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Compatibility of Elastomeric Parts with High Quality Jatropha Biodiesel (H-FAME)

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Abstract

This study has investigated the effects of high quality jatropha biodiesel called as H-FAME on the compatibility of elastomeric parts. To produce high quality biodiesel, jatropha biodiesel is upgraded by partially Hydrogenated Fatty Acid Methyl Ester (H-FAME) process. H-FAME blended with diesel at 10 % and pure diesel as the reference were used as the test fuels. The immersion test following SAE J1748 in conjunction with ASTM D471 standard was conducted. Commercial elastomeric parts which contact directly with the fuel in the vehicle were selected for immersion test. Viton, neoprene and nitrile butadiene rubber (NBR) were also soaked for comparison. The rubber parts were soaked for 1006 hours. The compatibility was analyzed by the percentage of weight change. The mechanical properties of materials such as tensile and hardness were measured. In addition, the surface structure was monitored by scanning electron microscope.

The results showed that commercial parts seemed to lose the weight while NBR and viton tended to increase. The rubbers which immersed in the H-FAME blend showed more swell than those of diesel fuel. Tensile strength was reduced with the lengthening immersion period and lower for the rubber soaked in the blend when compared with those of diesel. Viton could tolerate well with H-FAME.

***Keywords**:* Material compatibility, H-FAME, Jatropha, elastomer.

1. Introduction

Due to the energy security and environmental problems, alternative fuels such as biodiesel and ethanol derived from sustainable resources have stimulated many researchers to research their application instead of petroleum based fuels. Many researches showed the use of biodiesel in a diesel engine without a substantial reduction in engine performance or requiring engine modification [1, 2]. Higher specific fuel consumption of biodiesel was necessitated, due to its lower heating value, but lower exhaust emissions, such as CO and HC, were emitted [3]. Moreover, particulate matter was significantly reduced while increased NO_X emission was measured [3-5]. As the results, biodiesel has successfully been used in the current commercial engines. However, the application has limited 7 percent of biodiesel to blend with diesel as the maximum percentage according to the warrantee from original equipment manufacturers (OEM).

When replacing diesel with biodiesel, material compatibility is one of the most important issues to consider. Sheet steel showed the pitting corrosion whereas copper and leaded bronze were significantly eroded by biodiesel [6, 7]. The degradations of polymeric materials were investigated when using biodiesel derived from palm, soybean and rapeseed [8-10]. Biodiesel concentrations affected nitride rubber degradation. Higher biodiesel contents, nitrile rubber showed more swelling and lower tensile strength [11]. To improve the resistance of nitrile rubber, the percentage of acrylonitrile was increased [12]. Most of the researches have investigated the base elastomeric materials such as nitride, acrylonitrile butadiene and fluoro-viton. However, there is a few information of the compatibility of commercial parts which added a vast variety of additives to improve their quality.

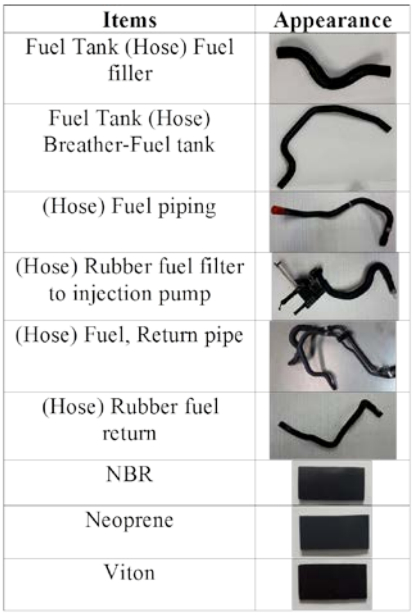
In order to increase the amount in blended fuel, the quality of biodiesel should be improved, in particular oxidation stability which is the major drawback. In addition, non-food biomass has been increasingly interested to produce biodiesel due to food security. Therefore, jatropha was used to produce biodiesel via transesterification process. Then, upgraded by partially Hydrogenated Fatty Acid Methyl Ester (H-FAME) process, high quality biodiesel called as H-FAME has been introduced and investigated its use in vehicles.

The current study has focused on the compatibility of elastomeric materials with high quality biodiesel produced from jatropha. For the purpose of the application in in-use vehicles, commercial parts in the present automotive were used to investigate the degradation. In order to use as the information for the OEM to accept it as a commercial fuel, biodiesel 10 % (B10) has been investigated and compared its effect with pure diesel.

2. Materials and methods

2.1 Elastomeric parts

The elastomeric automotive parts used to test the compatibility with biodiesel are the parts of a commercial light duty pick-up diesel truck, model year 2014. All test specimens were selected from the parts which contact directly with the fuel such as return pipe, fuel filler as shown in Fig 1. Due to the trade secrets, the component of the elastomeric parts could not be identified. Therefore, the specified polymer including acrylonitrile butadiene rubber (NBR), neoprene and viton were also experimented for the comparison.



Items	Appearance
Fuel Tank (Hose) Fuel filler	
Fuel Tank (Hose) Breather-Fuel tank	
(Hose) Fuel piping	
(Hose) Rubber fuel filter to injection pump	
(Hose) Fuel, Return pipe	
(Hose) Rubber fuel return	
NBR	
Neoprene	
Viton	

Fig. 1 Elastomeric parts for material compatibility with biodiesel test

2.2 Fuels

Conventional FAME from jatropha is upgraded by partial hydrogenation which decreases the number of double bonds in its molecule. The upgraded quality process increases the oxidation stability as shown in Table 1 and also detoxes the toxic (Phorbol ester) in jatropha biodiesel. H-FAME was blended with diesel at 10 % in the current study. For the reference, pure diesel (B0) without any additives was investigated as well.

Table. 1 Properties of test fuels

Properties	B0	B10	B100	Method
Density g/cm^3	0.829	0.834	0.876	ASTM D 4052
Acid Value mg/g	0.02	0.06	0.16	ASTM D 664
Gross Heat kJ/g	45.86	45.34	39.93	ASTM D 240
Copper strip corrosion	1a	1a	1b	ASTM D 130/IP 154
Water content ppm	36.76	76.47	385	ASTM D 6304
Oxidation Stability hr.	-	46.25	15.10	EN 14112

2.3 Immersion test

Immersion test, following SAE J1748 in conjunction with ASTM D417 was conducted. Five pieces of each sample parts were completely submerged in the test fuels in the air-tight glass bottles for 1006 hr. The test temperature was controlled at 55°± 2° C throughout the immersion period. The test fuels were replaced every day at first three day and then once a week. The elastomer parts were weighted by means of four digit weight scale with an accuracy of ±1 mg at 0, 22, 46, 70, 166, 670, 1006 h. Apparent percent weight increase is calculated as Eq. (1).

$$\frac{W_s\text{-}W_i}{W_i}\times 100 \qquad (1)$$

where W_s is the weight at measured hours and W_i is the original weight before immersion.

After the immersion test finished, the samples were left to dry by the air. Scanning electron microscope was used to monitor the surface of test specimens.

2.4 Mechanical test

Following ASTM D412 five pieces of NBR, neoprene and viton specimens were prepared for tensile test after the immersion period at 0, 22, 46, 70, 166, 670, 1006 h. Using Instron universal testing machine model 55R4502, the tensile tests were carried out with the strain rate of 500 mm/min. For commercial rubber parts, the specimens could not be shaped as the dumbbell (standard shape). Therefore, the tensile test did not perform.

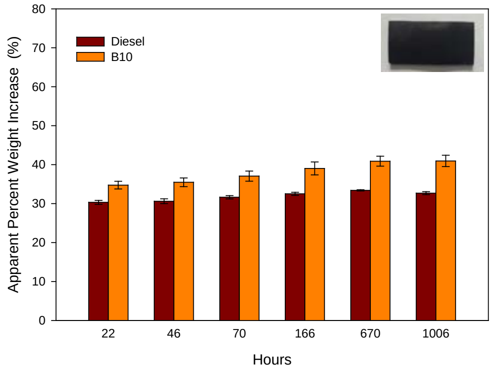
For hardness test, only the dried specimens of NBR, neoprene and viton after immersion duration of 1006 h were investigated according to ASTM D2240 shore durometer type A.

3. Results and Discussions

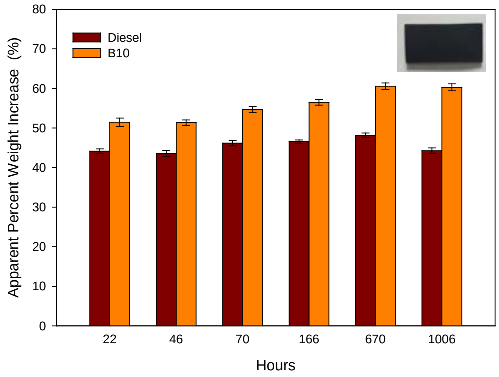
3.1 The changes of weight

Fig.2 shows the changes in mass (weight) of NBR, neoprene and viton rubber which exposed in the test fuels with varied immersion period. The results show that the weights of all elastomer coupons immersed with both fuels increase. Neoprene shows the most swell (~ 40 - 60 %) followed with NBR (~ 30 - 40%) while viton (~ 2 – 2.8 %) seems to resist well with the biodiesel application due to its constituent of higher cross-linking which limits the amount of fuel absorption [8]. The changes in mass could be classified into three regimes including fast absorption, slow linear absorption and constant mass/weight loss. NBR and neoprene show the fast absorption within 22 h after the immersion starts and then linearly uptake fuel until 670 h. Afterwards, the weights of rubbers immersed with diesel indicate the mass loss while the ones exposed to biodiesel remaine constant. In case of viton, the fast increased weights about 2 - 2.8 % occur from 22 to 166 h and then the mass remain almost constant afterwards.

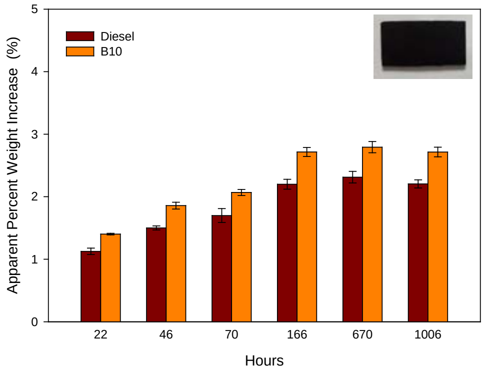
Fuel absorption and the relaxation of the elastomer chains are the cause of the increased weight; hence swelling. Biodiesel shows more apparent percent weight increase than that of diesel. This implies that more liquid biodiesel diffuses into the elastomers. Because of higher polarity of biodiesel from esters molecule, the positive ends of polar solvent (biodiesel) readily attracts the negative ends of solute materials following the rule of “like dissolves like” [8]. As the results, the higher dipole-dipole interaction is formed for biodiesel. Therefore, elastomeric materials exposed to biodiesel present higher swelling than those of diesel; in case of (i) NBR about 4.5 - 8.5 %, (ii) neoprene around 7 – 16 % and (iii) viton 0.3 – 0.5 %.



(a) NBR



(b) Neoprene

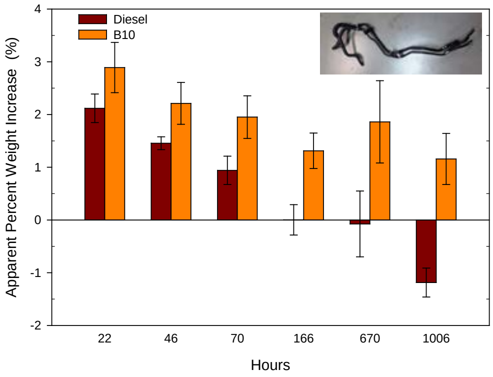


(c) Viton

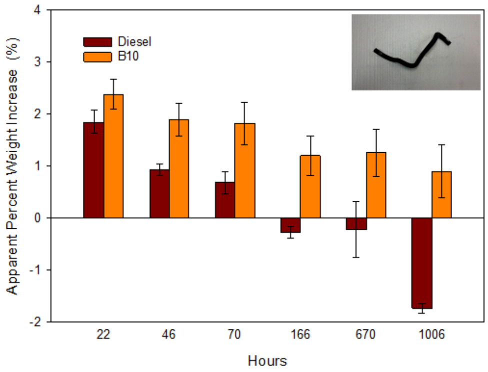
Fig. 2 Apparent percent weight increase of immersed (a) NBR (b) Neoprene (c) Viton

Fig. 3 and Fig. 4 present the changes in weight of automotive rubber parts which exposed in different fuels with varied immersion period. The elastomer degradation could be classified into two characteristics. The first one is shown in Fig. 3 in which the weights of return pipe and fuel return hose increase after the immersion test starts. In contrast, the latter phenomena show the decreased weight of fuel filler, breather-fuel tank hose, piping and fuel filter to injection pump hose as seen in Fig. 4. These two characteristics indicate fuel absorption or extraction process depended on the ingredients of the elastomers.

In case of absorption process (Fig.3), the apparent percent weight increase is increased just after the immersion test starts (22 h) and then it decreases when the exposure time lengthens. As discussed earlier, the process to increase the mass is the same as NBR and neoprene immersion in which biodiesel shows the grater effects. However, for the automotive rubber parts which composed of many substances, the solvent can extract and dissolute the soluble components such as fillers, oil, plasticizers, stabilizers or additives. Their dissolution characteristics are more dominant than fuel absorption. Therefore, the mass of those rubber parts are decreased. Finally, the weights of the elastomeric parts exposed to diesel are lower than the initial value (mass loss) while the ones immersed in biodiesel still increase because biofuel remains in the rubber structure.



(a) Return pipe

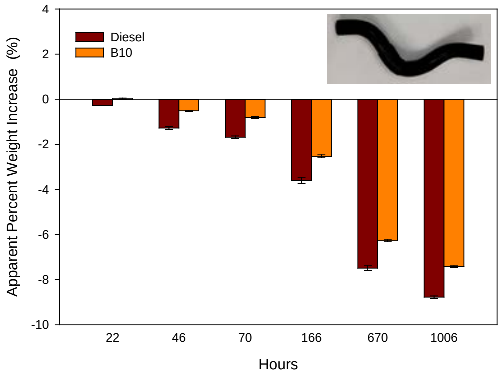


(b) Fuel return

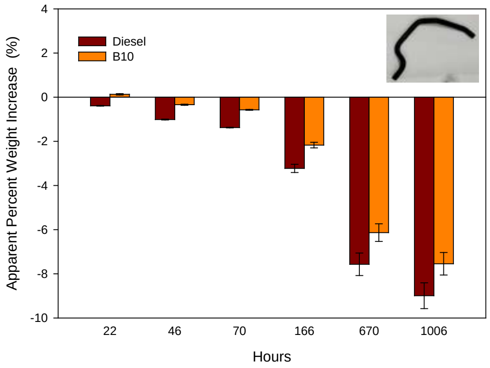
Fig. 3 Apparent percent weight increase of immersed (a) return pipe (b) fuel return

In case of extraction process (Fig.4), the elastomer structure seems to inhibit the fuel diffusion process. Specimens soaked with diesel fuel shows the mass loss more than those of biodiesel cases. There are two plausible explanations for this. For the first reason, diesel could extract the soluble components such as additives from the polymer more than biodiesel. On the other hand, more biodiesel but few amount of diesel diffuse into the rubber and remains in it at the same time as the extraction process occurs. The dissolution process is more dominant than absorption process. As the results, the weight loss of rubber in biodiesel is lower than diesel.

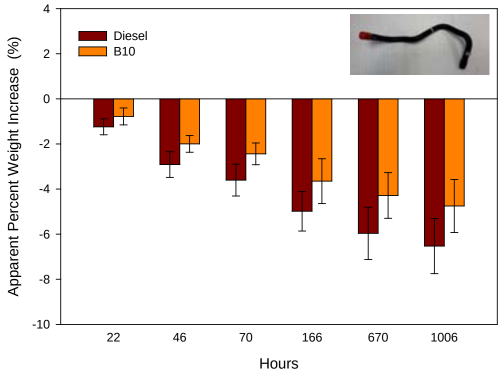
The weight changes of dried rubbers leaved to expose to the air are presented in Fig. 5. The higher weight losses of dried samples when compared to the changes in Fig. 4 indicate the fuel evaporation from the rubbers. Dried weights of elastomers immersed to diesel seem to indicate the higher extractable ability of diesel fuel. However, the current study could not ensure that all of the fuels completely evaporate from the rubber parts. Therefore, further experiment will be continued to clarify the cause.



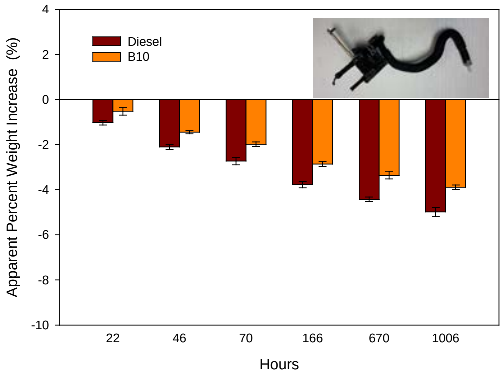
(a) Fuel filler



(b) Breather-fuel tank hose



(c) Piping



(d) Fuel filter to injection pump

Fig. 4 Apparent percent weight increase of immersed (a) fuel filler (b) breather-fuel tank hose (c) piping and (d) fuel filter to injection pump

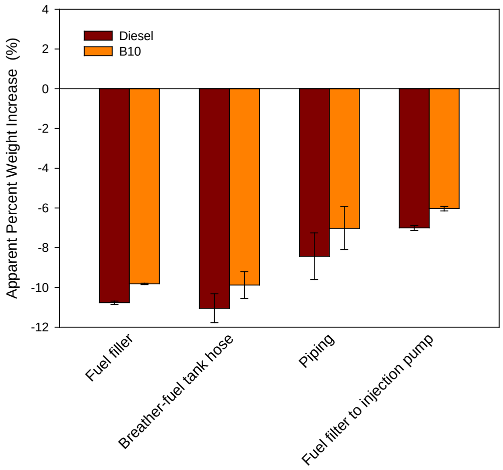
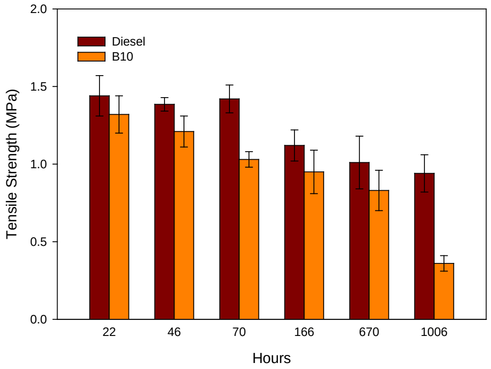


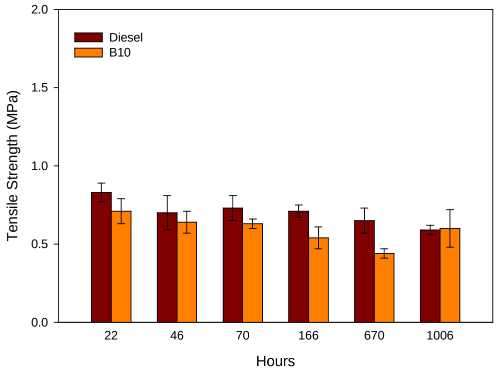
Fig. 5 Apparent percent weight increase of dried rubbers

3.2 The changes of mechanical properties

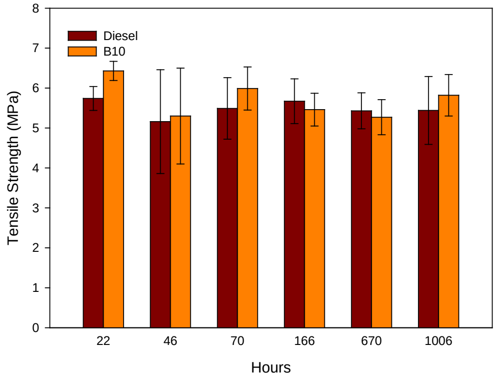
Fig.6 presents the tensile strength of the elastomeric samples which exposed to diesel and B10 with different immersion period. Viton shows the highest tensile strength followed with NBR and neoprene, respectively. When compared with the fresh samples, the tensile strengths of immersed neoprene show the most reduction (~ 80 – 86 %), followed with NBR (~ 65 – 80 %) and viton (~ 10 - 20 %). This correlates well with the changes of mass from the previous section. The higher swelling the lower tensile strength is observed.



(a) NBR



(b) Neoprene



(c) Viton

Fig. 6 Tensile strength of immersed (a) NBR (b) Neoprene (c) Viton

From Fig.6, biodiesel decreases the tensile strengths more than diesel around 6.5 % for NBR and about 2.4 % for neoprene. However, there is no effect of biodiesel shown in the tensile strength of viton. Hence, the effect of biodiesel on the higher weight increase around 0.3 - 0.5 % of viton could not affect its mechanical properties.

The reduction in cross-linking density is the cause of decreased tensile strength [13]. The effective number of network chains per unit volume of rubber decreases with the increased fuel absorption. Because more biodiesel diffuses into the polymeric samples, higher degradation of the rubber network occurs. Consequently, tensile strengths of rubber exposed to B10 are lower than those of diesel.

Fig. 7 presents the hardness value of fresh and dried elastomer exposed to diesel and biodiesel. Without immersion, all fresh rubbers show the similar hardness value. However, the hardness of NBR and neoprene reduces significantly after they are exposed to the fuels whereas slightly reduction is noticed for viton. Biodiesel decreases the hardness of NBR and neoprene more than diesel does. No significant difference is observed between viton exposed to biodiesel and diesel.

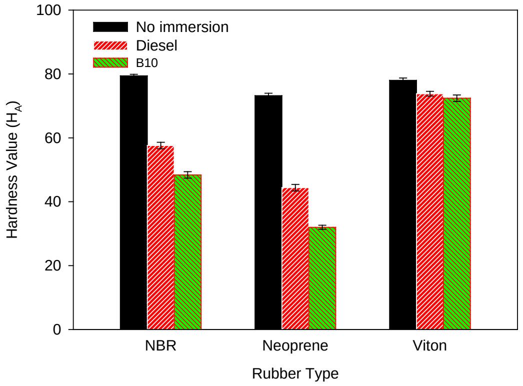


Fig. 7 Tensile strength of immersed (a) NBR (b) Neoprene (c) Viton

3.3 The change of material surfaces

Fig.8 displays the surfaces of fresh (leftmost) NBR, neoprene and viton compared to the ones exposed to B0 (middle) and B10 (rightmost). The spherical features seen in the fresh rubber disappear after the immersion in B0 and B10. These should be the carbon black particles which were found in the test fuels of 1006 h immersion. Hence, the rubbers are dissolved in the fuels. The pits and cracks occurred in immersed NBR and neoprene while viton did not present. However, the difference between B0 and B10 could not clearly notice.

4. Conclusions

The compatibility of elastomeric materials with high quality biodiesel from jatropha in the current study can be summarized as follows:

(1) Depended on the ingredient of elastomer, there are three patterns of material degradations; (i) weight increase due to fuel absorption, (ii) weight loss due to fuel extraction and (iii) weight increase before weight loss. Most of commercial parts showed the weight loss after the immersion test finished but all base rubbers indicated weight increase.

(2) B10 certainly diffused into the rubber materials more than diesel. However, further experiment is required to approve the higher extraction ability of diesel.

(3) The mechanical properties correlated well with the increased weight. Higher fuel absorption, lower mechanical properties were measured.

(4) The degradations of elastomer of commercial parts showed not much different between B0

and B10. Therefore, the use of B10 in the in use vehicles is possible.

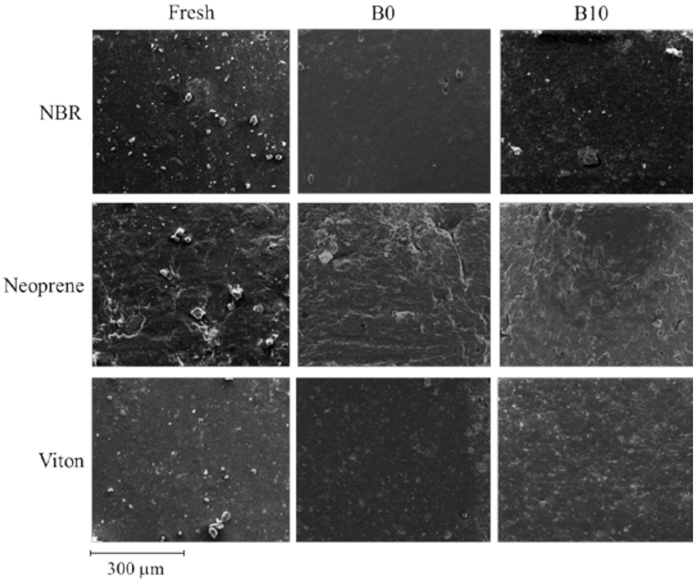


Fig. 8 SEM images of fresh NBR, neoprene and viton and exposed to B0 and B10

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6. References

[1] Laforgia, D. and Ardit,o V. (1995). Biodiesel fueled IDI engines: performance, emissions and heat release investigation, *Bioresource Technology*, vol. 51 , August 1994, pp. 53-59

[2] Mazumdar, B. and Agarwal, A.K. (2008). Performance, emission and combustion characteristics of biodiesel (waste cooking oil methy ester) fueled IDI diesel engine, *SAE Paper* No. 2008-01-1384

[3] Canakci, M. (2007). Combustion characteristics of a turbocharged DI compression ignition engine fueled with petroleum diesel fuels and biodiesel, *Bioresource Technology*, vol. 98 , April 2007, pp. 1167 – 1175

[4] Yomane, K., Asakawa, T., Numao, H. and Komori, M. (2004). Characteristics of DPF for diesel engine fueled with biodiesel fuel - first report: self-regeneration behavior of vehicle road test and engine bench rig test, *SAE Paper* No. 2004-01-1883

[5] Matti, M., Giuliano, J., Szente, J. and Tennison, P. (2010). Effects of B20 versus ULSD fuel on diesel engine PM emissions and aftertreatment performance, *SAE Paper* No. 2010-01-0790

[6] Tsuchiya, T., Shiotani, H., Goto, S., Sugiyama, G. and Maeda, A. (2006). Japanese standards for diesel fuel containing 5% FAME blended diesel fuels and its impact on corrosion. *SAE Paper* No. 2006-01-3303

[7] Haseeb, A.S.M.A., Masjuki, H.H., Ann, L.J. and Fazal, M.A. (2010). Corrosion characteristics of copper and leaded bronze in palm biodiesel. *Fuel Processing Technology* , vol. 9, March 2010, pp. 329-334

[8] Haseeb, A.S.M.A., Masjuki, H.H., Siang, C.T. and Fazal, M.A. (2010). Compatibility of elastomers in palm biodiesel. *Renewable Energy*, vol. 35, April 2010, pp. 2356 – 2361

[9] Terry, B., McCormick, R.L. and Natarajan, M. (2006). Impact of biodiesel blends on fuel system component durability. *SAE Paper* No. 2006-01-3279

[10] Haseed, A.S.M.A., Fazal, M.A., Jahirul, M.I. and Masjuki, H.H. (2011). Compatibility of automotive materials in biodiesel: A review, *Fuel*, vol. 90, March 2011, pp. 922-931

[11] Coronado, M., Montero, G., Valdez, B., Stoytcheva, M., Eliezer, A., Garcia, C., Campbell, H. And Perez, A. (2014). Degradation of nitrile rubber hose by biodiesel use, *Energy*, vol. 68, March 2014, pp. 364 – 369

[12] Linhares, F.N., Correa, H.L., Khalil, C.N., Leite, M.C.A.M. and Furtado, C.R.G. (2013). Study of the compatibility of nitrile rubber wiith Brazillian biodiesel, *Energy*, vol. 49, November 2013, pp. 102 – 106

[13] Akhlaghi, S., Hedenqvist, M.S., Conde Brana, M.T., Bellander, M. and Gedde, U.W. (2015). Deterioration of acrylonitrile butadiene rubber in rappeseed biodiesel, *Polymer Degradation and Stability*, vol. 111, November 2014, pp. 211 - 222