were damaged to a high extent in non-aged and one year aged B10 as a result of swelling up to 70 °C. FVMQ and PA can be evaluated as resistant in non-aged and one year aged B10 at 20 °C and 40 °C. However, FKM was evaluated as resistant up to 70 °C.
The exposure tests showed that all the elastomers tested were resistant in the premium-grade fuel Super at 20 °C. On increasing the temperature to 40 °C, only FKM, VMQ and PA were resistant to Super. At 70 °C FKM showed the best resistance.

1 Introduction

Biofuels are viewed as a major source of energy. In areas such as the European Union, where 80% of the oil based fuel is imported, there is also the desire to reduce dependence on external oil supplies. It is likely that biofuels will be used for an increasing proportion of the energy required for transportation in the near future. There are two principal types of biofuels currently being used [1]. These are ethanol instead of gasoline and biodiesel instead of diesel. Ethanol is produced from carbohydrates such as sugar cane, sugar beer and corn. Biodiesel is manufactured from oilseeds, predominantly rapeseed, oil palm and soy.

Changes in fuel composition and the introduction of alternative fuels often create problems of corrosion and degradation in materials.

Polymeric materials can suffer from damage or degradation due to the use of ethanol-blended fuels, which is attributable to the absorption of oxygenated hydrocarbons that mainly cause swelling. The amount of swelling depends on the nature of the solvent and the polymer. Besides the tendency of elastomers to swell, contact with ethanol may also alter the tensile strength and breaking elongation, causing weakening, cracking, leakage and brittle behaviour [2].

The polarity of biodiesel increases its solvency and facilitates permeation and extraction. Solvation, swelling and/or extraction lead to changes in the physical properties. Extraction alters the fuel chemistry. These chemical changes could also accelerate the degradation (hydrolysis and oxidation) of the polymeric material with the loss of additives and stabilizers [3, 4, 5].

The aim of this work is to determine the physical and chemical behaviour of different frequently used sealing materials in biofuels such as non-aged and aged biodiesel (FAME), E85 (fuel with 85% ethanol) and non-aged and aged B10 (heating oil with 10% biodiesel) in comparison with premium grade fuel at 20°C, 40°C and 70°C. The first results of the sealing material exposure tests in the fuels at 70°C were published in the paper for EUROCORR 2013 [6].

2 Experimental set-up

2.1 Preparation of test specimens

Vulcanized rubber plates of FKM (fluorocarbon rubber), EPDM (ethylene-propylene-diene rubber), CR (chloroprene rubber), CSM (chlorosulfonated polyethylene), NBR (acrylonitrile-butadiene rubber), IIR (butyl rubber), VMQ (methyl-vinyl-silicone rubber) and FVMQ (methyl-fluoro-silicone rubber) as well as plates of PA (polyamide) were used for the exposure tests. The physical properties of the elastomers are specified in Table 1.

At least five test specimens of each sealing material were cut out of the plates with the following dimensions according to DIN 53504 - Testing of rubber - Determination of tensile strength at break, tensile stress at yield, elongation at break and stress values in a tensile test [7]:

Total length: 110 mm
Breadth at the end: 12.5 mm
Length of the narrow parallel part: 25 mm
Breadth of the narrow parallel part: 4 mm
It should be noted that the thickness values of the test specimens varied.

Table 1: Physical properties of selected elastomers

Elastomer	FKM	FVMQ	VMQ	NBR	EPDM	CR	CSM	IIR
Property								
Density (g/cm^3) ISO 1183 [8]	1.84	1.6	1.18	1.4	1.4	1.4	1.3	1.27
Shore hardness A DIN 53505 [10]	76	70	65	70	68	67	62	57
Tensile strength (N/mm^2) DIN 53504, S2 [7]	12.1	6.8	9.8	15.7	10	8	10	8
Elongation at break (%) DIN 53504, S2 [7]	218	195	470	112	200	250	350	400
Temperature range	-15°C 200°C	-50°C 200°C	-50°C 200°C	-20°C 80°C	-40°C 125°C	-30°C 90°C	-35°C 125°C	-40°C 100°C

2.2 Exposure tests in biofuels and premium grade fuel

Five test specimens of each sealing material were exposed to the biofuels:

- non-aged and two years aged biodiesel produced from rapeseed,
- E85 (fuel with 85% ethanol),
- non-aged and one year aged B10 (heating oil with 10% biodiesel) and
- the premium-grade fuel Super with 5% ethanol

for 84 days at 70°C in specimen jars (diameter: 100 mm, height: 200 mm) with a sufficiently tight lid according to ISO 1817: 2005 – Rubber, vulcanized – Determination of the effect of liquids. The test specimens were fully immersed in the fuels [9].

2.3 Determination of change in mass and visual detection

The test specimens were weighed before and after exposure to the biofuels at the standard laboratory temperature of 23°C. After exposure the test specimens were inspected visually to detect damage such as greater swelling and volume change.

2.4 Determination of tensile properties

The tensile properties (tensile strength and breaking elongation) were determined according to DIN 53504 - Testing of rubber - determination of tensile strength at break, tensile stress at yield, elongation at break and stress values in a tensile test with the tensile testing equipment Zwick Z 005 immediately after exposure at the standard laboratory temperature of 23°C [7].

3. Results

3.1 Change in mass and tensile properties in E85

The weight gain of the test specimens caused by swelling increased with the temperature. The elastomers EPDM, NBR, CR and IIR were damaged by weight loss because ethanol is a solvent. The weight gain was in the range of 3% (FKM, FVMQ and CSM) to 9% (PA) and the highest weight loss was measured for NBR with -6% at 20°C. Increasing the temperature to 40°C, the weight gain was in the range of 3% (FVMQ) to 9% (PA). Further increase of the test temperature to 70°C led to a weight gain in the range of 3% (FVMQ) to 12% (NBR). However, the weight gain of the fluorinated elastomers FKM and FVMQ was at the lower end of this range. IIR test spec-

imens lost 2% and CR test specimens 4% of their original weight at 70℃ (see Figure 1).

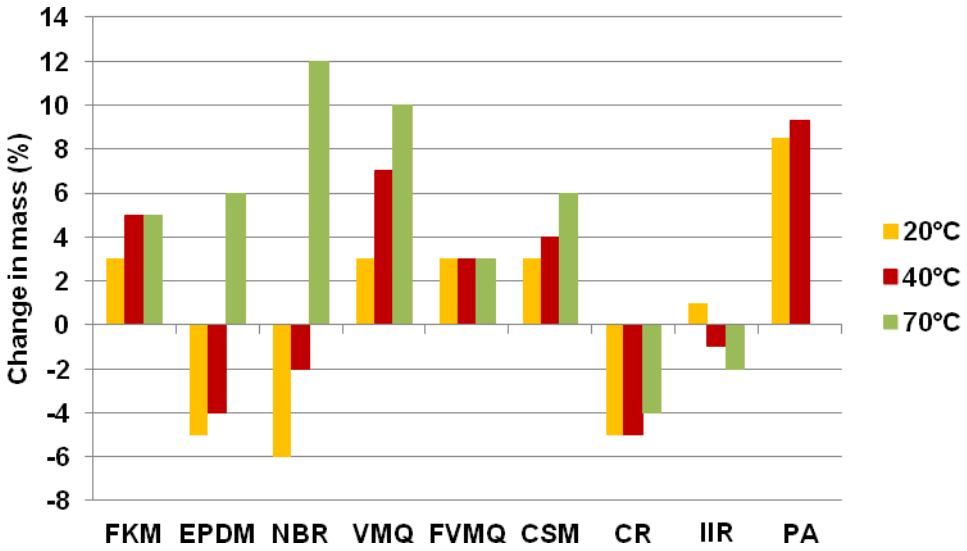

Figure 1: Change in mass of selected sealing materials after exposure to E85 for 84 days

Besides the tendency of elastomers to swell, contact with ethanol affected the tensile properties. Tensile strength decreased by 1% (VMQ) to 25% (CSM, CR) and breaking elongation by 8% (VMQ) to 39% (CR) at 20℃. The reduction in the percentage value of tensile strength and breaking elongation increased with a temperature increase to 40℃ and 70℃. At 40℃ tensile strength decreased by 9% (PA) to 52% (CR, EPDM) and breaking elongation by 6% to 54% (NBR) (see Figure 2). The lowest decreases in tensile strength of 39% and 22% and the lowest deceases in breaking elongation of 17% and 35% were measured for FKM and IIR respectively at 70℃.

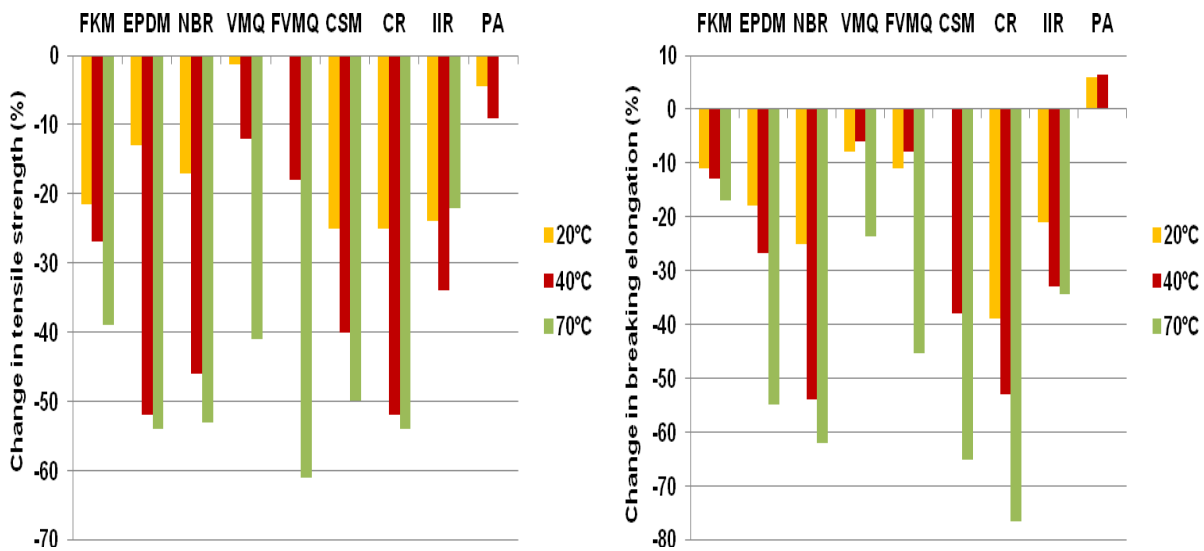

Figure 2: Change in tensile properties of selected sealing materials after exposure to E85 for 84 days

Summarizing the results, it can be stated that most of the sealing materials were damaged by E85, especially at 40 °C and 70 °C. PA showed the best resistance at 20 °C and 40 °C, and FKM and IIR at 70 °C.

3.2 Change in mass and tensile properties in biodiesel

When exposed to biodiesel produced from rapeseed, elastomers are affected in two ways: firstly, by absorption of liquid by the elastomers and, secondly, by dissolution of soluble components from the elastomers in the liquid medium. Swelling is the result of the high absorption by elastomers in comparison to their dissolution in the fuel. Test specimens of CSM, CR, EPDM, IIR and NBR are damaged to a high degree by swelling. The reason for high swelling in these elastomers is their polar nature when they are dissolved in the biodiesel with its polar ester group. Swelling can be retarded by adding cross-linking agents to the elastomers, and peroxides are commonly used in this function.
The weight gain of the elastomers varied between 0.3% (FKM) and 94% (IIR) in non-aged biodiesel and between 0.4% (FKM) and 107% (CR) in two years aged biodiesel at 20 °C. An increasing weight gain with increasing temperature was observed.
Weight gain in the range of 0.5% (FKM) to 164% (CSM) was measured in non-aged biodiesel, and weight gain in the range of 4% (FKM) to 140% (EPDM) was measured in 2 years aged biodiesel. The older the biodiesel, the higher the weight gain was at all test temperatures (see Figure 3).

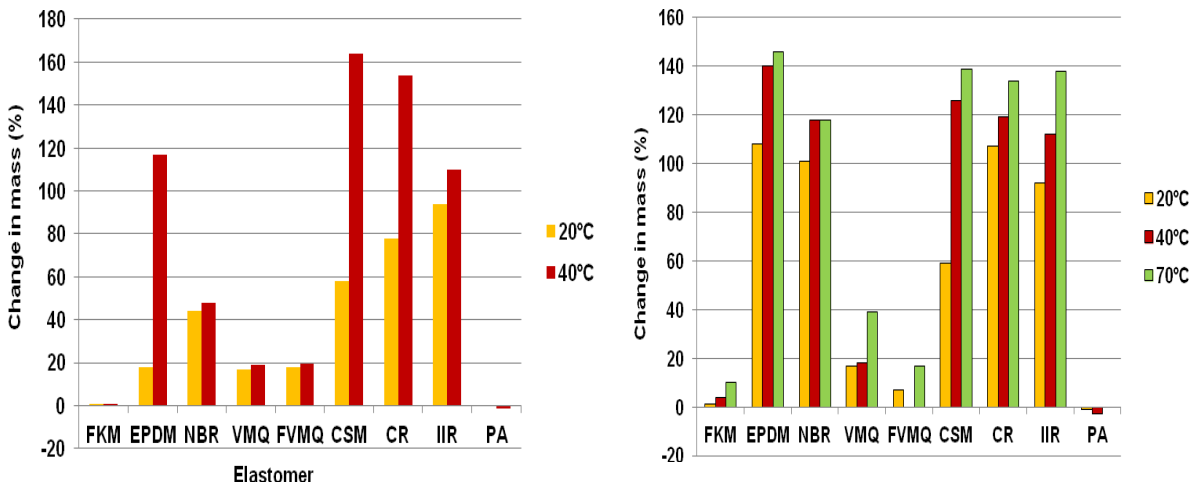

Figure 3: Change in mass of selected sealing materials after exposure to non-aged (left) and two years aged biodiesel (right) for 84 days

The tensile strength and breaking elongation decreased to a large extent in the case of CSM, CR, EPDM, IIR and NBR in non-aged as well as in two years aged biodiesel at 20 °C, 40 °C and 70 °C (see Figures 4 and 5). Together with PA, FKM showed high compatibility with a 0% (20 °C), 9% (40 °C) and 16% (70 °C) loss in tensile strength and a 6% (20 °C) and 8% (40 °C) in breaking elongation in two years aged biodiesel, which was attributed to the absence of polarity. A tensile strength gain of 2% was determined for FKM at 70 °C. The differences between the tensile strength and breaking elongation values after exposure of the FKM and PA test specimens to non-aged and two years aged biodiesel were slight.
The age of the biodiesel was not relevant for sealing materials which were generally not resistant to biodiesel.

The impact on the tensile properties only increased with the age of the biodiesel for VMQ.

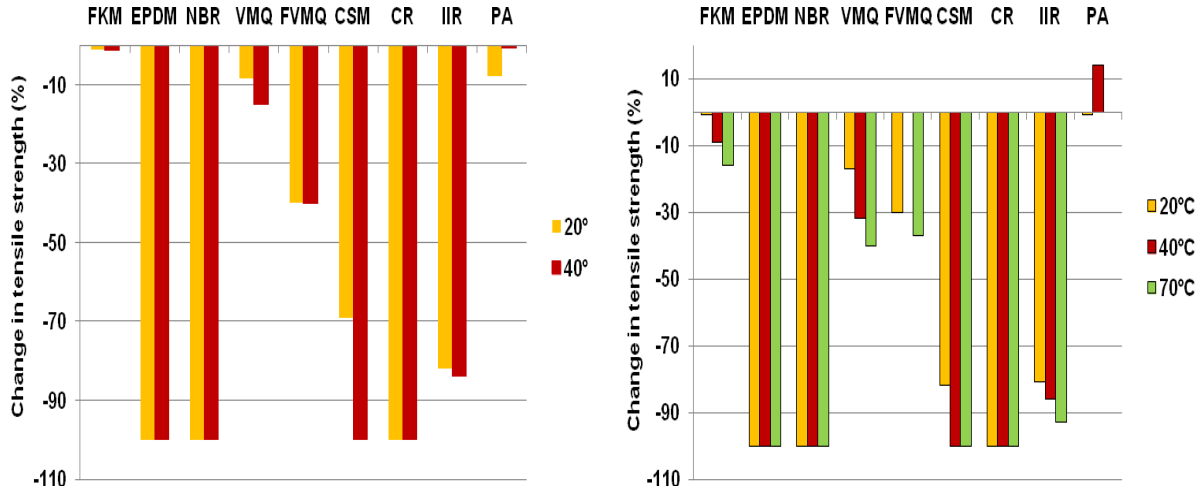

Figure 4: Change in tensile strength of selected sealing materials after exposure to non-aged biodiesel (left) and to 2 years aged biodiesel (right) for 84 days

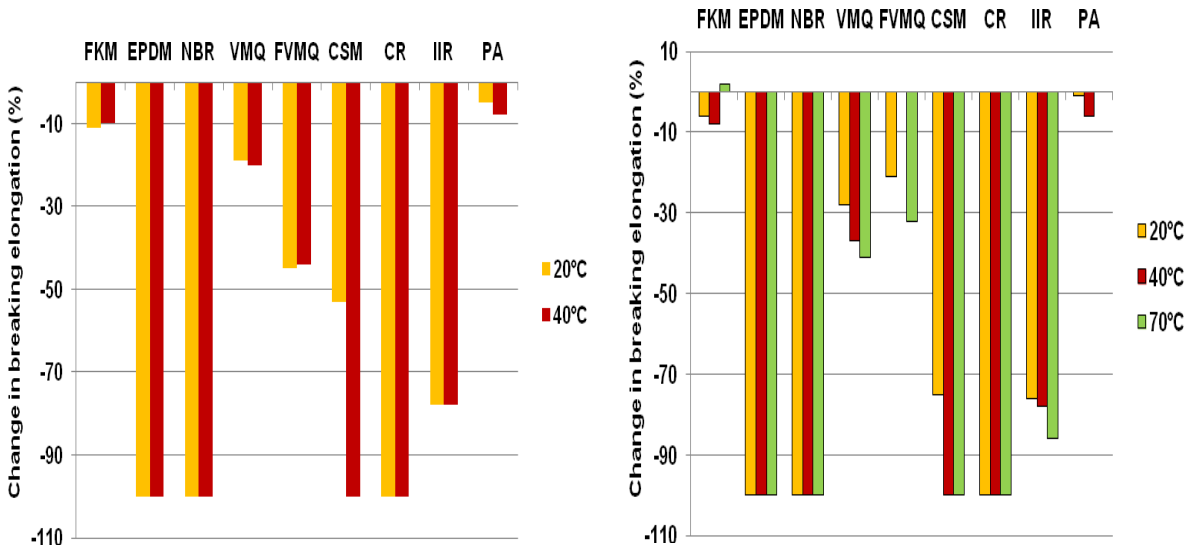

Figure 5: Change in breaking elongation of selected sealing materials after exposure to non-aged biodiesel (left) and 2 years aged biodiesel (right) for 84 days

3.3 Change in mass and tensile properties in B10

Test specimens of CSM, CR and IIR were damaged to a high degree by swelling in both non-aged and one year aged B10, which consists of 10% biodiesel (FAME) produced from rapeseed (see Figure 6).
The highest weight gain as a result of swelling was measured for CR with 240%, IIR with 192%, CSM with 106%, EPDM with 96% and VMQ with 54% in one year aged B10 at 70 °C, while the elastomers containing fluorine FKM (1%) and FVMQ (3%) absorbed much less B10 and swelled less. Weight gain was reduced by decreasing the temperature to 40 °C and 20 °C.

It is apparent that the weight gain of all the elastomers was higher in non-aged B10 than in one year aged B10 (see Figure 7). For IIR a weight gain of 264% was measured in non-aged B10 at 40 °C. The increase in weight in one year aged B10 amounted to 191% at this temperature.

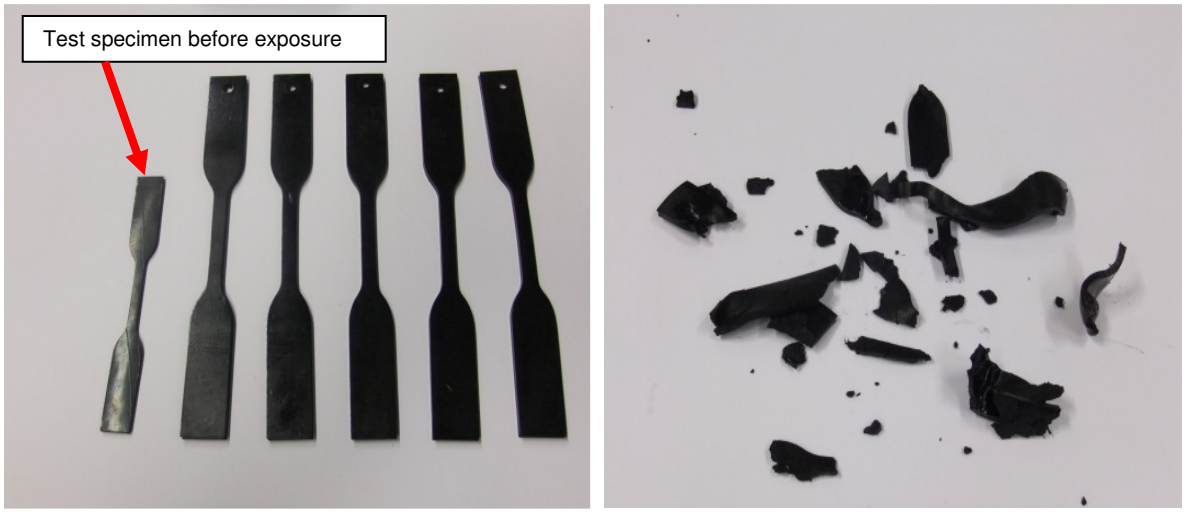

Figure 6: IIR test specimens after exposure to one year aged heating oil B10 at 20 °C (left) and CR test specimens after exposure to non-aged heating oil B10 at 40 °C (right) for 84 days

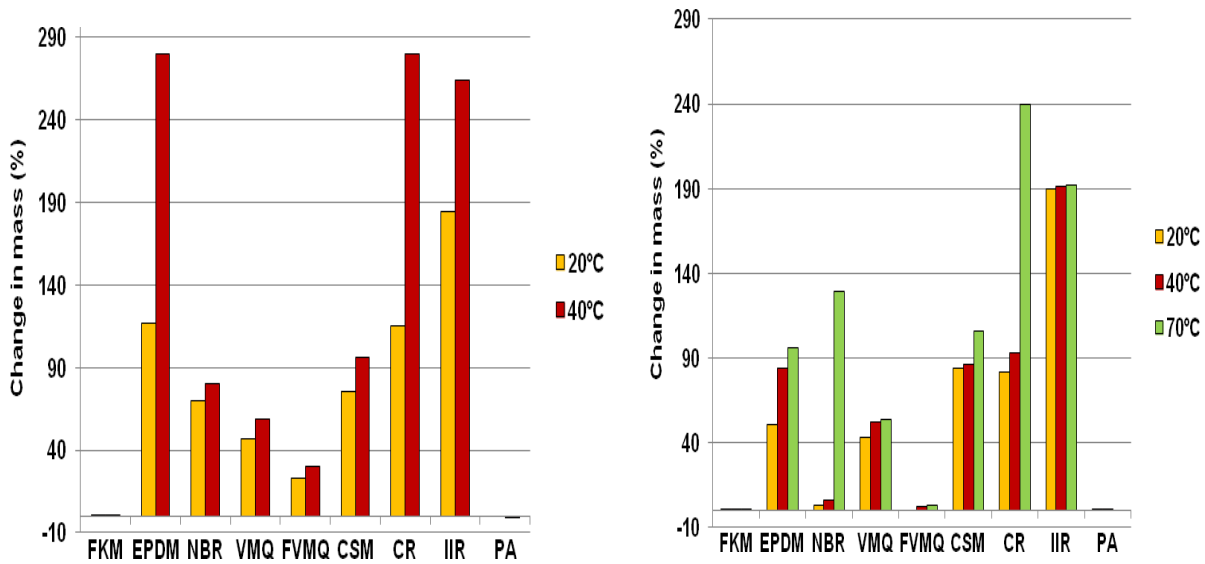

Figure 7: Change in mass of selected sealing materials after exposure to non-aged B10 (left) and to one year aged B10 (right) for 84 days

Test specimens of EPDM and CR disintegrated into smaller fragments after exposure to non-aged B10 at 40 °C. It was not possible to measure the tensile properties of CR test specimens due to the high degree of damage at 70 °C.
The most resistant sealing material FKM lost 0% in tensile strength at 20 °C, 1% at 40 °C and 23% at 70 °C in one year aged B10. FKM breaking elongation values were reduced by 0% at 20 °C, 1% at 40 °C and 16% at 70 °C.
FVMQ and PA can be evaluated as resistant in non-aged and one year aged B10 at 20 °C and 40 °C too because the tensile strength and breaking elongation loss was less than 15%.

As with biodiesel, the less resistant materials CSM, CR, EPDM, IIR and NBR lost 80-100% in tensile strength and breaking elongation in both non-aged and aged B10. The damaging impact of non-aged B10 was higher than that of one year aged B10 (see Figures 8 and 9).

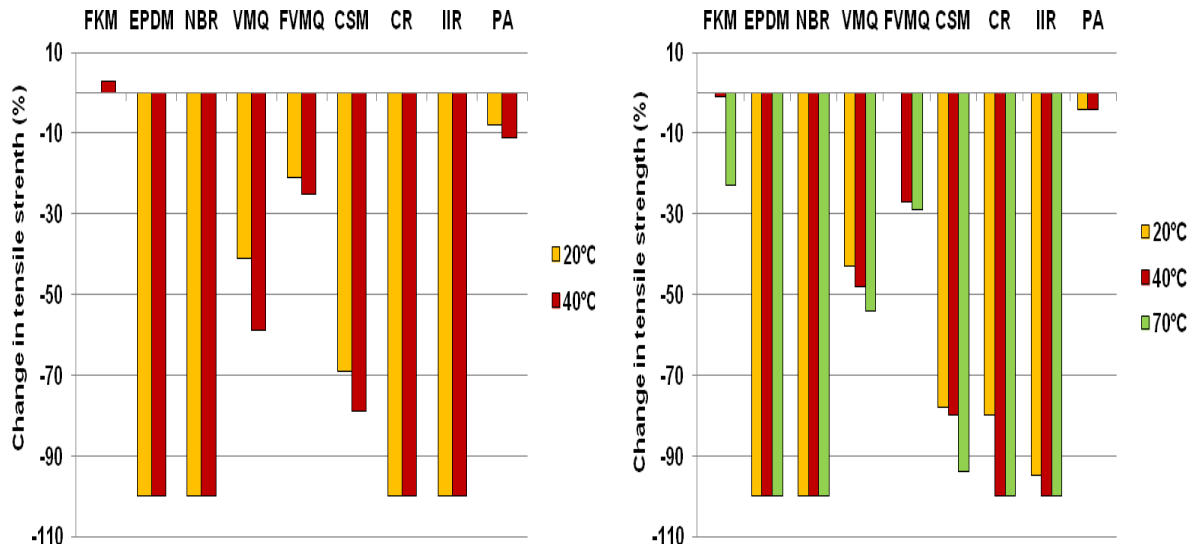

Figure 8: Change in tensile strength of selected sealing materials after exposure to non-aged B10 (left) and one year aged B10 (right) for 84 days

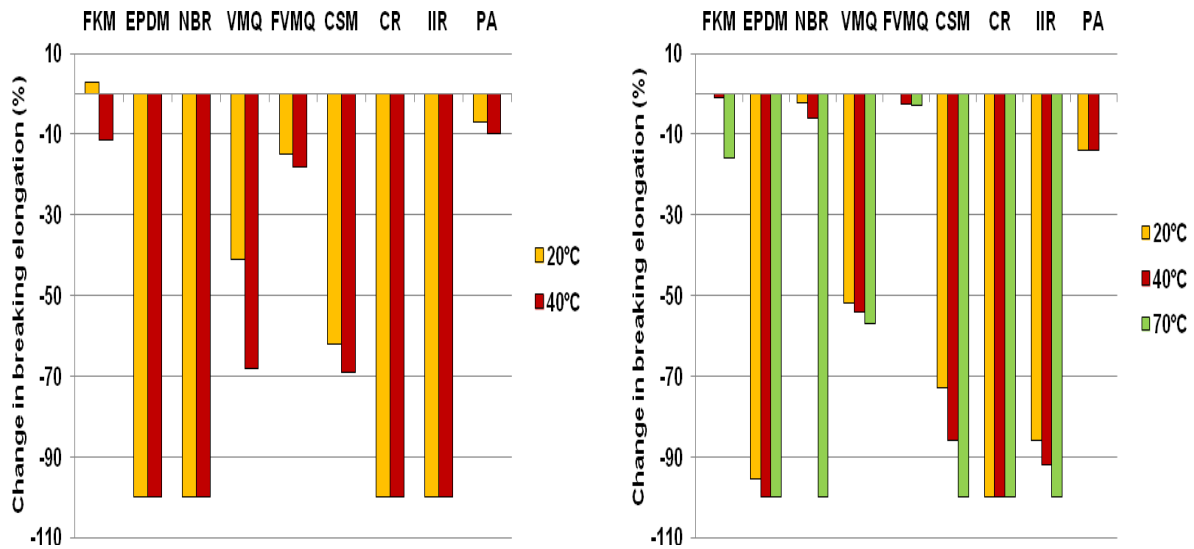

Figure 9: Change in breaking elongation of selected sealing materials after exposure to non-aged B10 (left) and one year aged B10 (right) for 84 days

3.4 Change in mass and tensile properties in the premium grade fuel Super

The premium grade fuel Super contains 5% ethanol, which is a solvent (see also 3.1). It is obvious that the damaging impact on the sealing materials increases with temperature. The weight gain was in the range of 1% (FKM, PA) to 55% (VMQ) at 20°C, 1.5% (FKM, PA) to 70% (VMQ) at 40°C and 6% (FKM) to 102% (VMQ) at 70°C. CR and IIR test specimens were destroyed at 70°C (see Figure 10).
The impact on the tensile properties increased with the temperature. The tensile strength loss was in the range of -4% (PA) to -23% (CR) at 20°C, -2% (PA) to - 49% (CR) at 40°C and -23% (FKM) to -100% (CR, EPDM, IIR and NBR) at 70°C.

Comparable results were achieved for the breaking elongation (see Figures 10 and 11). The exposure tests with PA at 70 °C are still not finished.

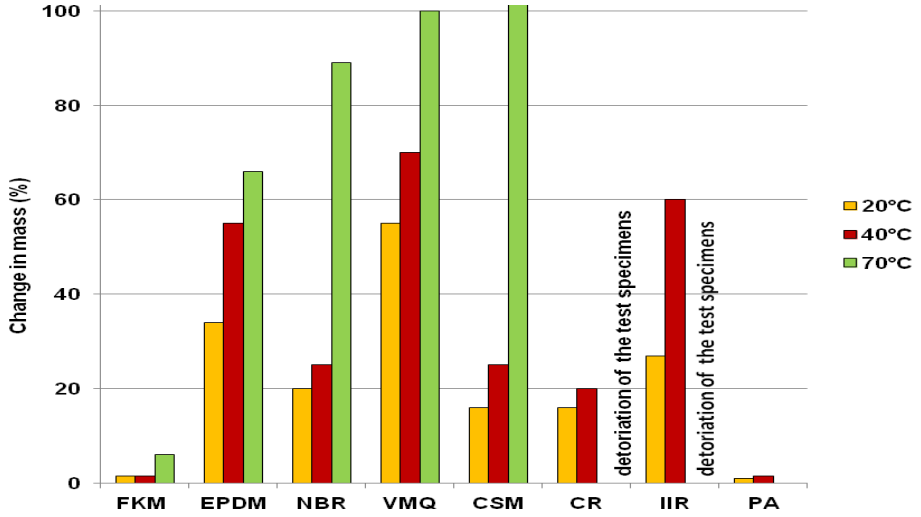

Figure 10: Change in mass of selected sealing materials after exposure to the premium grade Super for 84 days

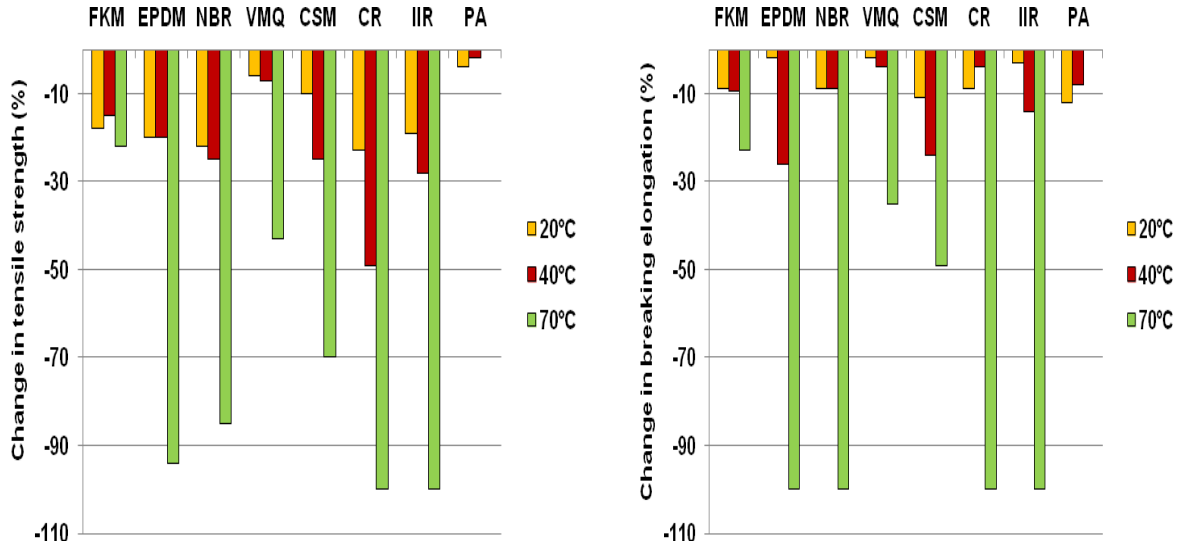

Figure 11: Change in tensile properties of selected sealing materials after exposure to the premium grade fuel Super for 84 days

4. Conclusions

Measurements of the variations in mass and tensile properties after exposure of the nine different sealing materials FKM (fluorocarbon rubber), EPDM (ethylene-propylene-diene rubber), CR (chloroprene rubber), CSM (chlorosulfonated polyethylene), NBR (acrylonitrile-butadiene rubber), IIR (butyl rubber), VMQ (methyl-vinyl-silicone rubber), FVMQ (methyl-fluoro-silicone rubber) and polyamide in E85, biodiesel (FAME), B10 (heating oil with 10% biodiesel) and the premium grade fuel Super showed clearly that FKM was the most resistant material in all three biofuels up to 70 °C. Damage to the materials was lower at 20 °C and 40 °C than at 70 °C. PA was a resistant material at 20 °C and 40 °C (tests at 70 °C are still not completed).

E85 was less aggressive than biodiesel and B10. The lowest decrease in tensile properties was determined for FKM, VMQ and PA, and the highest for NBR, CSM and CR at all test temperatures.
Most of the sealing materials were damaged by E85, especially at 40℃ and 70℃. PA showed the best resistance at 20℃ and 40℃, and FKM and IIR at 70℃.

Biodiesel fuels are easily oxidized and contain acids and water.
The age of the biodiesel was not relevant for the sealing materials CR, CSM, EPDM, IIR and NBR, which were generally not resistant to biodiesel.
FKM and PA showed high compatibility in non-aged and two years aged biodiesel, which was attributed to the absence of polarity.

FKM and FVMQ absorbed much less B10 and swelled less. CR, CSM, EPDM, IIR, NBR and VMQ were not resistant to B10 at all at 20℃, 40℃ and 70℃ as the decrease in the tensile properties was significantly over 50%.
FVMQ and PA could be evaluated as resistant in non-aged and one year aged B10 at 20℃ and 40℃, whereas FKM was resistant up to 70℃.
The damaging impact of non-aged B10 was higher than that of one year aged B10.

The premium grade fuel Super contains 5% ethanol, which is a solvent. The damaging impact on the sealing materials increased with temperature.
Whereas most of the sealing materials were evaluated as resistant in Super at 20℃, CR, EPDM, IIR, NBR and VMQ were not resistant in Super at 70℃. The tests showed that FKM was resistant up to 70℃, and PA was a resistant material at 20℃ and 40℃.

5 References

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