Palm and soybean biodiesel compatibility with fuel system elastomers

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The present study aims to investigate the impact of biodiesel on the degradation behavior and sealing ability of elastomers such as nitrile rubber (NBR) and fluorocarbon (FKM). Pressurized tests were carried out with biodiesel of palm and soybean oil and a system piston-cylinder of steel SAE 1045. The fluid pressure applied was 200 bar and the time test was 5 h. The results showed a decrease in mass of the NBR for all biodiesels. Upon exposure into biodiesel, both tensile strength and hardness were reduced but in different proportions for biodiesels tested. FKM exhibited good resistance to degradation and keeping its swelling ability. The surface of elastomers was a little modified showing pits and cracks.

1. Introduction

Recently, environmental degradation and the exhaustion of fossil fuels have increased the amount of research about alter-
native fuels. Biodiesel is one of the most used alternatives to solve this problem. It is renewable, biodegradable, non-toxic, and has properties similar to diesel fuel; however, it does not have sulfur and aromatics in its composition [1–4].

The biodiesel is defined as the mono-alkyl esters of vegetable oils or animal fats, produced by transesterification reactions. Vegetable oil mainly consists of triglyceride molecules which give oil its high viscosity. Due to the high viscosity of neat vegetable oils, they are not used as fuel. They cause operational problems in diesel engine, such as formation of deposits in fuel nozzle, because of the poorer atomization upon injection into the combustion chamber [1,4]. In order to reduce the viscosity to make the fuel usable in a diesel engine, neat oil is converted into three mono-
alkyl esters (three separated long chain carbon molecules) by transesterification (see Fig. 1). Normally this reaction is carried out using methanol in basic homogeneous catalysts which is faster than acidic catalysts [5]. The glycerol formed as product is removed.

There are many potential vegetable oils used as sources of biodiesel, they include soybean oil, sunflower oil, cottonseed oil, rapeseed oil, etc. [6–12]. Differences between diesel and biodiesel are due to their variation of chemical nature. Diesel is composed of hundreds of compounds boiling at differing temperatures while biodiesel contains a few compounds—primarily C16–18 carbon chain length alkyl esters (depending on the vegetable oil) [1,4]. The composition of a fuel has significant influence on its properties.

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Besides advantages showed before, the biodiesel has higher flash point and cetane number. In addition, it provides better lubricity as compared to that of diesel fuel [13–15]. The performance and emission characteristics of biodiesel engine are decisive. Combustion of biodiesel fuel in general produces lower smoke, particulate matter, carbon monoxide and hydrocarbon emissions than diesel, while the engine efficiency is either unaffacted or improved [3,10]. However, compatibility of biodiesel materials is being considered as a rising concern [1,3]. Due to its composition and unsaturated molecules, it is more oxidative and causes enhanced corrosion and material degradation.

In automobile applications, biodiesel has contact with various kinds of materials, which can be grouped in three major categories: (1) ferrous alloys, (2) non-ferrous alloys, and (3) polymers. Metallic materials can suffer corrosion and wear in contact with biodiesel. Polymers like plastics and elastomers can undergo degradation because of biodiesel use [3]. Currently, nitrile rubber (NBR), polychloroprene (CR), ethylene propylene diene monomer (EDPM), silicone rubber (S) and fluorocarbon (FKM) are the most common elastomer materials used in gasket, fuel hose, and o-ring. As compatibility of elastomers in biodiesel is the aim of this paper, some studies about this issue are furthermore discussed in this paper.

Bessee and Fey [16] evaluated the influence of different blends of methyl soyester and diesel on mechanical properties of elastomers, such as hardness, tensile strength, elongation and swelling. They verified that nitrile rubber, nylon 6/6, and high-density polypropylene exhibited change in mechanical properties listed above while Teflon, VITON 401-C, and VITON GFLT were unaffected.

Trakarnpruk and Porntangjittikit [5] investigated the biodiesel impact on six types of elastomer properties commonly found in fuel systems (NBR, HNBR, NBR/PVC, acrylic rubber, co-polymer FKM, and terpolymer FKM). The biodiesel was mixed with diesel to prepare B10 (10% blended with diesel). The study demonstrated...
little impact on the properties of co-polymer FKM, and terpolymer FKM, assuring consumer confidence in using B10.

Haseeb et al. [2] studied the degradation of different elastomers in palm diesel. After immersion tests, they verified that some properties like tensile strength, elongation, and hardness were significantly reduced for both nitrile rubber and polychloroprene while little changes were found for fluoro-VITON.

Also, Haseeb et al. [17] investigated the comparative degradation of physical properties for five types of elastomers (EPDM, NBR, CR, SR and PTFE) with palm biodiesel by static immersion tests in B0 (diesel), B10 (10% biodiesel in diesel), B20, B50 and B100 (100% biodiesel). Tensile strength and hardness were greatly reduced for EPDM and CR, but for SR, PTFE, and NBR the changes were not so significant. They conclude that the overall sequence of compatible elastomers in palm biodiesel is to be PTFE > SR > NBR > EPDM > CR.

All investigations above and others not mentioned describe static immersion test investigating the diffusion of liquid in stress-free rubber, but few investigations involve the swelling of polymer in the presence of stresses. Most of them deal with the interaction between diffusion of liquid and large deformation without explicitly relating them to cyclic and fatigue response of rubber [18,19]. Chai et al. [20] designed a compression device to evaluate the durability of industrial rubber components exposed to aggressive environment, e.g. oil in biofuel system, during their service. The apparatus is comprised of four rectangular stainless steel plates with spacer bars in between, which are designed so that the pre-compression can be introduced on the rubber specimens while they are immersed into diesel. They found that swelling in rubbers increases with the increase of palm biodiesel content and decreases with the increase of pre-compressive strain. Also, it was observed that the presence of biodiesel significantly reduces the mechanical strength of the rubber.

The present work aims to evaluate the degradation of elastomer used as O-ring in fuel injection system when biodiesel is the fuel. This analysis verified the effect of exposition to fuel and the presence of stresses by a device developed to simulate in elastomer service in fuel injection system. In the other words, the changes in mechanical properties and swelling are investigated.

2. Experimental

2.1. Synthesis and characterization of biodiesel

For synthesis of biodiesel were used soybean and palm vegetable oils, they were dried in oven at 110 °C for 4 h. Transesterification reactions were performed in a batch with a magnetic stirrer. The reaction mixture containing methanol, the catalyst (KOH), vegetable oil (soybean or palm oil), with the molar ration of alcohol/soybean oil/catalyst of 6:1:0.01 and alcohol/palm oil/catalyst of 12:1:0.025, was stirred for 1 h at environment temperature. After this time, the mixture was neutralized and washed many times with distilled water. The separation phase was carried out by gravity in a separator funnel and the biodiesel was dried for 4 h at 110 °C.

The density was determined with a pycnometer. The oxidative stability and induction period of biodiesel were determined by Rancimat method following the standard EN 14112. The humidity and acid value was determined by ASTM D671 method. The flash point was determined by ABNT NBR 14598.

Also, blends with diesel were prepared in proportions of 5 and 20% (B5 and B20). The diesel used was S50 from Petrobrás (50 ppm of sulfur).

2.2. Tribological test

The tribological system of injection pump was simulated by a device designed in order to observe the interaction between diffusion of biodiesel and deformation in elastomer during the service. Fig. 2 shows the device used to simulate the tribological contact.

The device has the following features:

- The compression was evaluated using a 1045 steel cylinder. A preload of 2500 N was applied in the cylinder. This load was determined in preliminary tests and it is the minimum load that should be applied in order to avoid opening of the system with expansion generated by the pressurization of fluid.
- Two types of O-rings were tested: NBR and FKM, both with inner diameter of 36.5 mm and thickness of 3.5 mm. These elastomers were chosen because they are the most common O-rings used in injection fuel system in Brazil. The NBR 80 (hardness 80 Shore A) is a nitrile compound with medium percentage of acrylonitrile from Mannefion and the FKM is a copolymer with 66% of fluorine, cure system is bisphenol, and its hardness is 75 Shore A from Parker Co. The O-rings were compressed by the cylinder.
- All devices were submitted to fluid pressure of 200 bar for 5 h. This pressure was determinate with preliminary tests and it corresponds to 80% of the breaking pressure of the elastomer with low pressure resistance, the NBR in this study. The test time was chosen in order to verify the effect of compression and fluid pressure and not only the diffusion. Also, Seehra et al. [21] carried out swelling test to grades of NBR elastomer and verified that in toluene, the elastomer attains a maximum increase in mass in about 6 h of test and decreases by 4% in about 7 days. On the other hand, with this time, it was possible to evaluate if fast tests are able to analyze the elastomer degradation, once those standards for elastomer compatibility analysis are specific for immersion test with long immersion times.
- The fluids used were diesel, palm and soybean biodiesel, and their blends with diesel (B5 and B20). All the tests were conducted at

![Fig. 2. Device of injection fuel system simulation.](image-url)
room temperature. To ensure repeatability of the results, each test condition was carried out three times.

2.3. Mechanical characterization

The changes in mechanical properties of the O-rings were evaluated by measurement of tensile strength and hardness, before and after the tribological tests. The hardness value of the sample was determined using a Kori durometer in Shore A scale. The indentations were made every 45°, in intervals from 0° to 270° for raw samples and interval from 0° to 180° for tested samples.

The value of tensile strength was measured according to ASTM D412 (strain rate of 500 mm/min and load of 5 kN) by using MesdanLab dynamometer.

2.4. Swelling measurement

The swelling of the elastomers was evaluated according to ASTM D3616. The samples were cut into strips of less than 1 mm in thickness and of about 5 mm long. They were immersed in different solvents (diesel, biodiesel and blends described in 2.1) for 100 h, room temperature of 25 °C and dark. About 0.4 g of the prepared sample were distributed over the screen that was placed into the borosilicate weighing bottle. To ensure repeatability of the results, at least three specimens were used to perform each test.

The mass changes were measured using a sensitive balance with accuracy of ± 0.1 mg. The weight change was determined by the weight of initial and final elastomers mass. The mechanical characterization was not done because of the small size of samples.

The mass loss was evaluated after drying of elastomers. They were kept in an oven at 108 °C for 24 h and were weighed afterwards.

3. Results and discussions

Biodiesel and its blends were tested to evaluate their impacts on the performance of elastomers in fuel injection system, more precisely O-rings. The compatibility between biodiesel and elastomers were discussed by mass changes, mechanical properties loss and microstructural change.

3.1. Biodiesel characterization

Important properties of the biodiesel produced from palm and soybean oil (B100) were found out and compared with that of diesel (Table 1). They were evaluated according to the ASTM or EN standard methods and the results are in accordance with ANP (Petroleum Brazilian Agency) regulations for biodiesel (B100).

Table 1

<table>
<thead>
<tr>
<th>Property</th>
<th>Methods</th>
<th>Diesel</th>
<th>B100 soybean</th>
<th>B100 palm</th>
<th>Limits *(ANP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 28 °C (kg/m³)</td>
<td>Pycnometer</td>
<td>853.8</td>
<td>855.0</td>
<td>887.1</td>
<td>850–900</td>
</tr>
<tr>
<td>Humidity (%/m)</td>
<td>ASTM D671</td>
<td>1.595</td>
<td>1.04</td>
<td>0.035</td>
<td>0.05</td>
</tr>
<tr>
<td>Viscosity (mm²/s) at 40 °C</td>
<td>ASTM D 445</td>
<td>2–5</td>
<td>0.35</td>
<td>153</td>
<td>≥100</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>ABNT NBR 14598/2007</td>
<td>64.7</td>
<td>130</td>
<td>153</td>
<td>&gt;60</td>
</tr>
<tr>
<td>Acid value (mg KOH/g)</td>
<td>ASTM D 664</td>
<td>0.373642</td>
<td>1.01107</td>
<td>≤0.8**</td>
<td></td>
</tr>
<tr>
<td>Oxidative estability (h)</td>
<td>EN 14112</td>
<td>12.2</td>
<td>≤6.0</td>
<td>≤47</td>
<td></td>
</tr>
</tbody>
</table>

** ASTM D6751.

3.2. Swelling of O-rings

Fig. 3 shows a comparison of different elastomers in terms of their changes in weight upon exposure in different biodiesel and its blends by swelling (Fig. 3a) and pressurized (Fig. 3b) tests. For both conditions, with the increase of biodiesel concentration it was possible to observe an increase in the weight of NBR for both biodiesels (soybean and palm), while for FKM this behavior was lighter; these weight changes were kept almost constant for all fuels studied. NBR elastomer changes in weight are higher in biodiesel (B100) when compared to those in diesel (B0). This increase in weight due to swelling resulted from the extent of more liquid absorption as compared to the extraction soluble components from elastomer [5]. On the other hand, the causes of light change in weight for FKM can be attributed to the absorption of lighter elements like diesel or biodiesel and at the same time, dissolution of soluble components such as plasticizers, stabilizers or additives from the elastomers. In addition, the increasing of cross-linking also limits the degree of polymer swelling by providing tie-points (constrains) that limit the amount of solvent that can be absorbed into the polymer [2].

Another important aspect is that different biodiesels of different sources (soybean and palm oils) that show the same behavior of swelling, so it is possible to conclude that little differences in raw oil composition and consequently biodiesel composition do not affect the swelling ability of elastomers.

Fig. 3b shows the changes in weight for different elastomers when tests under stress conditions (pressurized tests). The FKM keeps its weight almost constant for all fuels studied, type of
biodiesel and its blends are compatible with O-rings of FKM. On the other hand, the NBR proved susceptible to bio-diesel, increasing the biodiesel concentration the weight change increases. This behavior is similar to that obtained in immersion test. However, a reduction in weight change was observed, probably this fact is not only function of the diffusion time but the stress applied to system. Chai et al. [20] observed that the fuel uptake is affected by the compression with compressive stress leads to a decrease in the swelling of elastomer. The results of weight change agree with other works. After 30 days of immersion, Chai et al. [20] found a weight change of 3% and 7% for NBR immersed in palm biodiesel blends with 25% and 100%, respectively. The low weight change observed for FKM agrees with results presented in the literature [2,5].

Swelling in rubber is a purely mixing or interdiffusion process with no chemical attraction between rubber and liquid molecules [21,20]. The principle behind the swelling of the elastomer is “like dissolves like”, polar substances are more likely to dissolve in polar solvents [2]. Due to higher polarity of biodiesel than diesel, the degree of dipole–dipole interaction in biodiesel for solute (elastomers) seems to be higher than compared to diesel. The chemical differences between diesel and biodiesel determined this behavior; the esters increase the polarity of biodiesel. Thus, the high polarity of ester components in biodiesel allows the more polar elastomers (NBR) to dissolve to a greater extent. The absorption increases with the similarity between the structure of the polymer and solvent.

Fig. 4 shows mass loss of the elastomers upon exposure in different biodiesel after the drying process. FKM shows a constant behavior to all fuel, it is seen that the FKM has good compatibility, in terms of mass loss, with diesel and biodiesel. On the other hand, NBR was less compatible with biodiesel. The results indicated high NBR mass loss for B100 in both biodiesels. However, this result is more significant for soybean oil biofuel. The causes of reduction in mass for NBR can be discussed in terms of the dissolution of soluble components such as plasticizers, stabilizers, or additives from the elastomers in solvent (biodiesel and diesel). This mass loss for FKM was practically constant in all fuels with more variations about 0.25% observed in soybean oil blends (B5).

3.3. Mechanical properties

Fig. 5 shows the effects of fuel blends on the mechanical properties of elastomers. Upon exposure to biodiesel, both tensile strength and hardness were reduced as compared to that of raw samples. For NBR, hardness in B0 and B100 decreased as compared to that in raw material, but diesel showed higher decrease in value of hardness (about 9 Shore A). This behavior was observed when soybean biodiesel was used. If palm biodiesel is the fuel, the hardness decreases as compared to raw material, but all fuel (B0, B5, B20 and B100) show similar hardness values and they are higher than those obtained for soybean biodiesel and its blends. For FKM, little changes were found. Micallef [22] evaluated the compatibility of 8 types of fluorocarbon elastomers with diesel and a mixture of diesel with 30% biodiesel, the results showed that after 336 h of immersion at 150 °C, the reduction of hardness range from 2 to 4 Shore A, and the similar sample to FKM studied in this present work presented hardness reduction of 2 Shore A as observed for this elastomer in Fig. 5.

In order to understand the biodiesel effect on mechanical properties, it is important to consider that for common elastomers, carbon black and silica fillers can serve to improve the hardness, abrasion resistance, tensile properties and tear strength. The addition of curing agents and accelerators cause cross-linking between the polymer chains or backbone and they also determine the physical properties. According to Haseeb et al. [2] upon exposure of different elastomers into biodiesel, these cross-linking agent and/or filler seem to react with different components of biodiesel and thereby deteriorate the mechanical properties. In addition, hygroscopic nature of biodiesel may introduce water into polymer matrix. Diffusion of water into polymer matrix can also deteriorate the mechanical properties [17].

The strength tensile test was conducted to both elastomers under the same test conditions. Fig. 5 shows the changes in tensile strength for different elastomers and biodiesel. Obtained results show that after pressurized testing NBR loses tensile strength as compared to raw material. Also, different behavior is observed for different biodiesels, palm biodiesel, for example, show smaller losses of tensile strength than soybean biodiesel, mainly in B20 and B100 conditions. In this present study, decrease of tensile strength for NBR is comparatively higher than those for FKM; this may indicate higher disappearing of crosslinking for NBR after immersion into biodiesel. The values of hardness and tensile strength for both biodiesel were similar to raw FKM, indicating more compatibility of FKM with biodiesels studied in this work.

Overall, the results of mechanical properties changes are similar to those shown in swelling ability, so that the absorption of the fuel acts to reduce the mechanical properties of elastomers. Also, as these results are similar to those found for long-term swelling tests, it is possible to evaluate the compatibility of elastomers with fuel using few hours of pressurized test.

3.4. Morphology

The changes in surfaces of NBR after exposure to different biodiesel and their blends (B0, B5, B20 and B100) are shown in Fig. 6. Surface of NBR in B100 shows comparatively more pits and
fewer cracks as compared to other blends and raw NBR. Few changes in surfaces are observed for diesel. However, when high biodiesel concentration is used, the surface becomes more uniform. The cause of this observation can be the fact that elastomer can be dissolved in solvent (biodiesel) either by exhibiting a thick swollen layer or depending on how fast the osmotic pressure stress that builds up in the polymer matrix is relieved [2]. As NBR exhibit a good swelling, in the words, having more solubility in biodiesel, NBR shows more voids in B20 and B100 as compared to that in B0.

The FKM changes in surfaces after exposure to different biodiesel and their blends (B0, B5, B20 and B100) are shown in Fig. 7. The surface of FKM in all palm blends shows comparatively a little more pits and cracks as compared to raw FKM. As observed in NBR, few changes in surfaces are observed for diesel (B0). This fact is due to lower swelling ability of FKM with biodiesel, mainly with palm biodiesel.

4. Conclusions

The following conclusions can be drawn from results obtained to compatibility test of two types of elastomers and biodiesel described in this work, regarding materials more commonly used in fuel injection system in Brazil.

1. Weight change and mass loss for NBR increase with increasing the concentration of biodiesel while for FKM; these remain almost constant for all fuels. Also, little differences in oil raw
composition and consequently biodiesel composition do not affect the swelling ability of elastomers.

2. After compressed test with biodiesel pressurized, tensile strength and hardness were reduced for NBR elastomer while little changes were found for FKM.

3. Degradation of elastomer is due to higher polarity of biodiesel than diesel, this is attributed to carboxylic groups (ester) present in biodiesel composition.

4. Due to exposure to biodiesel, more changes on the NBR surface is observed as compared to those on FKM.

5. The type of FKM studied is more suitable for O-rings in injection system that uses biodiesel as fuel than NBR, due to its good compatibility with palm and soybean biodiesel.

6. Besides the short time of exposure in pressurized test (5 h), it was sufficient to understand elastomer behavior in contact with biofuel and under compressed conditions.

References


