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1. Introduction

Since past few decades, biodiesel, as a renewable alternative fuel is receiving much attention to substitute diesel partially or completely. It is composed of fatty acid alkyl esters derived from vegetable oils or animal fats [1,2]. Biodiesel having very close fuel properties than diesel is receiving much attention to substitute diesel partially or completely. It is composed of fatty acid alkyl esters derived from vegetable oils or animal fats [1,2]. Biodiesel having very close fuel properties than diesel is receiving much attention to substitute diesel partially or completely. It is composed of fatty acid alkyl esters derived from vegetable oils or animal fats [1,2]. Biodiesel having very close fuel properties than diesel is receiving much attention to substitute diesel partially or completely. It is composed of fatty acid alkyl esters derived from vegetable oils or animal fats [1,2]. Biodiesel having very close fuel properties than diesel is receiving much attention to substitute diesel partially or completely. It is composed of fatty acid alkyl esters derived from vegetable oils or animal fats [1,2]. Biodiesel having very close fuel properties than diesel is receiving much attention to substitute diesel partially or completely. It is composed of fatty acid alkyl esters derived from vegetable oils or animal fats [1,2]. Biodiesel having very close fuel properties than diesel is receiving much attention to substitute diesel partially or completely. It is composed of fatty acid alkyl esters derived from vegetable oils or animal fats [1,2]. Biodiesel having very close fuel properties than diesel is receiving much attention to substitute diesel partially or completely. It is composed of fatty acid alkyl esters derived from vegetable oils or animal fats [1,2]. Biodiesel having very close fuel properties than diesel is receiving much attention to substitute diesel partially or completely. It is composed of fatty acid alkyl esters derived from vegetable oils or animal fats [1,2]. Biodiesel having very close fuel properties than diesel is receiving much attention to substitute diesel partially or completely. It is composed of fatty acid alkyl esters derived from vegetable oils or animal fats [1,2]. Biodiesel having very close fuel properties than diesel is receiving much attention to substitute diesel partially or completely. It is composed of fatty acid alkyl esters derived from vegetable oils or animal fats [1,2]. Biodiesel having very close fuel properties than diesel is receiving much attention to substitute diesel partially or completely. It is composed of fatty acid alkyl esters derived from vegetable oils or animal fats [1,2]. Biodiesel having very close fuel properties than diesel is receiving much attention to substitute diesel partially or completely. It is composed of fatty acid alkyl esters derived from vegetable oils or animal fats [1,2]. Biodiesel having very close fuel properties than diesel is receiving much attention to substitute diesel partially or completely. It is composed of fatty acid alkyl esters derived from vegetable oils or animal fats [1,2].
2. Experimental

The palm biodiesel used in this study was supplied by Wesh-chem Technology Sdn Bhd, Malaysia. The analysis report provided by the supplier is summarized elsewhere [15]. The compatibility of five different elastomer materials viz, EPDM, NBR, CR, SR and PTFE with palm biodiesel was assessed by conducting static immersion tests in B0 (diesel), B10 (10% biodiesel in diesel), B20, B50 and B100 (100% biodiesel). The investigated elastomers were supplied by Malaysian Rubber Board.

For each elastomer, test was carried out at room temperature (25°C) for 1000 h. At the end of immersion, degradation behavior of different elastomers was characterized by measuring changes in weight, volume, hardness and tensile strength. Samples for tensile tests were prepared in the form of dumbbell shape with gauge length of 30 mm. Changes in weight were measured by balance with 4 decimal accuracy. Volume was calculated by measuring the height, width and length of the sample. Upon immersion, before measuring weight and volume, samples were dried by blotting with lint-free cloth followed by air drying by keeping on clean places at room temperature for 30–40 min. The value of tensile strength was measured according to ASTM D412 (strain rate of 500 mm/min) by using Instron Tensile Tester (5 kN). The hardness value of the sample was determined using Cogenix Dead Load Hardness Tester Model H-14. A 2.5 mm ball indenter was pressed on the sample and the hardness value was automatically

Fig. 1. Changes of volume for different elastomers after immersion at room temperature.
Compositional changes in biodiesel were determined by conducting Gas chromatography mass spectroscopy (GCMS).

3. Results

Fig. 1 shows the changes in volume of different elastomers upon exposure into different fuels. It is seen that biodiesel and its blends cause a greater swelling of CR and NBR compared with that caused by diesel. On the other hand, EPDM and SR swelled to a greater extent in diesel compared with that in biodiesel and its blends. It is also seen in Fig. 1 that PTFE showed a reduction in volume with an increase in the concentration of biodiesel. Like changes in volume, similar trends were found for the changes of weight for respective elastomers (Fig. 2). PTFE showed a slight weight loss, while all other materials show considerable weight gain.

Fig. 3 shows a comparison of different elastomers in terms of their respective volume and weight changes. It is seen that the compatibility, in terms of changes in weight and volumes, for both EPDM and SR are higher in biodiesel as compared to that in diesel. On the other hand, CR and NBR are less compatible with biodiesel. This can be attributed to the higher polarity of ester components in biodiesel which allows the more polar elastomers to dissolve to a greater extent.

Fig. 4 shows that upon exposure to biodiesel, tensile strength values are decreased to a greater extent for EPDM, CR, NBR than SR...
and PTFE elastomers. Almost similar trends were also found for respective elastomers for the change of hardness (Fig. 5).

Table 1 shows the compositional changes of EPDM and CR exposed biodiesel as compared to as-received biodiesel. It is seen that concentration of palmitate ester is higher in as-received biodiesel than that in EPDM and CR exposed biodiesel. On the other hand, percentage of Methyl Oleate is increased considerably upon exposure to both EPDM and CR. Elastomer or its constituents may play an important role to influence the change in composition of biodiesel.

4. Discussions

Elastomers are basically complex mixture of polar and non-polar substances including polymers, fillers, oil, plasticizer, stabilizers, curing agents, antioxidants, antizonants and processing aids [16,17]. When it is immersed in a solvent, the elastomer matrix has a tendency to swell. Swelling of EPDM, SR, CR and NBR upon exposure to fuel can be attributed to the absorption of solvent as well as relaxation of polymer chains. It is seen that the increasing trends of swelling in biodiesel blends and diesel for EPDM and SR are higher in the time range of 500–700 h. But in pure biodiesel, the increased volume remains almost constant for the time range 250–750 h. This demonstrates that EPDM and SR are more resistant to swelling in biodiesel than in diesel. On the other hand, swelling rates for CR and NBR are higher in biodiesel as compared to that in diesel. This indicates that CR and NBR are less compatible in biodiesel than that in diesel. Compositionally, NBR is a complex family of unsaturated copolymers of acrylonitrile (ACN) and butadiene, while CR refers to polymers of 2-chloro-1,3-butadiene or copolymers of 2-chloro-1,3-butadiene with one or more polymerizable monomers. For NBR, the greater the acrylonitrile content, the less the swell in fuels as it ensures increased crosslinks in the polymer backbone [18]. Similarly, glycol dimethacrylates is the crosslinking agent for polychloroprene which resists swelling. Impact of diesel and biodiesel on these different ingredients of elastomers bears different characteristics based on their dissolution capabilities as well as their molecular polarities.

There is a general rule describing the fact that polar substances are more likely to dissolve in polar solvents and non-polar substances are more likely to dissolve in non-polar solvents [19]. It is noted that the degree of polarity for EPDM and SR is less than that of CR and NBR [20], while PTFE shows no polarity [21]. For polar solvent, the positive ends of the molecules will attract the negative ends of the solute molecules thereby creating an intermolecular force known as dipole–dipole interaction. The degree of dipole–dipole interaction in biodiesel for polar solute seems to be higher as compared to that in diesel. This is because biodiesel has additional unique chemical difference arising from the increased polarity of esters as compared to diesel [22]. Therefore, swelling of highly polar elastomer material (e.g. CR, NBR) is comparatively larger in biodiesel than that in diesel fuel. Elastomers seem to swell/degrade in biodiesel through reactions with the polymer backbone and crosslinking system or by reactions with the filler system [23]. In practical cases, upon exposure to different metals, biodiesel becomes oxidized and thereby it can increase its polarity which may cause further degradation of elastomers. Generally, the influence of ester base fluids on deterioration of elastomer is more significant in comparison to that of mineral oils [25]. If the solvent–polymer interactions are more dominant than polymer–polymer interactions, maximum swelling can be obtained [26].

Beside this, even a non-polar solvent has the ability to solvate the solute molecules. In fact, each molecule has a weak intermolecular force called London Dispersion force by which positive nuclei of the solute molecule atoms will attract the negative

![Fig. 3. Changes of (a) volume and (b) weight for different elastomers after immersion at room temperature for 1000 h.](image)

![Fig. 4. Tensile strength (TS) for as-received elastomers and elastomers exposed to diesel (B0) and biodiesel (B100) at room temperature for 1000 h.](image)

![Fig. 5. Hardness (IRHD) for as-received elastomers and elastomers exposed to diesel (B0) and biodiesel (B100) at room temperature for 1000 h.](image)
electrons of the solvent molecule atoms [19]. The increase in volume (swelling) and weight may result from the absorption of higher amount of liquid as compared to the extraction of soluble components from elastomer. On the other hand, the causes of slight reduction in mass and volume for PTFE can be discussed in terms of the dissolution of soluble components such as plasticizers, stabilizers or additives from the elastomers. Decreasing of volume as a result of reduction in pore size distribution indicates the densification of network by providing further crosslinks [27]. In other words, increase of crosslinks can limit the degree of polymer swelling by providing tie-points (constrains) that limit the amount of solvent to be absorbed into the elastomer.

Crosslinking agents in elastomers are mostly peroxide based [28]. During crosslinking, peroxides typically react with the elastomer chains by removing hydrogen atoms from the carbon backbone of the polymer. Thus, it creates highly active radicals on the chain, which attach to a similar site on another chain. This forms a carbon to carbon crosslink. Upon exposure of different elastomers in biodiesel, crosslinking agent and/or filler can react with different components of biodiesel and thereby deteriorate the physical and mechanical properties. In addition, biodiesel exposed elastomer may lose its crosslink if hydrogen peroxide is formed by abstracting hydrogen from the components of biodiesel. Observations of compositional change of CR exposed biodiesel seem to indicate that hydrogen abstraction by CR from palmitale has converted a small amount of palmitale (16:0) into palmitoleate (16:1). This may partly cause for the reduction of palmitale from 44.272% to 40.79% and the increase of palmitoleate from 0.497% to 3.215%. Such type of change was not found for less polar EPDM exposed biodiesel. Concentration of different components in biodiesel such as methyl oleate, methyl linoleate, methyl linolenate etc. may also be changed due to presence of catalyst [29]. In present study, environmental factors (e.g. light, air) or certain constituents of elastomer may act as catalyst to increase the concentration of methyl oleate after exposure to elastomers. In fact, the entanglements of the long elastomer chains act as obstructions to the movement of the polymer chains. These obstructions enable the elastomer to sustain stable property. But, as a result of reaction between fillers and fuel, different mechanical properties can be influenced [30]. Results from change in hardness and tensile strength show that biodiesel is more aggressive than diesel. This can be attributed to the ester components of biodiesel. In addition, hygroscopic nature of biodiesel may introduce water into polymer matrix. Diffusion of water into polymer matrix can also deteriorate the mechanical properties [31]. Upon exposure to biodiesel, both tensile strength and hardness were reduced as compared to that of as-received samples. Decrease of tensile strength and hardness for EPDM and CR are comparatively higher than that for SR, NBR, PTFE. This suggests that after immersion into biodiesel higher degradation occurs for CR and EPDM. Change in volume of CR (80.48%) is comparatively higher than that of EPDM (49.48%). However, the sequence of biodiesel exposed elastomers that show more close hardness value to that of their respective as-received states is PTFE > SR > NBR. Similar sequence is also found for the tensile strength.

5. Conclusions

This study suggests the following conclusions:

1. Biodiesel and its blends swelled polychloroprene (CR) and nitrile rubber (NBR) to a greater extent than did diesel. On the other hand, ethylene propylene diene monomer (EPDM) and silicone rubber (SR) swelled to a greater extent in diesel compared with that in biodiesel and its blends. Polytetrafluoroethylene (PTFE) showed a slight reduction in weight and volume with an increase in the concentration of biodiesel.

2. Upon exposure into biodiesel, both tensile strength and hardness were greatly reduced for EPDM and CR as compared to that in as-received condition. But changes of these properties were not so significant for SR, PTFE and NBR.

3. The overall sequence of compatible elastomers in palm biodiesel is found to be: PTFE > silicone rubber (SR) > NBR > EPDM > polychloroprene (CR).

4. Although PTFE seems to be the most compatible materials among those tested, it undergoes a slight reduction of main constituents. The effects of such dissolution on fuel properties require further investigation.

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