A STUDY ON THE PHYSICAL AND MECHANICAL CHANGES OF NITRILE RUBBER IN PALM OIL BIODIESEL

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DECLARATION

I declare that this project report entitled "A Study on Physical and Mechanical Changes on Nitrile Rubber in Palm Oil Biodiesel" is the result of my own work except as cited in the references

Signature : ....

Name : ....

Date : ....

APPROVAL

I hereby declare that I have read this project report and in my opinion this report is sufficient in terms of scope and quality for the award of the degree of Bachelor of Mechanical Engineering.

Signature : ....

Supervisor's Name : ....

Date : ....

DEDICATION

To my late father and beloved mother

ABSTRACT

Biodiesel has attracted researchers' interest since its introduction as a green alternative fuel. Biodiesel is made from the transesterification of animal fats, plants, algae, or even waste cooking oil, which maximizes the use of natural resources while alleviating increasingly serious oil shortages and pollution. Biodiesel may be used directly in automobile engines without any modifications which may result in improving the combustion quality and lowering the hazardous emissions. Despite this, certain questions about biodiesel compatibility with fuel system elastomers remain unanswered and controversial. Gaskets, gasoline hoses, O-rings, and other components are now made from a variety of materials, most of which are entirely compatible with fossil fuels but not with biodiesel or biodiesel blends. There are few papers studied on the degradation on the different type of elastomer in various type of biodiesel or biodiesel blends. However, the information on the changes of elastomer in palm oil biodiesel is insufficient. Thus, in this study, the aim is to investigate on the physical and mechanical changes of the elastomer, nitrile rubber upon exposure on the palm oil biodiesel B30. A static immersion test in palm oil biodiesel B30 were carried out at room temperature (25°C) and high temperature (50°C) for 4 weeks (672h). Different in physical changes in mass is recorded at every 250h of immersion time. A set of comparison data on previous research involving palm oil biodiesel with various blend were analyzed and discussed on different in physical and mechanical changes in volume hardness respectively due to the insufficient amount of data. The experiment and comparison on the previous research found an increasing in trend line of the mass and volume changes While the hardness was found to have decreasing trend line on lower and higher blend biodiesel from that B30.

ABSTRAK

Biodiesel telah menarik minat penyelidik sejak diperkenalkan sebagai bahan api alternatif hijau.Biodiesel diperbuat daripada transesterifikasi lemak haiwan, tumbuh-tumbuhan, alga, atau bahkan minyak masak sisa, yang memaksimumkan penggunaan sumber asli 5tatic mengurangkan kekurangan dan pencemaran minyak yang semakin serius.Biodiesel boleh digunakan secara langsung dalam enjin kereta tanpa sebarang pengubahsuaian yang boleh mengakibatkan peningkatan kualiti pembakaran dan menurunkan pelepasan berbahaya.Walaupun begitu, soalan-soalan tertentu mengenai keserasian biodiesel dengan elastomers sistem bahan api kekal tidak terjawab dan kontroversi. Gasket, hos petrol, O-cincin, dan komponen lain kini diperbuat daripada pelbagai bahan, yang kebanyakannya serasi sepenuhnya dengan bahan api fosil tetapi tidak dengan biodiesel atau campuran biodiesel. Terdapat beberapa kertas yang dikaji mengenai kemerosotan pada jenis elastomer yang berbeza dalam pelbagai jenis biodiesel atau campuran biodiesel.Walau bagaimanapun, maklumat mengenai perubahan elastomer dalam biodiesel minyak sawit tidak mencukupi. Oleh itu, dalam kajian ini, tujuannya adalah untuk menyiasat perubahan fizikal dan mekanikal elastomer, getah nitrile apabila terdedah kepada biodiesel minyak sawit B30. Ujian refleksi 5tatic dalam biodiesel minyak sawit B30 telah dijalankan pada suhu bilik (25℃) dan suhu tinggi (50℃) selama 4 minggu (672j). Perbezaan dalam perubahan fizikal dalam jisim direkodkan pada setiap 250h masa rendaman. Satu set data perbandingan mengenai penyelidikan terdahulu yang melibatkan biodiesel minyak sawit dengan pelbagai campuran telah dianalisis dan dibincangkan tentang perubahan fizikal dan mekanikal dalam isipadu dan kekerasam masing-masing. Namun disebabkan oleh jumlah data yang tidak mencukupi, eksperimen dan perbandingan pada penyelidikan terdahulu mendapati peningkatan dalam garis trend perubahan jisim dan isipadu, manakala ciri kekerasan didapati penurunan garis trend pada biodiesel campuran yang lebih rendah dan lebih tinggi daripada B30 itu.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVATIONS

ACN	Acrylonitrile
ASTM D6751	American Society for Testing and Material for biodiesel blends
ASTM D471	American Society for Standard Test Method for Rubber Property
ASTM G31	American Society for Standard Guide for Laboratory Immersion Corrosion Testing of Metals
B5	Biodiesel 5%
B7	Biodiesel 7%
B10	Biodiesel 10%
B20	Biodiesel 20%
B30	Biodiesel 30%
B100	Biodiesel 100%
CR	Polychloroprene
EDPM	Ethylene Propylene Diene Monomer
EN14214	European Committee for Standardization for test methods of FAME
FDM	Fuel Delivery System
FKM	Fluorocarbon
IRHD	International Rubber Hardness Degree
ISO 1817	International Standard for Rubber, Vulcanized or Thermoplastic
KOH	Potassium Hydroxide
NBR	Nitrile Rubber
SR	Silicone Rubber

LIST OF SYMBOLS

g	Gram
h	Hours
H_2	Hardness sample after immersion
H_1	Hardness sample before immersion
mg	Milligram
ml	Milliliter
mm	Millimeter
M_1	Mass sample before immersion
M_2	Mass sample after immersion
wt%	Weight Percent
°C	Degree Celsius
%	Percentage

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Biodiesel is an alternative fuel besides fossil fuel due to its abundant resources and environmental benefits. The blended form of biodiesel with diesel was initiated from a minimum of 1% volume of biodiesel. Currently, the blending level has reached a maximum of 20% biodiesel volume, B20 (Chandran et al., 2016). In the automotive industry, the use of biodiesel has been steadily growing in the last few years, especially in France (where diesel oil blends are used commonly) and Germany (where pure biodiesel engines can be fueled) (Carraretto et al., 2004). However, in Malaysia, the use of biodiesel is still in low blends and not commonly used. Although biodiesel has certain advantages over fossil diesel, there are some drawbacks to it, especially for B20 and beyond, which depends on the chemical properties. It has been shown to damage the vehicle engine by clogging the fuel filter, corrode metal, and form engine and injector deposits (Tziourtzioumis & Stamatelos, 2019). A wide range of modular units, such as the fuel pump, fuel injector, engine, and exhaust system, are in direct touch with the fuel in a vehicle system. Despite the fact that attempts to use biodiesel to power existing diesel engines have been ongoing for more than a decade, the materials incompatibility that results in early failure of fuel delivery components, primarily line and hose leaks, continues to be a problem (Chandran et al., 2016).

Metals and rubbers make up the majority of the components in these engines in which the conventional automotive fuel systems were designed for petroleum-based fuels, thus moving to biofuels could cause rubber to swell and degrade, as well as metal parts to corrode

(Akhlaghi et al., 2015). Biodiesel comes into touch with a variety of materials in car applications, which can be divided into three categories: ferrous alloys, non-ferrous alloys, and polymers. When metals come into touch with biodiesel, they can corrode and wear out. Due to the biodiesel utilized, polymers such as plastics and elastomers can degrade. The most popular elastomer materials used in gaskets, gasoline hoses, and O-rings are nitrile rubber (NBR), polychloroprene (CR), ethylene propylene diene monomer (EDPM), silicone rubber (SR), and fluorocarbon (FKM). When exposed to heat, light, oxygen, chemicals, or other harsh conditions, most elastomers undergo considerable changes over time. These modifications could have a significant impact on its attributes and service life. Because biodiesel has a solvency feature, it can quickly destroy elastomer materials (Fazal et al., 2019)

According to certain research, when biodiesel was used as a fuel in diesel engines, the injection system suffered some damage, including swelling in the elastomeric seals in the injection distribution, which could lead to fuel leakage (Salete Martins Alves et al., 2017). The degradation of rubber seals, O-rings, gaskets, and hoses is now the most serious issue associated with biofuel incompatibility in the automotive industry.

1.2 PROBLEM STATEMENT

Research on diesel engines running on biodiesel has found that some problems will occur, resulting in material degradation. Some other issues also arise related to the injector deposit formed in the engine that cause injector chocking. The results of the swelling revealed an incompatibility between the elastomer and the fuel, resulting in a significant loss of elastomeric qualities and, as a result, a loss of sealing capacity. There has been a lot of evidence that elastomers deteriorate in biodiesel. In biodiesel, elastomers are degraded to a greater extent. The causes of degradation are discussed from numerous angles. Based on previous studies, the degradation of the elastomer materials is different on different percentage of biodiesel which involves results as tensile strength, elongation, mass changes and characterization. However, B30 palm oil still have a few information on the effect to the material which need to be study and analyze. This paper will review and compare the degradation and effect results of biodiesel B30 on the material elastomer with the method of static immersion test with previous studies that have been complete.

1.3 OBJECTIVE

The objectives of this project are as follows

1. To analyze the mass changes in biodiesel B30 compared to other type of blends.
2. To implement a comparative study for physical and mechanical changes of nitrile rubber in other types of biodiesel blends.

1.4 SCOPE OF PROJECT

The scopes of the project are:

1. Literature review on the degradation of elastomer in biodiesel
2. The materials used and the procedure to achieve the physical and mechanical changes of elastomer
3. Comparison of results involving of mass, volume, and hardness changes on NBR material with other research paper using palm oil biodiesel.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Biodiesel

In recent years, understanding of energy and environmental issues has inspired many researchers to explore the potential of using renewable fuels instead of petroleum and its derivatives. Biodiesel is one of the renewable fuels that obtained from vegetables oil and animal fats. Biodiesel fuel is classified as a mono-alkyl ester of fatty acids derived from plant oils or animal fats conforming to the requirements of ASTM D6751 or EN14214. The saturated and unsaturated content of biodiesels derived from various sources varies widely (Mathew & Thangaraja, 2018). In the production of biodiesel, the common crops oil used are rapeseed, canola, soybean, oil palm, sunflower, jatropha, safflower and more. The leading crops oil used in biodiesel production are rapeseed, palm and soybean (Nair, 2015) In this study, palm oil is used as the fuel in order to achieve the objectives. The oil palm is a tropical plant that reaches a height of 20–25 m and has a life cycle of around 25 years. The maximum production is achieved 8 years after planting and there are two kind of oil produced which first derived from the palm pulp called as palm kernel oil and second derived from the fruit is called palm oil proper. Several high oil-yield varieties have been developed with Indonesia and Malaysia as the main producers (Nair, 2015).

Other than being a renewable source, biodiesel have some advantages such as it deteriorates faster than diesel fuel which resulted in minimizing the environmental effects of biofuel spills. In addition, it lowers the emission of contaminants which made the health risk also can be lower. Furthermore, it is the only fuel that can replace diesel fuel in conventional diesel engine without have to modify. Biodiesel also can be mixed with diesel fuel at any proportions. Its fuel blends eliminate particulate matter, hydrocarbon, carbon monoxide and sulphur oxides (Romano & Sorichetti, 2011). Blends of biodiesel and traditional hydrocarbon-based diesel are generated by blending biodiesel and petroleum diesel in appropriate proportions under appropriate conditions. Diesel fuel blends are indicated as "Bx" where "x" is the amount of biodiesel in the blend. For example, B5 (lowest mix) indicates 5% of biodiesel and 95% diesel which make B100 as pure biodiesel. The most used in current biodiesel blends are B2, B5, B7, B20 and B100 (Romano & Sorichetti, 2011). The use of biodiesel from a minimum of 1 volume% biodiesel in the blended form with diesel was initiated. Today, the blending amount of biodiesel in diesel is up to 20 vol % (Chandran et al., 2016). Based on the findings of the established compatibility studies, the use of biodiesel in diesel engines above B20 is usually not fully explore (Omori et al., 2011). In order to optimize the use of biodiesel, in this study, a slightly higher percentage of biodiesel, B30 will be used. Recent years, biodiesel use has continuously increased in the automotive industry, especially in France and Germany where diesel oil mixtures are widely used. Some manufacturers (for example, Volkswagen, Audi, Mercedes-Benz) are currently guaranteeing their biodiesel engines (Carraretto et al., 2004).

However, biodiesel is still in low mixes (B5 and B7) in Malaysia and is not widely used although Malaysia have abundance supplies of palm oil which is a part of biodiesel. Although the usage of biodiesel is becoming more common, there are several issues related to biodiesel that need to be understood. Hanif (2004) has investigated the effect of palm oil Biodiesel, which reveals that the use of palm oil biodiesel resulted in an 11.93-13.48 % increase of fuel consumption by diesel engines, and a 2.96-5% decrease of thermal efficiency to 5.33 %. This shows that biodiesel has many different properties than diesel fuel. Figure 2.1 shows few of the problems that often occurs when using biodiesel. The cause to the degradation of biodiesel is found which related to the high temperatures and exposure of air and water to the biodiesel (Celik & Aydin, 2011). Other studies also mentioned that, oxidation stability of the biodiesel is also one of the factors which can caused the production of byproducts (Fang & McCormick, 2006). The focus problem in this study is the degradation of elastomer parts in fuel delivery system. Previous study found that when immersed in a solvent, such as biodiesel, the elastomeric material swells. Fuel lines in automobile combustion systems are generally comprised of elastomers, which degrade quickly and change their characteristics when exposed to biodiesel. As a result, biodiesel compatibility with these materials is a topic in the automotive industry that demands specific consideration (Coronado et al., 2014).

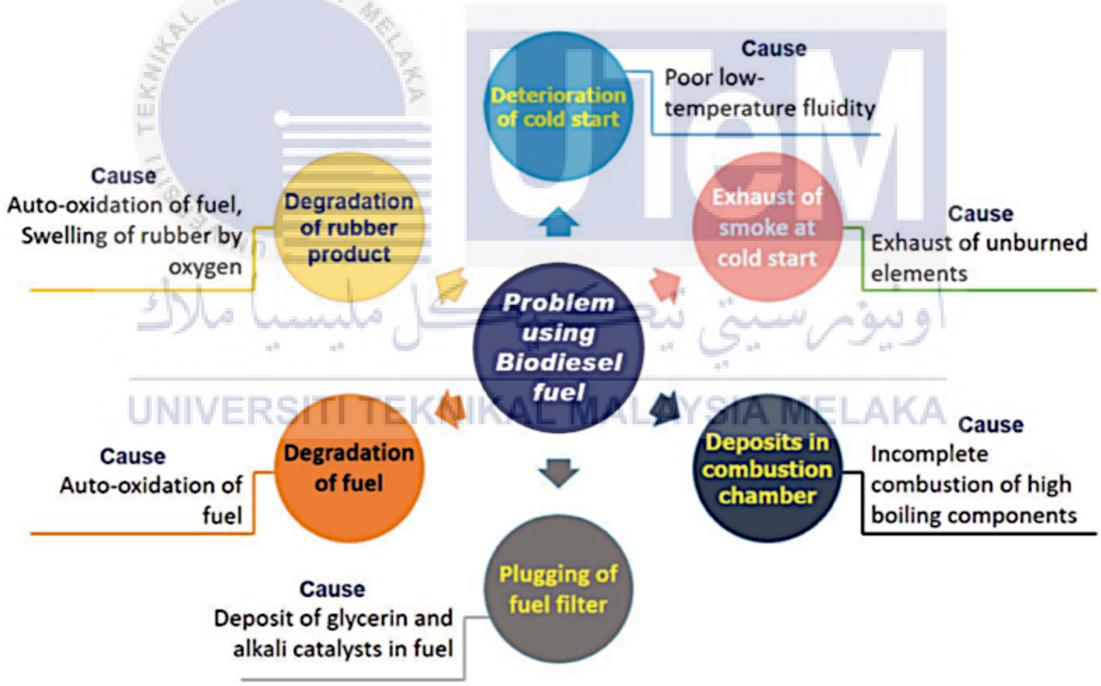


Figure 2.1: Few problems in using biodiesel (Hoang & Le, 2018)

2.2 Elastomer and Properties

Buna-N or NBR stands for nitrile rubber, which is a copolymer made up of butadiene monomers and acrylonitrile (ACN) as shown in Figure 2.2. Several qualities, such as petroleum oil and fuel resistance, tensile strength, hardness, and low temperature properties, are affected by the amount of ACN present. Increased ACN content improves petroleum oil and fuel resistance, tensile strength, and hardness, but at the expense of low temperature characteristics. The acrylonitrile monomer confers penetration resistance to a wide range of solvents and chemicals, while the butadiene component of the polymer contributes to the polymer's flexibility (Sellden, 2013).

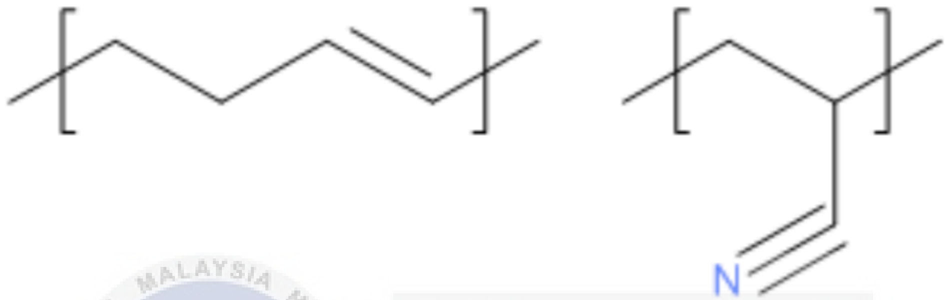


Figure 2.2: NBR units that are repeated. Butadiene unit on the left, acrylonitrile unit on the right.

The mechanical and chemical resistance properties of nitrile rubber vary according on the proportion of each monomer, reinforcing fillers, plasticizers, antioxidants, processing aids, cross-linking agents, and other curing and manufacturing processes, just as they do with any other polymer (Komariah et al., 2019). Unfortunately, the source and type of nitrile utilized in biodiesel testing is not disclosed in many of the literature. NBR is one of the most common elastomers used in the fuel system for sealing. NBR has a good resistance to petroleum-based fuels and lubricants due to the polarity of its acrylonitrile content (from 15% to 50%). Biofuels such as biodiesel and bioethanol, on the other hand, are more polar than fossil fuels (Akhlaghi et al., 2015). Nitrile rubber (NBR), polychloroprene (CR), ethylene propylene diene monomer (EPDM), silicone rubber (SR), and polytetrafluoroethylene are currently the most popular elastomer materials used in gaskets, fuel hoses, and O-rings. This is due to their flexibility, excellent barrier, physical qualities, and ease of manufacture, these materials are competitors for use in diesel engine fuel systems. (Tongroon et al., 2017). As elastomeric materials are widely employed in fuel lines as hoses and seals, their compatibility with new fuel chemistries must be evaluated. Figure 2.3 shows the position of some of the rubber components in a typical automotive gasoline system. These units are made up of components that are mostly made of metals and rubbers.

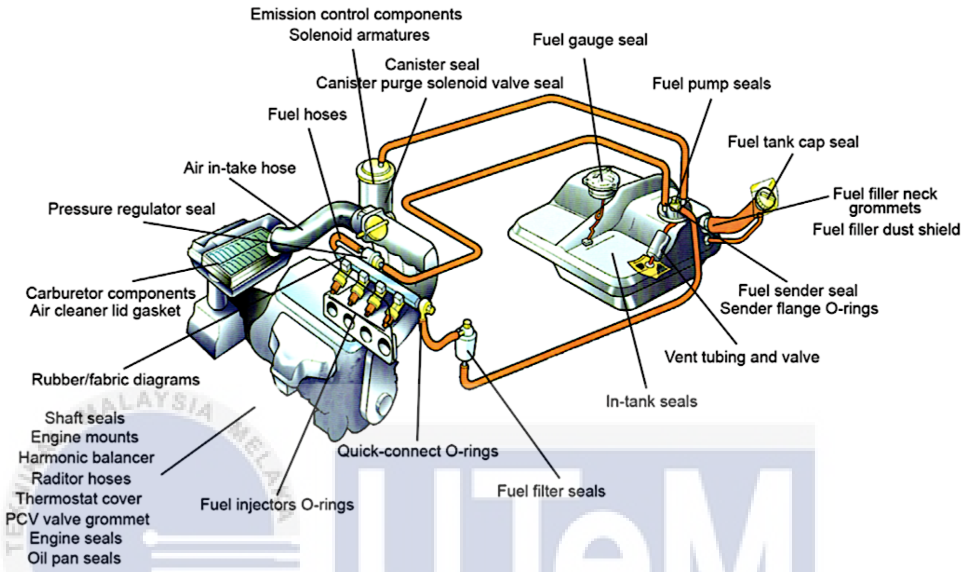
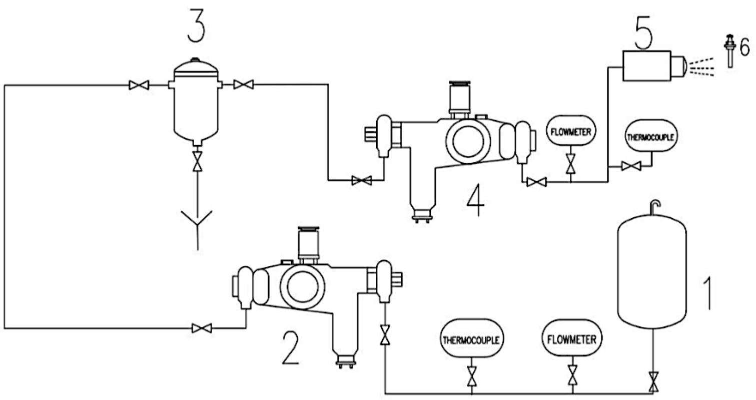


Figure 2.3: Location on where the rubber parts in a conventional fuel delivery system (Ariffin et al., 2018).

A good and compatible mechanical seal or packing is one practical technique for preventing leakage. O-rings are the most common seals used in machine design. The used of O-rings in fuel delivery system can be seen in Figure 2.4. A mechanical gasket in the shape of a torus or doughnut-shaped ring is known as an O-ring, sometimes known as a packing. O-rings are used to prevent the loss of a fluid or gas in either a static or dynamic application (Fernández et al., 2020). Fuel hose is also important part in the fuel delivery system. A hose for vehicle fuel lines consisting of a two-ply rubber tube created by extrusion and consisting of an inner layer of a hexafluoropropylene copolymer with vinylidene fluoride that is resistant to hydrocarbon fuels including sour gasoline and an exterior layer of a synthetic rubber.



Fuel tank
Fuel Supply Pump
Oil Filter
Injection Pump
Injector
Nozzle

Figure 2.4: O-rings used in parts of fuel delivery system (Komariah et al., 2019).

Polymeric materials in the fuel system have a significant risk of degrading, particularly when they come into touch with oil that has aggressive qualities. Elastomers are susceptible to chemical assault and can lose their physical qualities as well as their size and shape stability. Polymeric molecules, as is well known, are quite massive (on a molecular scale), and their distinctive and valuable features are largely due to their size. Any shortening of the chain reduces tensile strength and is a common cause of premature cracking. The ability of an O-ring to recall its shape is critical to its effectiveness. Because of material incompatibility with biodiesel and its mixtures, changes to engine seals, particularly fuel system O-rings, must be regulated (Rudbahs & Smigins, 2014).

2.2.1 Elastomer deteriorate in biodiesel

There has been a mountain of research that elastomers deteriorate in biodiesel. In biodiesel, elastomers are degraded to a greater extent. The reasons of degradation are discussed from numerous angles. As most elastomer materials come into contact with fuel, it undergoes physical or chemical changes. The degree of change is determined by the material’s ability to absorb a fuel or by the chemicals dissolved or removed by the fuel. This can cause a variety of changes in the physical properties of the material, such as swelling, shrinkage, embrittlement, and changes in tensile strength It was investigated the corrosivity, elastomer compatibility, toxicity, and biodegradability of numerous oxygenated diesel fuels and discovered a wide range of impacts depending on the oxygenate chemistry (Terry et al., 2006). The application determines the maximum allowable physical change, and some degree of change is normally tolerated. According to Sem (2004) stated that biodiesel B100 has a greater propensity to break down or oxidize rubbers and plastics because to its high oxygen content. The unstable hydroperoxides generated during the oxidation of biodiesel damage elastomeric materials. Biodiesel mixes higher than B20 can harm fuel system components including hoses and pump seals, which contain biodiesel-incompatible elastomers. Biodiesel can produce structural changes in volume and mass, as well as changes in mechanical properties such as elongation, hardness, and tensile stress in polymers, in addition to swelling. It is important to know that the changes in physical qualities generated by contact with biodiesel are caused not only by the molecular structure, but also by the fact that it is extremely sensitive to certain environmental variables (Rudbahs & Smigins, 2014). According to Saiful et al. (2020), the enhanced polarity of biodiesel combined with the carboxylic (ester) functional group in biodiesel creation resulted in elastomer degradation, with biodiesel concentration influencing elastomer properties and causing swelling, cracking, and fracture events. In a study by Sellden (2013), it is found that after each of the 1008h exposures in fuels to check all of the samples in B100, have swollen as shown in Figure 2.5. NBR 2 appeared to swell the greatest, whereas NBR 3 appeared to swell the least.