



SBR elastomer response to renewable diesel blends: An experimental investigation

Andrias Rahman WIMADA^{1,*}, Ni Putu Dian NITAMIWATI¹, Fatimah Tresna PRATIWI¹, Maharani Dewi SOLIKHAH¹, Bina Restituta BARUS², Eki Dwi WIJANARKO³, Riesta ANGGARANI⁴, Lies ASIYAH⁴, Setyo WIDODO⁴, Arfie THAHAR⁵, and Soni Solistia WIRAWAN¹

¹ Research Center for Energy Conversion and Conservation, National Research and Innovation Agency, South Tangerang, 15314, Indonesia

² Center of the Technology Services, National Research and Innovation Agency, Jakarta, 10330, Indonesia

³ Directorate Bioenergy, Directorate General of the New, Renewable Energy and Energy Conservation, Ministry of Energy and Mineral Resources, Jakarta, 10320, Indonesia

⁴ Testing Center for Oil and Gas LEMIGAS, Ministry of Energy and Mineral Resources Republic of Indonesia, Jakarta, 12230, Indonesia

⁵ Palm Oil Plantation Fund Management Agency (BPDPKS), 10310, Indonesia

*Corresponding author e-mail: andr030@brin.go.id

Received date:

3 April 2024

Revised date:

26 July 2024

Accepted date:

22 October 2024

Keywords:

Biodiesel;
HVO;
Elastomers;
Swelling;
Polymer content

Abstract

To investigate the impact of Styrene Butadiene Rubber (SBR) exposure to renewable fuels during handling and storage processes, compatibility tests were conducted on three different renewable fuel mixtures: 30% biodiesel, 40% biodiesel, and 30% biodiesel + 10% hydrogenated vegetable oil. These tests involved static immersion experiments conducted at room temperature for a duration of 1000 h, following the ASTM D471 standards. Before and after the immersion tests, the physical properties and visually assessed elastomers concentrations were investigated by varying the SBR content. Additionally, the post-immersion fuel properties were examined. The results showed that mass and volume swelling increased with the SBR-to-bound sulfur ratio. Enhanced mechanical strength was observed, particularly in cases with medium SBR content, which correlated with higher carbon black concentrations. The increasingly subtle morphological appearance was also captured via SEM. After immersion, fuel characterization showed that parameters such as acid number and water content remained stable without significant alterations.

1. Introduction

The need for fossil fuels continues to increase despite the decline in reserves and petroleum production. In addition to limitations in quantity, fossil energy has a major impact on global warming because it increases the accumulation of greenhouse gas emissions in the atmosphere. This is the basis for global initiative to use and produce clean, sustainable, low-cost energy, as advocated by sustainable development goals [1].

A promising alternative to fossil fuels is biofuels because they are renewable and more environmentally friendly and can be derived from a range of local natural oil resources. One alternative fuel to replace diesel fuel is biodiesel, which is a fatty acid methyl ester (FAME) compound resulting from the reaction between vegetable oil or animal fat and alcohol with the aid of a catalyst (acid, base, or enzyme) or without a catalyst [2-4]. Biodiesel has great potential to meet the world's increasing energy needs, primarily because of its abundant availability of raw materials, environmentally friendly characteristics, and renewable properties [5]. Biodiesel has a higher cetane number than diesel fuel, so the use of biodiesel can reduce emissions. A study by Reksowardojo *et al.* [6] mentioned that the use of B20 (20% of biodiesel and 80% of diesel) reduces emissions of carbon monoxide (CO), hydrocarbon (HC), and particulate matter (PM).

Another type of biofuel that can be utilized as a substitute for diesel fuel is hydrotreated vegetable oil (HVO). HVO is produced from vegetable materials with a hydrogenation process technology to produce fuel like diesel fuel. The advantages of HVO are higher cetane number, sulfur-free, aromatic-free, and glycerol-free [7,8]. HVO fuel also positively impacts emissions, where the PM value decreased by 43%, solid particle number shows a number about 40% lower, and particle size 23% smaller than diesel fuel [7]. The use of HVO in diesel vehicles is possible without engine modification because its properties are similar to that of diesel [9]. However, the use of pure HVO in diesel engines still has weaknesses, such as lower volumetric calorific value, so volumetric fuel consumption of HVO is about 3% to 6% higher than diesel fuel [7,10].

At present, both varieties of biofuels can be utilized as a blend with diesel fuel. Pure biodiesel is denoted as B100, while mixed biodiesel is denoted as Bxx where xx states for the percentage of biodiesel in the mixture with diesel fuel. The addition of HVO to the mixture of biodiesel and diesel fuel provides an improvement from some of the shortcomings of biodiesel. The quality of the biofuel mixture improves hence it reaches standard requirements, such as Euro 2 and Euro 4 [11]. In terms of emission, the mixture of biodiesel and HVO fuel can significantly reduce CO and HC emissions [12].

Currently, Indonesia has implemented the highest biodiesel-diesel fuel mix of B35, with 35% biodiesel and 65% diesel fuel, since February 1st, 2023 [13]. Biodiesel is currently utilized in the United States (maximum B20), Malaysia (B10 since 2020), Thailand (B10 since 2020), and China (maximum B5) [14]. To provide the technical acceptability of biofuels in blends, the biofuel quality has been improved, supported by testing on diesel engines and regulation of biodiesel specifications.

To maintain the biofuel blend quality, it is essential to prevent fuel contamination and degradation, especially during handling and storage. This concern arises due to the inherent properties of biodiesel, which contains methyl esters. These compounds possess solvent-like characteristics and can interact with materials such as elastomers when they encounter biodiesel and its mixtures. It is necessary to identify and study the damage mechanisms that occur when fluid diffuses into the elastomer, impacting structural changes and modification of physical properties. This problem may lead to fuel leaks and contamination in the fuel system.

The study involves several types of elastomeric materials often found in pipe joints, valves, and other parts of the fuel system. The negative impact of biodiesel use on elastomeric materials in the fuel supply system is at high service temperatures. It can cause severe operational problems such as fuel leaks and fuel pump failure [15]. Different elastomer degradation behaviors were studied on ethylene propylene diene monomer (EPDM) elastomer types, silicone rubber (SR), polychloroprene (CR), polytetrafluorethylene (PTFE), and nitrile rubber (NBR) after exposure to diesel and biodiesel. The result was a sequence of elastomer types that are compatible with biodiesel as follows: PTFE > SR > NBR > EPDM > CR [16,17]. Most of the research studied elastomer compatibility at low mixtures, while research on elastomer compatibility at high mixtures was still very limited. A comparative study of the compatibility of EPDM elastomers in biodiesel blends [17,18] showed changes in the mass, volume, and mechanical properties of the elastomers after immersion.

However, the effect of adding high-ratio biodiesel blends with elastomer materials has not been thoroughly studied. Bialecki *et al.*

[19] made a comparison when NBR and fluoroelastomer (FKM) were immersed in HVO. The result shows no significant change in mass. Bockey [20] also stated that the addition of HVO had a better interaction effect on elastomers. These studies imply that the use of HVO may improve the solvency effect of biodiesel in diesel fuel blends.

In addition, to achieve Net Zero Emissions, the use of renewable fuel mixtures will continue to increase. Therefore, it needs to be anticipated by studying the effects of elastomers due to the use of this fuel at a higher ratio. Consequently, the objective of this research was to examine the suitability of elastomer handling and storage systems in accordance with ASTM D471 standards, specifically for 40% blends of diesel-biodiesel and diesel-biodiesel-HVO, as opposed to the 30% biodiesel blend. The elastomer to be tested was SBR (styrene-butadiene rubber), a material frequently encountered and employed in fuel storage applications, particularly in hose and seal/gaskets [21]. SBR is a low-cost general-purpose rubber, and its characteristics are influenced by the amount of styrene. SBR, is synthesized from various hydrocarbons derived from petroleum [22]. This synthetic rubber offers the advantages of favorable mechanical properties and an affordable price. Changes in physical properties observed include mass change, volume change, hardness, measurement of tensile strength, and morphological appearance.

2. Materials and methods

2.1 Materials

The diesel fuel and HVO used were obtained from PT Kilang Pertamina Internasional, while palm oil-based biodiesel was obtained from the Indonesia Biofuels Producer Association (APROBI). In this study, the fuel blends of B30 (30% biodiesel and 70% diesel fuel), B40 (40% biodiesel and 60% diesel fuel), and B30D10 (30% biodiesel, 10% HVO, and 60% diesel fuel) were used. The specifications for biodiesel, HVO, and diesel fuel used were based on a standard that applies in Indonesia [23-25]. Furthermore, the fuel blends were tested according to the parameters in Table 1.

Table 1. Parameter of Diesel-Biodiesel and Diesel-Biodiesel-HVO Blends.

Properties	Method
FAME content, volume%	ASTM D7371
Total acid number, mg KOH·g ⁻¹	ASTM D664
Water content, ppm	ASTM D6304
Density at 15°C, kg·m ⁻³	ASTM D4052
Kinematic Viscosity at 40 °C, mm ² ·s ⁻¹	ASTM D445
Cloud Point	ASTM D2500
Color	ASTM D1500
Cleanliness	ASTM D7619
Oxidation stability, min	EN 15751
Aniline point, °C	ASTM D611
Aromatics, wt%	ASTM D2140

Table 1. Elastomer composition characteristic test.

Properties	Method
Acetone extract	ASTM D297-15 Clausul 19
Ash content	ASTM D297-15 Clausul 35
Total sulfur content	ASTM D297-15 Clausul 32
Free sulfur content	ASTM D297-15 Clausul 29
Carbon content	-
Polymer content	-

The study examined SBR elastomers with varying polymer content, and the characterization test parameters for the SBR used in this research are provided in Table 2. The materials of SBR are obtained from the local market.

2.2 Experimentation

The shape and dimensions of SBR from the local market can vary greatly depending on the specific application. Typically, SBR is available in sheets, rolls, or pre-cut shapes such as rings, strips, or special shapes. In this research, SBR in sheet form was utilized with dimensions of about 2400 mm in length and 1200 mm in width with a thickness of 2 mm.

Specimen preparation was conducted before the immersion test. Elastomeric specimens were cut with a height of 50 mm, a width of 25 mm, and a thickness of 2 mm to examine changes in mass and volume (see Figure 1(a)). The tensile test specimens were prepared and tested according to ASTM D412 Die C (see Figure 1(b)) [26]. The hardness specimens were prepared with a length of 5 mm, a width of 3 mm, and a thickness of 2 mm.

Following the preparation, all specimens were immersed in a fuel solution (B30, B40, and B30D10). Three elastomers were placed in a sealed glass container with three specimens of each type. The specimen was hung on 316L stainless steel wire. Each container was filled with the fuel blend until all specimen parts were immersed. The specimens were immersed for 0, 71, 167, 671, and 1007 h at room temperature (23°C).

2.3 Material compatibility analysis

A material is considered compatible for its application if changes that could affect its function and performance do not occur. Certain manufacturers, such as Parker O-Ring, require changes (tensile strength) of no more than $\pm 15\%$ [27].

Material compatibility was analyzed by measuring mass, volume, tensile strength, and hardness. The quality of immersion fuel after immersion was also tested. The test method uses ASTM D471 standards [28]. Equation (1-3) were used to determine swelling mass, swelling volume, and tensile strength, respectively.

$$\Delta M, \% = \frac{(M_2 - M_1)}{M_1} \times 100 \quad (1)$$

where:

- ΔM = change in mass, %
- M_1 = initial mass of specimen in air, g
- M_2 = mass of specimen in air after immersion, g

$$\Delta L, \% = \frac{(L - L_0)}{L_0} \times 100 \quad (2)$$

where (A similar equation was applied for width and thickness):

- ΔL = change in length, %
- L_0 = initial length of specimen, mm
- L = length of specimen after immersion, mm

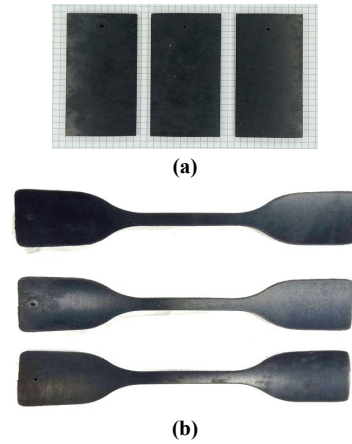


Figure 1. Elastomer specimens for mass and volume swelling tests (a) and tensile strength tests (b).

$$\Delta \sigma, \% = \frac{(\sigma_2 - \sigma_1)}{\sigma_1} \times 100 \quad (3)$$

where:

- $\Delta \sigma$ = change in tensile strength, %
- σ_1 = initial tensile strength of specimen in air, Mpa
- σ_2 = tensile strength of specimen in air after immersion, Mpa

Mass was measured using a Shimadzu AUW 220 balance with an accuracy of 0.1 mg. The elastomer volume was calculated by measuring the dimensions (length \times width \times thickness). Tensile strength was tested using the Universal Testing Machine (UTM) Shimadzu AGS 10 kNG. Hardness measurement was analyzed based on ASTM D2240 [29] using a Shore A type Durometer.

2.4 Fuel quality analysis

Fuel analysis is important to determine the impact of fuel contact with elastomers on fuel quality. The parameters analyzed by the following method were water content (ASTM D6304), total acid number (ASTM D664), color (ASTM D1500), and oxidation stability (EN 15751).

3. Results and discussion

3.1 Polymer characteristics

When producing rubber items through the vulcanization process, various additives, including fillers, plasticizers, antioxidants, colorants, and flame retardants, were incorporated alongside vulcanization accelerators. The elasticity of elastomers can be enhanced through the intricate process of vulcanization. This process involves the formation of chemical bonds, specifically primary cross-links, which bind chains of rubber molecules together, creating a three-dimensional molecular network [22]. These additional components serve the purpose of enhancing specific characteristics or lowering manufacturing expenses [30]. Therefore, the polymer content, ash content, carbon content, and acetone extract of the specimens were analyzed as provided in Table 3.

Table 2. Test results for characteristics of elastomer composition.

Properties	SBR1	SBR2	SBR3
Polymer content (wt%)	31.72	41.93	49.83
Ash content (wt%)	42.56	21.93	21.35
Carbon content (wt%)	16.17	26.35	22.56
Acetone extract (wt%)	9.55	9.79	6.26
Total	100	100	100

3.1.1 Polymer content

Polymer content is a test carried out to determine the characteristics and main components of natural or synthetic raw rubber, which is calculated by subtracting the amount of non-rubber elements by 100%. SBR is a copolymer with a random structure, and its characteristics are influenced by the quantity of styrene. Commercial SBR rubber uses a target-bound styrene content of 23.5 wt%. To improve some of the properties of SBR, it is blended with polar elastomers like acrylonitrile butadiene rubber (NBR), chloroprene rubber, and natural rubber (NR). The non-polar nature of SBR makes it also not susceptible to use with certain filler materials [21].

3.1.2 Ash content

Ash content is a parameter to determine the approximate number of inorganic fillers in elastomers. Fillers commonly used in rubber matrices are silica, clay, calcium carbonate, and kaolin [31]. Silica is a filler used in rubber materials, which varies depending on its use. Silica filler functions as a reinforcement or increase in volume or weight. Fillers whose function is to increase weight are generally used to reduce production raw material costs. In addition, the use of silica aims to build a strong filler network and low interaction with the polymer [32]. Based on the test results, the ash content for the three elastomers was obtained as follows: 42.56 wt%, 21.93 wt%, and 21.35 wt%, respectively. The types of fillers contained are silica, carbonate, and sulfate.

3.1.3 Carbon content

Carbon content is a parameter that also indicates the amount of filler in the elastomer. Carbon is a common organic filler added to elastomers. Selection of the carbon black-rubber system, the rubber effectively occupies and safeguards the voids within each aggregate, preventing deformation. As a result, it functions as an integral part of the filler rather than being part of the flexible matrix. Research conducted by Rahmiani *et al.* [32] also stated that the addition of commercial fillers, such as carbon black, to the rubber phase matrix can strengthen the properties of the polymer and reduce costs, especially by reducing the amount of polymer used. As a result of this phenomenon, the effective volume of the filler increases significantly and, of course, improves the tensile strength, tear resistance, abrasion resistance, and modulus. In short, it can be said that the addition of carbon filler is a strengthening material. Incorporating fillers into rubber compounds significantly impacts the static and dynamic performance of rubber specimens [33]. The highest carbon content in the test sample was 26.35 wt% found in the SBR2 sample, 22.56 wt% in the SBR3 sample, and 16.17 wt% in the SBR1 sample.

3.1.4 Acetone extract

Acetone extract is used to determine the composition of other ingredients from the rubber vulcanization process, apart from the polymer and filler content. These other ingredients include accelerators, bound sulfur, antioxidants, and plasticizers. Accelerators are chemical compounds that, when added to the rubber compound before the vulcanization process, will speed up the vulcanization process. In addition, the use of accelerators will reduce the amount of vulcanization material used. During sulfur vulcanization of rubber, the accelerator controls the onset of vulcanization, the rate of vulcanization, and the amount and type of sulfur crossflow formed.

Sulfur is one of the materials that is often used as a Cross-Linking Agent (CLA). Sulfur will form cross-links with the rubber (cross-links), which at the beginning of the cross-link formation results in interactions between parts until an active complex is formed in the rubber matrix in the form of an active cross-links agent. Their inherent flexibility facilitates the stretching of elastomers to lengths significantly greater than their original formation. However, the cross-linking of elastomers serves as a barrier, preventing the polymer chains from separating easily [34]. The introduction of plasticizers represents a passive approach to enhancing polymers' flexibility, ductility, and toughness while concurrently reducing their hardness and stiffness. Plasticizers are usually used on polymers that are intrinsically brittle at room temperature, they lower the glass transition temperature, so that at room conditions the polymer can be used in applications that require a certain level of flexibility [32].

The main chain structures of elastomers are interconnected in polymer chain structures. In other words, there are cross-links between the main chains. Cross-links between molecular chains are the result of reactions from cross-linking materials in the form of sulfur. The sulfur content in elastomers is divided into two parts: bound sulfur and free sulfur. Sulfur content, especially bound sulfur, influences the degree of cross-linking. The degree of cross-linking will affect the free volume, impacting the tightness and mechanical properties [32]. Furthermore, apart from the mentioned chemical components, an elevation in cross-link density can be achieved through the curing process [35].

The bound sulfur content between SBR1 and SBR3 has the same value, namely 1.66 wt%, but there are differences in the polymer content. SBR3 has a polymer content value of 26.97 wt% which is higher than SBR1, which is 11.94 wt%. With the same bound sulfur content value, SBR1 has lower cross-linking, so it has a greater free volume than SBR2, which has an impact on its swelling value.

Meanwhile, the swelling value in SBR2 is smaller than in SBR3 since the polymer content is smaller and has greater bound sulfur than SBR3. SBR2 has more cross-links and lower free volume compared to SBR3, which impacts its swelling properties. Based on

the test results, the acetone extract values for the three elastomers were as follows: 9.55 wt%, 9.79 wt%, and 6.26 wt%.

3.2 Swelling test

3.2.1 Swelling mass

After immersion, the elastomers showed an increase in mass in B30, B40, and B30D10 immersion, as shown in Figure 3. The weight gain of the elastomeric immersed in B40 was relatively higher than that of B30 and B30D10 (Figure 2(a)). SBR3 showed the most significant weight change compared to SBR2 and SBR1, which were 65.77 wt%, 50.53 wt%, and 39.28 wt%, respectively, after 1007 h. Our results was comparable to previous study conducted by Sorate *et al.* [17], where the elastomer experienced significant mass swelling after immersion in B100. The weight gain resulted from the infiltration of liquid fuel into the elastomeric matrix, wherein fuel molecules occupy the voids within the elastomer. When saturation conditions was obtained, certain segments of the polymer molecules may undergo degradation [40].

Bialecki *et al.* and Linhares *et al.* [19], [36] also conveyed the same observation, the increases in mass and volume are associated with elastomer swelling due to the adsorption of fuel and relaxing of the polymer, as well as the affinity of the related chains between the fuel and the elastomer. Trakarnpruk and Porntangjitlikit [37] also stated that biodiesel is easily absorbed into elastomers, breaking down the polymer chain bonds.

On the other hand, the addition of bio-hydrocarbon (D10) to the biodiesel mixture reduced the swelling process by 2 wt%, 4 wt%, and 3 wt% in SBR1, SBR2, and SBR3, respectively.

3.2.2 Swelling volume

Similar to the swelling mass, the two types of elastomers experienced an increase in volume, especially at B40. Sorate *et al.* [17] has investigated that this was due to liquid dipole-dipole interactions and elastomers. The higher polarity of biodiesel than diesel fuel results in stronger dipole-dipole interactions with elastomers in B40 than B30 and B30D10, owing to its greater concentration in the blend. This

elastomeric swelling is in response to the cross-linkage after exposure to fuel. Biodiesel contains acid, ester, and phenolic compounds, which will react with inorganic fillers such as carbonate compounds, one of the fillers in elastomer samples.

Swelling in elastomers starts when the fuel is absorbed by the surface of the elastomer, which then penetrates the elastomer and occupies the pores or free volume found between the molecular chains and cross-links. Then, the fuel diffuses into the elastomer, which causes the elastomer to swell because the fuel is trapped in the pores of the elastomer chain network [39]. Elastomer dimensions that do not return to their original shape (before immersion) can also be caused by broken cross-links connecting of the main molecular chains in the elastomer, so that the molecular chains do not return to their original position or are far apart, resulting in a larger free volume which has an impact on the volume or dimensions expansion of the elastomer [38].

However, the extent of swelling will depend on the chemical behavior of the elastomeric constituents. The greatest swelling can be obtained if soluble polymer collaborations predominate over polymer connections [39]. In this case, shown in Figure 2(b), SBR3 has a larger swelling volume value for the three fuel types. The volume change in the elastomer is greater than the change in mass. This is possible because there is a large free volume, which causes mobility in the main molecular chain, which impacts swelling.

Based on Table 1, the ratio of SBR content to bound sulfur content can be calculated, which is presented in Table 4. These two parameters can influence the swelling effect of elastomer on fuel exposure. The ratio of polymer and sulfur content in the polymer will affect the amount of cross-linking, which will impact the free volume. The free volume of the elastomer will affect the swelling level.

By comparing the analysis results of the SBR to bound sulfur ratio with mass and volume expansion in Figure 2(a-b), the lower the ratio of SBR to bound sulfur, the lower the expansion effect. To minimize the swelling impact of SBR on the fuel mixture, it is suggested that a lower SBR ratio be used. Other studies also showed higher physical cross-link density values for carbon black-filled elastomers than for unfilled ones. This is because carbon black limits the mobility of the rubber chain, in addition to the inherent entanglement of the rubber chain.

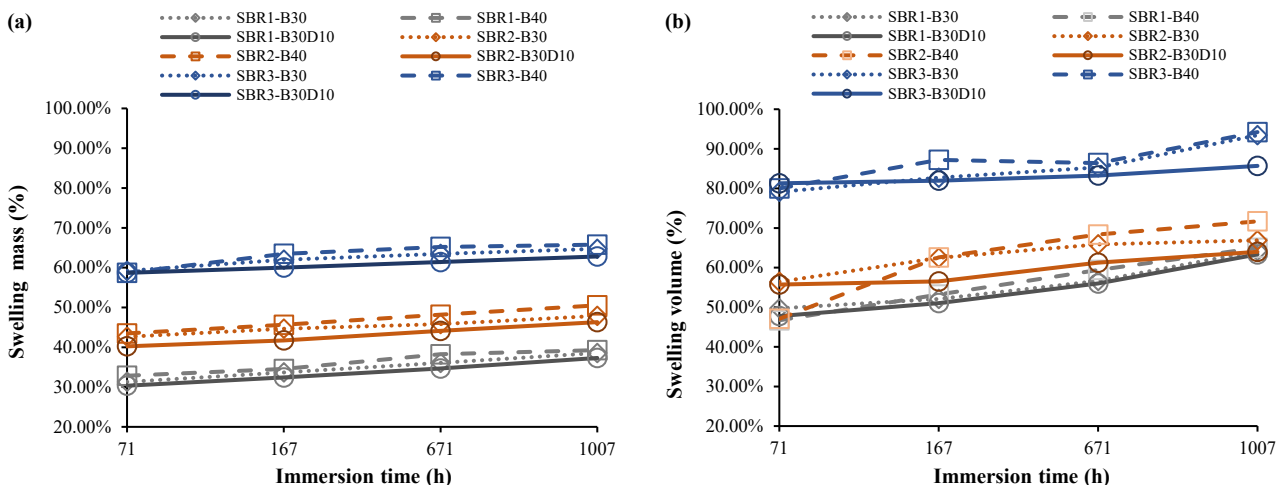


Figure 2. Swelling mass (a), and volume (b) of elastomer after immersion 1007 h.

Table 3. Calculation table for the ratio of SBR : Bound sulfur.

Parameter	SBR1	SBR2	SBR3
Polymer content (wt%)	31.72	41.93	49.83
SBR content (wt%)	11.94	17.53	26.97
Total sulfur content (wt%):			
Bound sulfur (wt%)	1.66	2.24	1.66
Free sulfur content (wt%)	0.0028	0.0029	0.0028
SBR : Bound sulfur ratio	7.20	7.84	16.27

Based on the outcomes of the elasticity test involving three different elastomers and various fuel types, the elastomer exposed to B30D10 fuel exhibited the least significant increase in mass and volume compared to its counterparts exposed to B30 and B40 fuels. The flexible nature of polymers, especially elastomers, reflects the presence of free volume in the polymer chain. When the elastomer encounters fuel, it begins with the absorption of fuel on its surface, followed by the penetration of the polymer, filling the pores and available space. Subsequently, the fuel molecules gradually diffuse deeper into the polymer material. The elastomer swells because fuel molecules become trapped in the pores and penetrate the polymer chain network. The distance between the chains increases with the presence of fuel molecules between polymer chains [40]. FAME fuel has a high oxygen content, viscosity, and density compared to HVO, so that the FAME mixed fuel can accelerate the rate of diffusion, which causes the decomposition of polymer chains [41].

3.3 Mechanical characteristic

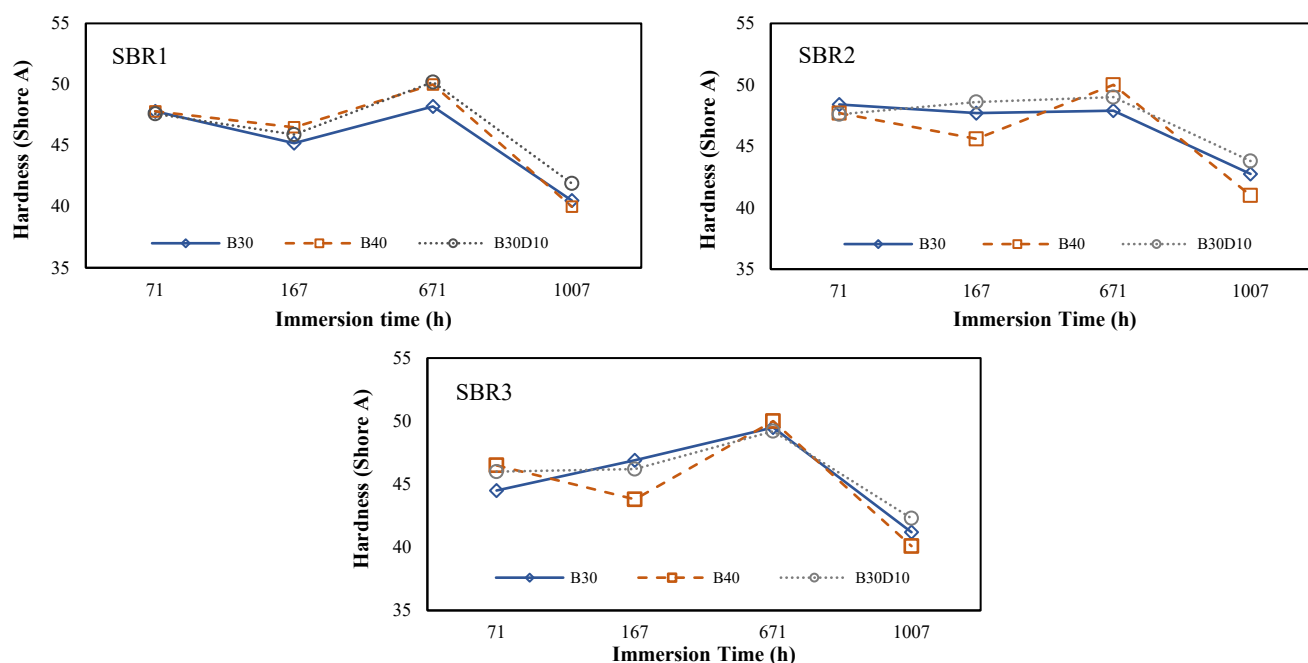
3.3.1 Hardness change

Immersion of the elastomers for 1007 hours resulted in a decrease in hardness, which is shown in Figure 3. In the process of elastomer synthesis, preservatives and accelerators are added to increase the physical properties of the elastomer, which then forms cross-linked bonds. This compound then reacts to the biodiesel contained in the

fuel. Immersion in a solvent mixture of biodiesel fuel causes these materials to dissolve into the fuel and causes reduced physical and mechanical properties [17,19]. SBR rubber compounds are commonly compounded with aromatic mineral oil of the T-RAE (Treated Residual Aromatic Extract) type as a plasticizer. Considering the solubility parameter, biodiesel has properties similar to T-RAE [42]. Through immersion, biodiesel has the potential to extract T-RAE from SBR rubber, causing a decrease in hardness. This can be observed after immersion for 1007 h in all types of SBR.

The carbon content in elastomers influences increasing mechanical strength, in this case, hardness. In SBR2, the carbon black value obtained was 26.35 wt%, while SBR3 was 22.56 wt%, and SBR1 was 16.17 wt%. The three SBRs experienced almost the same decreasing pattern for hardness levels for all types of fuel mixtures. From the hardness measurement results, SBR2 has the highest value, followed by SBR3 and SBR1.

Fillers added to elastomer composites to improve mechanical properties, thermal stability, and solvent resistance have attracted much attention among researchers. One of the filler materials for elastomers is silica, which has the advantages of low processing costs and high efficiency. However, there is a note in the elastomer production process, namely that the filler materials must be well distributed in the matrix, so the tensile strength of the resulting composite will also increase. However, if the distribution of particles in the polymer matrix is not symmetrical, the tensile strength of the composite will decrease due to the formation of concentrated stress points in the matrix [43].

**Figure 3.** Hardness values of sample after 1007 h.

3.3.2 Tensile strength

Similar to hardness results, the strength of the elastomer experienced a significant decrease in strength after being soaked for 1007 h. (Figure 4). A significant decrease in tensile strength was observed in SBR2 when soaked in B30 and B40, possibly due to the greater loss of cross-links between its polymer chains during immersion. On the other hand, in the case of SBR2, there is a relatively smaller decrease in tensile strength upon immersion in B30D10. Figure 5 shows a reduction in the strength of the two elastomeric specimens after being soaked for 1007 h. The greatest reduction occurred in the B40-immersed elastomer, which was -86% for SBR2 and -83% for SBR1. Based on O-Parker standard values [24], all types of SBR elastomer do not meet the limit value of -15% for use in dynamic components that require strength properties.

3.4 Surface morphology

Furthermore, surface observations were conducted to better support the observations made from mechanical tests, and the three samples were analyzed by scanning electron microscopy (SEM). A specialized microscope is selected based on the specific requirements and scale of the studied changes and objects.

Figure 6 shows observations of the elastomer surface carried out using SEM. Three samples of SBR soaked in B30, B40, and B30D10 for 71 h and 1007 h experienced high levels of damage and degradation compared to the initial sample (0 h). Allegations lead to affinity factors between biodiesel and elastomer that may cause elastomer degradation.

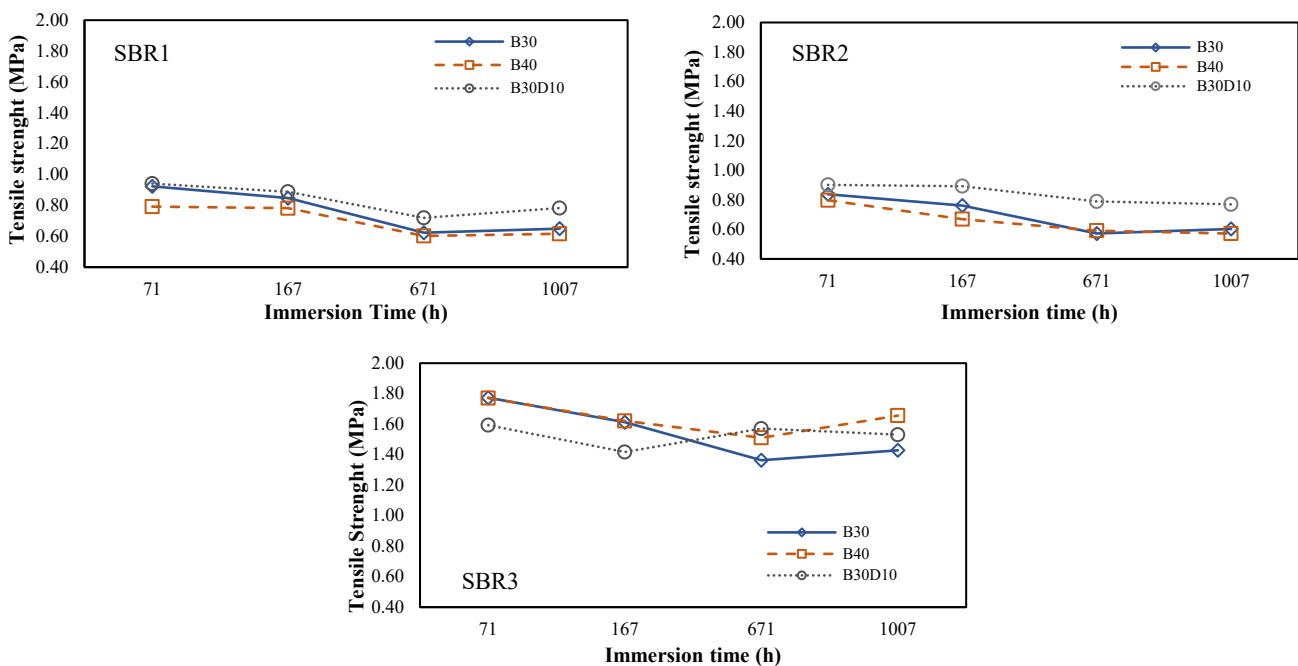


Figure 4. Tensile strength values before immersion and after 1007 h.

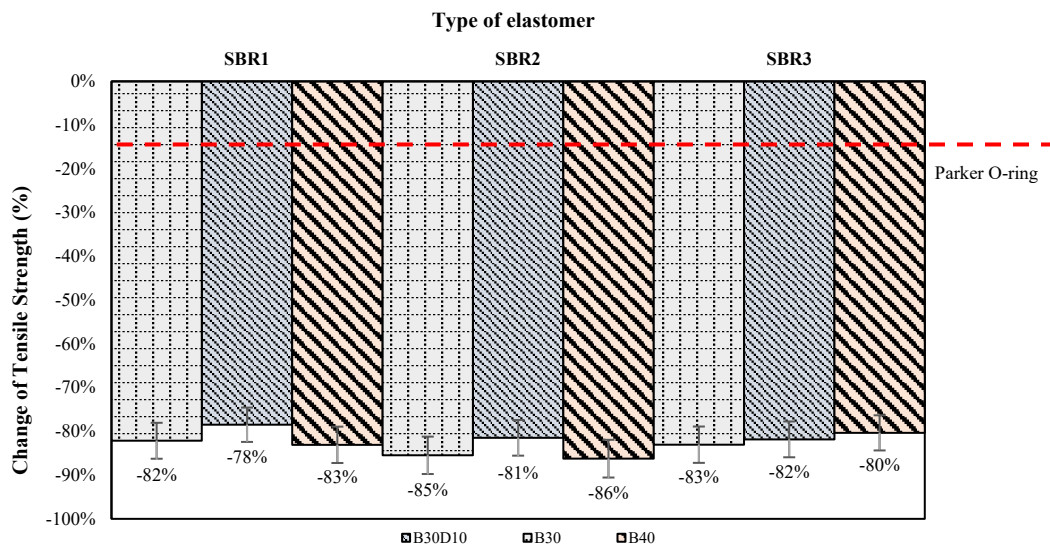


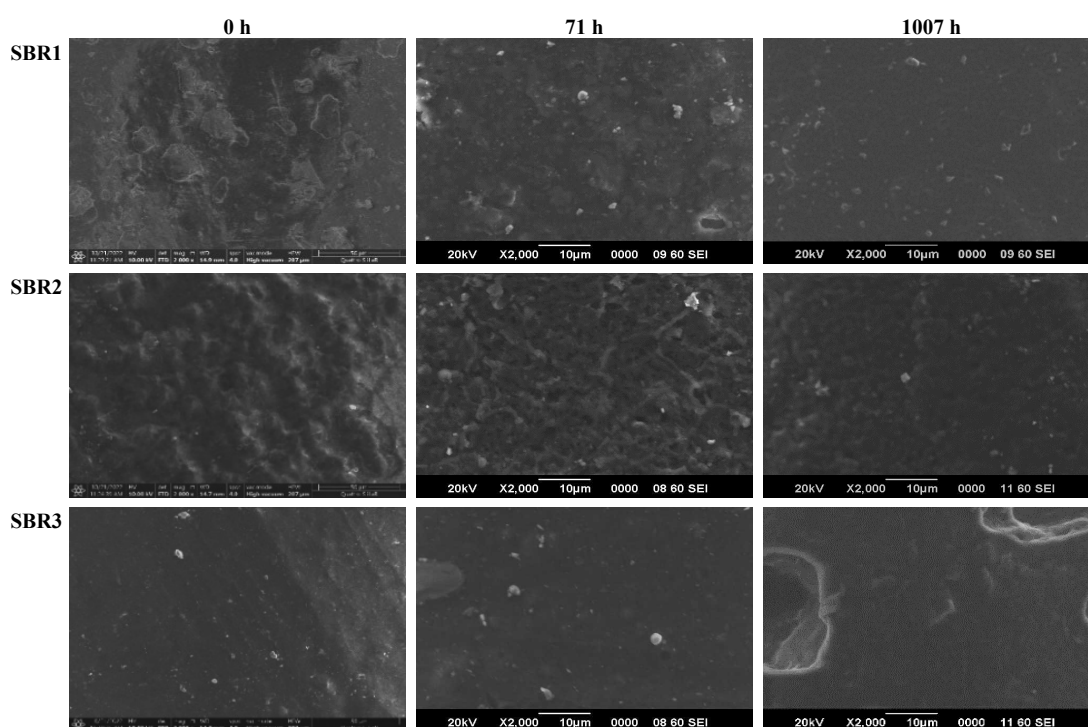
Figure 5. Change of tensile strength of SBR after immersion for 1007 h.

Table 4 Summaries of p-value after 1007 h of immersion.

Properties	p-value (CI=95%)	
	Among elastomers	Among fuels
Mass swelling	2.46 E-06	0.0109
Volume swelling	0.00026	0.0781
Hardness	0.00649	0.0026
Tensile	0.00056	0.3317

Table 5. Oxidation stability of the fuel after immersion.

Immersion period (h)	Oxidation stability (h)								
	B30			B40			B30D10		
	SBR1	SBR2	SBR3	SBR1	SBR2	SBR3	SBR1	SBR2	SBR3
71	>35	>35	2.48	>35	>35	1.81	>35	>35	2.63
167	>35	>35	2.34	>35	>35	1.7	>35	>35	1.62
671	>35	>35	2.42	>35	>35	2.24	>35	>35	2.88
1007	>35	>35	3.47	>35	>35	2.05	>35	>35	3.36

**Figure 6.** Surface SEM photomicrographs of SBR at 0 h, 71 h, and 1007 h immersion in B30.

To determine how significant elastomer compositions and fuel types affect elastomer characteristics after immersion, statistical analysis using Two-Way ANOVA was applied. Table 5 shows the p-value data after 1007 h of immersion. The differences in composition for each elastomer cause significant changes in all test parameters. However, the differences in fuel types only significantly affect mass swelling and hardness.

3.5 Fuel characteristics

The impact of elastomers on fuel quality was further studied. Several crucial parameters in fuel that may be affected by elastomer degradation include water content, acid number, color, and oxidation stability. Among these four parameters, noticeable changes were observed among different elastomers in the color and oxidation

stability parameters. Figure 7 shows that the water content of B30D10 is lower than B30 and B40 over time or immersion. Thus, the change in water content is predicted to be influenced not by the elastomers but rather by the type of fuel used. The water affinity of HVO is lower than the biodiesel blend since HVO only consists of paraffinic hydrocarbon, which is highly non-polar [10]. This result means that 10% Hydrogenated Vegetable Oil (HVO) in the fuel blend positively prevents significant increases in water content over time. The increase in water content over time is mainly attributed to the hygroscopic nature of biodiesel, which can easily absorb water from the surroundings, as it plays a role in the fuel mixture. This observation is further supported by the analysis results of blank samples (fuels without elastomers), which exhibited a concurrent increase with the immersion duration. Similarly, the elastomer composition did not significantly affect the change in acid number. This can be observed in Figure 8.

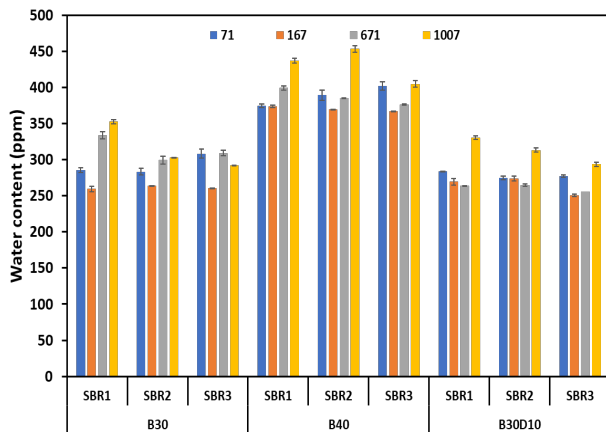


Figure 7. Fuel water content after immersion of elastomers.

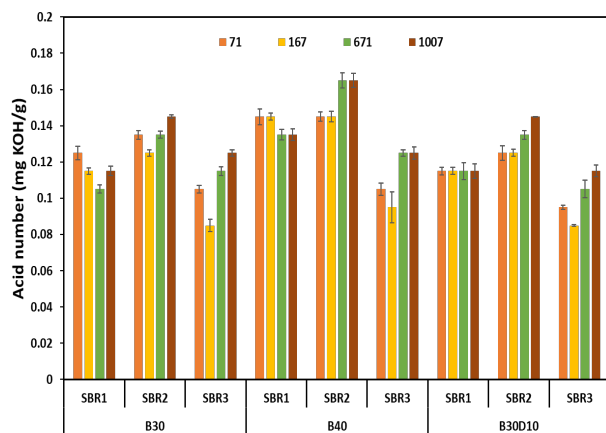


Figure 8. Fuel acid number after immersion of elastomers.

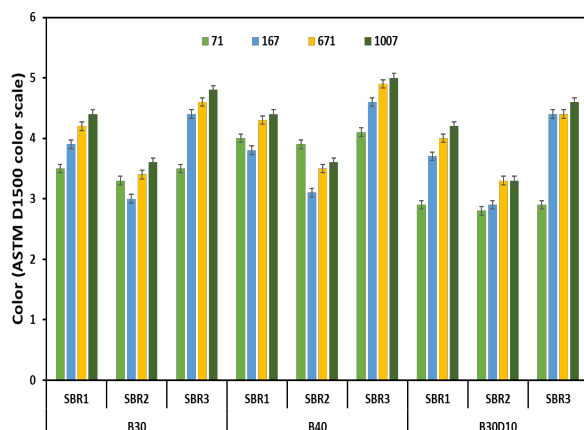


Figure 9. Fuel color after immersion of elastomers.

In addition to their constituent polymers, elastomers also contain ingredients such as plasticizers, stabilizers, and UV protectors [44]. Elastomer degradation can lead to the dissolution of materials within the elastomer, resulting in color changes. Changes in fuel color (Figure 9) revealed that the color of B30, B40, and B30D10 fuels with all elastomers increased with the prolonged immersion time. The sequence of the highest to lowest increase in the color index is as follows: SBR3 > SBR1 > SBR2. Based on these results, the increase in color is not influenced by the polymer concentration (SBR) but rather due to the dissolution of other compounds in the filler. The

highest color increase is obtained in the following sequence: B40 > B30 > B30D10. Based on the phenomenon "like dissolves like," the polarity of the compounds causing the color increase in the fuel is more like biodiesel. Unfortunately, the composition of filler compounds within the elastomer was not analyzed in detail, so the specific types of compounds responsible for the color change in the fuel cannot be determined.

The oxidation stability depicted in Table 4 showed that neither SBR1 nor SBR2 significantly impacted the oxidation stability of the fuel. This indicates that during the immersion period of up to 1007 h, the elastomer did not undergo degradation, resulting in the absence of products such as carboxylic acids, aldehydes, ketones, and epoxides that could potentially reduce oxidation stability [45].

This can be correlated with the swelling phenomenon in SBR1 and SBR2 elastomers, which is not as pronounced as in SBR3. Swelling occurs due to the diffusion of fuel molecules into the free volume of the elastomer, leading to degradation and the production of hydroperoxide products that dissolve in the fuel, causing a sharp decrease in oxidation stability. The degradation of SBR can initiate with the breaking of C=C bonds in the polymer or C-S bonds in the crosslinker. If C-S bond cleavage occurs in the termination stage, it will result in a dead-end thiol [46].

Based on the results of fuel characteristics after immersion, when comparing the effects of different fuel types, it can be observed that the addition of 10% HVO (Hydrogenated Vegetable Oil) to the fuel mixture does not significantly improve SBR compatibility. However, the addition of HVO has a positive effect on inhibiting the increase in water content over time.

4. Conclusions

Applying high biodiesel blends requires attention, especially to handling and storage activities. Based on these problems, a suitability study has been conducted on SBR with contents of 12.0862% (SBR1), 17.3219% (SBR2), and 26.9247% (SBR3) in biodiesel-diesel fuel mixtures with higher ratios and diesel-biodiesel-HVO mixtures. Elastomer degradation behavior was obtained and presented in mass swelling, volume swelling, hardness, tensile strength, and fuel characteristics.

It was found that the SBR3 elastomer showed the greatest increase in mass and volume swelling, influenced by the ratio of SBR to bound sulfur. The highest level of hardness was found in SBR2. The hardness of elastomers is influenced by carbon black concentration, with higher carbon black concentrations leading to increased mechanical strength. The interaction between the elastomer and the fuel can be observed in the SEM results analysis, where the morphology of the elastomer becomes smoother with immersion time. The characteristics of the fuel after immersion, such as acid number and water content were relatively stable and do not experience significant changes. However, the most significant changes in color and oxidation stability were observed in the case of SBR3. The oxidation stability of all fuels immersed in SBR3 decreased from more than 35 h to less than 4 h.

By comparing the result of the analysis of fuel characteristics after immersion, it becomes evident that introducing 10% Hydrogenated Vegetable Oil (HVO) into the biodiesel blend has a positive effect in preventing significant increases in water content over time.

Acknowledgment

The authors would like to express their gratitude and highest appreciation to the Testing Center for Oil and Gas LEMIGAS as well as Directorate Bioenergy, Directorate General of the New, Renewable Energy and Energy Conservation Department, Ministry of Energy and Mineral Resources, Oil Palm Plantation Fund Management Agency (BPDPKS) Indonesia, PT Pertamina (Persero), Indonesia Biofuels Producer Association (APROBI), National Research and Innovation Agency (BRIN), and IKABI for their support in this project. The authors also acknowledge the facilities, scientific and technical support from Laboratory for Fuel and Engineering Design, National Research and Innovation Agency through E- Layanan Sains-BRIN.

References

- [1] United Nation, "The Sustainable Development Goals Report," 2022.
- [2] G. Knothe, and J. Van Gerpen, *Biodiesel Handbook*. AOCS Publishing, 2005.
- [3] B. Norjannah, H. C. Ong, H. H. Masjuki, J. C. Juan, and W. T. Chong, "Enzymatic transesterification for biodiesel production: A comprehensive review," *RSC Advances*, vol. 6, no. 65, pp. 60034-60055, 2016.
- [4] M. Mittelbach, and C. Remschmidt, "Fuel stability," in *Biodiesel: The comprehensive handbook*, 1st ed., Vienna (AUT): Boersedruck Ges.m.b.H, 2004, p. 148.
- [5] H. M. Mahmudul, F. Y. Hagos, R. Mamat, A. A. Adam, W. F. W. Ishak, and R. Alenezi, "Production, characterization and performance of biodiesel as an alternative fuel in diesel engines – A review," *Renewable and Sustainable Energy Reviews*, vol. 72, no. November 2016, pp. 497-509, 2017.
- [6] I. K. Reksowardojo, H. Setiaprada, R. Fajar, E. Wibowo, and D. Kusdiana, "An investigation of laboratory and road test of common rail injection vehicles fueled with B20 biodiesel," *Energies (Basel)*, vol. 13, no. 22, 2020.
- [7] D. Singh, K. A. Subramanian, and M. O. Garg, "Comprehensive review of combustion, performance and emissions characteristics of a compression ignition engine fueled with hydroprocessed renewable diesel," *Renewable and Sustainable Energy Reviews*, vol. 81, no. July 2016, pp. 2947-2954, 2018.
- [8] C. McCaffery, H. Zhu, C. M. S. Ahmed, A. Canchola, J. Y. Chen, L. Chengguo, K. C. Johnson, T. D. Durbin, Y-H. Lin, G. Karavalakis, "Effects of hydrogenated vegetable oil (HVO) and HVO/biodiesel blends on the physicochemical and toxicological properties of emissions from an off-road heavy-duty diesel engine," *Fuel*, vol. 323, no. April, p. 124283, 2022.
- [9] P. Zeman, V. Honig, M. Kotek, J. Taborsky, M. Obergruber, J. Marik, V. Hartova, and M. Pechout, "Hydrotreated vegetable oil as a fuel from waste materials," *Catalysts*, vol. 9, no. 4, pp. 1-16, 2019.
- [10] T. Hartikka, M. Kuronen, and K. Ulla, *Technical Performance of HVO (Hydrotreated Vegetable Oil) in Diesel Engines*, vol. 9. 2012.
- [11] S. Mustika, and W. Wahyu Purwanto, "Multi-objective optimization of blending strategy of FAME, HVO, and petroleum diesel," *IOP Conference Series: Materials Science and Engineering*, vol. 1143, no. 1, p. 012046, 2021.
- [12] B. Rochmanto, H. Setiaprada, and M. Ekasari, "Kajian emisi dan konsumsi bahan bakar dalam penggunaan campuran bahan bakar biosolar pada kendaraan penumpang," *Rotor*, vol. 13, no. 2, 2020.
- [13] MEMR, "Surat Edaran - No.10.E/EK.05/DJE/2022-tentang implementasi penahapan pemanfaatan bahan bakar nabati jenis biodiesel sebagai campuran bahan bakar minyak jenis minyak solar dalam kerangka pembiayaan oleh BPDPKS," 2022.
- [14] A. Syafiuddin, J. H. Chong, A. Yuniarto, and T. Hadibarata, "The current scenario and challenges of biodiesel production in Asian countries: A review," *Bioresource Technology Reports*, vol. 12, no. November, p. 100608, 2020.
- [15] X. F. Wei, Q. Meng, K. J. Kallio, R. T. Olsson, and M. S. Hedenqvist, "Ageing properties of a polyoxymethylene copolymer exposed to (bio) diesel and hydrogenated vegetable oil (HVO) in demanding high temperature conditions," *Polymer Degradation and Stability*, vol. 185, Mar. 2021.
- [16] A. S. M. A. Haseeb, T. S. Jun, M. A. Fazal, and H. H. Masjuki, "Degradation of physical properties of different elastomers upon exposure to palm biodiesel," *Energy*, vol. 36, no. 3, pp. 1814-1819, 2011.
- [17] K. A. Sorate, P. V. Bhale, and B. Z. Dhaolakiya, "A material compatibility study of automotive elastomers with high FFA based biodiesel," *Energy Procedia*, vol. 75, pp. 105-110, 2015.
- [18] D. S. Maharani, A. R. Wimada, A. G. Arisanti, F. Karuana, H. Ghazidin, H. P. Putra, F. T. Pratiwi, and B. B. Restituta, "Influence of B30 palm-based biodiesel blends upon degradation of elastomers," in *IOP Conference Series: Earth and Environmental Science*, Institute of Physics, 2022.
- [19] T. Bialecki, A. Sitkiewicz, B. Giemza, J. Sarnecki, M. Skolniak, and B. Gawron, "Compatibility of different automotive elastomers in paraffinic diesel fuel," *Applied Sciences (Switzerland)*, vol. 11, no. 23, 2021.
- [20] D. Bockey, "The significance and perspective of biodiesel production - A European and global view," *OCL - Oilseeds and fats, Crops and Lipids*, vol. 26, 2019.
- [21] A. Abdel-Hakim, S. A. el-Mogy, and A. I. Abou-Kandil, "Novel modification of styrene butadiene rubber/acrylic rubber blends to improve mechanical, dynamic mechanical, and swelling behavior for oil sealing applications," *Polymers and Polymer Composites*, vol. 29, no. 9_suppl, pp. S959-S968, 2021.
- [22] A. Dorigato, D. Rigotti, and G. Fredi, "Recent advances in the devulcanization technologies of industrially relevant sulfur-vulcanized elastomers," *Advanced Industrial and Engineering Polymer Research*, vol. 6, no. 3, pp. 288-309, 2023.
- [23] EBTKE, *Standar dan Mutu (Spesifikasi) Bahan Bakar Nabati (Biofuel) Jenis Biodiesel sebagai Bahan Bakar Lain yang Dipasarkan di Dalam Negeri D. EBTKE-ESDM Keputusan Dirjen EBTKE No.195.K/EK.05/DJE/2022 jo. Keputusan Dirjen EBTKE No.207.K/EK.05/DJE/2022*. 2022. EBTKE, 2022.
- [24] EBTKE, *Standar dan Mutu (Spesifikasi) Bahan Bakar Nabati Jenis Diesel Biohidrokarbon sebagai Bahan Bakar Lain yang Dipasarkan di Dalam Negeri*. EBTKE, 2022.

- [25] Migas, *Standar dan Mutu (Spesifikasi) Bahan Bakar Minyak Jenis Solar yang Dipasarkan di Dalam Negeri, SK Dirjen Migas No. 146.K/10/DJM/2020*. Migas, 2020.
- [26] Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers—Tension, ASTM D412-16.
- [27] Parker O-Ring Handbook ORD 5700,” 2018. [Online]. Available: www.parkerorings.com
- [28] Standard Test Method for Rubber Property - Effect of Liquids, ASTM D471 – 16a.
- [29] Standard Test Method for Rubber Property-Durometer Hardness, ASTM D2240.
- [30] M. D. Stelescu, M. Sonmez, L. Alexandrescu, M. Nituica, D. F. Gurau, and M. Georgescu, “Structure and properties of blends based on vulcanized rubber waste and styrene-butadiene-styrene thermoplastic elastomer,” *Journal of Rubber Research*, vol. 25, no. 5, pp. 421-434, 2022.
- [31] B. Szadkowski, A. Marzec, and P. Rybiński, “Silane treatment as an effective way of improving the reinforcing activity of carbon nano-fibers in nitrile rubber composites,” *Materials*, vol. 13, no. 16, 2020.
- [32] W. D. Callister and J. G. David Rethwisch, *Materials Science and Engineering: An Introduction*, Wiley, 2013.
- [33] J. Fröhlich, W. Niedermeier, and H. D. Luginsland, “The effect of filler-filler and filler-elastomer interaction on rubber reinforcement,” *Composites Part A: Applied Science and Manufacturing*, vol. 36, no. 4, pp. 449-460, 2005.
- [34] I. M. Alarifi, “A comprehensive review on advancements of elastomers for engineering applications,” *Advanced Industrial and Engineering Polymer Research*, vol. 6, no. 4, pp. 451-464, 2023.
- [35] J. Kruželák, A. Kvasničáková, and I. Hudec, “Peroxide curing systems applied for cross-linking of rubber compounds based on SBR,” *Advanced Industrial and Engineering Polymer Research*, vol. 3, no. 3, pp. 120-128, 2020.
- [36] F. N. Linhares, H. L. Corrêa, C. N. Khalil, M. C. Amorim Moreira Leite, and C. R. Guimarães Furtado, “Study of the compatibility of nitrile rubber with Brazilian biodiesel,” *Energy*, vol. 49, no. 1, pp. 102-106, 2013.
- [37] W. Trakarnpruk and S. Porntangjitlikit, “Palm oil biodiesel synthesized with potassium loaded calcined hydrotalcite and effect of biodiesel blend on elastomer properties,” *Renew Energy*, vol. 33, no. 7, pp. 1558-1563, 2008.
- [38] A. R. Wimada, M. D. Sholihah, F. Karuana, A. G. Arisanti, H. Ghazidin, and M. Chalid “Pengaruh bahan bakar campuran biodiesel berbahan dasar minyak sawit terhadap elastomer NBR,” *Jurnal Rekayasa Material, Manufaktur dan Energi*, vol. 6, no. 1, pp. 66-71, 2023.
- [39] R. Gurani, and S. N. Kurbet, “Experimental investigation on compatibility of elastomeric materials with biodiesel,” *International Journal of Engineering Research & Technology (IJERT)*, vol. 06, no. 16, 2018.
- [40] W. Balasooriya, B. Schrittester, G. Pinter, and T. Schwarz, “Induced material degradation of elastomers in harsh environments,” *Polymer Testing*, vol. 69, pp. 107-115, 2018.
- [41] J. Hunicz, P. Krzaczek, M. Gęca, A. Rybak, and M. Mikulski, “Comparative study of combustion and emissions of diesel engine fuelled with FAME and HVO,” *Combustion Engines*, vol. 184, no. 1, pp. 72-78, 2021.
- [42] F. Cataldo, O. Ursini, and G. Angelini, “Biodiesel as a plasticizer of a SBR-based tire tread formulation,” *ISRN Polymer Science*, vol. 2013, pp. 1-9, 2013.
- [43] M. Sadeghalvaad, E. Dabiri, S. Zahmatkesh, and P. Afsharimoghadam, “Preparation and properties evaluation of nitrile rubber nano-composites reinforced with organo-clay, CaCO₃, and SiO₂ nano-fillers,” *Polymer Bulletin*, vol. 76, no. 8, pp. 3819-3839, 2019.
- [44] V. Marturano, P. Cerruti, and V. Ambrogi, “Polymer additives,” *Physical Sciences Reviews*, vol. 2, no. 6, pp. 1-22, 2019.
- [45] I.-S. Kim, B.-W. Lee, K.-S. Sohn, J. Yoon, and J.-H. Lee, “Characterization of the UV Oxidation of raw natural rubber thin film using image and FT-IR analysis,” *Elastomers and Composites*, vol. 51, no. 1, pp. 1-9, 2016.
- [46] M. G. Aboelkheir, J. G. Lima Junior, R. D. Toledo Filho, F. G. Souza Junior, and C. Y. dos Santos Siqueira, “Thermo-oxidative degradation of vulcanized SBR: A comparison between ultraviolet (UV) and microwave as recovery techniques,” *Journal of Polymer Research*, vol. 28, no. 4, 2021.