Degradation of aviation sealing materials in rapeseed biodiesel

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ABSTRACT: Nowadays, the airline industry and worldwide companies in the aerospace industry have been forced to find new ecological alternatives to traditional fuels to substitute as aviation fuels and kerosene. In aero turbo engines, rubber seals based on nitrile–butadiene rubber (NBR) with different contents of acrylonitrile are the most commonly used for the production of seals. This NBR is characterized by excellent physical and mechanical properties. In this article, we present the effects of critical operating conditions and the addition of the methyl ester of rapeseed oil to aviation fuel in relation to seals for aircraft engines. In this study, we evaluated changes in the physical and mechanical properties of rubber blends that were produced from NBR rubber. The exact composition and material properties were obtained from the producer. Static immersion tests in B10 (10% biodiesel in diesel), B50 (50% biodiesel in diesel), B75 (75% biodiesel in diesel), and B100 (100% biodiesel) were carried out at a higher temperature (100°C) for 500 h and at laboratory temperature (23 ± 2°C) for 3000 h. At the end of the immersion test, the degradation behavior was investigated by the measurement of the relative changes in the weight, hardness, tensile strength, and elongation. The change in the rubber surface morphology was studied by optimal microscopy and with a digital camera. The results show that the extent of rubber blend degradation was observed for samples that were exposed to a higher concentration of biodiesel and to a higher temperature. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42254.

INTRODUCTION

Biodiesel, which is a relatively clean-burning, renewable fuel produced from new and used animal and vegetable oil, could be used to replace at least a portion of the diesel fuel consumed worldwide. The performance of biodiesel under cold conditions is markedly worse in comparison with the performance of petroleum diesel. At low temperatures, biodiesel forms wax crystals, which can clog fuel lines and filters in a vehicle fuel system.[1] In aircraft applications, biodiesel is in contact with various materials, such as plastic or elastomers. Haseeb et al.[2] investigated the degradation of the physical and mechanical properties of five types of polymers [ethylene propylene diene monomer (EPDM), nitrile–butadiene rubber (NBR), polychloroprene rubber (CR), SR, and polytetrafluoroethylene (PTFE)] with palm biodiesel by static immersion tests in B0 (diesel), B10 (10% biodiesel in diesel), B20 (20% biodiesel in diesel), B50 (50% biodiesel in diesel), and B100 (100% biodiesel). Tensile strength and hardness were greatly reduced in the case of EPDM and CR, but for silicone rubber (Q), PTFE, and NBR, the changes were not so significant. The authors of the mentioned article concluded that the overall sequence of compatible elastomers in palm biodiesel was as follows: PTFE > SR > NBR > EPDM > CR.

Trakarnpruk and Porntangjitlikit[3] investigated the influence of biodiesel on six types of elastomer that are commonly used in fuel systems [hydrogenated nitrile-butadiene rubber (HNBR), NBR, NBR/polyvinyl chloride (PVC), copolymer fluoroelastomer (FKM), terpolymer FKM, and acrylic rubber]. The content of biodiesel in diesel was 1:9. The authors concluded that the properties of NBR, NBR/PVC, and acrylic rubber were affected more than the other elastomers. The copolymer FKM and terpolymer FKM showed little property change.

Chai et al.[4] designed a compression device to evaluate the durability of industrial rubber components exposed to an aggressive environment, for example, oil in a biofuel system during their service. The apparatus was made up of four rectangular stainless steel plates with spacer bars in between, and thus, precompression was introduced for the rubber specimens while they were immersed into diesel. Chai et al. found that swelling in the rubbers increased with increasing palm biodiesel content and decreased with increasing precompressive strain. We also observed that the presence of biodiesel significantly decreased the mechanical strength of the rubber.

Linhares et al.[5] evaluated the resistance of different NBRs in contact with Brazilian biofuels. In this study, samples with different contents of acrylonitrile (28, 33, and 45%) were used. Biofuels were prepared from coconut oil and castor bean oil. The samples with lower acrylonitrile contents (28 and 33%)

Table I. Analysis Report for Methyl Ester of Rapeseed Oil

Test	Method	Units	Result
Density at 15°C	EN ISO 12185	kg/m^3	886.2
Viscosity at 40°C	EN ISO 12185	mm^2/s	4.19
Flash point	EN ISO 3104	°C	184
Cetane number	EN ISO 3679	—	57.8
Total ester content	EN ISO 5165	% (m/m)	96.8
Iodine value	EN 14111	g of I$_2$/100 g	81.52
Acid value	EN 14104	mg of KOH/g	0.013
Sulfur content	EN ISO 20846	mg/kg	<10
Monoglyceride	EN 14105	% (m/m)	0.28
Diglyceride	EN 14105	% (m/m)	<0.05
Triglyceride	EN 14105	% (m/m)	<0.07
Water content	EN ISO 12937	mg/kg	75
Methanol content	EN 14110	% (m/m)	<0.01
Total glycerol	EN 14105	% (m/m)	0.12

showed low resistance to both pure biofuels. The mechanical properties of the NBR composed of 45% acrylonitrile appeared unchanged even after immersion in biodiesel oils.

Haseeb et al.[6] examined the effect of palm biodiesel on the deterioration behavior of elastomers, such as NBR, polychloroprene, and fluoroelastomer which were produced by VITON company (fluoro-VITON). Static immersion tests in B0 (diesel), B10 (10% biodiesel in diesel), and B100 (100% biodiesel) were carried out at room temperature (25°C) and at 50°C for 500 h. The extent of degradation of elastomers was higher for both polychloroprene and NBR, whereas fluoro-VITON exhibited good resistance in palm biodiesel.

EXPERIMENTAL

The tested specimens were made of rubber blends, which are commonly used for the production of rubber seals for aero turbo engines in the aviation industry. We did not change the composition of the rubber blends because our samples were supplied directly by the producer, so the exact composition was known by the producer. These rubber seals were resistant to oil and oil products, and the exact formulation is shown in the literature.[7] The fuel solutions consisted of methyl esters of rapeseed oil (FAME; Merocco, Leopoldov, Slovakia) and aviation fuel (JET A1; Slovnaft, Bratislava, Slovakia). The material data of rapeseed biodiesel are shown in Table I.

RESULTS AND DISCUSSION

Experimental measurements were performed at the Faculty of Industrial Technology in Púchov with the cooperation with the Faculty of Aeronautics, Technical University, in Košice. The object of this study was to investigate the influence of four concentrations of added biofuel FAME into the aviation fuel JET A1 and monitor the impact of such fuel on the rubber blends in aero turbo engines. In our study, the changes in the physical and mechanical properties of the rubber blends were investigated, and moreover, the change in the surface morphology was

observed by optical microscopy and with a digital camera. The rubber blends were exposed to a higher temperature (+100°C) and to laboratory temperature (23 ± 2°C). The samples became brittle at 100°C; therefore, it was not possible to perform tensile testing for them. The fuel composition and conditions of measurement are shown in Table II. These parameters were measured for the rubber blends: the relative change in weight (ISO 1817), relative change in hardness (ISO 48), tensile properties (ISO 37), crosslinking density,[8] and change in the surface morphology by optical microscopy and with a digital camera. The selection of the temperature (+100°C) was based on the simulation of the real operating conditions, which were observed for aviation engines. The samples were cured by sulfur at 150°C for 60 min in the shape of double-sided blades.

Properties of the Rubber Blends Exposed to Fuel Mixtures at Laboratory Temperature

The results of the measurements related to changes in the weight and hardness of rubber blends that were exposed to laboratory temperature (23 ± 2°C) are shown in Table III.

Increasing the volume of FAME in aviation fuel, which had the influence on the rubber blends of a plasticizer, caused a decrease in the rubber seal hardness (Table III). FAME had the influence on the rubber matrix as an internal plasticizer, and thus, the mobility of the macromolecules probably increased. The hardness of the samples had a tendency to decrease with dependence on time in relation to the impact of fuel. This effect was caused by the higher distances between the individual macromolecules, and this problem was closely connected to the plasticizing effect of FAME. The mentioned initial increase was closely connected with the swelling of rubbers, and it included an increase in the total volume of the samples. Subsequently, there was the occurrence of a weight decrease; this resulted in the stabilization of dissolution equilibrium, and this decrease in weight was probably caused by the dissolution and leaching of some soluble parts of rubber seals (mainly nonrubber additives were dissolved). Finally, the weight increased again, and this was caused by the swelling of rubber in liquid, or it could have been caused by the possible chemical reaction of rubber with the liquid. In fuel engines, hydroperoxides that are present in biofuels are decomposed into free-radical products, especially in the
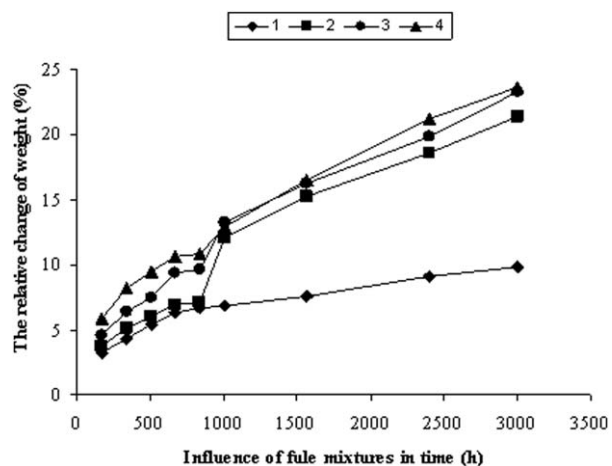
Table II. Test Conditions

Sample	Content of FAME (%)	Temperature (°C)
0	Standard (without the effect of fuel mixtures)	
1	10	23 ± 2
2	50	23 ± 2
3	75	23 ± 2
4	100	23 ± 2
5	10	100 ± 2
6	50	100 ± 2
7	75	100 ± 2
8	100	100 ± 2

**Table III.** Relative Changes in the Specific Weight and Hardness at Laboratory Temperature

Influence of FAME in time (h)	Relative change in weight (%)				Relative change in hardness (%)			
	1	2	3	4	1	2	3	4
168	3.26	3.78	4.56	5.90	0	−6.38	−7.55	−7.60
336	4.32	5.12	6.41	8.20	−2.84	−5.72	−9.43	−10.19
504	5.38	6.09	7.50	9.50	0	−7.51	−9.55	−11.02
672	6.34	6.92	9.35	10.63	1.06	−8.64	−11.69	−11.78
840	6.70	7.14	9.69	10.86	0	−8.64	−12.82	−12.55
1008	6.88	12.11	13.28	12.87	1.06	−11.28	−13.21	−13.30
1560	7.61	15.25	16.22	16.55	−0.70	−12.79	−15.00	−15.45
2400	9.12	18.55	19.82	21.20	−4.97	−14.12	−15.09	−16.72
3000	9.85	21.40	23.33	23.67	−3.55	−15.79	−16.61	−15.58

presence of water, oxygen, and metal ions. These substances are often present in commercial biodiesels. Free radicals bind hydrogen atoms from an alkyl esters chains, and these radicals form allylic radicals. Subsequently, by reaction with molecular oxygen, allylic radicals form peroxide radicals, and these peroxide radicals form allylic hydroperoxides by the elimination of further hydrogen atoms. After the penetration of these hydroperoxides into the structure of rubber blends, carboxylic acid salts, metal halides, and Lewis acids can be formed. These factors can cause the degradation of sealing materials in aviation transport.[9]

As shown in Figures 1 and 2, we determined that sample 1 (with a content of 10 vol % FAME in the aviation fuel) reached the minimum values changes in swelling and hardness. Moreover, the highest hardness changes were observed for samples that were exposed to the fuel mixtures B50, B75, and B100, which represented FAME in aviation fuel (samples 2, 3, and 4). This phenomenon was probably caused by the washing out of nonrubber additives from the rubber blends or by the increase in the filler content in the samples from the aspect of the density of the blends. In comparison with the conventional diesel fuels, esters were characterized by increased polarity, and this polarity also influenced the degradation of the rubber blends.

Shown in Table IV are the results of the mechanical properties of the rubber blends that were exposed to biofuel FAME in the aviation fuel JET A1 at laboratory temperature. The reduction of the tensile properties was caused by the increased absorption of liquid by the rubber and by the extraction of the soluble constituents of the rubber mixtures. In comparison to conventional diesel fuels, esters are characterized by an increased polarity, and this polarity also influenced the degradation of the rubber
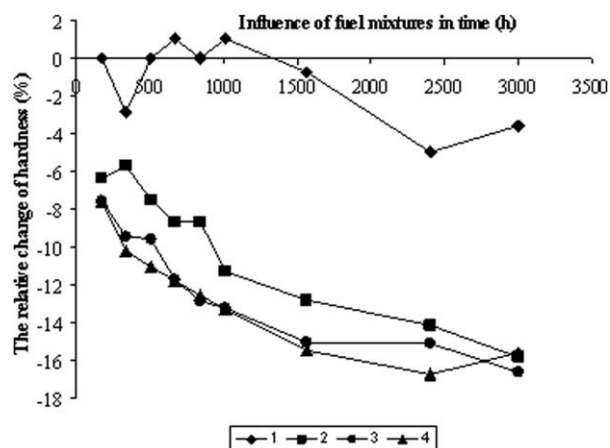
Figure 2. Relative change in hardness after immersion at laboratory temperature.

Table IV. Changes in the Mechanical Properties of the Rubber Blends at Laboratory Temperature

Sample	Tensile strength (MPa)	Elongation (%)	Density (g/cm^3)	Hardness (IRHD)
0	17.9	123	1.344	94.7
1	15.5	128	1.316	89.7
2	13.5	124	1.294	75
3	13.8	124	1.284	73.66
4	12.3	119	1.272	74

IRHD: International rubber hardness degree.

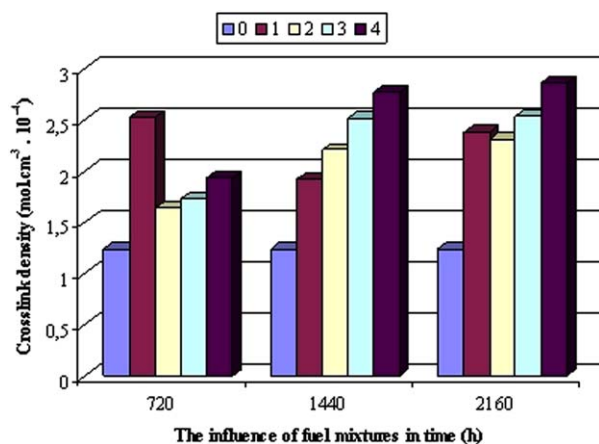**Figure 1.** Relative change in weight after immersion at laboratory temperature.

Figure 3. Crosslink density of the rubber blends at laboratory temperature for 3000 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

blends. A ZWICK/ROEL Z2.5 instrument was used for the measurement of the tensile properties, and the rate of the moveable jaw of this device was 500 mm/min.

The next measurements (Figure 3) showed that the addition of biodiesel to the aviation fuel JET A1 and the long-term effect of
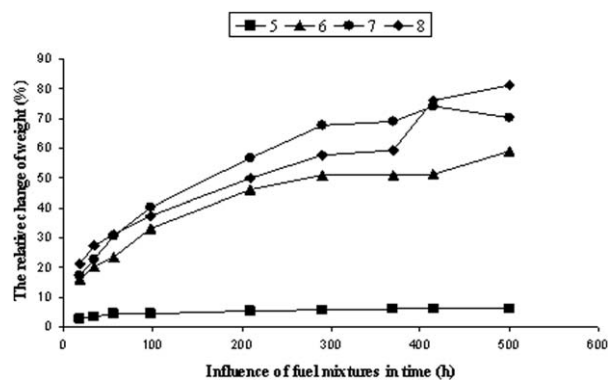

Figure 5. Relative change in weight after immersion at 100°C.

fuel mixtures increased the crosslinking density values. This means that these used samples of fuel did not affect the incurred crosslinking grid directly. There was only the occurrence of the decomposition of the individual components of the rubber mixtures that were used for production of these rubber seals. The values of crosslinking density decreased; this was caused by the damage of rubber chains in the vulcanizate structure under the influence of the penetration of solvent into the polymeric matrix. The three-dimensional spatial grid was formed during the vulcanization, and it was caused by the
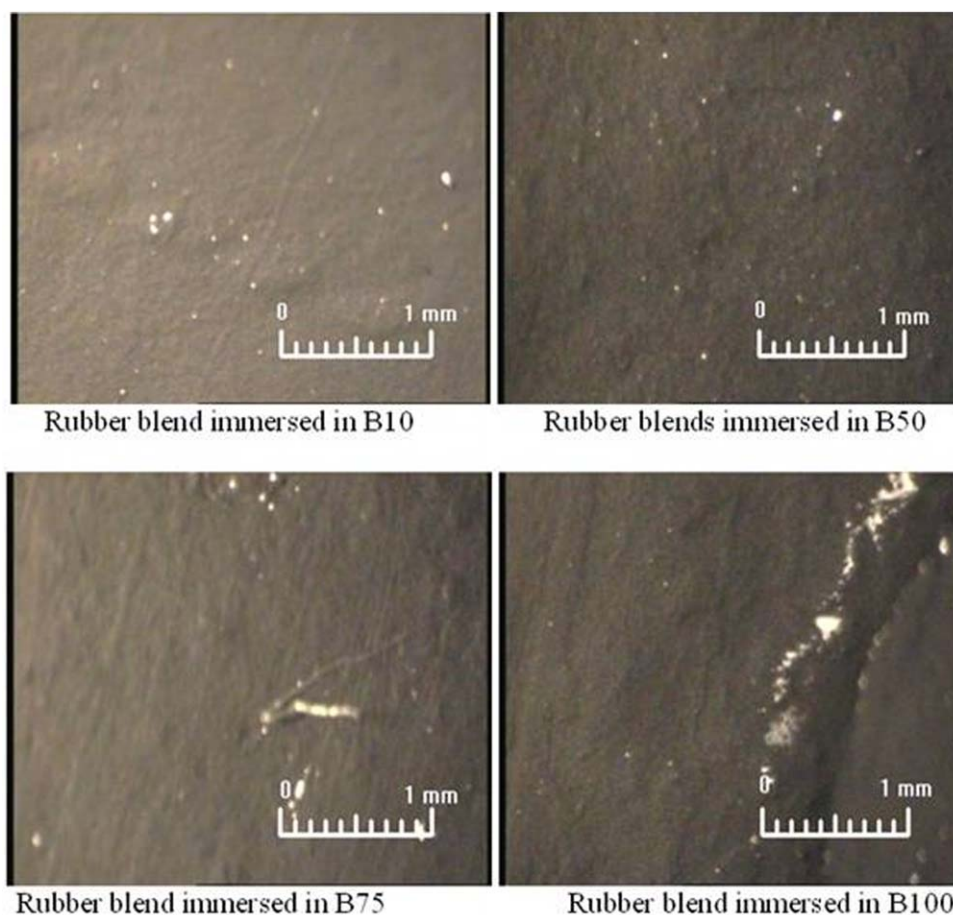

Figure 4. Images of the surface of the rubber blends upon exposure in B10, B50, B75, and B100 at laboratory temperature for 3000 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

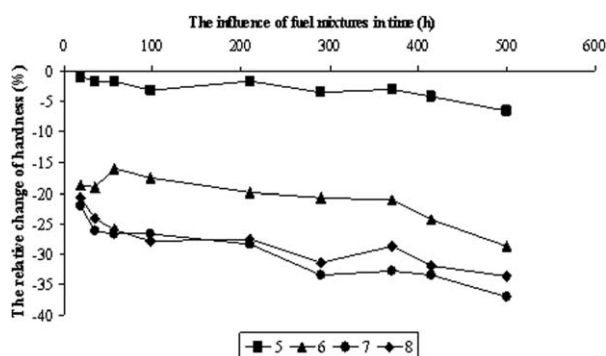**Table V.** Relative Changes in the Specific Weight and Hardness at 100°C

Influence of FAME in time (h)	Relative change of weight (%)				Relative change of hardness (%)			
	5	6	7	8	5	6	7	8
19	2.85	16.25	17.28	21.22	−1.04	−18.70	−22.05	−20.75
35	3.52	20.37	22.75	27.50	−1.73	−19.09	−26.24	−24.15
57	4.49	23.55	30.54	31.24	−1.74	−16.03	−26.61	−26.04
98	4.67	33.21	40.22	37.41	−3.13	−17.55	−26.64	−27.93
210	5.46	46.17	56.66	49.84	−1.74	−19.85	−28.33	−27.54
290	5.83	50.82	67.63	57.85	−3.48	−20.75	−33.44	−31.33
370	6.13	51.01	68.88	59.48	−3.09	−21.13	−32.77	−28.68
415	6.10	51.20	74.25	76.12	−4.17	−24.22	−33.45	−31.88
500	6.25	59.17	70.22	81.23	−6.60	−28.63	−36.88	−33.59

formation of chemical bonds between linear rubber chains. To determine the swelling of our samples, the 1% solution of the antioxidant N-isopropyl-N′-phenyl-p-phenylene diamine in xylene was used to stabilize the rubber chains.[8] The rubber chains were loaded markedly during the process of swelling.

At the end, each sample was thoroughly dried by filter paper, then washed in acetone and investigated by optical microscopy and digital camera. This equipment was used for the investigation of the sample surfaces that were exposed to biofuels at laboratory temperature. The degradation of the surface morphology was not observed for the samples compared to that at higher temperature. Photographs of the rubber blends used in our test are shown in Figure 4. The surfaces of the rubber blends were investigated at a magnification of 20×. The worst results were observed for samples that were immersed in pure biodiesel. The degradation of the sample surfaces was not observed, and this corresponded to previous studies, where the authors presented that the optimum addition of biofuel into aviation fuel was up to 30 vol %.[10–13]

Properties of the Rubber Blends Exposed to Fuel Mixtures at 100°C

The rubber dumbbell shapes became brittle and shiny (it was easy to break them) after 500 h, and during the mentioned time, the rubber blends were exposed to a higher temperature and liquid mixtures of biofuel FAME with aviation fuel JET A1.

Therefore, it was not possible to perform tensile tests for them. In the pure biodiesel at higher temperature, a higher extraction of soluble constituents occurred in comparison to that at laboratory temperature (Figure 5).

In comparison to the conventional diesel fuels, the esters were characterized by increased polarity, and this polarity also influenced the property deterioration of the rubber blends. The change in the weight of the rubber blends was within the range 6–85 vol %, and this was much greater than that at laboratory temperature (Table V).

The most significant change in weight was observed for samples 6, 7, and 8, which were exposed to fuel with the addition of 50, 75, and 100 vol % FAME, and this means that the mixture of biofuel and aviation fuel and the higher temperature had a destructive influence on these rubber blends (Figure 6).

The decrease in hardness was approximately the same for both test conditions, and there was not any substantial effect on the hardness by fuel composition. Shown in Figure 7 is a photograph of the rubber blends that were exposed to the pure rapeseed biodiesel at 100°C. According to the mentioned facts, the higher temperature accelerated the degradation of these rubber blends.

Figure 6. Relative change in hardness after immersion at 100°C.
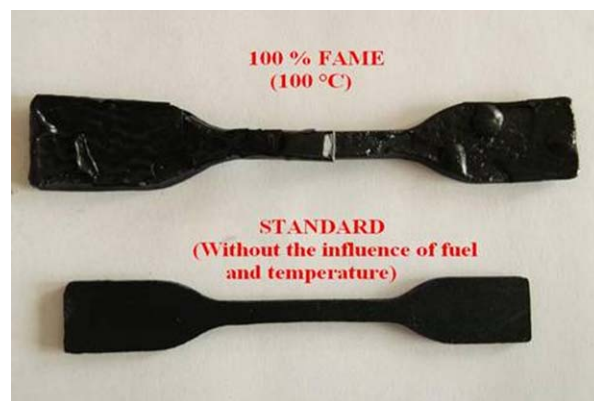
Figure 7. Photograph of the rubber blends that were exposed to pure rapeseed biodiesel at 100°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
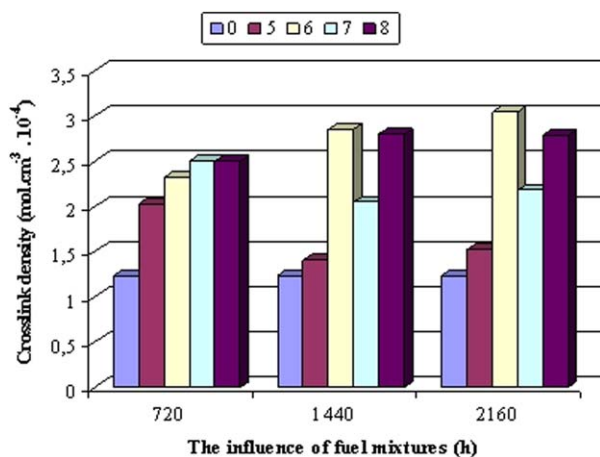
Figure 8. Crosslink density of the rubber blends at 100°C for 500 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The value of the crosslinking density of the standard sample, designated as 0, was 1.24×10^{-3} mol/cm^3. The crosslinking density increased at 100°C and was attributed to the fact that the vulcanization curve showed a growing tendency. Therefore, it was possible that the elevated temperature (100°C) had a permanent influence on the vulcanization network (Figure 8).

Shown in Figure 9 are the rubber blends that were exposed to the fuel with biofuel addition and the higher temperature. These blends showed more pits and cracks at 100°C than those exposed to laboratory temperature. The reason for the formation of pits and cracks was attributed to the macromolecular chain scission, crosslinking, or introduction of polar oxygen groups into elastomers. The surfaces of the rubber blends were investigated at a magnification of 45×. According to Ueberreiter,[14] rubber sealing materials can be dissolved, and this dissolution process could be caused either by the exhibition of a thick swollen layer or by extensive cracking. This depended on how fast the osmotic pressure stress that built up in the polymer matrix was relieved.

CONCLUSIONS

The degradation of rubber materials in biofuel mixtures was investigated by a static immersion test. In addition to focusing on the impact of the FAME content in fuel, we also paid attention to observing the changes in the properties of the rubber blends at laboratory temperature (23 ± 2°C) and a higher temperature (+100°C), and these changes were connected with the more complex simulation of real conditions of the blend use. Upon exposure of the rubber materials to the addition of FAME in the aviation fuel JET A1 at high temperature (100°C), more pits and cracks were formed than at laboratory temperature.[15] The surfaces of the samples exposed to biofuels were
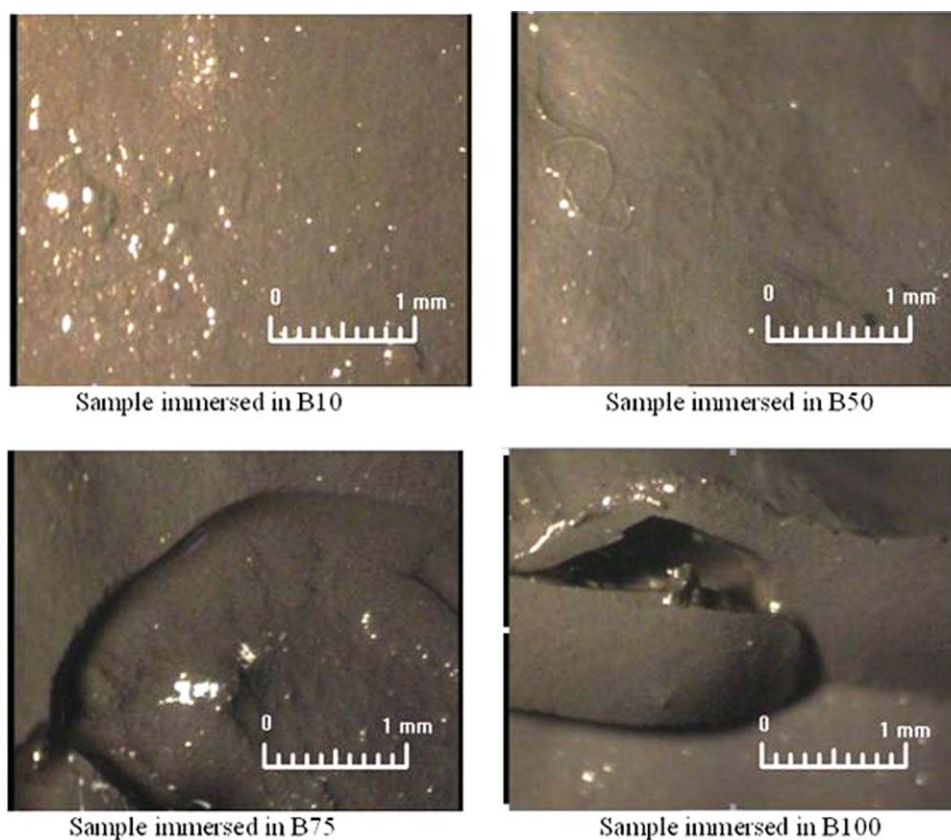

Figure 9. Images of the surface of the rubber blends upon exposure in B10, B50, B75, and B100 at laboratory temperature for 3000 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

investigated by optical microscopy and with a digital camera. The degradation of the surface morphology was observed at the higher temperature. The results show that a higher temperature accelerated the destruction of rubber sealing materials when there was an increase of the FAME content in the fuel. The worst results were reached for samples that were immersed in the pure biodiesel.

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