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O-Rings Material Deterioration due to Contact with Biodiesel Blends in a Dynamic Fuel Flow

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Abstract. O-rings are a primary component made from polymeric materials in most diesel engine systems. For oil-fuelled operations, O-rings tend to degrade after exposure to fuel in certain operating condition and periods. Degradation of O-rings can cause engine leakage. This study is intended to test the O-rings material which contacted with biodiesel in dynamic flow by considering the potential deterioration caused. The use of biodiesel may contribute to accelerating deterioration of O-rings. The boiler fuel system was duplicated in this test, where the biodiesel used was palm oil based. The O-rings tested are made of materials of Fluorocarbon elastomer (FKM), Nitrile Rubber (NR) and Silicone Rubber (SR). The effects on O-rings were observed on changes in mass, volume, and thickness. The material compatibility is indicated by elongation, swelling and chemical resistance of elastomers with various fuel flow rates. The fuel flow with high volumetric rate tends to damage the O-rings faster as effected on the immersion test. FKM-Viton performed as materials with the best physical and chemical resistance. Dynamic fuel flow in the engine system showed that SR is deteriorated faster than NBR and FKM. The resistance of O-ring material to fuel in the system is not linearly influenced by the amount of biodiesel in the fuel.

1. Introduction

The increasing interest in the use of alternative fuels instead of the fossil-based diesel fuels has led to the development of a broad range of biodiesel. Recently, biodiesel is widely used as fuel in industrial and commercial machines in the form of blends with petrodiesel at 20-25%. The polymer-biodiesel compatibility has been one of the important issue concerned in biodiesel applications. In the diesel engine fuel system, fuel passes through three subsystems: fuel feed, combustion and exhaust sub-system. The fuel feed sub-system helps to draw fuel from the tank and to deliver it to the injectors of various cylinders. In modern industrial engine machine applications with the principle of rotation, compression and using liquid fuels, mechanical seals play a key role in sealing process fluids in, keeping contaminants out and prevent the machine from failure caused by leakage. Any leakage will reduce efficiency and cause power loss.

One of a practical strategy to prevent leakage is using a proper and compatible mechanical seal or packing. The most common seals used in machine design are O-rings. An O-ring, also known as a packing, is a mechanical gasket in the shape of a torus or doughnut-shaped ring. O-rings may be used in the static or dynamic application, it is used to prevent the loss of a fluid or gas. The seal assembly consists of an elastomer O-ring and a gland. O-ring selection is based on chemical compatibility, application temperature, sealing pressure, lubrication requirements, durometer, size and cost [1]. Polymeric material in the fuel system has high potential to degrade, especially when in contact with oil flow with aggressive properties. Elastomers are vulnerable attack by various chemicals and can undergo degradation of their physical properties and stability in size or shape. As known, polymeric molecules are very large (on the molecular scale), and its unique and useful properties are mainly a result of the molecular size. Any loss in chain length lowers tensile strength and is a primary cause of premature cracking [2].

The interactions with oil fuels can cause physical changes in polymeric materials, especially over long periods and certain thermal conditions. Currently, the most common elastomer materials that are used in O-ring are nitrile rubber (NBR), polychloroprene (CR), ethylene propylene diene monomer (EPDM), silicone rubber (SR), poly-tetrafluoroethylene (PTFE), etc [3]. These are rival materials for their uses in diesel engine fuel systems because of their flexibility, excellent barrier, physical properties and ease of fabrication [4][5].

An important factor in the effectiveness of any O-ring is its ability to remember its shape. Changes to the engine seals particularly on fuel system o-rings then need to be controlled because of material incompatibility with biodiesel and its blends. Degradation behavior of O-rings from three different materials upon exposure to diesel and palm biodiesel in static and dynamic fuel flow was studied in this work.

2. Polymer aging problem caused by biodiesel

There are much convincing research showed that elastomers degrade in biodiesel. Elastomers undergo degradation to a greater extent in biodiesel. The causes of degradation are explained in various perspectives. According to Sem [6], due to the high oxygen content of B100, the ability of Biodiesel (B100) to break down or oxidize rubbers and plastics is enhanced. The hydroperoxides formed during the oxidation of the biodiesel are unstable and attack elastomeric materials. Using biodiesel blends higher than B20 can damage fuel systems components such as hoses and pump seals, which contain elastomers incompatible with biodiesel [7][8][9]. Besides the swelling, biodiesel can also cause structural changes in volume and mass, and changes in mechanical properties such as elongation, hardness, and tensile stress in polymers [4]. The changes in physical properties due to contact with biodiesel are not only originating caused by the molecular structure but because it is very sensitive to some environmental factors [10].

Another factor that can potentially contribute to the deterioration of polymeric materials caused by biodiesel is the presence of acidity, like free fatty acids (FFA), which are present in the triglycerides found in the biodiesel and the presence of water in Biodiesel [11].

Biodiesel is hydroscopic, meaning it attracts moisture. Once it comes in contact with moisture, it can hydrolyze and form a variety of organic acids which are partly responsible for its compatibility problems with a various seal, elastomers, and metals. [8]. The water content in excess quantity in biodiesel is known to cause a potential increase in hydrolysis reactions. The presence of residues of basic catalysts (that can also catalyze the hydrolysis), can also drive the formation of FFA in the biodiesel and increase the water affinity of the biodiesel. Another source of acidity in biodiesel is associated with the oxidation that it can suffer. As it has been established, one characteristic of biodiesel is the poor oxidative stability of the unsaturated fatty acids that comprise the methyl ester [10][11]. The characteristics of the material degradation process depend on the heating rate, polypropylene accelerates the decomposition of the organic matter in the oil.

Many studies conducted to test the effect of biodiesel on polymeric materials. The use of biodiesel can cause the deterioration and degradation of many polymeric materials samples in the form of O-rings and other. Akhlagi [12] found that during the high-temperature autoclave aging, the NBR swelled less in biodiesel, and showed a small decrease in the strain-at break due to the cleavage of rubber chains. The FKM rubbers absorbed biodiesel faster, and to a greater extent, with increasing oxygen concentration.

A study by Beesee examined the performance of polymeric materials in soybean oil and sunflower oil biodiesel by static immersion test at 60^{O}C for 125 days observing a significant weight gain of about 5%. They found that some physical properties of the materials (nylon 6/6, nitrile rubber, and high-density polypropylene), were affected after being immersed in biodiesel blends at 51.7 ^{O}C for 694 h. Teflon and Viton had insignificant changes in physical properties after exposure to biodiesel [13].

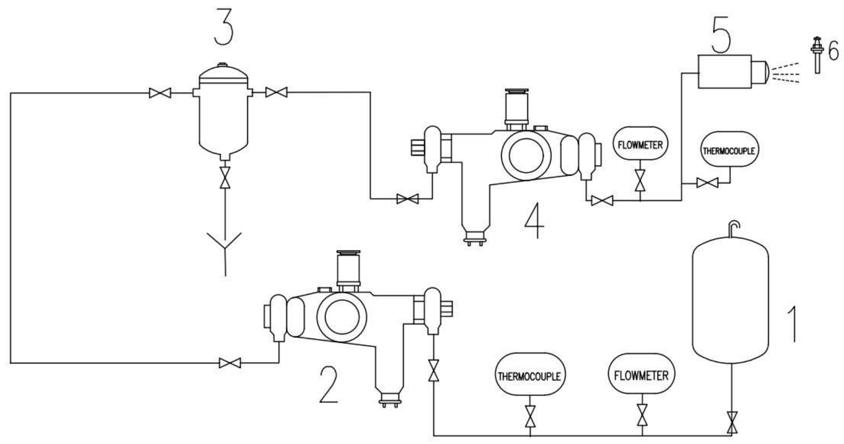
Haseeb et al. [4] investigated the impact of palm biodiesel on the degradation and deterioration of nitrile rubber (NBR), polychloroprene, and fluoro-Viton A by static immersion test at 50 ^{O}C for 500 h. In this work, no significant changes found in the volume, mass, tensile stress, elongation, and hardness for the three polymers tested. From another study, it is stated that the degradation of elastomeric materials occurred due to contact with different mixtures of palm biodiesel and diesel oil at 25 ^{O}C for 1000 hours. The observation on polytetrafluoroethylene (PTFE) showed a reduction in mass and volume, while EPDM (ethylene propylene diene monomer) presented a decrease in hardness and tensile stress in mixtures with higher concentrations of biodiesel [4][11].

An immersion test performed by Bhardwaja et al., [14] at room temperature for 500 hours. Common elastomers like natural rubber, nitrile, chloroprene/neoprene, etc. are not suitable for use in biodiesel. The static immersion tests were conducted in 70 ºC over 672 hours to evaluate the compatibility of various synthetic polymers (PE, PP, PVC, Viton, and SBR) upon exposure to B25 and B50 [14]. Similar compatibility tests were performed on conventional diesel for comparative purposes. The hardness of elastomers (mainly SBR but also Viton) was affected after long exposure periods to bio-oil blends. In contrast, exposure of elastomers to bio-oil blends had a limited effect on breaking strength and elongation capacity of the elastomers. The resistance to degradation of breaking strength and elongation properties in the case of plastic polymers followed the following order: PE > PVC > PP [15].

The loss in mechanical properties of NBR was studied by Trakarnpruk et al. They conclude it might be because of the great affinity of biodiesel for those samples. Biodiesel has been considered to be a good solvent mostly likely because of this affinity; however, this affinity is detrimental to the use of biodiesel in diesel engines [15]. This phenomenon could have caused the substantial decrease in tensile strength, tear strength and hardness of any polymeric samples contacted to Biodiesel [16]. Comparative test on liquid fuel of fossil diesel, biodiesel and blend of those fuels (B30) were done by Rudbahs and Smigins. The tests were carried out at room temperature (20 °C) for 1000 h. The research results showed that O-rings produced from such material as FKM could be not influenced by biodiesel and its blend seriously. The most impacted material was EPDM, which showed an increase in the thickness of O-rings by 30 %, outside diameter by 22 % and reduction of elongation using all types of fuels [17]. Fluorocarbons (Viton) have shown good resistance and are recommended for used in biodiesel based on several tests [14][15][17].

3. Experiment

In this work, the O-rings are taken form the elements in boiler fuel systems, especially from oil pumps and filters. There are 3 (three) types of O-ring materials tested, namely Silicone Rubber (SR), Nitrile Rubber (NBR) and Fluorocarbon Viton (FKM-V). The fuel used is B100, B20, and petroleum diesel oil (B0). Variations in fuel flow rate are set at 150 to 750 mL per minute. Immersion test (static flow) is carried out for a period of 1250 hours. For testing on dynamic flow, the flow rate is controlled by engineering the fuel flow pump and control valve. The scheme for a series of test equipment can be seen in figure 1.



Fuel tank
Fuel Supply Pump
Oil Filter
Injection Pump
Injector
Nozzle

Figure 1. O-rings test apparatus (in Boiler Fuel System).

Physical changes in the O-ring materials are detected through changes in weight, volume, length in thickness test and others. Changes in the O-ring mass are expressed in the following equation;

$$\Delta m = \frac{m_2 - m_1}{m1} \, x \, 100\,\% \quad (1)$$

where: m_2 = mass of sampel after fuel contact (gr), m_1 = mass of sample after fuel contact (gr).
The Elongation E_b was calculated by the formula;

$$E_b = \frac{(C_b - C_{j)}}{C_j} .100\% \quad \textbf{(2)}$$

where: E_b – elongation (%); C_b – end inner circumference of the O-ring (mm); C_j – the initial internal perimeter of the O-ring (mm).

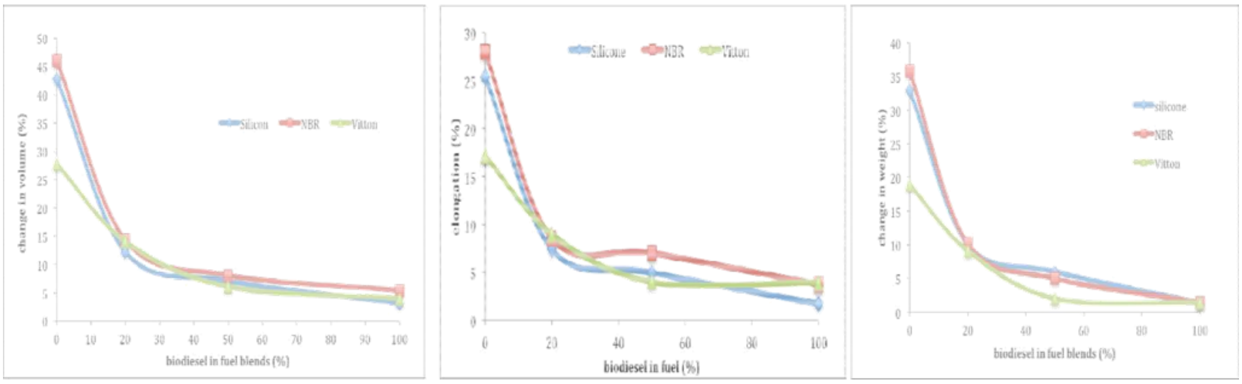
The degradation effects on the polymer were analyzed following ASTM D471, D751, and ASTM D2240. ASTM D471 describes the method for evaluating the effects on the rubber materials caused by exposure to standardized fuels, oils, and other liquids. While ASTM D2240 is taken for Rubber Property-Durometer Hardness and ASTM D751 for Coated Fabrics.

4. Result and discussion

The deterioration of the O-rings was observed after 1250 hours of immersion contact and after operation takes place in 48 hours in dynamic flow. The volume of change is in correlation with swelling and elongation, while, the weight loss is in accordance with the materials abrasion resistance. Chemical compatibility of each elastomer can be determined through the material resistance to each treatment.

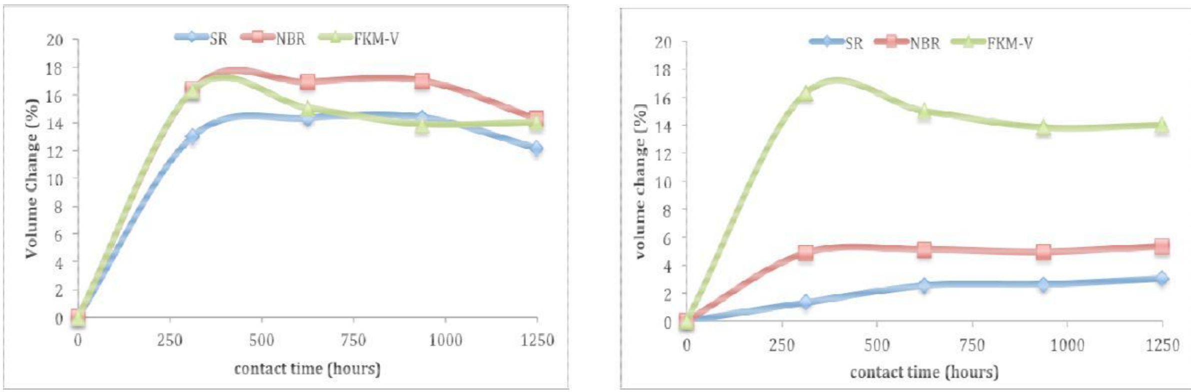
4.1. Physical changes in O-rings in various biodiesel blends

An interesting fact was found that the biodiesel blends with petroleum diesel oil show a larger volume change rather than neat biodiesel. This condition is tested on static/immersion mode for 1250 hours. The immersion of o-rings in pure Biodiesel (B100) turns out to cause a lighter degradation effect than soaking in diesel oil or the blends. This condition may be affected by fuel storage conditions and environmental factors (ambient temperature, air humidity and/or sunlight intensity) to the physical properties of the fuel use during the test.



(a) volume change (b) elongation (c) weight change

Figure 2. Profile of physical changes in O-rings during immersion time contact with B20 (a) volume change, (b) elongation, (c) weight.



(a) B20 (b) B100

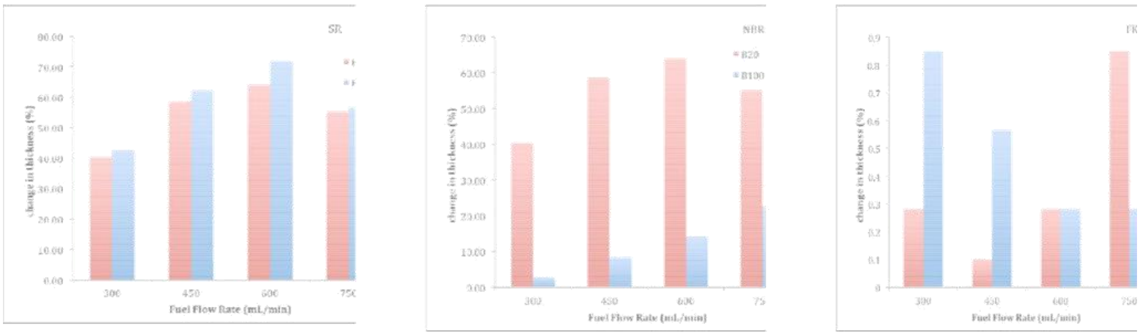
Figure 3. Profile change in O-rings volume during contact immersion time with B20 and B100.

In figure 3, it is clearly shown that the longer fuel contact with O-rings material, the relative volume change will increase mainly in the first contact of 300 hours. The highest volume change occurred in the O-rings made from NBR after contact with B20, while the magnitude of changes in the volume of O-rings from FKM material had the same tendency both when contacting B20 and with B100.

4.2. The changes in O-ring size and elongation at a various fuel flow rate

As seen in figure 4, the changes in O-rings thickness are most evident in SR material. The resistance of SR with B20 and B100 both is much lower than the NBR and FKM. The changes in thickness at SR averaged at intervals of 54-59%, while in NBR is on average of 12-15%. FKM-Viton material shows the best resistance with an average change of 0.35-0.49%.

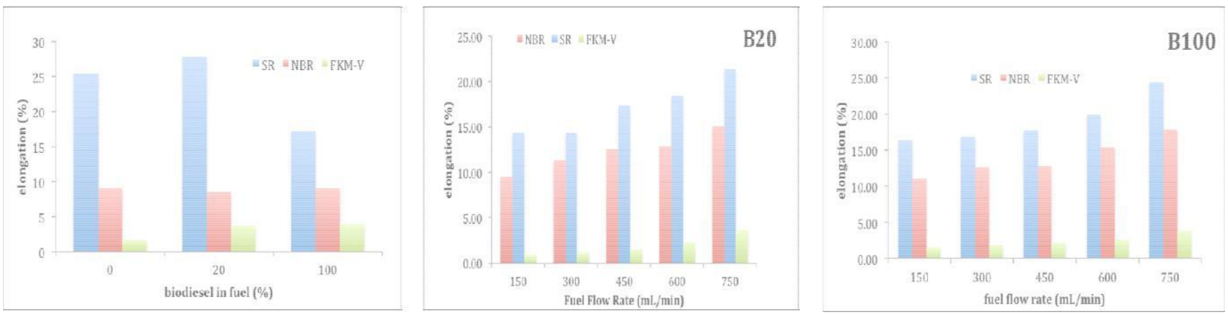
In the NBR-based O-ring, it is found that elastomeric contact with B20 shows a worse effect of physical changes compared to contact with neat biodiesel (B100). It indicates that damage to polymer materials due to fuel contact is not always caused by the high portion of biodiesel in fuel but possibly due to other multiple effects. The chemical resistance of O-ring material to biodiesel, diesel oil, and the blends may not be affected linearly with the amount of Biodiesel in the fuel. O-rings of SR material and NBR which are in contact with dynamic B20 and B100 flow, show a greater volume change effect than B100 in the static flow.



(a) SR (b) NBR (c) FKM Viton **Figure 4**. Changes in O-rings size (thickness) at a different fuel flow rate of B20 and B100.

According to the Chemical Compatibility Guide Rating [2] a change of less than 10% indicates that the elastomer may exhibit slight swelling and/or loss of physical properties under severe conditions. In this test, FKM-Viton showed changes of 0.35-0.5% so that it is recommended for use in oil fuels even with pure biodiesel (B100). Meanwhile, material that shows a change in the 10-30% interval showed that it might exhibit swelling in addition to changing physical properties. This material may be suitable only for static applications. NBR O-rings showed an interval change of 12-16% in both fuel blends.

For changes that are included in the noticeable change category, which shows a change of 30-50%. Under certain conditions, NBR includes materials that may be partially not compatible with oil fuel. O-rings made of SR shows an average change of more than 58% in dynamic flow. This indicates the occurrence of the excessive change. Thus SR has ensured that it is not suitable for the service at all to use diesel oil fuel. These elastomers may not be fully compatible in all applications in fuels blend with low or even without biodiesel.



(a) elongation on different biodiesel blends (b) on different flow rate in contact with B20 (c) on different flow rate in contact with B100

Figure 5. Elongation (%) of O-rings at the different condition of fuel blend and fuel flow rate.

Elongation profiles of various fuel conditions are shown in Figure 4. For o-rings with silicon material, degradation occurs higher after contact with both with B20 than B100, while the NBR and FKM materials are relatively stable, as seen in figure 5(a). This suggests that polymer degradation is not absolutely due to the inherent physical properties of biodiesel but conditionally depends on the interaction of fuel blend and the nature of the fuel at the time of testing (possibly triggered by contamination).

Observations on the O-rings after dynamic flow contact with B20 and B100 show that there is a linear tendency to increase the flow rate with swelling potential in all types of material as seen on figures 5(b) and 5(c). The physical changes resulting from the SR and NBR o-ring contacts on dynamic flow rates are relatively similar to those caused by immersed contacts, which should be expected to be much lower. This condition may occur due to the influence of increasing fuel temperature cause by engine rotation or flow friction so that polymer degradation become faster. On the other hand, it is believed that the degradation of elastomer is sensitive to temperature [18]. In general, immersion of elastomers and contact fuels with higher flow rate increased the percentage of elongation. This can be attributed to the reduced entanglements in the polymeric chains upon contacts. The amount of swelling or volume change depends upon the chemical behaviour of the elastomer.

5. Conclusion

1. O-rings deterioration was found occurred due to engine operation with biodiesel as fuel (B20 and B100). It is detected from a change in volume swell, weight change, thickness change and elongation of O rings.

2. A massive change was found in O-rings made of Silicon Rubber and Nitrile Rubber at the completion of static immersion and dynamic flow test.

3. The shape and rate of deterioration in the three O-rings materials due to contact with B20 and B100 in the static and dynamic flow are relatively in the same pattern. It shows that resistance to chemical abrasion of o-rings material is still not absolute due to the inherent nature of biodiesel.

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