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Palm and soybean biodiesel compatibility with fuel system elastomers

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ABSTRACT

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 alternative 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-akyl 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.

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 unaffected 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-densitiy polypropylene exhibited change in mechanical properties listed above while Teflon, VITON 401-C, and VITON GFLT were unaffected.

Trakarnpruk and Porntangjitlikit [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

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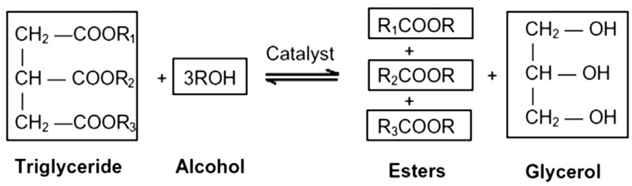

Fig. 1. Transesterification reaction for producing biodiesel (esters) from vegetable oil (triglyceride).

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 Manneflon 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

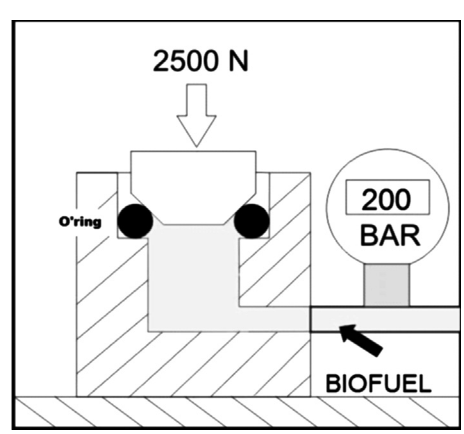

Fig. 2. Device of injection fuel system simulation.