

# Compatibility of Metals and Elastomers in Biodiesel: A review

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## Abstract:

Recently biodiesel as an alternative fuel is getting more significance to replace diesel fuel partially and help reduce environmental pollution. However, corrosion of automotive materials in biodiesel is a major concern as this can reduce of engine life. This paper reviews the effects of corrosion on the engine parts that come in contact with biodiesel and its diesel blends. In metals copper, brass, bronze shows high level of corrosion in biodiesel and biodiesel blends on the other side aluminium shows low corrosion. Stainless steel has high resistance to corrosion as compare to copper, aluminium and copper alloys in biodiesel. Common methods adopted for measurement of corrosion include weight loss through Static emersion tests and electrochemical techniques by electrochemical impedance spectroscopy or on Potentiostat/Galvanostat. Biodiesel composed of saturated and unsaturated alkyl ester fatty acids when exposed to air, heat, light

and metallic contaminants can cause auto oxidation. The process ultimately leads to the formation of corrosive acids and deposits that cause a slow degradation of metal and elastomers. Elastomers such as nitrile rubber (NBR), EPDM, PVC, fluoro-viton, silicon rubber also show degradation nature in biodiesel. Static immersion test carried out to find out the degradation of elastomers in biodiesel for a particular time and temperature. The level of degradation has been finding out by measuring property change in elastomers at the end of test. A massive change was found in tensile strength, volume swell, hardness, compression set, weight change and elongation of elastomers at the completion of static immersion test. Results showed that the extent of degradation was higher for PVC, silicon rubber, EPDM and NBR while fluoro-viton exhibited good resistance to degradation and was least attacked.

**Key Words:** Corrosion, Static immersion, Stainless steel, Aluminium, Copper, Mild Steel, Bronze, biodiesel, Wear, Elastomers.

## Introduction:

As a result of increasing environmental concern and diminishing petroleum reserves, there is a growing trend to substitute biodiesel for conventional diesel fuel. As an alternative fuel, though biodiesel have some technical advantages over diesel fuel, the former appears to be more corrosive than diesel. The corrosive nature of biodiesel can be more aggravated if

Free water and free fatty acid are present in it. As compared to diesel, biodiesel is more prone to absorb water which tends to condense on metal surface and may cause enhanced

corrosion. Beside this, auto-oxidation of biodiesel can also enhance its corrosive characteristics and degradation of fuel properties. The use of biodiesel as an alternative fuel in compression ignition (CI) engines instead of petrodiesel (also known as 'mineral diesel', but hereafter referred to as 'diesel') has advantages as well as disadvantages. One of the advantages of using biodiesel as a fuel is its high

cetane number and absence of sulfur and aromatics.

Among the disadvantages is its low fuel density in comparison to mineral diesel, which requires a higher amount of fuel to achieve the same power to drive the engine [1]. Until now, CI engines were suited only for a low-ratio blend of biodiesel with diesel because of corrosion. Corrosion is the disintegration of a material as it reacts with other materials with which it comes into contact. According to Nernst's theory, all metals have a tendency to pass into solution. However, the extent of corrosion varies for metal ions depending on its oxidation potential and various prevailing conditions (temperature, water content, etc.) in the fuel. Metal ions, when present in fuel, can cause corrosion [2].

Kaul et al. [3] investigated the corrosiveness of different biodiesel (i.e. *Jatropha curcas*, *Karanja*, *Mahua* and *Salvadora*) as compared to that of diesel fuel. They found that biodiesel from *Jatropha curcas* and *Salvadora* were more aggressive for both ferrous and non-ferrous metal. Geller et al. [4] have reported that as compared to ferrous alloys, copper alloys are more prone to be attracted by corrosion into fat based biodiesel. In an another study, pitting corrosion was found on the bronze sintered filters integrated oil nozzle after 10 h operation with biodiesel at 70 °C [5].

Hence, recently, corrosion aspect of biodiesel as fuel has been tested by researchers for its viability in CI engines. Biodiesel is generally prepared from acid or alkali catalysts that are either homogeneous or heterogeneous [6]. Homogeneous acid catalysts, such as sulfuric acid, which are generally used for acid esterification, and impart corrosive nature to biodiesel fuel [7]. This is generally overcome by using solid acid catalysts which are easily separated from biodiesel and hence do not make the fuel corrosive [8–10]. Biodiesel also ought to be of high purity for its compatibility in CI engines. Therefore, incomplete conversion or inadequate purification (by water washing or other means) may result in impurities such as glycerol, free fatty acids, alcohol, and catalyst,

causing deposits in the engine, corrosion, and ultimately failure of the fuel [11].

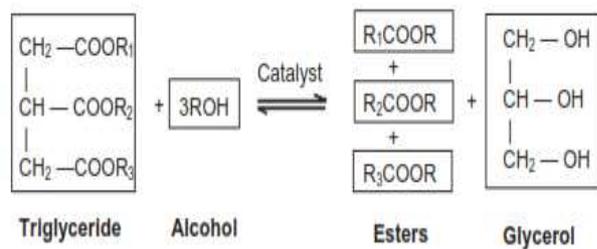
Biodiesel has a good lubricity and hence, it has a higher tendency as compared to mineral diesel to dissolve the metallic parts in the fuel. Thus, the study of corrosion with biodiesel as fuel and search for corrosion inhibitors becomes an important aspect for the enhanced endurance of biodiesel as a fuel in the compression ignition engine. An excellent review on the compatibility of automotive materials in biodiesel has been done by Haseeb et al. [12].

Diesel engine components are made from a variety of metals, non-metals, and elastomers. The main parts of the engine/vehicle that come in contact with fuel are fuel tank, fuel feed pump, fuel lines, fuel filter, fuel pump, fuel injector cylinder, piston assembly, and exhaust system. These engine/vehicle parts are made of metallic (i.e., steel, stainless steel, copper, aluminum, copper-based alloy, aluminum-based alloy, iron-based alloy, gray-cast iron, special cast iron, cast aluminum, forged aluminum, sand-cast aluminum, die-cast aluminum, and aluminum fiber) and non-metallic materials (i.e., elastomer, plastics, paint, coating, cork, rubber, ceramic fiber, and even paper). The fuel comes in contact with the various engine parts and its accessories at varying temperature, velocity, load, sliding, and physical state. It has been found that either the impurities in biodiesel or the deterioration of biodiesel through oxidation enhances the corrosiveness of the fuel.

## Production of Biodiesel:

Biodiesel can be produced from straight vegetable oil, animal oil/fats and waste cooking oil. The process used to convert these oils to biodiesel is called transesterification.

Vegetable oils/animal fats mainly consist of triglyceride molecules. The structure of one such molecule is shown schematically in Fig. 1

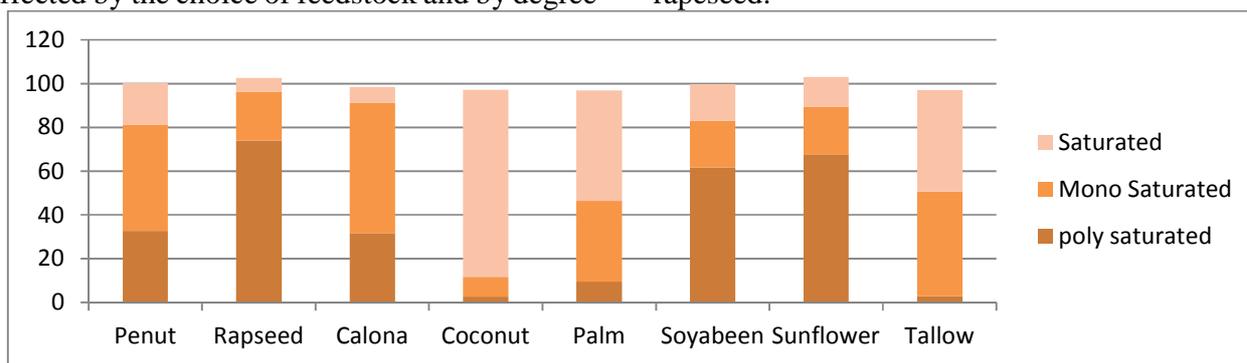


**Fig.1.** Transesterification reaction ( from Ref. [12])

esters (three separated long chain carbon molecules) by transesterification as shown in Fig. 1. Glycerol is removed as by-product and esters are known as biodiesel. These esters have several acronyms to describe the short chain biodiesel fuels as SME (soyabean oil methyl ester), RME (rapeseed methyl ester), FAME (fatty acid methyl ester, encompasses oils from many sources: all types of vegetable oils and animal fats), POME (palm oil methyl ester) etc. The total ester content is a measure of the completeness of the transesterification reaction [13]. The content of esters for different types of biodiesel depends on the type of feedstock used to produce biodiesel. Fuel properties such as cetane number (CN), viscosity, cloud and pour points, degree of saturation depend on the varieties and amounts of esters. The presence of impurities remaining after processing also affects the fuel properties. Therefore, properties of biodiesel are generally affected by the choice of feedstock and by degree

R1, R2, and R3 represent the hydrocarbon chains (more than 10 carbon atoms) of the fatty acid of the triglyceride. Glycerides make the oil thick and sticky with higher viscosity. In order to reduce the viscosity to make the fuel usable in a diesel engine, pure oil is converted from natural oil triglyceride into three mono-alkyl of refinement. For biodiesel, as an alternative to diesel fuel, a higher CN is desirable whereas higher viscosity and higher cloud and pour points are undesirable.

The fatty acid profile of biodiesel is identical to that of its parent oil or fat [14]. Biodiesels obtained from different sources contain different types and amounts of unsaturated and saturated fatty acids. Unsaturated fatty acids with double bonds in their structures are more susceptible to oxidation. Fig. 2 shows the bar diagram of total amount of saturated and mono- and poly-unsaturated fatty acids in different types of biodiesel. It is seen that biodiesel from coconut oil, palm oil and tallow contain more saturated acids whereas biodiesel from soybean, sunflower, rapeseed, calona etc. contain more unsaturated fatty acids. Thus coconut or palm oil based biodiesel is expected to be less prone to oxidation than biodiesel from soybean or rapeseed.



	Penut	Rapeseed	Calona	Coconut	Palm	Soyabean	Sunflower	Tallow
Saturated	19.1	6.2	7.3	85.4	50.4	16.7	13.4	46.3
Mono saturated	48.4	22.3	59.4	9.1	37	21.4	21.7	47.8
Poly Saturated	32.7	74	31.7	2.6	9.5	61.7	67.8	2.85

**Fig.2.** Saturated, mono- and poly-unsaturated fatty acid contents for different biodiesel. ( from Ref. [15,16,17]).

## Engine component materials that comes in contact with fuel in automobiles:

In diesel engine fuel system, fuel passes through three subsystems: fuel feed, combustion and exhaust sub-system. Basic components of these sub-systems are shown in Fig. 3.

The fuel feed sub-system helps to draw fuel from the tank and to deliver it to the injectors of various cylinders. It consists of diesel tank, preliminary fuel filter, feed pump, filter, an injector pump, injectors and connecting lines. From tank, fuel feed pump delivers fuel to the injection pump through filter. The injection pump feeds high-pressure lines to the fuel nozzles for injection into the cylinders

[18]. In in-line pumps and injectors, there is less reliance on the fuel for lubrication, however there are some sliding components at where fuel itself provides lubricity (e.g. plunger and barrel). In combustion zone, fuel is burnt once it is injected. This sub-system consists of cylinder block, cylinder liner, cylinder head, inlet valve, exhaust valve, piston, piston rings, piston pin and connecting rod. The piston compresses the air and raises its temperature above 500°C. The diameter of the piston is slightly smaller than

cylinder which allows the piston to slide up and down in the cylinder. To prevent the gap between piston and cylinder wall, piston rings are installed around the piston. The rings are split at single point. Engine exhaust system consists of mainly exhaust manifold, catalytic converter and muffler. After combustion the exhaust gas flows through the catalytic converter and the muffler. The catalytic converter converts most of the pollutant in the exhaust gas to harmless substances. The muffler reduces exhaust noise. During the flow of fuel in different sub-systems, fuel comes in contact with a wide variety of metallic and non-metallic materials. Different types of materials commonly used in diesel engine fuel system. Metallic materials include ferrous like steel, cast irons and non-ferrous like aluminum alloys and copper alloys. Elastomer, plastics, paints, paper etc. are the most common nonmetallic materials. Fuel comes in contact with these materials under different temperature, velocity, and load as well as in different sliding and physical state and thereby causes corrosion, wear, and degradation of metals.

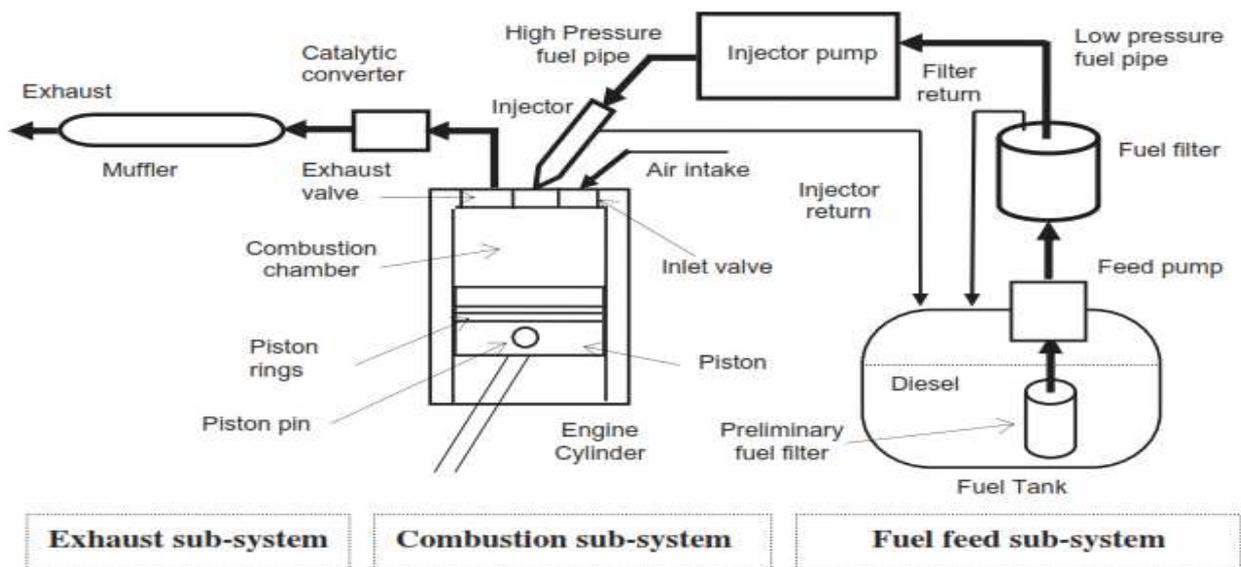


Fig. 3. Schematic diagram of a typical diesel engine fuel system. (From Ref. [12]).

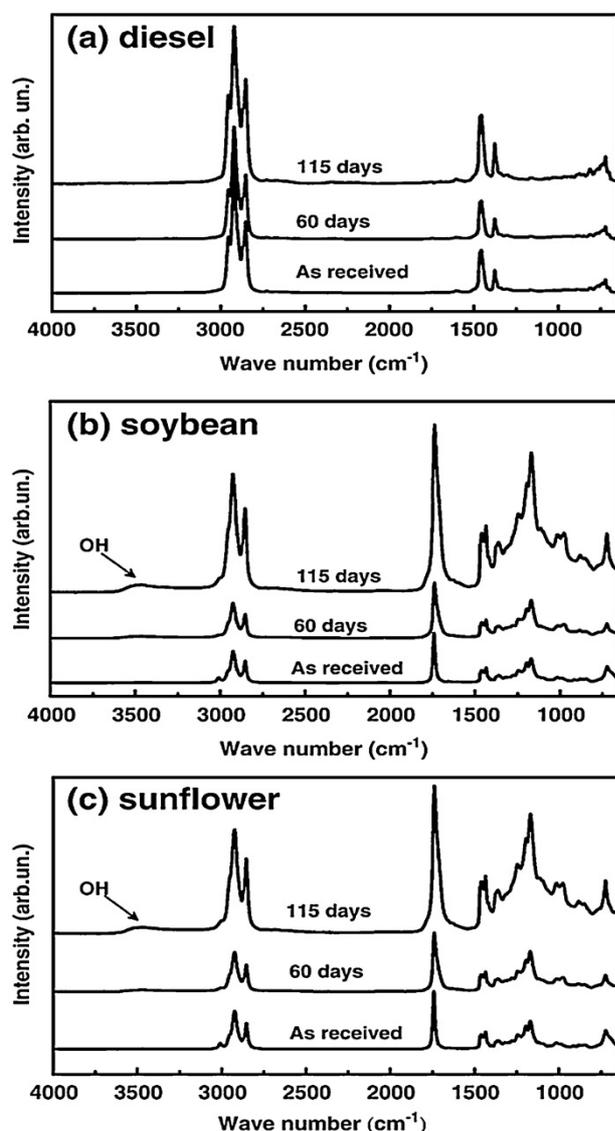
## Metal and alloys corrosion in biodiesel:

Currently, the level of corrosion in biodiesel fuel is specified by the 'copper strip corrosion test' and determined by ASTM D 93 specifications [19]. A polished copper strip is immersed in a specified volume of biodiesel for a specific time and temperature. The copper strip is then removed and washed. The color of the strip is then assessed as per the ASTM standard [20]. However, the 'copper strip corrosion test' provides limited information with respect to corrosiveness as it measures the level of corrosion that will occur when copper is present as metal. Corrosion in engine parts that are made of metals, alloys, and elastomers on contact with biodiesel occur due to the chemical composition of biodiesel that is comprised of unsaturated molecules that easily undergo oxidation. Factors that influence the performance and engine durability of a CI engine run on B0 (100% pure or 'neat' diesel) or a biodiesel blend are presence of oxygen in the functional groups (moieties), free fatty acids, degree of unsaturation, and hygroscopic nature (ability to attract and hold water) of the biodiesel [21]. The level of corrosion also depends on the type of alloy in contact with biodiesel fuel. In general, copper alloys have been found to be more corrosive than the ferrous alloys [21]. Apart from biodiesel, corrosion also occurs in engines operating on ethanol. Agarwal [22] reported corrosion in engine carburetors exposed to ethanol by three ways: general corrosion, dry corrosion, and wet corrosion. General corrosion results from ionic impurities such as chloride ions and acetic acid. Dry corrosion results from polarity of the molecule. Wet corrosion arises due to azeotropic water and oxidizes various metals [22]. In biodiesel-run engines, a high chrome stainless steel has been used to make oil nozzles and was found to be resistant to corrosion when exposed to biodiesel. The oil burner filter components made of copper and copper alloys were found to corrode in biodiesel, resulting in the fuel being

contaminated with copper ions. The copper content increased from 0.1 to 21 ppm after 2 h contact with the fuel when analyzed on Inductively Coupled Plasma (ICP). Corrosion was observed on the bronze filter incorporated in the oil nozzle after 10 h operation using biodiesel at 70 °C. Pitting corrosion was also observed after several hours of operation with biodiesel fuel [23].

Geller et al. [24] reported that copper and brass are prone to corrosion as observed by weight loss through pitting and deposits covering the surface. Corrosion of steel, however, is not very clear and data differ [24]. Steel is an alloy comprised mostly of iron and has a carbon content ranging from 0.2 to 2.1% by weight. The carbon content in the steel could be a reason for its high resistance to corrosion due to the fact that carbon has a high corrosion resistance [25]. Steel, until now, has been found to show high resistance to corrosion in biodiesel blends as evidenced from electrochemical impedance spectroscopy (EIS). However, Prieto et al. [26] reported that biodiesel is more conductive electrically compared to gasoline and diesel and may cause galvanic metal corrosion in steel. Corrosion of metal and metal alloys varies with feedstock used for synthesis of biodiesel. This is due to differences in the chemical composition of the feedstock that show various degrees of corrosiveness. Maru et al. [27] tested strips of structural carbon steel (CS) and high density polyethylene (HDPE) exposed to soybean biodiesel, sunflower biodiesel, and diesel using static emersion tests (SET), observing weight loss, and observing the surface by optical, scanning electron, and atomic force microscopy. The time span of the test was between 60 and 115 days. Although the weight of the CS strips did not change with exposure to biodiesel for 60 days, the soybean biodiesel was found to be more compatible with carbon steel than sunflower biodiesel and even diesel. The weight loss that occurred in carbon steel after 115

days was quite low (around  $10^{-5}$  g) and only slightly higher in biodiesel. The Fourier Transform Infra Red (FTIR) Spectroscopy spectra revealed the formation of secondary products due to degradation of the fuel. The C=O peak was broadened and hydroxyl peaks sharpened with time (Fig. 4). Degradation of fuel was also observed in diesel, which has been attributed to its sulfur content, resulting in the formation of iron sulfide. In the HDPE strip exposed to biodiesel and diesel, a gain in weight and discoloration was observed. The gain in weight occurred during the first 75 days and then remained constant.

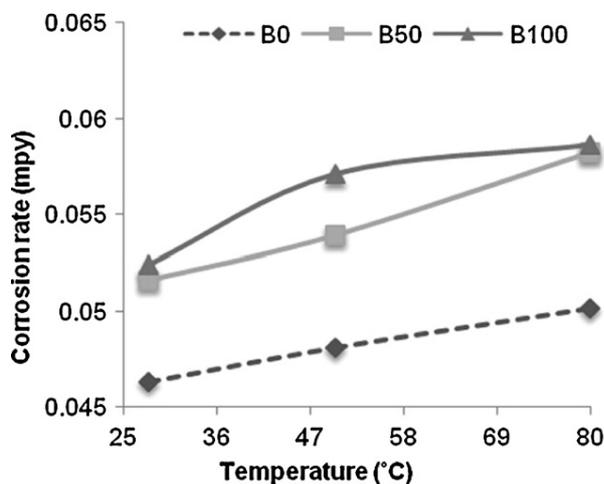


**Fig. 4.** FT-IR spectra of fluids before and after immersion tests. (a) Diesel; (b) soybean; (c) sunflower [27].

Corrosion becomes an important aspect in usage of biodiesel fuel because many of the engine parts are composed of metals such as aluminum, copper and its alloys, and stainless steel [28] that may be prone to corrosion. Percent aluminum in engine components includes piston (100%), cylinder heads (70%), and engine blocks (19%). Pumps and injectors are often composed of copper and its alloys. Parts composed of stainless steel include fuel filter, valve bodies, nozzle, and pump ring [29,30]. Fuel degradation varies with the specific metal used. Based on the observation that biodiesel degrades through moisture absorption, auto-oxidation, and microbial attack during storage, Fazal et al. [31] tested corrosion of aluminum, copper, and stainless steel in petrodiesel and palm biodiesel. The static immersion test conducted on B100 and diesel was done at 80 °C for 600 and 1200 h and an agitation rate of 250 rpm. The corrosion rate in copper, aluminum, and carbon steel has been found to be 0.586, 0.202, and 0.015 mils per year (mpy), respectively in palm biodiesel. In diesel, the rate of corrosion was less and found to be less than 0.3 mpy for copper, less than 0.15 mpy for aluminum, and was almost the same for carbon steel (0.015 mpy) [31]. In an earlier study, Haseeb et al. [32] reported the rate of corrosion to be only 0.053 mpy for copper strips at 60 °C. The enhanced rate of corrosion has been attributed to higher temperature and to the agitation of metal specimen in the fluid provided during the test [33, 34]. In a recent study, Fazal et al. [35] tested the effect of corrosion on mild steel dipped in biodiesel and diesel at temperatures of 27, 50, and 80°C. Corrosion rate increased with increasing temperature in the diesel (B0) and biodiesel, especially B50 and B100 (Fig. 5). The study of surface morphology of the test coupons suggested that the depth attack was more prominent with metal surfaces exposed to biodiesel than those exposed to diesel.

Elemental analysis of the metal samples also revealed presence of oxygen on their surfaces, which increased at higher temperature, indicating oxidation of the metal surface. X-ray

diffraction (XRD) analysis revealed two phases in diesel exposed metal:  $\text{Fe}(\text{OH})_3$  and  $\text{Fe}_2\text{O}_3$ . In the biodiesel-exposed metal, a new, third,  $\text{Fe}_2\text{O}_2\text{CO}_3$  phase was observed in addition to  $\text{Fe}(\text{OH})_3$  and  $\text{Fe}_2\text{O}_3$ . The formation of the  $\text{Fe}_2\text{O}_2\text{CO}_3$  phase has been attributed to absorption of water, oxygen, and carbon dioxide from the atmosphere.



**Fig. 5.** Corrosion rate of mild steel after exposure to diesel (B0), B50, and B100 for 1200 h at 27, 50, and 80 °C [35].

Corrosion of metals can also trigger/catalyze other undesirable reactions leading the instability and degradation of biodiesel. ASTM D130 is currently used to measure the corrosion of biodiesel by copper strip tarnish test. During the test, copper strips are immersed into the sample being evaluated. At the end of the exposure period, the strips are compared to standardized reference strips and rated on a scale of slight tarnish 1A, B to heavy tarnish 4A–C [36]. Some test results available in the literature are summarized in Table 1. In most cases, such tests in biodiesel indicate 1A which represents marginal corrosion. It is thus seen that the results cannot distinguish between different types of biodiesel as well as different concentration of biodiesel in blends. Similarly, TAN value is

another parameter measured by titration to indicate the total acid number. For biodiesel, the standard calls for a maximum acid number of 0.80 mg KOH/g [36]. The acid number is directly related to the free fatty acid content. Higher the free fatty acid content and is considered as a measure of corrosiveness of biodiesel. For biodiesel, total acid content increases as it is oxidized specially while in service. Besides, the acid number can become a serious issue when feed stocks with high free fatty acids are used to produce biodiesel. It has been suggested that both of these indicators are not reliable indicators of the corrosiveness of biodiesel [37,38]. The corrosive nature of biodiesel can also stem from impurities like water, methanol, free glycerol, free fatty acid, catalyst (Na and K) remaining after processing and also from the reversibility of the chemical reaction which produces the esters. Under certain conditions absorbed water can convert some of the esters back to fatty acid plus methanol. These acids can then react with metals and causes [37].

Very few research studies are available on the corrosion of metals in biodiesel. Haseeb et al. [39] investigated corrosion characteristics of copper and leaded bronze in palm biodiesel. They found that in biodiesel, copper was more susceptible to corrosion than leaded bronze. They also added that oxidized biodiesel was more corrosive than as-received biodiesel. Tsuchiya et al. [37] investigated corrosion of terne sheet steel by immersion in diesel and 5% FAME blended diesel fuel at 80 °C. Terne sheet is a Pb–8% Sn coated rolled steel sheet which is commonly used to fabricate fuel tank. After 500 h, they found pitting corrosion on the surface of the sample immersed in 5% FAME blended diesel (Fig.6). They observed that corrosion occurred even in 2% FAME biodiesel. They opined that TAN value was not enough to explain the corrosive nature of FAME. They suggested that oxidation process reconverts esters into fatty acids such as formic acid, acetic acid, prop ionic acid, caproic acid which are highly corrosive. Sgroi et al. [40] reported on the corrosive effect of biodiesel on sintered bronze filter of an oil nozzle. They

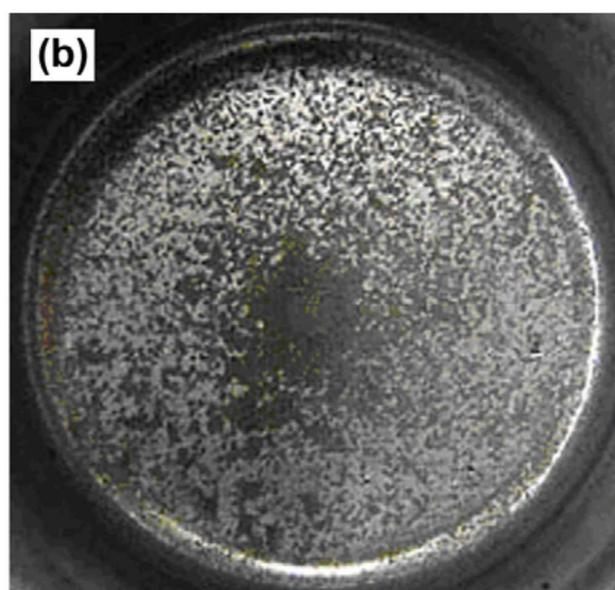
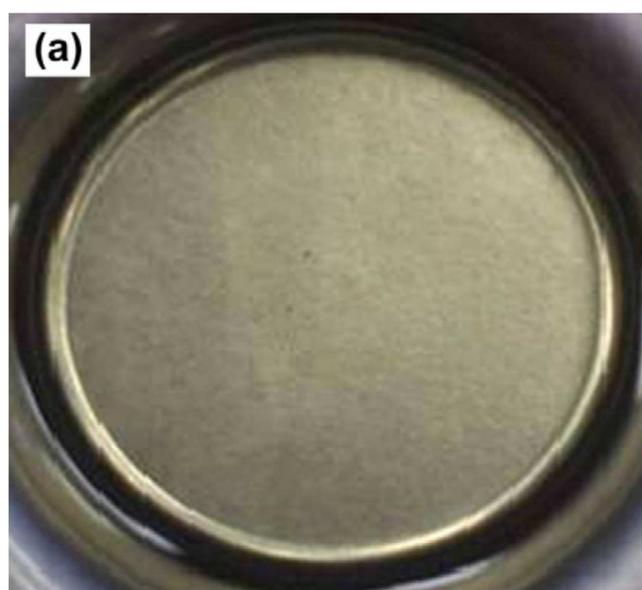
observed that pitting corrosion occurred on bronze when the nozzle operated at 70°C for several hours. Corrosive nature of biodiesel seems to be attributed to its free fatty acid

components and impurities remaining after processing. In addition, biodiesel is hygroscopic in nature and can absorb moisture from air and thereby can increase the water content [47]

**Table 1**

Copper strip corrosion test result

Fuel	Experimental result	Test Method	Reference
B0 (Diesel)	1A	ASTM D 130	Kanneth Proc [41]
B20 (methyl soyate)	1A	ASTM D 6751	Mazzoleni et al.[42]
B20 (soyabeen oil)	1A	ASTM D 130(IP 154)	Terry [44]
B100 (rapseed oil )	1A	EN ISO 2160	Dinkov et al.[45]
B100 (ethyl soyate)	1A	ASTM D 130	Clark et al.[46]
B100 (cotton seed oil)	1A	ASTM D 130	Rashid et al.[43]



**Fig.6** Appearance of terne cup after immersion in (a) diesel and (b) B5 for 500 h [37]

In addition to the scientific literature, reports on materials compatibility issues are also available which are mainly produced by industrial stakeholders and government agencies. In one such report it has been suggested [47] that copper, brass, bronze, lead, tin and zinc are corroded by biodiesel. These elements accelerate oxidation of biodiesel and hence should be avoided in fuel system. Stainless steel, carbon steel and aluminum, on the other hand, have been suggested to be used in biodiesel.

Ballote et al. [48] used electrochemical techniques to determine the effect of corrosion in biodiesel samples exposed to aluminum during different stages of washing. The corrosion process occurred in the same manner as if aluminum was exposed to aqueous or ethanol alkaline solution. The electrochemical measurements were done by Potentiostat/Galvanostat in a 3 electrode cell. During the initial wash, the open circuit potential ( $E_{ocp}$ ) showed a high negative value ( $-600$  mV), which might have occurred due to reaction of aluminum with biodiesel. Repeated washing of biodiesel by water resulted in a positive of  $E_{ocp}$  value, which was attributed to the use of potassium hydroxide or sodium hydroxide as homogeneous catalyst which forms  $Al(OH)_3$  as a passive layer. The corrosion potential ( $E_{corr}$ ) was negative (below  $-500$  mV) through six washing cycles, but increased to  $-50$  mV after the seventh wash cycle. The corrosion current density also decreased with the number of wash cycles (from  $10$  nA/cm<sup>2</sup> to  $0.10$  nA/cm<sup>2</sup>).

Kaul et al. [3] did a static immersion test (SIT) on the diesel piston liner and piston metal that came into contact with the biodiesel fuel. The SIT was conducted for 300 days at room temperature, which varied between  $15$  and  $40$  °C, and corrosion rate (mpy) and penetration (mdd) were determined. Weight losses resulting from corrosion in the piston liner exposed to Salvadora, Jatropha, Karanja, and Mahua biodiesel were  $6.1$ ,  $3.6$ ,  $0.3$ , and  $0.3$  mg,

respectively. A high weight loss of  $2.1$  mg was also observed in piston metal exposed to Salvadora biodiesel, followed decreasingly by Jatropha biodiesel ( $0.2$  mg), then Karanja and Mahua biodiesel ( $0.1$  mg). Corrosion rate and penetration were high in Salvadora and Jatropha biodiesel. An increase in Total Acid Number due to oxidation of the fuel was observed with Jatropha, Karanja, and Mahua, which led to increased corrosion. With Salvadora, however, the increase in corrosion was attributed to presence of a high concentration ( $1600$  ppm) of sulfur. Although they reported that the extent of corrosion was within the permissible limits and no gum formation was observed.

Based on the studies done so far, it can be said that biodiesel is more corrosive than diesel. The corrosiveness of biodiesel increases with the concentration of biodiesel in the blend. Copper alloys are more susceptible to corrosion than ferrous alloys and aluminum alloys. Lead alloys on terne steel sheet are also affected by biodiesel. The presence of impurities and water increases the corrosion tendency of biodiesel. There are concerns that the currently used indicators of corrosiveness of biodiesel e.g. copper strip corrosion and TAN value that are prescribed by different standards are not effective enough. Clearly at present, there is a serious lack of scientific data on corrosion of automotive metals and alloys in biodiesel based on which confident decisions could be made. Corrosive nature of biodiesel under wide spectrum of compositional, environmental and operating variables should be investigated.

### **Degradation of Elastomers in biodiesel:**

The compatibility of seal and hose materials commonly used in automotive fuel systems using conventional hydrocarbon fuels (petrodiesel) has long been established. However, there is less information available on the compatibility of fuel system elastomers with biodiesel fuels. Concern

arises from the fact that petrodiesel and biodiesel have much different chemical structures and consequent different effects on elastomers. Besides, biodiesel is susceptible to oxidation upon exposure to air as well as storage conditions and the amount of unsaturation of fatty acids. Being oxidized, it produces hydroperoxides at the unsaturated points of the fatty acids and these hydroperoxides later decompose to aldehydes, ketones, shorter chain carboxylic acids [49]. Esters, the main components of biodiesel, can also be easily hydrolyzed in the presence of water to form carboxylic acids. All these products including the chemical composition of biodiesel affect the swelling characteristic of elastomer depending not only on its composition but also on the formulation of the compound [50].

For diesel engine, usually hoses are produced from rubber modified polyolefin whereas gaskets are produced from gasket paper, non-asbestos, rubber, ethylene-propylene-diene monomer (EPDM), nitrile, Buna, neoprene, flexible graphite, viton, silicone, metal, mica, felt or plastic polymer, like Teflon, (PTFE), ethylene polymer etc. The common seal materials are polyurethane, nitrile rubber, Buna-N, EPDM, silicon rubber, virgin polytetrafluoroethylene (PTFE), aluminum etc. Many of these materials used in diesel engine are not compatible with biodiesel. Trakarnpruk and Porntangjitlikit [51] carried out immersion tests with six types of elastomers like nitrile rubber (NBR), hydrogenated nitrile butadiene rubber (HNBR), NBR/PVC, acrylic rubber, co-polymer fluoroelastomer (FKM), and terpolymer FKM in B10 (palm biodiesel) for upto 1008 h at 100 °C. They showed that mass and volume increased with respect to time for all test samples except NBR and NBR/ PVC. Only for these two (NBR and NBR/PVC) mass and volume were decreased with time.

Materials compatibility may also vary depending on feedstock of biodiesel. Frame and McCormick [52] investigated the degradation characteristics of elastomers like peroxide-cured nitrile rubber (N1059), nitrile rubber (N674), high aceto-nitrile content rubber (N0497), fluorocarbon filled with

carbon black (V747) and fluorocarbon without carbon black (V884) in diesel, diesel blend with 15% ethanol and 20% soy-derived biodiesel. They observed that these elastomers were fully compatible with B20 and diesel but not in 15% ethanol blend.

Haseeb et al. [53] did a SIT on three elastomers (nitrile rubber, polychloroprene, and fluoro-viton A) for compatibility with palm biodiesel at 25 and 50 °C for 500 h. The effect of biodiesel on corrosion was determined by measuring mass, volume, tensile strength, hardness, and elongation. Nitrile rubber and polychloroprene swelled and degraded in biodiesel; the reaction occurred between the polymer backbone and cross-linking system or with the filler system. However, the mass and volume of fluoro-viton A remained almost unchanged in biodiesel as well as diesel (Fig. 7). The absorption solvent and the relaxation of polymer chains increased mass and swelling of the nitrile rubber and polychloroprene. Increased crosslinking agent results in more swelling. In polychloroprene, glycol dimethacrylates present as cross-linking agent resulted in lower swelling in fuels compared to nitrile rubber. Swelling increased with increase in biodiesel content in the fuel. Elastomers include polar as well as non-polar substances. Thus, the polar end of the biodiesel (present in esters) interacts with the elastomers through dipole-dipole interaction, causing them to swell. This has been attributed to higher liquid absorption as compared to the extraction of soluble components from the elastomer. Increasing temperature had varying effect on elastomers. While increased swelling was observed in nitrile rubber, decreased swelling was observed in polychloroprene and almost no change was observed in fluoroviton A at 50 °C. The reason attributed for loss in mass and volume in polychloroprene is its containing polychloroprene, which is stable at low temperature and thus its polar group gets dissolved in biodiesel, causing reduced weight and volume. A decrease in tensile strength was observed in nitrile rubber and polychloroprene. However, no change in tensile strength was

observed in fluoro-viton. Analysis by FTIR spectrometry showed presence of carbon–carbon double bonds that may have resulted from reaction between the methylene or vinyl groups of nitrile rubber. The degradation of nitrile rubber and polychloroprene in biodiesel has been attributed to the carboxylic polar groups present in biodiesel

In order to investigate the oxidation effect, Terry [54] conducted experiments with different types of elastomers like sulfur cured acrylonitrile butadiene nitrile rubber (NO674-70), peroxide cured acrylonitrile butadiene nitrile rubber (NB104-75), hydrogenated nitrile polymer (KB162-80), fluorocarbon polymer with 67% fluorine content (VB153-75), fluorocarbon polymer with 66% fluorine content (V1164-75) in different types of feedstock blends like rapeseed methyl ester (B5, B20) and soybean methyl ester (B5, B20, oxidized B5, oxidized B20). He found that NB104- 75, NO674-70 and KB162-80 showed higher volume swell and little decrease in hardness in B20 oxidized SME. Dimensional changes were higher in oxidized B5 and B20. These results most likely proved that oxidized products caused comparatively more degradation of elastomers. Tensile strength was decreased for each elastomer only little in all the fuels.

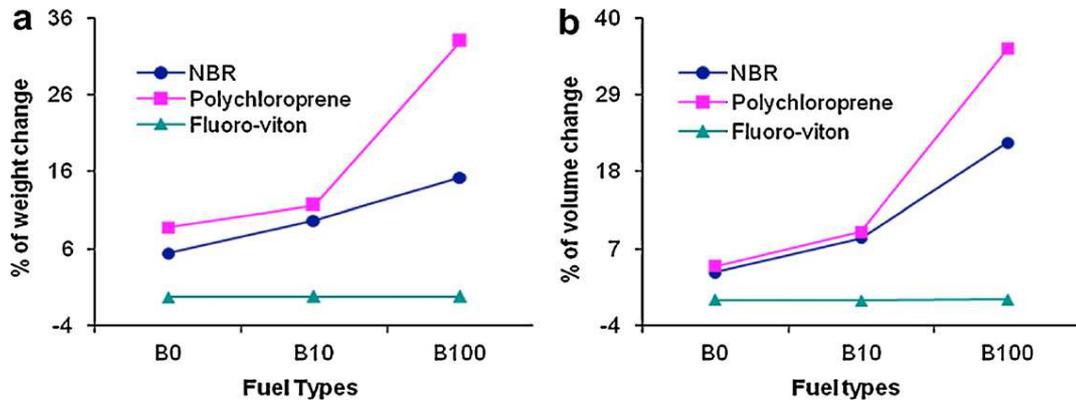
According to Baranescu [55] most of the elastomers used with conventional diesel swell by absorption of aromatic compounds. It is also reported in his study that biodiesel may leach aromatics as well as additives designed to prevent hardening and cracking.

Haseeb et al. [56] tested the physical properties of various elastomers on their exposure to diesel and biodiesel (prepared from palm oil). The elastomers tested were ethylene propylene diene monomer (EPDM), silicone rubber (SR), polychloroprene (CR), polytetrafluoroethylene (PTFE), and nitrile rubber (NBR). A SIT was carried out for B0, B10, B20, and B50 biodiesel at 25 °C for 1000 h. The physical properties of weight/volume loss, hardness, and tensile strength were determined after every 250 h of immersion. While biodiesel blends were found to

cause high swelling in CR and NBR elastomers, the EPDM and SR elastomers swelled more in diesel than in biodiesel. PTFE elastomer showed slight loss in weight and volume, whereas other elastomers showed considerable gain in weight due to swelling. The reason attributed for high swelling in CR and NBR elastomers was the polar nature of the elastomers that dissolved in the biodiesel with its polar ester group. Exposure to metals may have caused oxidation of the fuel, which enhanced its polarity and further degraded the elastomers. When exposed to biodiesel, elastomers are affected in two ways: first by absorption of liquid by elastomers and second, by dissolution of soluble components from the elastomers in the liquid medium. Swelling was the result of high absorption amount by elastomers in comparison to their dissolution in the fuel. The tensile strength of biodiesel decreased to a large extent in the case of EPDM and CR. A minor decrease in tensile strength was observed in SR, PTFE and NBR elastomers. Among all of the elastomers, PTFE showed high compatibility with biodiesel that was attributed to absence in its polarity, although it also underwent reduction in its constituents. Swelling of the elastomers in biodiesel fuel can be retarded by adding cross-linking agents in the elastomers. Peroxides are commonly added as cross-linking agents [57].

All these guideline suggest that fluorocarbon (e.g. PTFE), acetal etc. are compatible for use in biodiesel. Viton, EPDM etc. can also be used depending upon conditions. However, some common types of elastomer like nitrile rubber NBR, SBR, chloroprene, neoprene, natural rubber etc. are not suitable for use in biodiesel. Mechanisms of degradation of polymer in biodiesel are not well understood yet. The effects of fatty acid structure (e.g. degree of saturation and biodiesel purity) on elastomer compatibility do not appear to have been examined. Highly unstable free fatty acids as well as unreacted mono-, di-, and triglycerides, glycerol, and methanol may have a great impact on elastomers which require systematic investigations. These

aspects of compatibility with elastomers are a topic for future research.



**Fig. 7.** Changes in: (a) weight and (b) volume of different elastomers after immersion at room temperature for 500 h [53].

### Conclusion:

Biodiesel has chemical characteristics that are distinct from that of petroleum diesel. It is therefore expected that they will interact with materials differently. Compositional differences of biodiesel derived from different feed stocks complicate the situation. In automobile fuel systems, numerous materials come in contact with fuel. These can be mainly grouped into ferrous alloys, non-ferrous alloys and elastomers. Among these groups of materials, elastomers undergo degradation to a greater extent in biodiesel. Common elastomers like natural rubber, nitrile, chloroprene/neoprene etc. are not suitable for use in biodiesel. Fluorocarbons have shown good resistance and are recommended for used in biodiesel. Exact mechanisms of degradation of elastomers in biodiesel and the effects of different biodiesel constituents require systematic investigations. Between the other two groups of materials, viz. ferrous alloys and non-ferrous alloys, the former are more resistant to attack in biodiesel. Among non-ferrous alloys, copper alloys and lead alloys are the most vulnerable which appear to be followed by aluminum.

Metallic components in automobiles can undergo corrosive, tribological or both forms (tribo-corrosion) of attacks depending on their functionality. Corrosion studies done so far

suggest that biodiesel is more corrosive than diesel. However, there is no conclusive evidence as to whether the extent of corrosion encountered in biodiesel is within limits acceptable for automotive components. The corrosiveness of biodiesel increases with the concentration of biodiesel in the blend and the extent of oxidation. Copper alloys are more susceptible to corrosion than ferrous alloys and aluminum alloys. Lead alloy coating on terne steel sheet which is used for automotive fuel tanks is severely affected by biodiesel. The presence of impurities and water increases the corrosion tendency of biodiesel. There are concerns that the currently used indicators of corrosiveness of biodiesel e.g. copper strip corrosion and TAN value that are prescribed by different standards are not effective enough. Corrosive nature of biodiesel under wide spectrum of compositional, environmental and operating variables should be investigated.

As for the tribological degradation of metallic components in biodiesel, short term laboratory studies have shown that biodiesel offers beneficial properties in terms of lower wear and friction. However, oxidation of the biodiesel and higher test temperatures adversely affect its tribological properties. A number of long term wear durability tests have been conducted using

static engine as well as on-road tests. Most of these studies mainly evaluated engine component wear in biodiesel in terms of the contents of different elements in lubricants. In general, these studies show low or similar wear for many elements in biodiesel compared with diesel. Fe, the main constituents of the most critical components in automobiles, shows less or similar wear, except for one study which involved higher blend (100%). On the other hand, Cu shows higher wear in many cases. Pb and Al follow copper in terms of decreasing trend in the number of studies where higher wear was reported for these metals. The lubricant analysis technique for wear evaluation provides only overall indication of the extent of wear. It does not furnish provide a better understanding of corrosion for application. A few inhibitors (ethylenediamine, tert-butylamine, and n-butylamine) have been found to be effective in the formation of a stable metal oxide as protective layer and thus retarding corrosion in biodiesel. An antioxidant, tert-

information on the extent of damage of individual components which is important in the prediction of component life. Such information can be obtained by examining the individual wear components in an engine. A handful of studies involving such engine teardown investigations did not find excessive in lower blends (6B20) of biodiesel as compared with diesel. However, higher wear was reported for piston rings in 100% biodiesel. Corrosion of metallic parts and elastomers takes a long duration. Current studies done on metal samples commonly used in CI engines have been done for a limited period of time (1000 h or 300 days). Further testing carried out for longer durations is needed to

butylhydroquinone, was also found to retard the corrosion of copper coupon in biodiesel along with enhancing the oxidation stability of the fuel. Further studies on the effectiveness of inhibitors added to biodiesel are needed.

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