AN EVALUATION OF ELASTOMER COMPATIBILITY IN HIGH QUALITY BIODIESEL

KAMPANART POORAHONG

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENT FOR THE DEGREE OF
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หัวข้อวิทยานิพนธ์	การประเมินความเข้ากันได้ของยางสังเคราะห์ในน้ำมันไบโอดีเซลคุณภาพสูง
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อาจารย์ที่ปรึกษาวิทยานิพนธ์ร่วม	Prof. Dr. Hidenori Kosaka

บทคัดย่อ

น้ำมันไบโอดีเซล เป็นหนึ่งในพลังงานทางเลือกที่ได้รับความสนใจสูงในหลาย ๆ ภาคส่วน เพื่อใช้ในเครื่องยนต์ดีเซล แต่อย่างไรก็ตาม น้ำมันไบโอดีเซลมีข้อเสียเมื่อเทียบกับน้ำมันปิโตรเลียมดีเซล คือ มีเสถียรภาพต่อการทนทานต่อการเกิดปฏิกิริยาออกซิเดชั่นต่ำ จึงได้เกิดการปรับปรุงเพื่อเพิ่มประสิทธิภาพในการเพิ่มเสถียรภาพต่อการเกิดปฏิกิริยาออกซิเดชั่น โดยการลดจำนวนของพันธะคู่ในโซ่ของกรดไขมัน จึงทำให้น้ำมันไบโอดีเซลที่ได้รับการปรับปรุงคุณภาพแล้วนี้ มีความทนทานต่อการเกิดปฏิกิริยาออกซิเดชั่นได้นานขึ้น ในการประกาศใช้น้ำมันไบโอดีเซลที่ได้รับการปรับปรุงคุณภาพแล้วนี้ เพื่อจัดจำหน่ายโดยทั่วไปในตลาดนั้น จำเป็นต้องได้รับการทดสอบความเหมาะสมและเข้ากันได้กับการทำงานของเครื่องยนต์ และชิ้นส่วนวัสดุยานยนต์ ในการศึกษานี้ตั้งเป้าหมายเพื่อที่จะศึกษาความเข้ากันได้ของน้ำมันไบโอดีเซลที่ได้รับการปรับปรุงคุณภาพแล้วนี้ กับยางไนไตรล์ ซึ่งเป็นวัสดุที่นิยมนำมาผลิตในการชิ้นส่วนยานยนต์ และอาจเกิดการเสียหายได้ง่ายเมื่อมีการเปลี่ยนชนิดของน้ำมันเชื้อเพลิง จากการศึกษาพบว่า ความเข้ากันได้ของน้ำมันไบโอดีเซลกับชิ้นส่วนยางไนไตรล์ขึ้นอยู่กับองค์ประกอบภายในของทั้งสองวัสดุ โดยใช้ค่า Hansen solubility parameters ในการอธิบายองค์ประกอบต่าง ๆ ต่อการเสียสภาพของยางที่เกิดจากการบวมและละลายเมื่อสัมผัสกับน้ำมันไบโอดีเซลที่ได้รับการปรับปรุงคุณภาพนี้ และจากการตรวจสอบน้ำมันไบโอดีเซลที่ได้รับการปรับปรุงคุณภาพแล้ว มีความทนทานต่อการเกิดปฏิกิริยาออกซิเดชั่นสูงขึ้นมาก และมีความสามารถในการละลายต่ำลง ทำให้สามารถลดการเสื่อมของยางไนไตรล์เมื่อเทียบกับการสัมผัสกับน้ำมันไบโอดีเซลทั่วไปได้

Thesis Tittle	An Evaluation of Elastomer Compatibility in High Quality Biodiesel
Student	Mr. Kampanart Poorahong
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Degree	Master of Engineering
Program	Automotive Engineering (International Program)
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ABSTRACT

Biodiesel is one of the most concerned as alternative energy to uses with diesel engine. Nevertheless, the biodiesel has disadvantage properties from petroleum diesel such as the low storage stability and injector clog up over time. An enhanced of conventional biodiesel by partially hydrogenation process to improve the oxidation stability and minimized impurity of biodiesel. The partially hydrogenation process is the method uses hydrogen to minimize the double bond of unsaturated fatty acid of biodiesel. To implement the partially hydrogenated biodiesel, the study support of compatibility with the engine and vehicle composition is necessary to be done and evidential to approve the usability first. This study aims to support the compatibility of partially hydrogenated biodiesel with the nitrile rubber, which common uses materials to produced vehicle parts. The study reveals the partially hydrogenated biodiesel has better oxidation stability than palm biodiesel. The compatibility between biodiesel and nitrile rubber depends on strength of chemical structure, oxidative degradation of materials and refreshing fuel over time. The compatibility of partially hydrogenation biodiesel with nitrile rubbers also better than palm biodiesel due to less degradation over time and less solubility with nitrile rubber. However, pure partially hydrogenated biodiesel still worst compatibility with rubber when compared to petroleum diesel.

ACKNOWLEDGEMENT

I would like to express my very great appreciation to Dr. Manida Tongroon, my research advisor, Asst.Prof.Dr. Chinda Charoenphonphanich and Prof. Dr.Hidenori Kosaka as co-advisor and this work might not succeed without her patient guidance, enthusiastic encouragement and useful critiques of this research. Also, I would like to thank Asst. Prof. Dr. Preecha Karin and P'Pha from King Mongkut's Institute of Technology Ladkrabang (KMITL) for their advice and assistance through graduation. My grateful thanks are also extended to P'Aum for advice and assistance about chemistry.

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Kampanart Poorahong

TABLE OF CONTENTS

Chapter **Page**

TABLE OF CONTENTS

(Continued)

Chapter **Page**

TABLE OF CONTENTS

(Continued)

Chapter **Page**

LIST OF TABLES

Table **Page**

LIST OF FIGURES

Figure Page

LIST OF FIGURES

(continued)

Figure Page

LIST OF FIGURES

(continued)

Figure Page

LIST OF FIGURES

(continued)

Figure Page

LIST OF FIGURES

(continued)

Figure **Page**

LIST OF SYMBOLS

δ_D	Dispersion Cohesion (solubility) Parameter
δ_P	Hydrogen Bonding Cohesion (solubility) Parameter
δ_H	Polar Cohesion (solubility) Parameter
d_s	Solubility Distance
R_a	Interaction Radius
M	Mass
V	Volume
v_e	The Effective Number of Chains in A Real Network Per Unit Volume
V_r	Volume Fraction of Polymer
V_1	Molecular Volume of Solvent
χ_1	Polymer-Solvent Interaction Parameter
ρ	Density of Materials
A	Absorbance Intensity
σ	Ultimate Tensile Strength
e	Elongation

LIST OF DEFINITIONS

FAME	Fatty Acid Methyl Ester
PV	Peroxide Value
TAN	Total Acid Number
NBR	Acrylonitrile – Butadiene Rubber
RED	Relative Energy Distance
MG	Monoglyceride
SG	Sterol glucoside
HSP	Hansen Solubility Parameter
EDS	Energy Dispersive X-ray Spectrometer
SEM	Scanning electron microscopy
GC	Gas Chromatography
TGA	Thermogravimetry Analysis
IR	Infrared Spectroscopy
PFA	Perfluoroalkoxy Alkanes
Acc	Accelerated Ageing Condition
P-FAME	Palm Fatty Acid Methyl Ester – Refer to Palm Biodiesel
PH-FAME	Partially Hydrogenated Fatty Acid Methyl Ester – Refer to Partially Hydrogenated Biodiesel

CHAPTER 1

INTRODUCTION

1.1 Research Background

Biofuels have an important role as an alternative energy in the transportation sector in the past decades due to the limitation and the high pollution of fossil fuels. Biofuels are derived from agricultural or industrial waste. There are many types of biofuel such as biogas, ethanol and biodiesel for fossil fuel substitution. Biodiesel is one of the most concerned in public transportation such as bus, truck and train, and agriculture engine to subsidize petroleum diesel. Biodiesel derived from vegetable oil or waste cooking oil, formed to fatty acid methyl ester (FAME). Biodiesel can be produced from many feedstocks, depending on the region due to agriculture productivity, such as soybean, rapeseed, jatropha and palm. As the results of the different feedstocks, the physical/chemical properties of biodiesel are not the same, for instance, the oxidation stability which depended on the carbon structure chain. The advantages of biodiesel over the petroleum diesel are the improved lubricity, lower emissions and biodegradability. However, biodiesel also has some disadvantages such as higher pour and cloud point, degradation over the time past because of the oxidation and less compatibility with synthetic rubber due to the higher polarity than petroleum diesel.

When biodiesel is degraded by oxidizing with oxygen in the environment, the properties of biodiesel are changed including the increase of peroxide value (PV), total acid number (TAN), and water content. In addition, the long chain of carbon structure is produced and cause the gum formation which increases the kinematic viscosity of biodiesel [1]. As the results, the oxidation product may cause the malfunction of the vehicle using biodiesel. Thus, the amount of biodiesel blended with petroleum diesel has been limited by 7 % by volume in Thailand. However, the higher blending ratio of biodiesel has been promoted by government due to ecology, economy and energy security concerns. To increase the amount of biodiesel used in the vehicle, the partial hydrogenation process is used to improve the quality of biodiesel by reducing the amount of unsaturated double bond in the fatty acid chain to increase oxidation stability and eliminating the impurity which is the cause of injector clogging in the diesel engine. Biodiesel after upgraded via partial hydrogenation process has been investigated its properties. The results show that partially hydrogenated biodiesel has better properties such as higher cetane number, lubricity, oxidation stability and can reduce the emission from the combustion of the engine, but worse in the cold flow properties when compared with conventional biodiesel [2]. This implies that the use of high percentage of partially hydrogenated biodiesel blended with diesel is possible. However, there is no information of material compatibility of partially hydrogenated biodiesel available in the literature. Therefore, the research of the compatibility of material used in the engine contacted with the partially hydrogenated biodiesel is required to ensure the use of high percentage of partially hydrogenated biodiesel in the vehicle without the problem. Thus, this research has investigated the compatibility of the rubber with the partially hydrogenated biodiesel. Moreover, the degradation of the rubber when contacted with partially hydrogenated biodiesel is clarified and compared with the conventional biodiesel.

1.2 Research Objective

1. To study the compatibility of biodiesel blended diesel and different base including petroleum diesel, palm biodiesel and partially hydrogenated biodiesel with varied acrylonitrile butadiene rubber.
2. To determine the composition and its oxidation stability of biodiesel after partially hydrogenation process.
3. To study oxidation stability and degradation product of palm biodiesel and partially hydrogenated biodiesel by accelerated ageing method.
4. To study the compatibility of the accelerated ageing palm biodiesel and partially hydrogenated biodiesel with the nitrile rubber and the degradation mechanism of the rubber during immersion.
5. To study and evaluate the commercial nitrile rubber sheet and compared the effect of the rubber after compatibility test with palm biodiesel and partially hydrogenated biodiesel.

1.3 Thesis Outlines

The thesis outlines start with the background and important of this research topic. This part explains how important to study material (NBR) compatibility with partially hydrogenated biodiesel and what different from others study.

The second part of outline is literature review. The previous research about degradation of biodiesel and the rubber, and how is corelated is explained in the first section. And the materials compatibility test with different biofuels and test condition is explained in another part.

In the next chapter is represent the methodologies are used for study the material compatibility with biodiesel, including the test materials specification, swelling experiment, ageing condition and study degradation by various method.

Chapter 4 is shown the test result and discussion. This chapter split into 4 part. First, the solubility parameter of biodiesel and its effect to material compatibility. The next section is discussed the degradation partially hydrogenated biodiesel during accelerated ageing condition by bubbling using air zero (Linde) at 5 L/h and compare with the conventional biodiesel at the same condition. Then, the effect of accelerated ageing condition biodiesel to NBR compatibility is studied with the same accelerated ageing condition. And final part of this chapter, the swelling experiment of NBR sheet into biodiesel, partially hydrogenated biodiesel and conventional petroleum diesel for comparison, is explained and discussion about the effect of refreshing fuel during the test period. Finally,

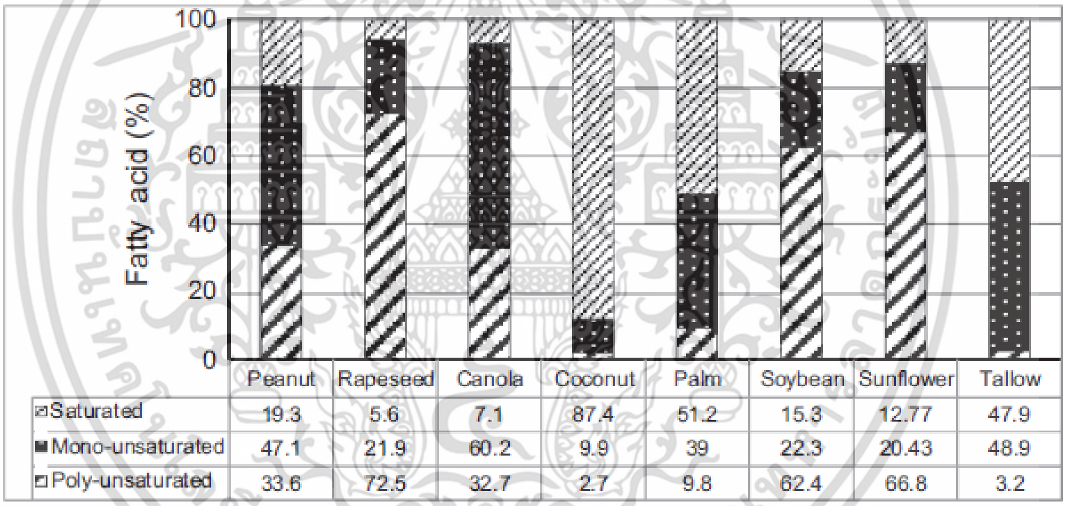
The last chapter is conclusion of this study. The degradation of biodiesel and NBR samples is summarized in this chapter. And discussion about future research of materials compatibility testing with different condition.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction of Partially Hydrogenated Biodiesel

Biodiesel derived from agriculture corps oil, animal fats or waste cooking oil through transesterification process to enhance the properties to ensure the liquid suit to use in diesel engine as fuel. The variation of source has an effect to the different of composition and contents between each supply, result in different fuel properties such as cold flowability, viscosity and oxidation stability. The different composition of varied feedstock of biodiesels [3] are show in the Figure 2.1.



	Peanut	Rapeseed	Canola	Coconut	Palm	Soybean	Sunflower	Tallow
▨ Saturated	19.3	5.6	7.1	87.4	51.2	15.3	12.77	47.9
■ Mono-unsaturated	47.1	21.9	60.2	9.9	39	22.3	20.43	48.9
▧ Poly-unsaturated	33.6	72.5	32.7	2.7	9.8	62.4	66.8	3.2

Figure 2.1 Saturated, mono- and polyunsaturated fatty acid contents for different biodiesel [3].

The composition of biodiesel in form of fatty acid methyl ester, has many forms depends on amount of double bond of carbon in fatty acid shows in Figure 2.2. The different unsaturated fatty acid resists the oxidative reaction differently. As show in the Figure 2.3, amount of double bond corelated with oxidation stability, the lower amount of double bond increased the oxidation stability [4].

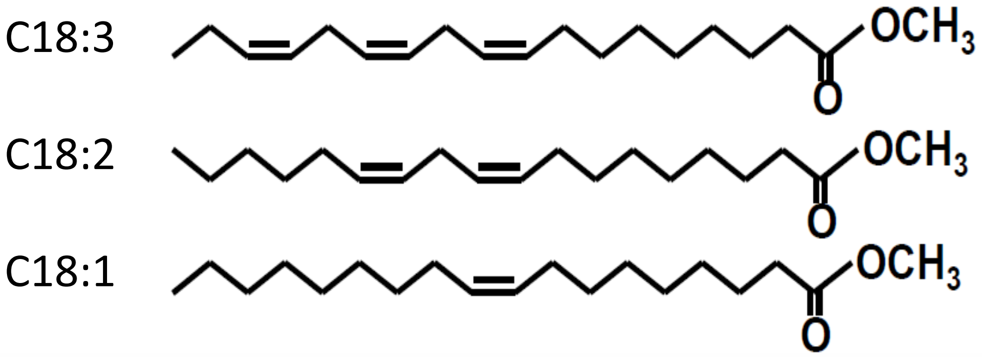


Figure 2.2 Structure of unsaturated fatty acid

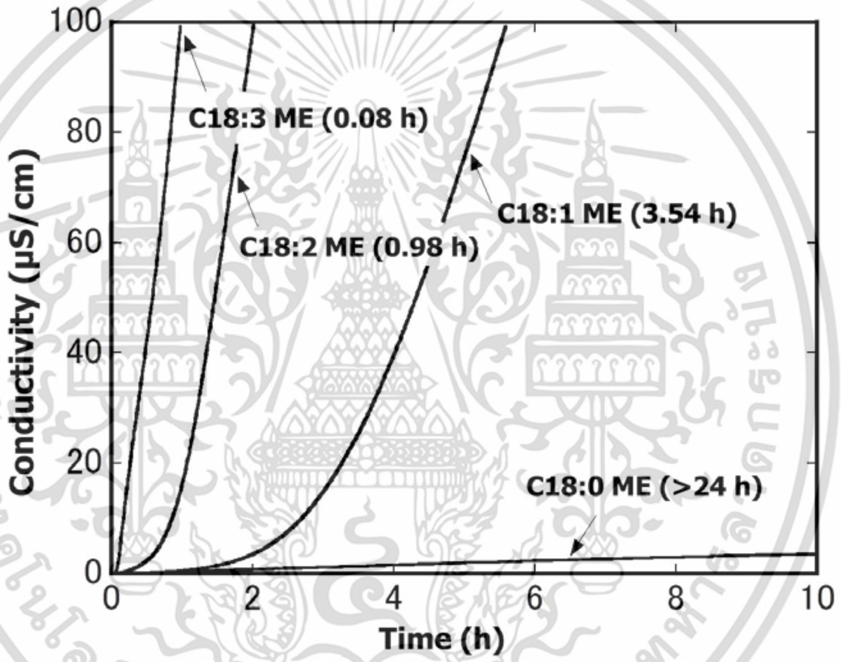
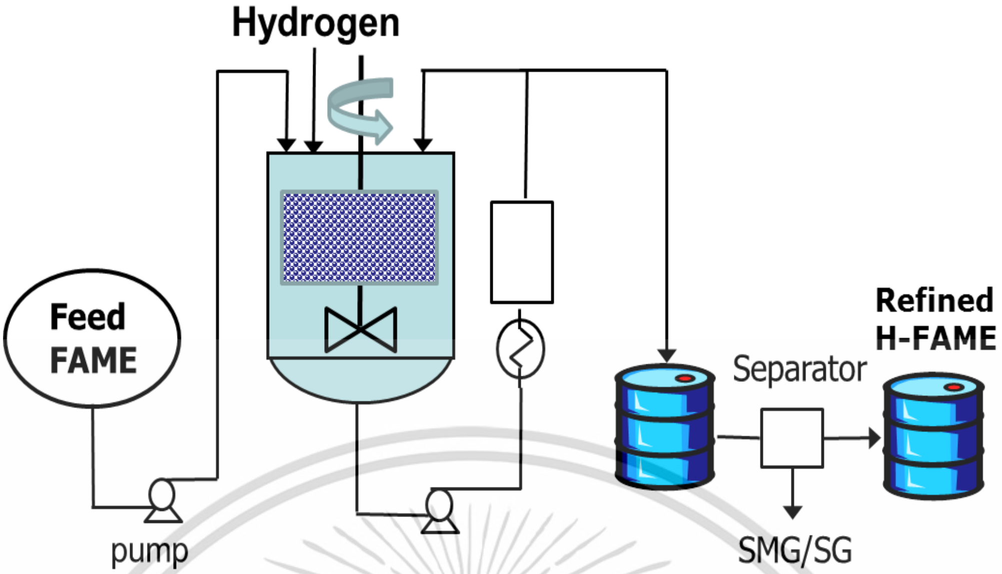


Figure 2.3 Oxidation stability of Various FAME measured by Rancimat Test [4].

To enhance the oxidation stability of the biodiesel, partially hydrogenation method is affordably concerned method by using hydrogen reduced the amount of double bond in fatty acid, result in increasing of oxidation stability of fuel. The schematic diagram of hydrogenation process is shown in the Figure 2.4



Source: Yuji YOSHIMURA. 2015. “Introduction of H-FAME Technology.”, WS on higher blending of biodiesel. Bangkok

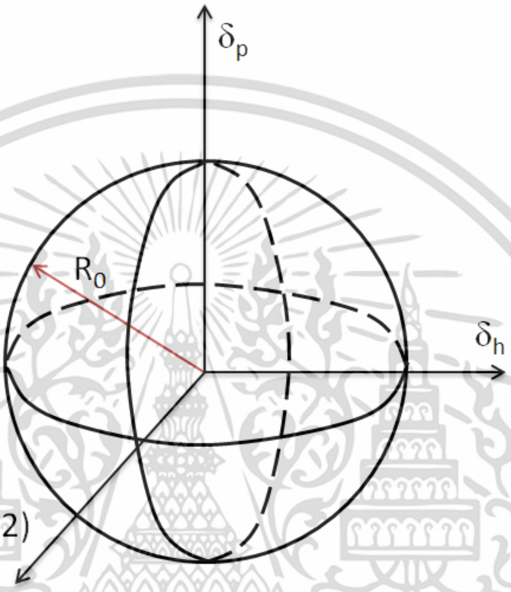
Figure 2.4 Schematics diagram of partially hydrogenation process to enhance the biodiesel

The biodiesel after partially hydrogenation process has better oxidation stability, less amount of precipitate compound such as remove Monoglyceride (MG) and Sterol glucoside (SG), but also poor cold flowability due to high cloud point.

2.2 Solubility Parameters of Materials

The solubility of materials is used for selected the suitable materials to solvent by considered to the degree of similarity (affinity) of binding forces that exist between the materials. Hansen Solubility Parameters (HSP) is one of the famous methods used as predication of choosing materials to suitability for using for several solvent based on atomic dispersion (δ_D), polarity (δ_P), and hydrogen bonding (δ_H) force biding in structure of both solvent and the materials to use with.

The swelling behavior of material exposed to solvent such as biodiesel or any fuel can be explained by using HSPs, the high affinities between materials seems to attractive each other and become to combined and dissolve. To visualize the solubility of solutes materials, the three parameters of HSP define the location of center of a sphere in 3 dimension plane of binding force called Hansen-sphere, and the radius called interaction radius (R_a) defined to create the sphere shows in the Figure 2.5. The closer coordinate of HSP value to the center of the sphere defines as high affinities to the solute materials, meanwhile the coordinate of HSP of solvent outside the sphere is defines as a bad solvent to materials. The good solvent seems to be absorbed and dissolve the materials such as the polymer and rubber better than the bad solvent, result in destruction of material structure and unsuitable for uses.



Source: http://polymerdatabase.com/polymer%20physics/Hansen%20Solubility%20Sphere.html

Figure 2.5 Hansen Solubility Sphere

The similarity between materials is quantified by the differences between the HSPs for the materials and solvent. This difference is termed the solubility distance (d_S) and, for a polymer (p) and a liquid (l), is determined by equation (2.1) (Hansen, 2007)

$$d_s = \sqrt{4\left(\delta_{D(p)} - \delta_{D(l)}\right)^2 + \left(\delta_{P(p)} - \delta_{P(l)}\right)^2 + \left(\delta_{H(p)} - \delta_{H(l)}\right)^2} \qquad (2.1)$$

As d_S decreases, the solvent become more soluble as the distance between the center and HSP of solvent are closer to each other as mention in Figure 2.5. The ratio between the solubility distance and interaction radius (d_S/R_a) is also called the relative energy distance (RED) used to express the mutual affinity of the material and solvent, If the RED number is equal or less than 1 means the solvent has high affinities with the materials, result in attractive between molecule of solvent and polymer. And if the RED number is more than 1 indicate the low affinities of materials. Some of the HSP value and interaction radius of polymer from many studies are show in the Table 2.1 and Table 2.2. For the rubber compatibility to use with fuel, the lower affinities between materials and fuel prefer to be produced suitable product, because the rubber absorbs and swell less when exposed to the fuel.

Table 2.1 The HSP value of composition of FAME, biodiesel, biodiesel degradation product and petroleum diesel

Materials	Composition	δ_d (MPa$^{1/2}$)	δ_p (MPa$^{1/2}$)	δ_h (MPa$^{1/2}$)
Major Fatty Acid Methyl Ester	Lauric acid	16	3.2	3.9
	Myristic acid	16.1	2.7	3.5
	Methyl palmitate (C16:0)	16	2.7	3.2
	Methyl stearate (C18:0)	16.1	2.3	3
	Methyl oleate (C18:1)	16.3	2.4	3.2
	Methyl linoleate (C18:2)	16.6	2.4	3.6
	Methyl linolenate (C18:3)	16.8	2.5	3.8
Biodiesel	Soybean biodiesel	16.4	3.1	6.1
	Palm Biodiesel	16.1	3.1	6.0
	Rapeseed	16.2	2.9	6.1
Biodiesel Degradation Products	Methyl hydroperoxide	15.0	15.0	30.0
	Acetaldehyde	14.7	12.5	7.9
	Formic acid	17.0	2.0	2.0
Diesel		17.0	2.0	2.0

Source: [5] [6] [7]

Table 2.2 The HSP of natural rubber, nitrile rubber and its compositions.

Elastomer type	Hansen Solubility Parameter, $MPa^{1/2}$			
	δ_d ($MPa^{1/2}$)	δ_p ($MPa^{1/2}$)	δ_h ($MPa^{1/2}$)	Interaction Radius (R_a)
Natural rubber	16.4	3.1	4.1	6.8
Nitrile rubber (Buna N)	20.4	12.4	4.1	13.9
Acrylonitrile	16.0	12.8	6.8	N/A
Butadiene	14.8	2.8	5.6	N/A

Sources: Charles M. Hansen, Hansen Solubility Parameters: A User's Handbook, 2nd Edition, 2007

2.3 Rubber Swelling Behavior of Rubber and Compatibility with Liquid Fuel

The study the compatibility of rubber with liquid such as fuel, most base on the swelling of the rubber when exposed to fuel and varied the temperature and duration. All of biodiesel has less compatibility with nitrile rubber than petroleum diesel. The higher biodiesel content blended with petroleum diesel has been absorbed more than less content of biodiesel [8] [9], the result of these work shows in the Figure 2.6

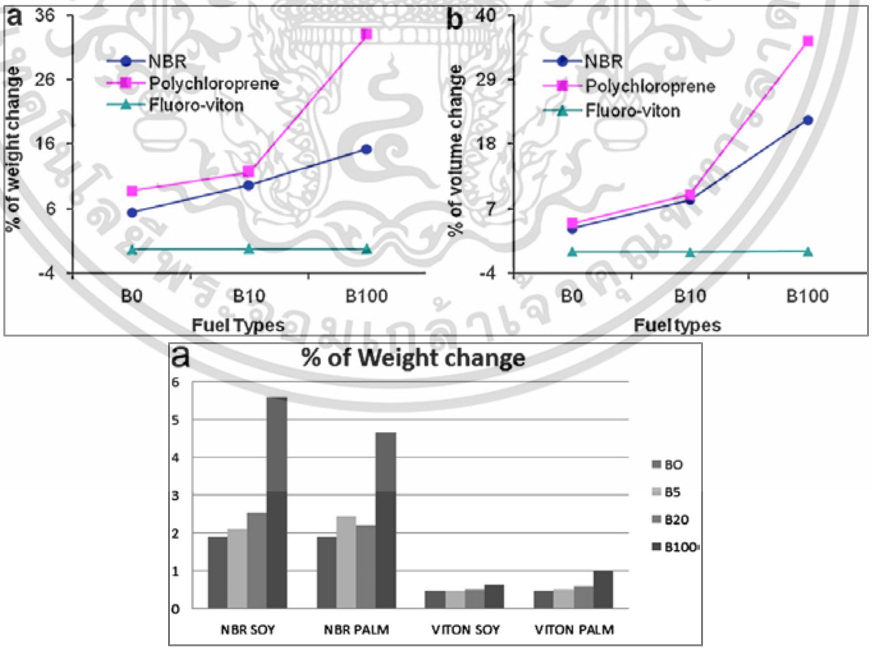


Figure 2.6 Variant of rubber test the compatibility with biodiesel blended, (Upper) - [8]; (Lower) - [9]

The composition of biodiesel also has an effect to the swelling of nitrile rubber due to different of HSPs value as mention in the Table 2.2. The study shows large of FAME composition has better compatibility with the rubber and the rubber, but double bond structure has worst compatibility to the rubber and the petroleum diesel is the most suitable to uses with nitrile rubber [10], result of the experiment shows in the Figure 2.7. As mention in (2.1), biodiesel has many compositions of fatty acid, which could result in different in material compatibility with nitrile rubber.

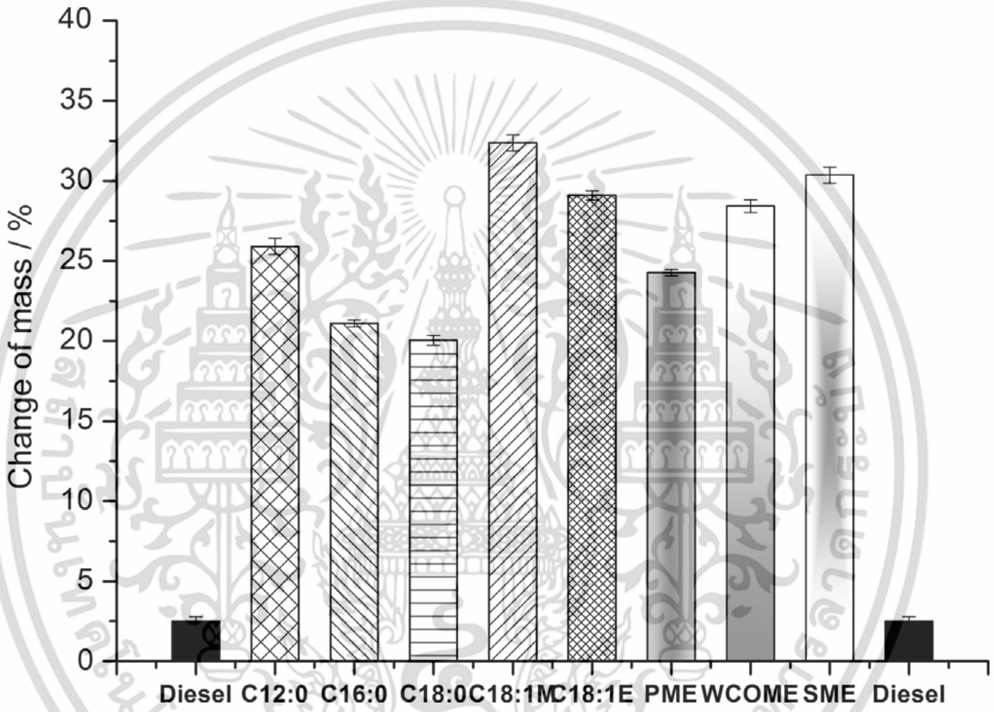


Figure 2.7 Change of mass of rubber sample after immersed in different fuels for 1 week at room temperature [10].

The rubber after immersed or exposed to fuel, the swelling behavior could divide into two state. Firstly, fast fuel uptake state, the mass of rubber increased rapidly during first contact with the fuel. Then, the mass change of the rubber is more stable. Some of mass change of the immersion rubber in the function of exposed time is shown in the Figure 2.8 [11].

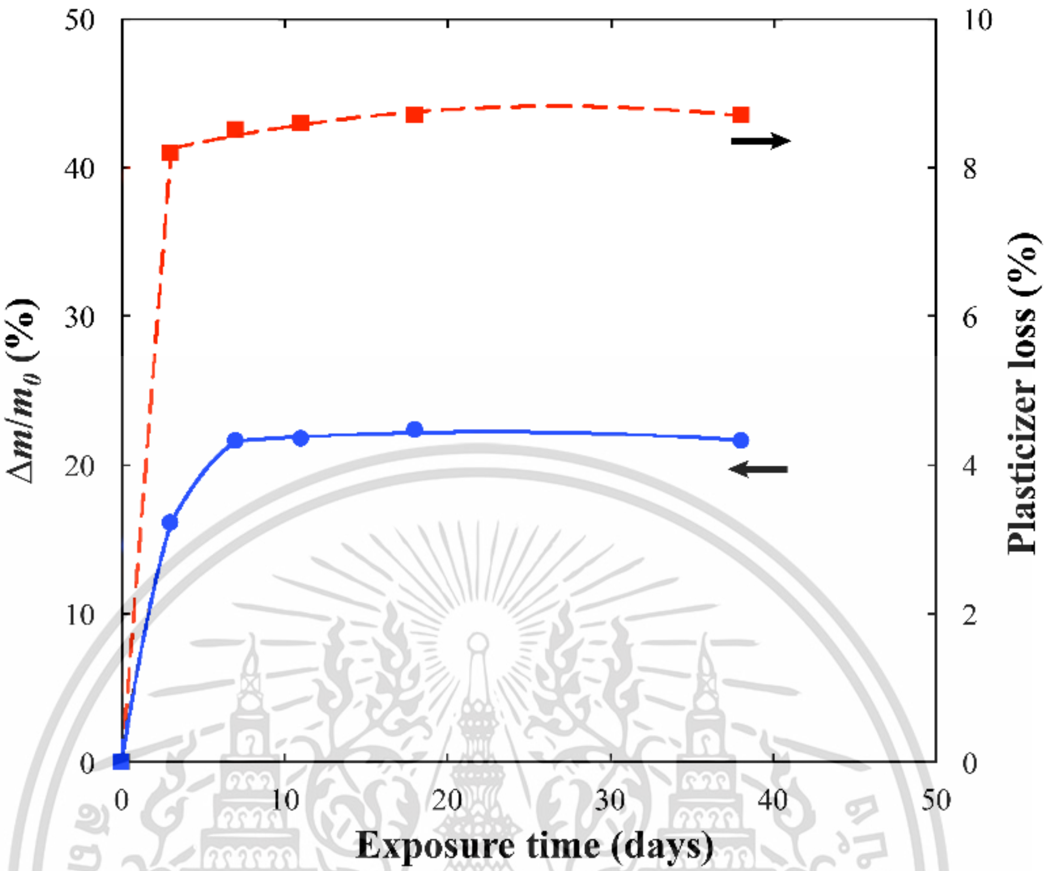


Figure 2.8 The biodiesel uptake and plasticizer loss of NBR at 150 °C and pO2 = 21 kPa on autoclave ageing, plotted as a function of exposure time [11].

Several works have been studied the degradation by determined the morphology of nitrile rubber exposed to biodiesel. After nitrile rubber has been exposed to biodiesel, several small holes then reveals overall surface shows in the Figure 2.9 and Figure 2.10 [12] [13]. These small holes assume to the compositions of nitrile rubber has been dissolve by the biodiesel.

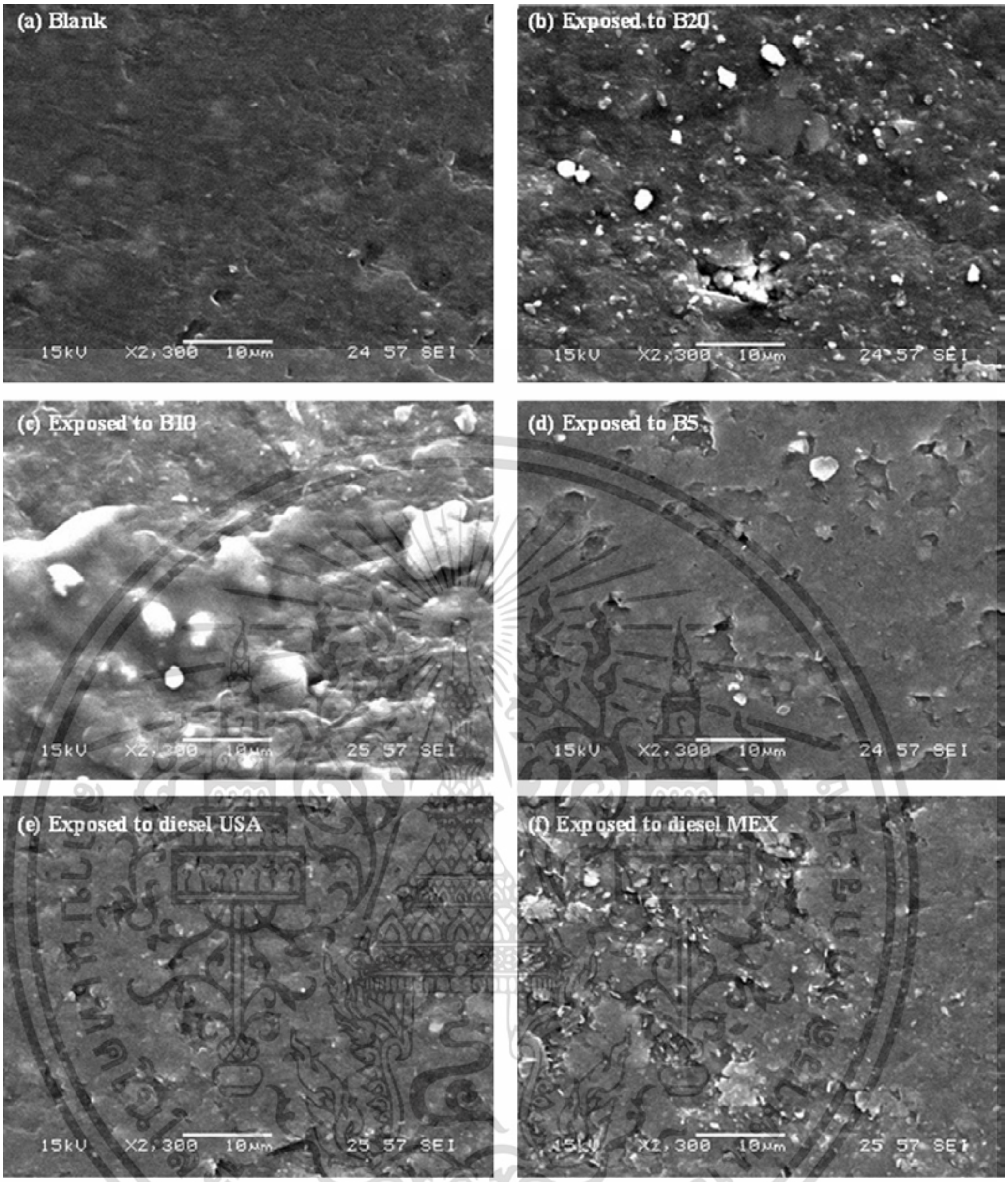


Figure 2.9 Scanning electron micrographs of material surfaces: (a) blank; (b) exposed to B20; (c) exposed to B10; (d) exposed to B5; (e) exposed to diesel USA; and (f) exposed to diesel MEX [12].

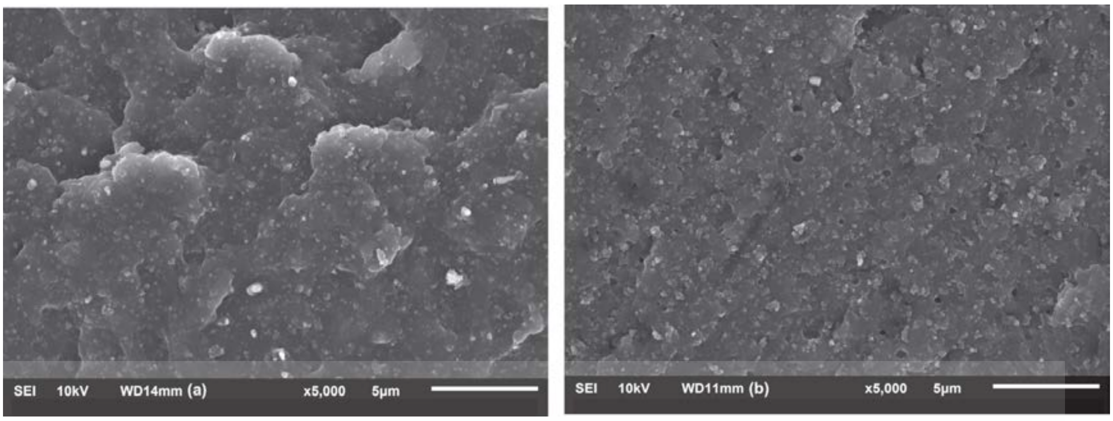


Figure 2.10 SEM photomicrographs of fracture surface from low-TMTD-composition: (a) non-immersed; (b) after immersion in soybean biodiesel for 22 h [13].

2.4 Chemical Degradation of Biodiesel and Rubber

The biodiesel could be degraded over time when unsuitable stored and exposed to heat, air or light. oxidation is a multi-step reaction process where primary products (conjugated diene hydroperoxides) decompose and chemically interact with each other to form numerous secondary oxidation products and result in change of peroxide value, acid value, viscosity, ester content and polymer content. The initiator radicals (I·) react with the fatty acid substrate (RH) removing hydrogen from a carbon atom of the fatty acid chain, to form a new carbon-based fatty acid radical (R·). Initiator radicals (I·) are formed by various mechanisms including (i) thermal dissociation of hydroperoxides (ROOH) present as impurities, (ii) metal (M) catalyzed decomposition of hydroperoxides and (iii) be catalyzed by exposure to light as called 'photo-oxidation'[14].

The polymer also degraded when stored unproperly and exposed to heat, light or oxygen. The polymer degraded over time during service life. The result of degraded rubber is declined in mechanical properties caused by changes to the molecular and composition of the polymer. The rubber could be embrittlement, softening, color changes and cracking, depend on types of polymer[15].

Both biodiesel and polymer are the organics compound, result in similar oxidative degradation pathway. The General examples of primary oxidation reaction of biodiesel and polybutadiene as an example of polymer are show in the Table 2.3.

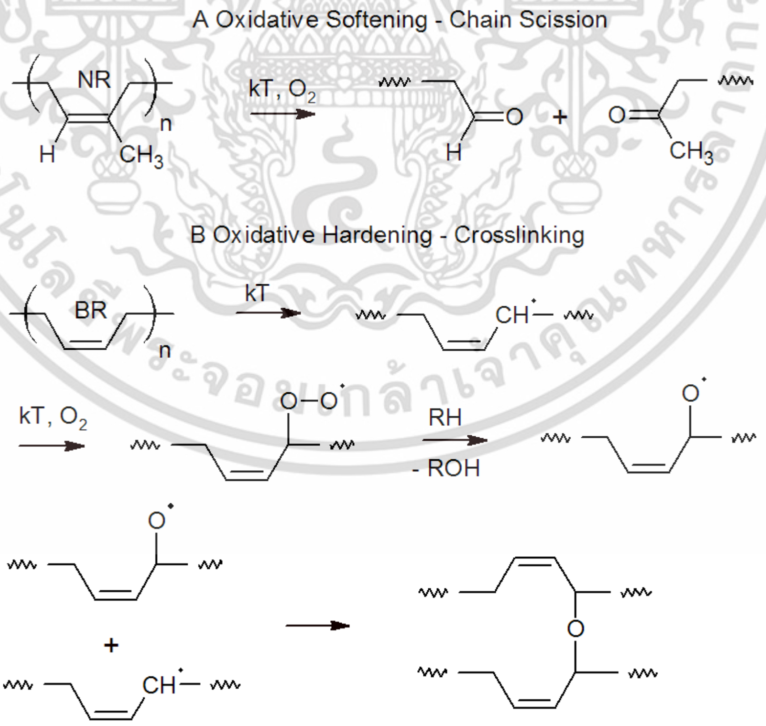
Table 2.3 Comparative of primary oxidation of biodiesel and polymer

Biodiesel [1]	**Polymer** [16]
Initiation	
RH + I· $\rightarrow$ R· + IH	
ROOH $\rightarrow$ RO· + OH·	Polybutadiene $\xrightarrow{\text{(kinetic energy)}}$ R·
ROOH + $M^{2}+$ $\rightarrow$ RO· + OH· + $M^{3}+$	ROOH $\rightarrow$ RO· + HO·
ROOH + $M^{3}+$ $\rightarrow$ ROO· + H^{+} + $M^{2}+$	2ROOH $\rightarrow$ RO· + ROO· + H2O
Propagation	
R· + O2 $\rightarrow$ ROO·	R· + O2 $\rightarrow$ ROO·
ROO· + RH $\rightarrow$ ROOH + R·	ROO· + RH $\rightarrow$ ROOH+R·
Termination	
R· + R· $\rightarrow$ R – R	R· + R· $\rightarrow$ R – R
ROO· + ROO· $\rightarrow$ stable products	R· + OR· $\rightarrow$ ROR
	R· + ROO· $\rightarrow$ ROOR

Figure 2.11 demonstrate the hardening or softening of polymer oxidative degradation. For example, polyisoprene or natural rubber usually softens when exposed to heat and oxygen whereas polybutadiene undergoes oxidative hardening. Hardening is much more common because free radicals produced when rubber is exposed to heat, oxygen and/or light rapidly combine and, in this process, form new crosslinks. On the other hand, polymers with pendent bulky side groups will get strain softening because radical recombination reactions are less likely to occur due to steric hindrance. Instead, these polymers degrade by chain scission caused by disproportionation and hydrogen abstraction [17]

Figure 2.12 shows the infrared spectra of nitrile rubber before and after heating at 200°C in and varied the heating duration of the samples [18]. The studied is use as predicted the service life of nitrile rubber by heating the rubber. The absorbance of the C=C (1,4 trans- bonding, 965 cm^{-1}) and the nitrile group (2233 cm^{-1}) changed with the heating time. In addition, the absorbance of hydroxyl groups at 3350 cm^{-1} and 3470 cm^{-1} and that of the carbonyl group at 1719 cm^{-1} increased with the heating time. Moreover, the extremely broad carbonyl group absorption band at 1719 cm^{-1} may indicate that the absorption band of carboxylate ester (1729 cm^{-1}) or α, β - unsaturated ketone (1690 cm^{-1}) contributes to this absorption band. The appearance of a shoulder peak at 1763 cm^{-1} was also observed, which is thought to be attributed to the carbonyl group absorption as a result of the generation of carboxylic acid at a carbon bonded to the nitrile group.

A thermal treatment of polyacrylonitrile results in an internal cyclization reaction of a nitrile group (polyimide formation), followed by dehydrogenation to form a highly conjugated structure[19]. An immediate decrease (consumption) in the nitrile group (2233 cm^{-1}) indicates cyclization, and a strong decrease in aliphatic hydrogens (2920 cm^{-1} and 1450 cm^{-1}) suggests concurrent aromatization. The rapid growth of a band at 1600 cm^{-1} is attributed to imide formation (cyclization). The thermal degradation of NBR produces several functional groups, such as carbonyl and carboxyl groups, due to oxidation reactions, as mentioned above. An investigation of this degradation has been carried out by the qualitative and quantitative analyze for these degradation products caused by oxidation.



Source: http://polymerdatabase.com/polymer%20chemistry/Thermal%20Degradation%20Elastomers.html

Figure 2.11 General mechanism of thermal degradation

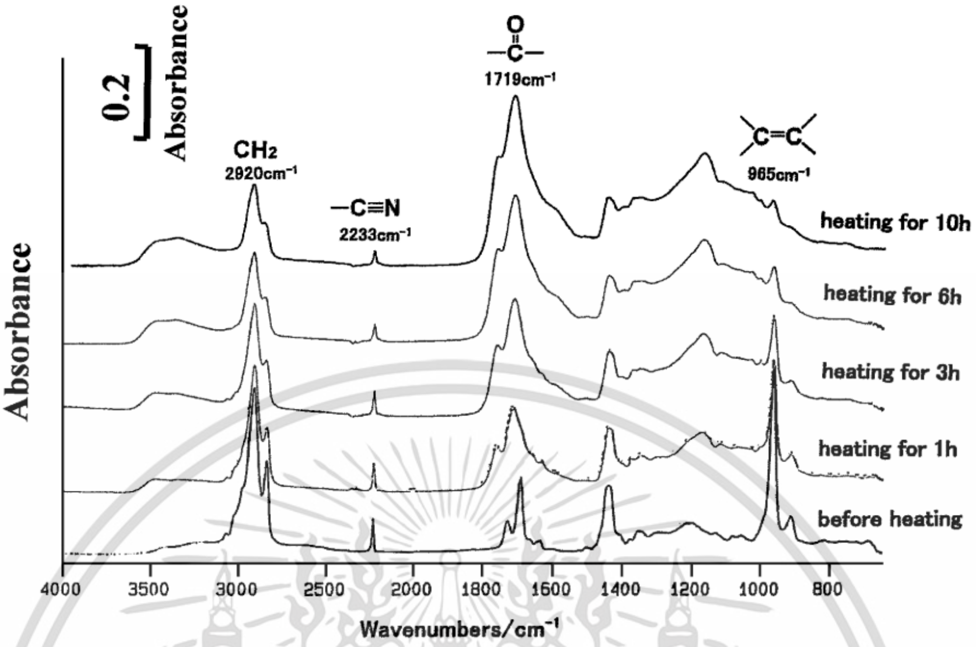


Figure 2.12 FT-IR spectra of NBR samples before and after heating at 200°C [18].

Figure 2.13 show the comparison of degradation via IR spectra of NBR before and after exposure to biodiesel and Hydrotreated Vegetable Oil (HVO) [20]. The intensity of the 1,2 vinyl and 1,4 trans double bonds, at respectively 930-941 cm^{-1} and 974-995 cm^{-1}, decreased with increasing exposure time. Oxidation products were formed after exposure to biodiesel: (i) carbonyl bonds of ester groups at 1758 cm^{-1}, (ii) carbonyl bonds of carboxylate groups at 1802 cm^{-1}, (iii) C-O-C groups of epoxidized species at 1195-1349 cm^{-1}[21]. A very small number of carbonyl groups were evident in the HVO-exposed rubber at 1775 cm^{-1}. The oxidation of the rubber in HVO was much slower and less pronounced than that in biodiesel. suggesting that the biodiesel was involved in the oxidative reactions of the rubber, and thus promoted oxidation. Nitrile groups do not generally change during the oxidation of NBR [22] but the IR spectra of the biodiesel-aged samples showed a decrease in the intensity of the C≡N stretching band at 2253 cm^{-1} with increasing exposure time, presumably due to hydrolysis of nitrile group by zinc cations resulted from the dissolution of ZnO particles in biodiesel.

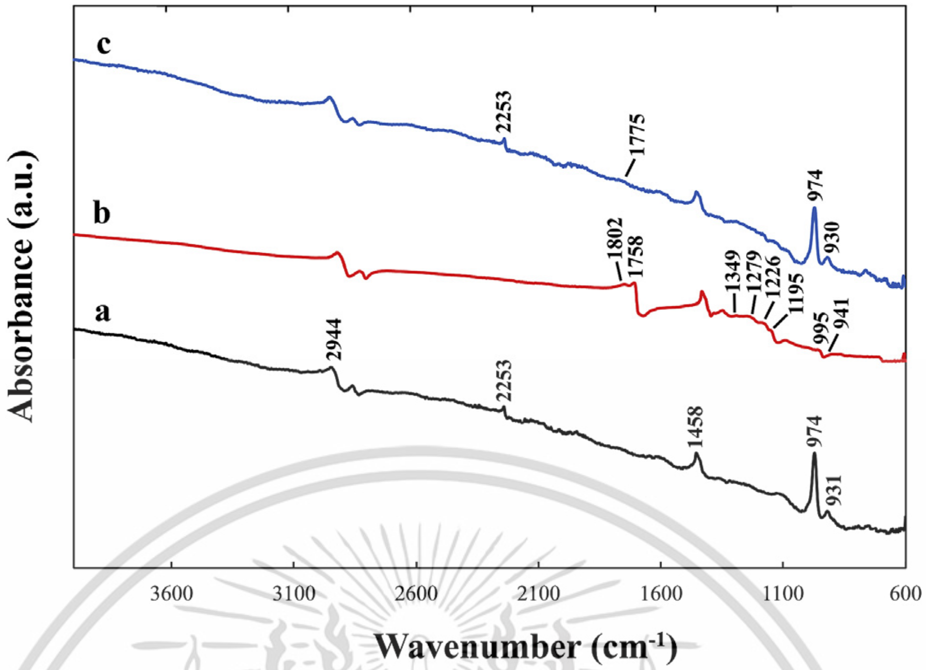


Figure 2.13 Infrared spectra of: (a) fresh (unexposed) NBR (black line), and NBR aged in: (b) biodiesel at 80 °C for 62 days (red); (c) HVO at 75 °C for 52 days (blue) [20].

In summary, the new developed biodiesel by partially hydrogenation process the conventional biodiesel to reduce the amount of unsaturated fatty acid contents which depended on the source of oil used as feedstock, result in better storage stability and decreasing of impurity caused the problem in vehicle such as filter clocking. The partially hydrogenated biodiesel is not be used widely yet, lacks study to support to implement and using commercially such as effects to engine performance and materials compatibility. Many studied supports the composition and contents of biodiesel is influence to the materials compatibility with the polymer including rubber. Also, the primary oxidative degradation of the biodiesel and the oxidative degradation of the rubber are similar as both of materials are organics compound and weak to the unproper environment such as heat and light. This work is proceeded to study on the effects of enhanced oxidative stability of biodiesel to compatibility with the nitrile rubber, which is the most concerned as weakest and easiest degraded materials used to produced vehicle parts by the change of fuel into high polar fuel such as biodiesel.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Fuel

Three fuels have been used in this study. First, the neat diesel, used as the base fuel for blending with biodiesel and used as the reference for compatibility study, was supplied from Bangchak Corporation Public Co., Ltd. Second, palm biodiesel used to blend with neat diesel at any blending ratio and used in the form of neat fuel for compatibility study was supplied from Global Green Chemicals Public Co., Ltd., Thailand. No stabilizer nor additives were added into this biodiesel. The last one is, partially hydrogenated biodiesel which produced at Thailand Institute of Scientific and Technological Research (TISTR), from palm biodiesel feedstock. The partially hydrogenated biodiesel is an upgrade of conventional palm biodiesel through partially hydrogenation process to minimize amount of methylene group or any double bond in fatty acid chain, which easy be oxidized from unproper environment.

The partially hydrogenated biodiesel was produced by using 95 L of palm biodiesel, hydrogenated in 0.32 MPa partial pressure of hydrogen at 85 °C by using 6%wt Pd/Al_2O_3 as a catalyst. The amount of hydrogen consumed during this process is 0.1% wt. After the hydrogenation process finishes, 2.7 kg silica alumina was added into the crude partially hydrogenated biodiesel to remove MG and SG. This process is called "adsorption". Then, the partially hydrogenated biodiesel is filtered to separate the saturated MG and silica alumina. The entire processes are shown in Figure 3.1.

3.2 Nitrile Rubbers

Three specifications of nitrile rubber sheet with 2 mm. thickness were used in this study. First, the black nitrile rubber sheet (a commercially product), called NBR 1 is supplied from Masterpac-Asia Co., Ltd. Its content was examined by thermogravimetry analysis. The black rubber contains 38 wt% of polymer, 20 wt% of carbon black, 2.5 wt% of volatile compounds and 39 wt% of ash (containing $CaCO_3$ identified by Energy Dispersive X-ray Spectrometer (EDS))

The other two nitrile rubber sheet specimens are made from the high and medium amount of acrylonitrile content (40% and 33%) in base polymer, cured by peroxide system in order to neglect the sulphur content for further analysis. NBR2 is the name for high amount of acrylonitrile while the medium one is labelled as NBR3 throughout this research. All specifications of test specimens are shown in the Table 3.1 and the appearances of rubbers are presented in the Figure 3.2. The rubbers were prepared by cutting into 3×4 cm for swelling and characterize determination and into die cut type C according to ASTM D412 for tensile test.

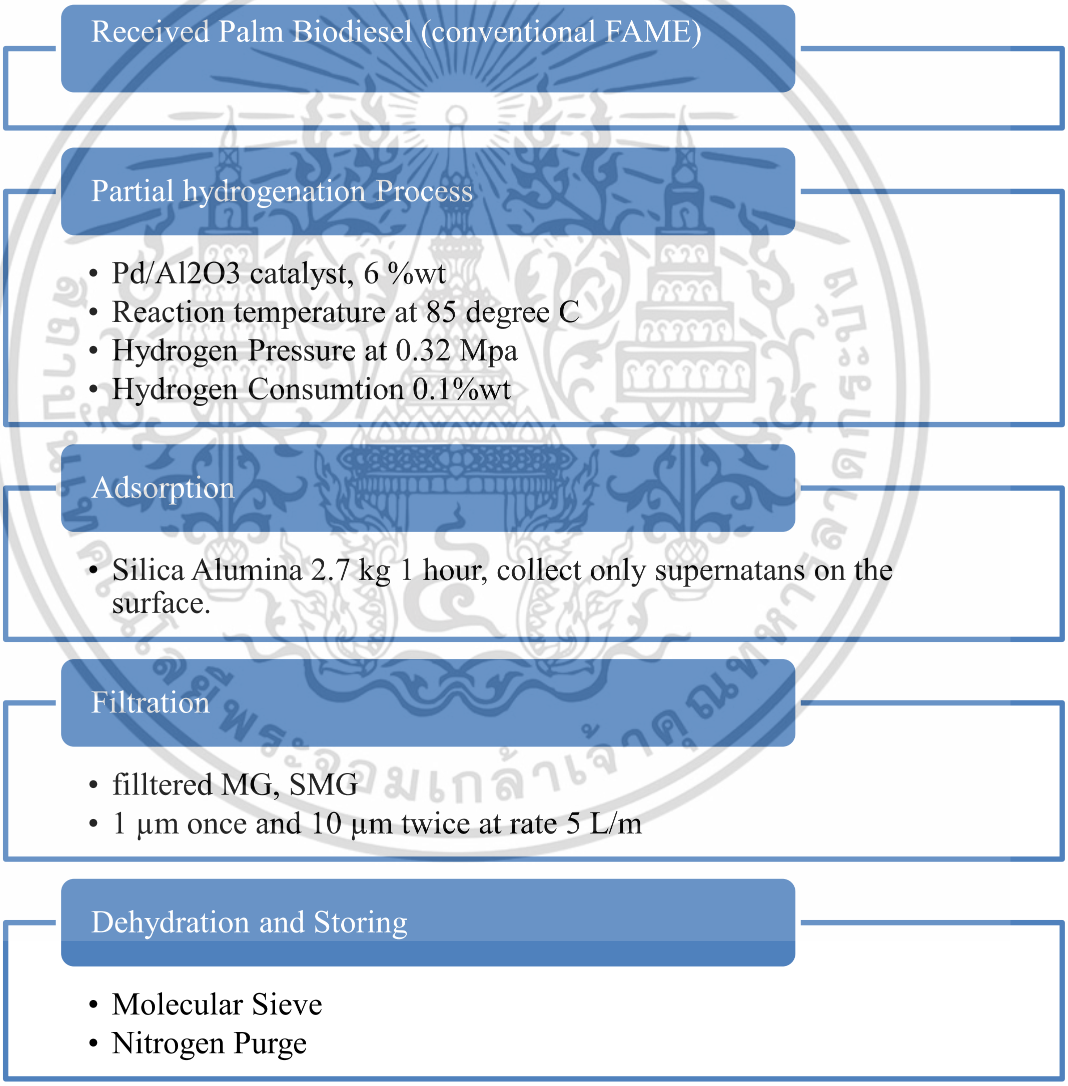


Figure 3.1 Partially hydrogenation processes to enhanced conventional biodiesel stability

Figure 3.2 NBR1-commercial NBR, NBR2 and NBR3 from left to right (Upper), cut by die cut type C for tensile test according to ASTM D412

Table 3.1 The specification of NBR test specimens

Sample	ACN (%)	Density (g/cm3)	Mooney Viscosity ML (1+4) 100°C	Tensile Strength (MPa)	Elongation (%)	Hardness (Shore A)
NBR1	NA	1.49	NA	4.68	162.82	65
NBR2	40	1.05	50	2.67	125	52
NBR3	33	1.02	45	2.72	137	50

3.3 Immersion Equipment

Shcott Duran wide mount with size of 250 ml and 1000 ml bottles with cap and sealing ring were used to contained fuel and immersed the rubbers in this study. The nitrile rubber samples were separated and hang in the bottle with stainless wire. The assembly of test equipment and test specimens shows in the Figure 3.3

Figure 3.3 1000 ml (left) and 250 ml (right) Shcott Duran bottle

3.4 Heating Unit

2 heating units were used for experiment set up to heat the bottle contained fuel and rubbers. Firstly, Heating oven from Memmert UF110 used as heating unit for 250 ml Schott Duran wide mount bottles at 55±2°C with forced ventilation. The other device is Memmert One 45 oil bath with cover. Heating oil bath was filled with silicone oil and used as heating unit for both 250 ml and 1000 ml Schott Duran wide mount bottles at 85°C.

Figure 3.4 Heating oven (Memmert UF110) (left), Oil Bath (Memmert One 4) (right)

3.5 Swelling Measurement

3.5.1 Analytical Balancer

The mass and volume of the rubber samples were determined by using 4 decimal places in grams by Sartorius CP224S analytical balancer with density determination kits shows in the Figure 3.5. The samples were cleaned by quickly dip in acetone and blot dry with lint free paper before weighted.

Figure 3.5 Sartorius CP224S analytical balance (left), density determination kits (right)

3.5.2 Calculation Method

The test samples were taken out from the immersion bottle then quickly dipped in acetone and blotted with a towel paper to remove the remained liquid on the sample surfaces. The relative change in mass (*ΔM*) and volume (*ΔV*) of the sample is calculated by equation (3.1) and equation (3.2) respectively, where M1 is the initial mass of samples in air as received and M2 is the mass after the immersion test period. M3 is the initial mass of samples and M4 is the mass after immersion test, weighted in the water to calculate the volume as followed Archimedes' principle.

$$\Delta M, \% = \frac{M_2 - M_1}{M_1} \times 100 \tag{3.1}$$

$$\Delta V, \% = \frac{(M_2 - M_4) - (M_1 - M_3)}{(M_1 - M_3)} \times 100 \tag{3.2}$$

3.6 Mechanical Properties

3.6.1 Mechanical Properties Test

The test samples were prepared from the rubber sheet with 2 mm thickness, punched to the dumbbell shape using a type-c die cut, according to ASTM D412 before the test. Tensile test was performed at room temperature by an Instron 5500 Universal Testing Machine shown in the Figure 3.6, using a 100 N load cell and crosshead speed of 500 mm/min. The tensile properties were averaged from the measuring value of three to five specimens for each test condition.

Figure 3.6 Instron 5500 Universal Testing Machine

3.6.2 Hardness test

The hardness of immersed samples was determined using Instron Shore durometer type A presented in

Figure **3.7**, according to ASTM D2240-15. Two pieces of 2 mm rubber sheet were stacked together to increase the thickness of test specimens to ensure that there is no hole happen due to the test, thus improving the accuracy.

Figure 3.7 Instron Shore durometer type A

3.7 Crosslink Density

The crosslink density of the samples was determined, according to ASTM D6814-02 calculated from Flory-Rehner equation (3.3), polymer-solvent interaction in the equation represent in Table 3.2. The samples were soaked in benzene (QRëC, New Zealand) until reaching equilibrium at room temperature. During soaking period, the solution is changed at every 24 h. At equilibrium, the samples were taken out and blotted with lint free paper, then samples were weighted in the closed-tared bottle. Later the samples were drying at 70°C with force ventilation oven overnight. The density of dried rubber was measured in ethanol (polymer density). The effective number of chains in a real network per unit volume (v_e) was calculated by equation (3.3).

$$v_e = \frac{-[ln(1-V_r)+V_r+\chi_1 V_r^2]}{V_1(V_r^{1/3}-V_r)/2} \tag{3.3}$$

Where $\chi 1$ is polymer-solvent interaction parameter as shown in Table 3.1, $V1$ is molecular volume of solvent and V_r is the volume fraction of polymer in a swollen network at equilibrium with pure solvent and calculated by equation (3.4)

$$V_r = \frac{(M_r)/(\rho_r)}{(M_r)/(\rho_r) + (W_s/\rho_s)} \tag{3.4}$$

where M_r is the mass of dried rubber, M_s is the mass of solvent swelled by rubber, ρ_r is the density of dried rubber and ρ_s is the density of the solvent.

Table 3.2 Solvents for Swelling Rubber (NBR)

Acrylonitrile: Butadiene	Solvent	Interaction Parameter
82:18	Benzene	0.390 (at 25°C)
70:30	Benzene	0.486 (at 25°C)
61:39	Benzene	0.564 (at 25°C)

Source: Rodriguez, F., Principle of Polymer Systems, 2nd Ed., McGraw-Hill, New York, 1982, Ch. 2.

3.8 Thermogravimetric Analysis

The composition and content of the rubbers was determined by thermogravimetry (Shimadzu DTG-60AH) by measured mass of the sample over time as the temperature change. The analysis is divided into three steps. Firstly, the samples were heated from room temperature to 800°C in nitrogen gas. Then, the samples were cooled down to 300°C while maintaining the nitrogen flow. Finally, the samples were reheated up to 800°C in oxygen to oxidize the carbon black and other compositions in the rubber sheet. The scanning rate was 20°C min-1 every state and the gas flow rate were 100 mL min^{-1}.

3.9 Infrared Spectroscopy

Infrared spectroscopy is the analysis of organic and inorganic functional group in molecules interacting with infrared light. IR spectra was determined the change of functional group of the rubbers and biodiesel before and after experiments. The infrared spectra of the NBR samples were obtained by a Nicolet™ iS50 FTIR

Spectrometer using attenuated total reflection (ATR) as shown in Figure 3.8. The spectrums of the samples were collected at wavelength between 4000 – 400 cm^{-1} at a resolution of 4 cm^{-1} with a scanning number of 32.

Figure 3.8 Nicolet™ iS50 FTIR

3.10 Gas Chromatography

The compositions of biodiesel were determined at National Metal and Materials Technology Center (MTEC), Thailand, by gas chromatography (GC-2010, Shimadzu). The sample solution is heated to vaporized without decomposition and uses carrier gas to separate and analyze compounds of sample across the long column shows in the Figure 3.9. Both palm biodiesel and partially hydrogenated biodiesel were prepared by dissolving 100 mg of sample into 10 mL of toluene in individual vial. Helium gas was used as the carrier gas and Agilent J&W HP-88 with 0.25 mm inner diameter, 100 meters and 0.20μm film thickness was used as column 140 to determine the composition of biodiesel. The initial heating temperature is 140°C were heating with rate 4°C/min up to 240°C and hold the temperature for 15 minutes.

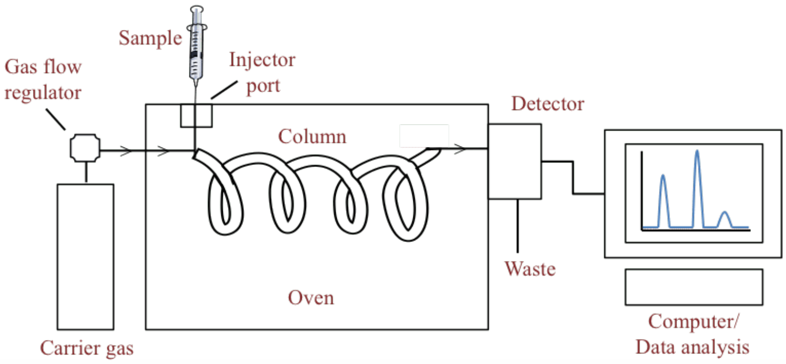


Figure 3.9 Gas chromatography configuration

3.11 Scanning Electron Microscopy

The morphology of NBR surface was studied using Hitachi SU5000 scanning electron microscope in Figure 3.10A. The samples were extracted the imbedded biodiesel by immersing them in benzene until reaching equilibrium condition. Then, the samples were dried in the force ventilation oven at 70°C overnight. Subsequently, the dried samples were coated with gold by Quorum rotary pumped coater Q150R as presented in Figure 3.10B with sputter current of 15 mA for 30 s. The micrographs were taken at an acceleration voltage of 10 kV in low vacuum mode.

Figure 3.10 Hitachi Schottky Field Emission Scanning Electron Microscope SU5000 and Quorum rotary pumped coater Q150R

3.12 Method to Determine Degradation of Biodiesel

3.12.1 Peroxide Value

Peroxide form, the primary product of biodiesel degradation, is increased as the initially product of degradation, then decrease upon further oxidation. The degradation of palm biodiesel and partially hydrogenated biodiesel was determined from peroxide content. The peroxide value was measured by in-house titration method, modified from ASTM D3703. A standard 0.01 N of sodium thiosulphate pentahydrate (QRëC, New Zealand) was used to titrate biodiesel sample which dissolved in 45 mL 2,2,4-trimethylpentane (Fisher, England) and acetic acid (RCI Labscan, Thailand) in the ratio of 5:4, 2 mL saturated potassium iodide, 100 mL water and 5 mL starch solution.

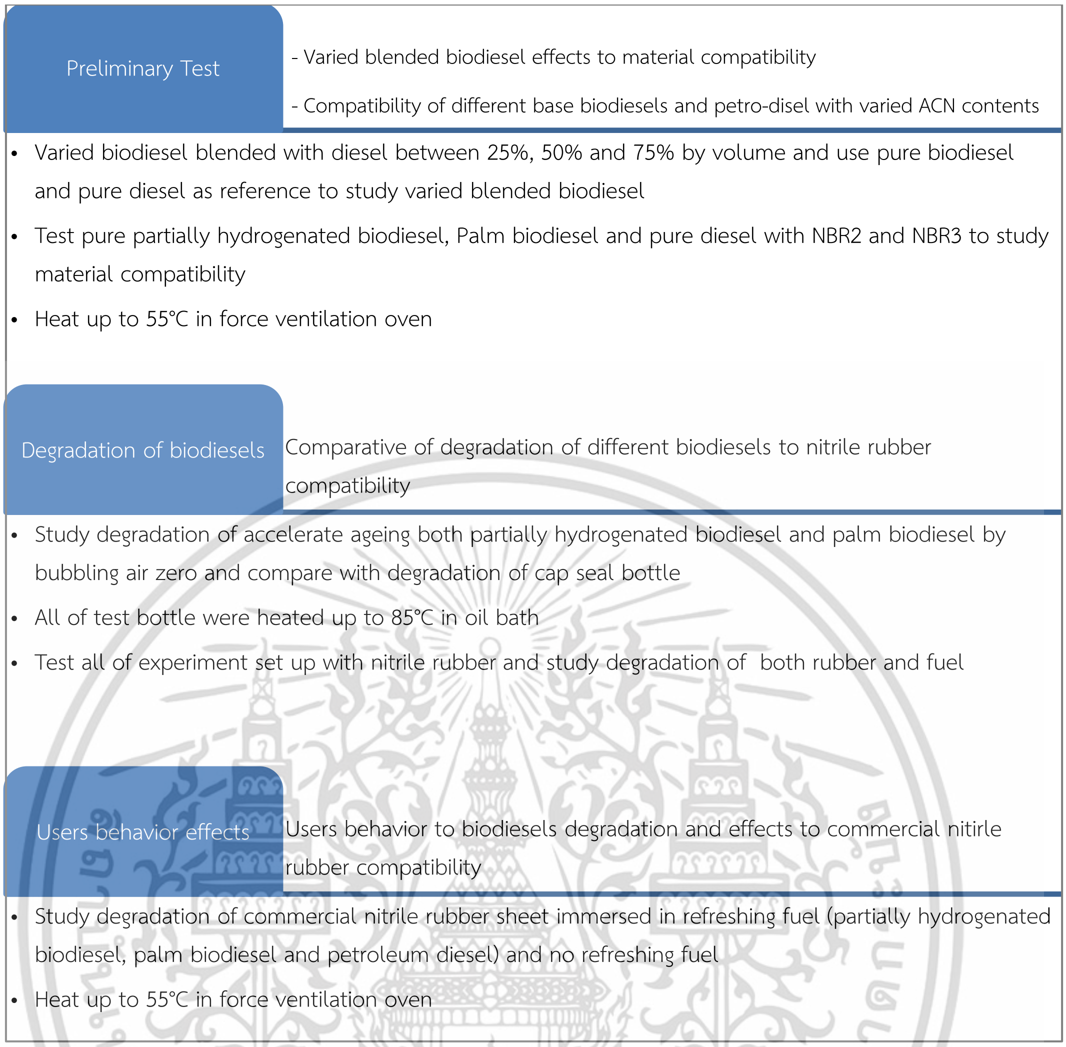
3.12.2 Acid Value

Acid value is the oxidation product from primary product and proceed to decompose then inter-react to form numerous secondary oxidation products including short chain carboxylic acid. Acid value represents to amount of secondary product of biodiesel oxidation which including many aldehydes, alcohols and higher molecular weight oligomers. The acidic compositions in biodiesel were measured according to ASTM D664. Biodiesel in the 100 mL of toluene (QRëC, New Zealand) , isopropyl alcohol(QRëC, New Zealand) and water in ratio 100:99:1 and used p-naphtholbenzein as an indicatior, were titrated by Metrohm 809 Titrando, Metrohm 800 Dosino dispensing system and Metrohm 801 magnetic stirrer, the equipment set up are shown in the Figure 3.11.

Figure 3.11 Metrohm automatic titration equipment

3.13 Test Condition

The study of nitrile rubber compatibility divide into 3 section of experiment. Firstly, the compatibility study from materials solubility parameters between biodiesel blended to nitrile rubber and different biodiesels and diesel to varied acrylonitrile content of the rubber has been studied as preliminary. The next section, comparative of degradation between conventional palm biodiesel and enhanced palm biodiesel from partially hydrogenation process to compatibility with nitrile rubber. Finally, the study of refilling behaviors of users to the degradation of commercial nitrile rubber sheet. The experiment set up detailed shows in the Figure 3.12



Preliminary Test

- Varied blended biodiesel effects to material compatibility
- Compatibility of different base biodiesels and petro-disel with varied ACN contents

- Varied biodiesel blended with diesel between 25%, 50% and 75% by volume and use pure biodiesel and pure diesel as reference to study varied blended biodiesel
- Test pure partially hydrogenated biodiesel, Palm biodiesel and pure diesel with NBR2 and NBR3 to study material compatibility
- Heat up to 55°C in force ventilation oven

Degradation of biodiesels

Comparative of degradation of different biodiesels to nitrile rubber compatibility

- Study degradation of accelerate ageing both partially hydrogenated biodiesel and palm biodiesel by bubbling air zero and compare with degradation of cap seal bottle
- All of test bottle were heated up to 85°C in oil bath
- Test all of experiment set up with nitrile rubber and study degradation of both rubber and fuel

Users behavior effects

Users behavior to biodiesels degradation and effects to commercial nitirle rubber compatibility

- Study degradation of commercial nitrile rubber sheet immersed in refreshing fuel (partially hydrogenated biodiesel, palm biodiesel and petroleum diesel) and no refreshing fuel
- Heat up to 55°C in force ventilation oven

Figure 3.12 Schematic of the experiment detailed process

3.13.1 Rubber Swelling and Fuel Absorption Test

The preliminary test divide into two section. Firstly, the experiment has been set up by soaking three specimens of NBR2 into 250 ml of biodiesel blended fuels at different ratios ranging from 25 – 75 percent in 25 % increments. In addition, pure biodiesel and neat diesel have been used as the reference. The samples were separated and hang of stainless wired as show in the Figure 3.13 . The bottles have been closed by sealing ring and cap to prevent air contact during the experiment. The whole bottles were kept in the 55°C force ventilation oven for 28 days. The samples were monitored the mas by weighted as detailed in the Table 3.3

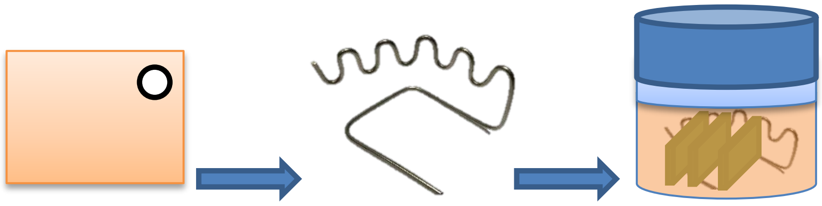


Figure 3.13 The assembly of the rubber hang by stainless wire in the bottles

Table 3.3 Experiment detailed for compatibility varied blending ratio of biodiesels and diesel with nitrile rubber

Test material	NBR2 (40% of ACN)
Fuel	- 25 Diesel/75 Biodiesel (v/v) - 50 Diesel/50 Biodiesel (v/v) - 75 Diesel/25 Biodiesel (v/v) - Pure petroleum diesel - Pure biodiesel
Temperature	55°C in force ventilation oven
Duration	28 days
Evaluation	Mass change: 3, 7, 14, 28 days

Then, the base diesel and biodiesels were used to study compatibility test with varied acrylonitrile contents in nitrile rubber sheet (NBR2 with 40% of ACN and NBR3 with 33% of ACN). Three specimens of each rubber were soaked in 250 ml of pure base fuel and closed the bottle by cap with sealing ring as show in the Figure 3.13. The rubbers exposed to the test fuel were kept in the oil bath at 85°C for 28 days for both experiments. During immersion period, the rubber degradation was monitored in terms of the mass change. The detailed of experiment set up show in the Table 3.4

Table 3.4 Experiment detailed for compatibility of different diesels with varied acrylonitrile content of nitrile rubber

Test material	- NBR2 (40% of ACN) - NBR3 (33% of ACN)
Fuel	- Petroleum diesel - Palm biodiesel - Partially hydrogenated biodiesel
Temperature	85°C in oil bath
Duration	28 days
Evaluation	Mass change: 1, 2, 3, 7, 14, 28 days

3.13.2 The Comparative of Biodiesels Degradation and Effects to the Degradation of The Nitrile Rubber

Both neat palm biodiesel and partially hydrogenated biodiesel, filled in a 1 L Scott Duran wide mouth bottle with the sealing cap, were tested at four different ageing conditions; (i) without the test specimens, the bottle caps were drilled and inserted the Perfluoroalkoxy alkanes (PFA) tube for bubbling the air zero gas (Linde, Thailand) with a flow rate of 5 L per hour (ii) without the test specimens, the bottles were tighten with the sealing cap to prevent the fuel degradation by the oxidation with the ambient air. The test condition of (i) and (ii) are detailed in the table Table 3.5. (iii) with the 5 test specimens of NBR2, the bottle caps were flowed the air zero gas like the case (i) and (iv) with the 5 test specimens of NBR2, the bottles were controlled to prevent the air leak into the bottle like case (ii). The test condition of (iii) and (iv) are detailed in the Table 3.6. All test bottles were kept in the oil bath to control the test temperature at 85°C for 4 weeks. At each week, the fuels were taken out 100 mL to determine the degradation of the sample. In addition, the NBR2s immerged in each test fuel were examined to verify their degradation.

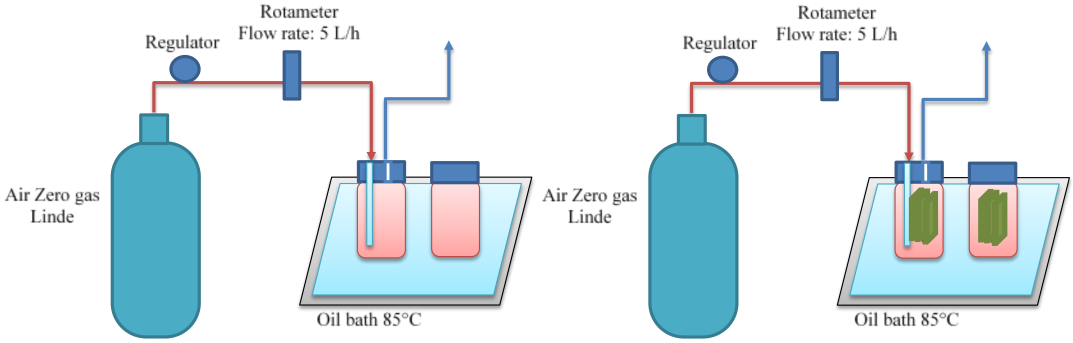


Figure 3.14 The schematic diagram for study the degradation of accelerate ageing biodiesel (left), and study its compatibility with nitrile rubber (right)

Table 3.5 Experiment detailed for study the degradation of accelerate ageing biodiesel

Condition	- Bubbling air zero (Linde) 5 l/h in the bottom of bottle - Sealing cap bottle
Fuel	- Palm biodiesel - Partially hydrogenated biodiesel
Temperature	85°C in oil bath
Duration	42 days
Evaluation	- Peroxide value: 3, 7, 14, 21, 28 days - Acid value: 3, 7, 14, 21, 28 days - IR: 3, 7, 14, 21, 28 days

Table 3.6 Experiment detailed for study the material compatibility of accelerate ageing biodiesel

Test material	- NBR2 (40% of ACN)
Condition	- Bubbling air zero (Linde) 5 l/h in the bottom of bottle - Sealing cap bottle
Fuel	- Palm biodiesel - Partially hydrogenated biodiesel
Temperature	85°C in oil bath
Duration	28 days
Evaluation	- Mass change: 1, 2, 3, 7, 14, 28 days - IR spectra: 3, 7, 14, 28 days - Mechanicals test: 3, 7, 14 days - Crosslink density: 7, 28 days - SEM and TGA: 28 days

3.13.3 The Compatibility of a Commercial Nitrile Rubber Sheet with Different Base Diesels

The commercial product NBR1 were exposed to neat diesel, palm biodiesel and partially hydrogenated biodiesel. At each fuel test was filled into two bottles in which three test specimens were placed, thus indicating six bottles used in this study and separating into two groups; each group includes all test fuels soaked with the NBR1 and assembly on stainless wired and put in the bottle with closed sealing ring and cap as same as 3.13.1. All bottles were placed into the oven to control the temperature at 55°C for 4 weeks period. The first group was flushed the fresh new fuel for every third three days and once weekly until 4 weeks as suggested by SAE J1748 standard. The latter group used the same fuel from the beginning until 4 weeks without replacing the fresh new fuels. All details of test condition are listed in Table 3.7

Table 3.7 Experiment detailed for commercial nitrile rubber sheet with different base diesels

Test material	NBR1 commercial nitrile rubber sheet
Fuel	- Petroleum diesel - Palm biodiesel - Partially hydrogenated biodiesel
Temperature	55°C in force ventilation oven
Condition	- Refreshing first three days, once a week later - Not refreshing overall test
Duration	28 days
Evaluation	- Mass change: 1, 2, 3, 7, 14, 28 days - Mechanical test: 7, 28 days - Crosslink density: 7, 28 days - TGA: 28 days

CHAPTER 4

RESULTS AND DISCUSSIONS

The results of the compatibility of nitrile rubber with different biodiesel have been divided into four parts. Firstly, the swelling tests of varied parameters of biodiesel and nitrile rubber have been conducted to study the correlate between these parameters and how its effect oil uptake of the rubber. In the second part, the degradation of partially hydrogenated biodiesel compositions and its degradation behaviors has been discussed and compared with conventional biodiesel. The experiments were accelerated at the high temperature and increasing air exposure. The degradation of biodiesels has been determined by measuring viscosity, peroxide contents and acid value as well as analyzing the functional groups of molecules structure by an infrared (IR) spectrometer. Then, the high acrylonitrile rubber, has been used as base rubber to test the compatibility with the accelerated degrading biodiesels. The rubber specimen has been determined the degradation by measuring oil uptake of specimens, the change in mechanical properties including tensile strength and hardness, thermogravimetric analysis, the morphology by SEM and IR analysis as same as biodiesels. Finally, the commercial grade of nitrile rubber sheets was conducted the compatibility test with both biodiesels and petroleum diesel with different condition to simulate the different application when using biodiesel as a fuel

4.1 The Compatibility Between Different Parameters of Both Materials

The easiest way to investigate the compatibility of the rubber with liquid fuels is to determine from the liquid penetration into the rubber matrix. The compatibility of the rubber is strongly depended on its own contents and the compositions of liquid fuels. To understand the compatibility of different material compositions, the experiments have been conducted into two parts. Firstly, the effect of biodiesel concentration in the blended fuels on the rubber degradation has been investigated as the preliminary test. Then, the relation of the material compatibility between the rubber content by varying the amount of acrylonitrile in conjunction with the fuel composition with different structure (conventional and upgraded biodiesel) has been clarified.

4.1.1 The Solubility of Biodiesel and Nitrile Rubber

In general, biodiesel is blended with petroleum diesel in order to use as the fuel in the diesel engine. The preliminarily test of the effect of biodiesel on rubber degradation has been conducted in this section. Only one grade of NBR rubber (NBR2) with 40% of acrylonitrile content was used as the specimens to conduct its compatibility test with one type of palm biodiesel. The experiment has been set up by soaking NBR2 into biodiesel blended fuels at different ratios ranging from 25 – 75 percent in 25 % increments. In addition, pure biodiesel and neat diesel have been used as the reference. The rubbers exposed to the test fuel were kept in the oven at 55°C for 28 days. During immersion period, the rubber degradation was monitored in terms of the mass change at day 3, 7, 14 and 28 as shown in Figure 4.1.

The results show that after the rubbers contact with biodiesel blended fuel, they turn to swelling with the mass increased (the positive value of mass change). When increasing the biodiesel content in blended fuel, the uptake of fuel into the rubber increases for every duration of the immersion test. Comparing the gap between day 3 (the light blue) and day 28 (the dark blue), the rubber immersed in the pure biodiesel gained the higher weight than those rubber soaked in the low content biodiesel fuels. This implies that biodiesel could degrade the rubber contacting it with the higher rate than diesel does. Therefore, to use biodiesel as the fuel with the high percentage content, material used to contact with the fuels have to be carefully investigated. Some additive may be added into the nitrile rubber to increase the resistance with biodiesel.

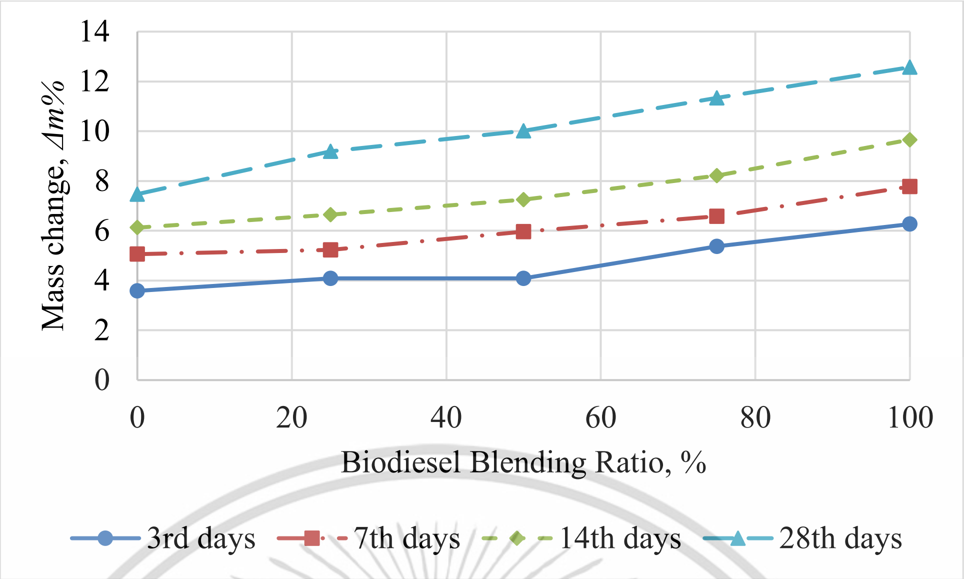


Figure 4.1 The mass change of NBR2 for 7 days and 28 days of immersion test at 55°C

Figure 4.2 indicates that when the percentage of biodiesel blended in diesel increases, the affinities between nitrile rubber and biodiesel blended fuel increases (the RED in the green dash line decreases). The high affinities between material leads to the fuel uptake into the rubber easily which corresponding well with the highest mass change of the rubber exposed to neat biodiesel in Figure 4.1. In conclusion, the amount of fuel absorbed by nitrile rubber is according to the affinities of solubility parameters between materials, the lower solubility distance (high affinities) between materials has higher of fuel absorbed. However, the experiments are not considered the degradation of chemical structure of both materials and any failure of rubber properties.

In addition to the RED between nitrile rubber and biodiesel, the RED of natural rubber/biodiesel is also shown in Figure 4.2. With the lower RED value, natural rubber can resist to biodiesel less than nitrile rubber. However, the highest affinity of natural rubber occurs at about 60% of biodiesel content. This means that neat biodiesel will not be the cause of material degradation for some case. In addition, nature rubber could not be used as the materials in the engine using biodiesel blended fuels.

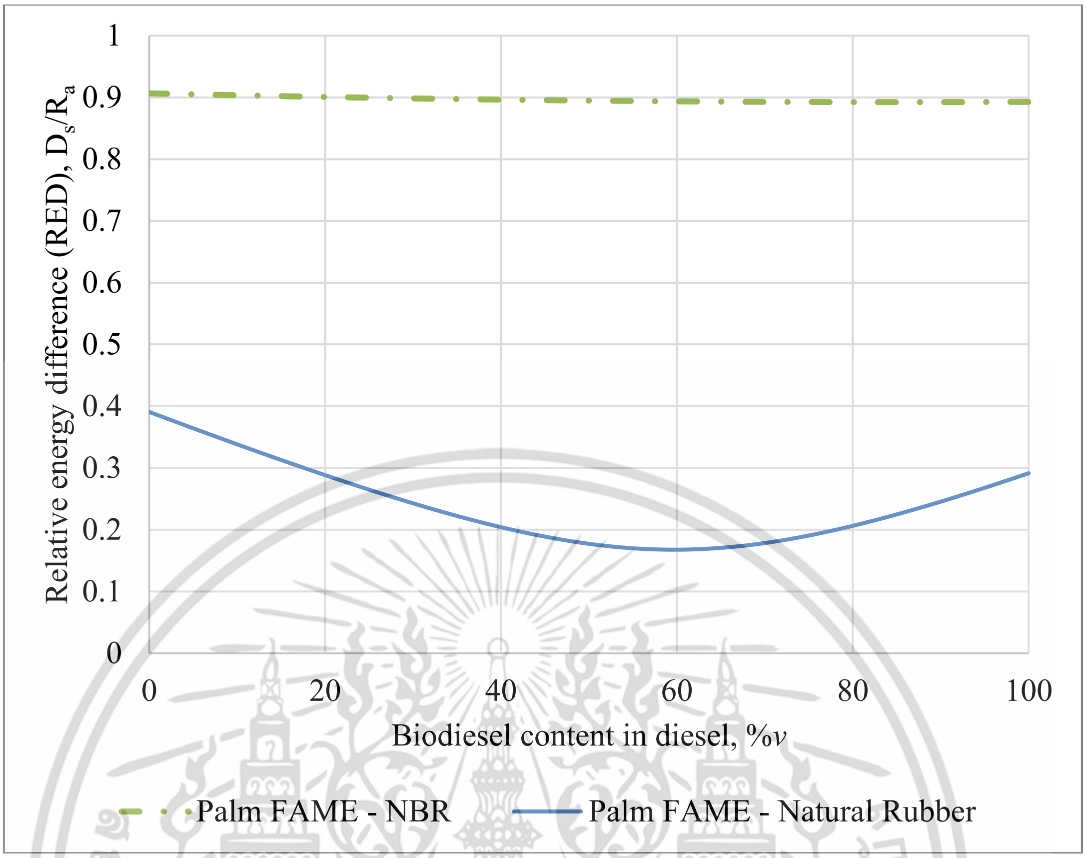


Figure 4.2 Relative energy difference ratio between polymer (NBR and Natural rubber) and varied of biodiesel blended with diesel

4.1.2 The Solubility of Varied Biodiesel Blended to Nitrile Rubber

According to the preliminary test in 4.1.1, neat biodiesel has the most effect on nitrile degradation. This section has been studied to clarify the important content of rubber and composition of the fuels in order to improve the nitrile rubber for using with the biodiesel fuels. The NBR2 with 40% of ACN and NBR3 with 33% of ACN have been used as the sample rubbers for the swelling test. Only neat fuel has been used in this study because they showed the most effect on the nitrile rubber. The samples were immersed under two different biodiesel composition (i) palm biodiesel (conventional biodiesel), and (ii) partially hydrogenated biodiesel (upgraded biodiesel) in the 250 ml wide mount bottle, stored in the oven at 55°C for 28 days. In addition, pure diesel is also used as the reference. Unlike the preliminary test, the rubber degradation was monitored at every day from the first three day after the immersion test started due to the rapidly change. Then, the rubbers were weighted once a week because of the gradually change.

Figure 4.3 shows the change of rubber mass which indicates the uptake of fuel into the rubber specimens with varying immersion period. Figure 4.3A presents the characteristic of fuel absorption of high acrylonitrile content rubber (NBR2) while the low acrylonitrile one (NBR3) is shown in Figure 4.3B. Both figures indicate that the uptake process can be divided into three intervals. Initially, the uptake of fuel into both rubbers showed the rapid rate during the first three days of immersion. In the next phase, the mass of rubber is slightly increased or constant, once it reaches equilibrium point of absorption. Finally, the different rubbers showed the different characteristics; one is dissolved but another is swelled.

In the Figure 4.3A, the NBR2 samples rapidly adsorb all three test fuels at the first 3 days and then the mass of rubber slightly increases until reaching 7th day. Palm biodiesel shows the most effect on the swelling while petroleum-based diesel presents the lowest influence. From 7th to 21st day after immersion, both types of biodiesel result in the slightly increased rubber mass while the mass of the rubber soaked in the diesel keeps constant. In the last phase, the swelling rates of NBR2 has increase for all test fuels, in which palm biodiesel has the most and diesel has the least effect.

Figure 4.3B shows the high rate of fuel absorption into NBR3. After the immersion test started, the fuel was rapidly absorbed into the rubber. It reached the equilibrium since the third day of immersion, faster than NBR2 which attained within 7 day. Like the NBR2 case, NBR3 immersed in palm biodiesel showed the highest rate of absorption whereas the lowest is the one soaked in the petroleum diesel. Unlike NBR2, NBR3 exposed partially hydrogenated biodiesel showed the absorption rate near the conventional biodiesel but much higher than diesel. Once the fuel absorption reached the equilibrium, the NBR3 immersed in the palm biodiesel still slightly increased. In contrast, the NBR3 immersed in partially hydrogenated biodiesel and petroleum diesel were not change in mass during day 3 to day 14. Finally, the mass of NBR3 immersed into the palm biodiesel was decreased from day 14 to day 21 and then slightly increased again (day 21- day 28). In the meanwhile, the mass of rubber immersed under partially hydrogenated biodiesel was decreased between day 14 and day 21 as same as immersed in palm biodiesel. However, those NBR3 kept the mass constant in the period of day 21 to day 28. For NBR3 exposed to petroleum diesel, the mass was continuously decreased after day 14.

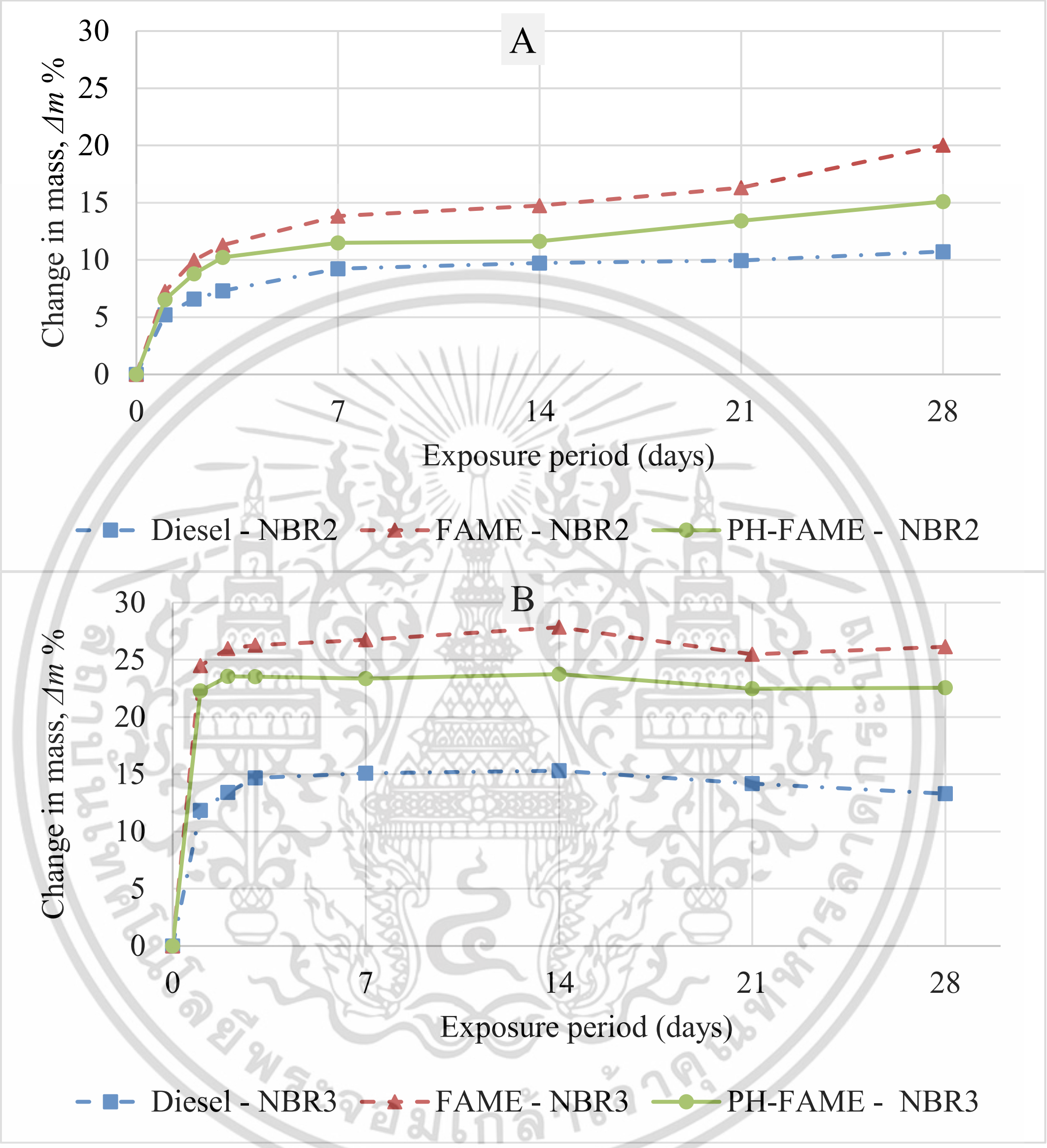


Figure 4.3 The mass change of A) NBR2 and B) NBR3 when exposed to base fuel at 85°C for 1 and 4 weeks.

From the immersion experiment of both based-rubber in three test fuels, the mass changes exhibit two behaviors of exposed rubbers; (i) the increasing of mass due to the rubber absorbed the fuel and (ii) the decreasing of mass because of the rubber dissolved into the fuel. The swelling behavior rapidly occurs immediately after the rubber and fuel contact to each other. The absorption rate and extent of the swelling is depended on many factors such as the structure of the rubber and compositions of the fuel. A high acrylonitrile content rubber is known as the high compatibility rubber in order to use with fuel. When it contacted with the fuel, its properties are hardly changed. As the results, NBR2 has the slower rate and lower amount sorption of biodiesel. A low acrylonitrile content rubber rapidly absorbs the fuel with the high amount until reaching its equilibrium. After one or two week of equilibrium condition, the dissolving/swelling process continues to progress. Meanwhile, NBR3 has the faster rate and higher amount of sorption of three fuels when contact, the mass of the specimens reached its equilibrium point faster than NBR2 and decreased later. In conclusion, the behavior of swell/dissolve of NBR3 is revealed its lower compatibility with any fuels than NBR2.

The occurrence of swelling and dissolving of nitrile rubber immersed in fuel can be explained by the similarity between structure of each materials, meaning rubber and fuel for this study. Materials having high similarity can attract each other higher than dissimilarity materials. The similarity of materials can be described by the solubility parameters of each material and calculated the interactive between materials. As describe in (2.2), the relative energy distance indicates the affinities between solvent and non-solvent material. Materials exhibiting the high affinities are expected to be attract each other higher than the lower one. As the result, the high amount of fuel is easily taken into the rubber matrix.

Because the relative energy distance (R_0) of the rubbers with different ratio of acrylonitrile and butadiene has not been provided individually because its liquid state when they are not copolymer, the solubility distance between both materials was calculated to visualize the affinity of materials instead. When the solubility distance of two materials is shorter, those materials have the high affinity between each other. Figure 4.4 presents the solubility distance between palm biodiesel/petroleum diesel and the most common concentration of acrylonitrile from 20 to 50 percent in the butadiene rubber reference to commercial blending specification [6]. The result shows that for all acrylonitrile contents the solubility distance of nitrile rubber and palm biodiesel (the red-dash line) is shorter than nitrile rubber and diesel (the solid blue line). This indicates that the affinity between nitrile rubber/biodiesel higher than nitrile rubber/diesel and results in the larger change in mass of rubber immersed under biodiesel in Figure 4.1.

Considering the effect of the amount of acrylonitrile content in the rubber, when the percentage of acrylonitrile content increases, the solubility distance increases thus lowering the affinity between rubber and the fuels. This leads to the high resistance of NBR2 to all three test fuels. Therefore, when biodiesel is applied in the diesel engine, a high acrylonitrile rubber is the material suitable to use.

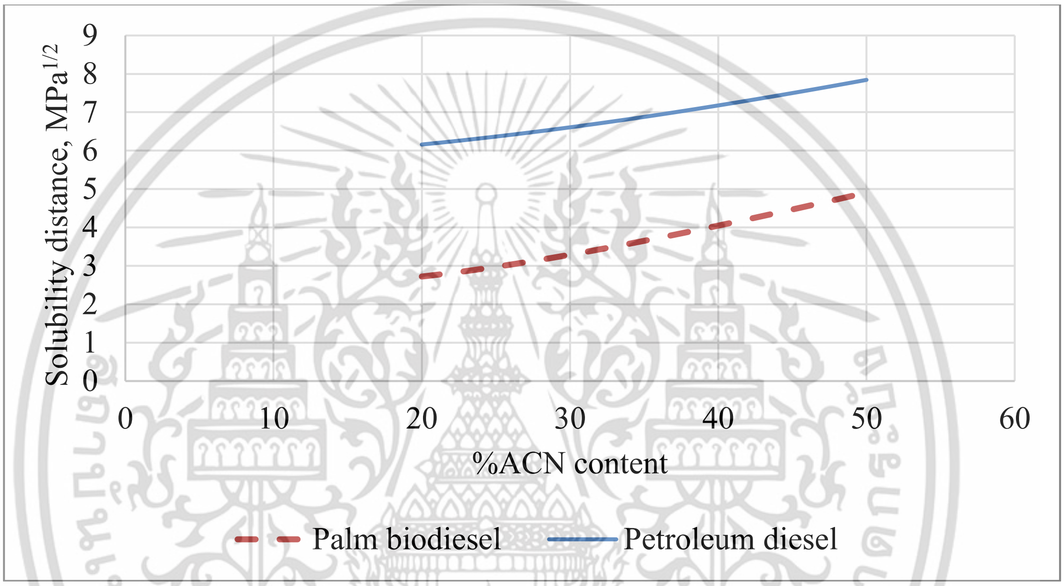


Figure 4.4 Solubility distance between fuel and varied contents of acrylonitrile and butadiene

To clearly understand biodiesel composition on rubber degradation, Figure 4.5 shows the Hansen solubility parameters sphere of Nitrile rubber, Natural rubber [5] and compositions of FAME in biodiesel [23] to reveal the affinity between the rubbers and FAME composition. The big orange circle presets to the HSP sphere of nitrile rubber while the small yellow circle indicate the to the HSP sphere of natural rubber. The sphere of HSP uses to indicate the solubility potential of solvent, the good solubility is when the HSP of solvent located inside the sphere and bad solubility solvent at outside of sphere.

As shows in Figure 4.5, the nitrile rubber has different polar parameter from the others materials due to nitrile triple bond from acrylonitrile in the polymers, made the nitrile rubber has resistance to swelling of fuel when contact with non-polar liquid such as neat diesel. Even the compositions of FAME have similarity with nitrile rubber than neat diesel, the distance between center of sphere still further than the center of natural rubber and the others fuel, causing the high swelling and low compatibility behavior of materials.

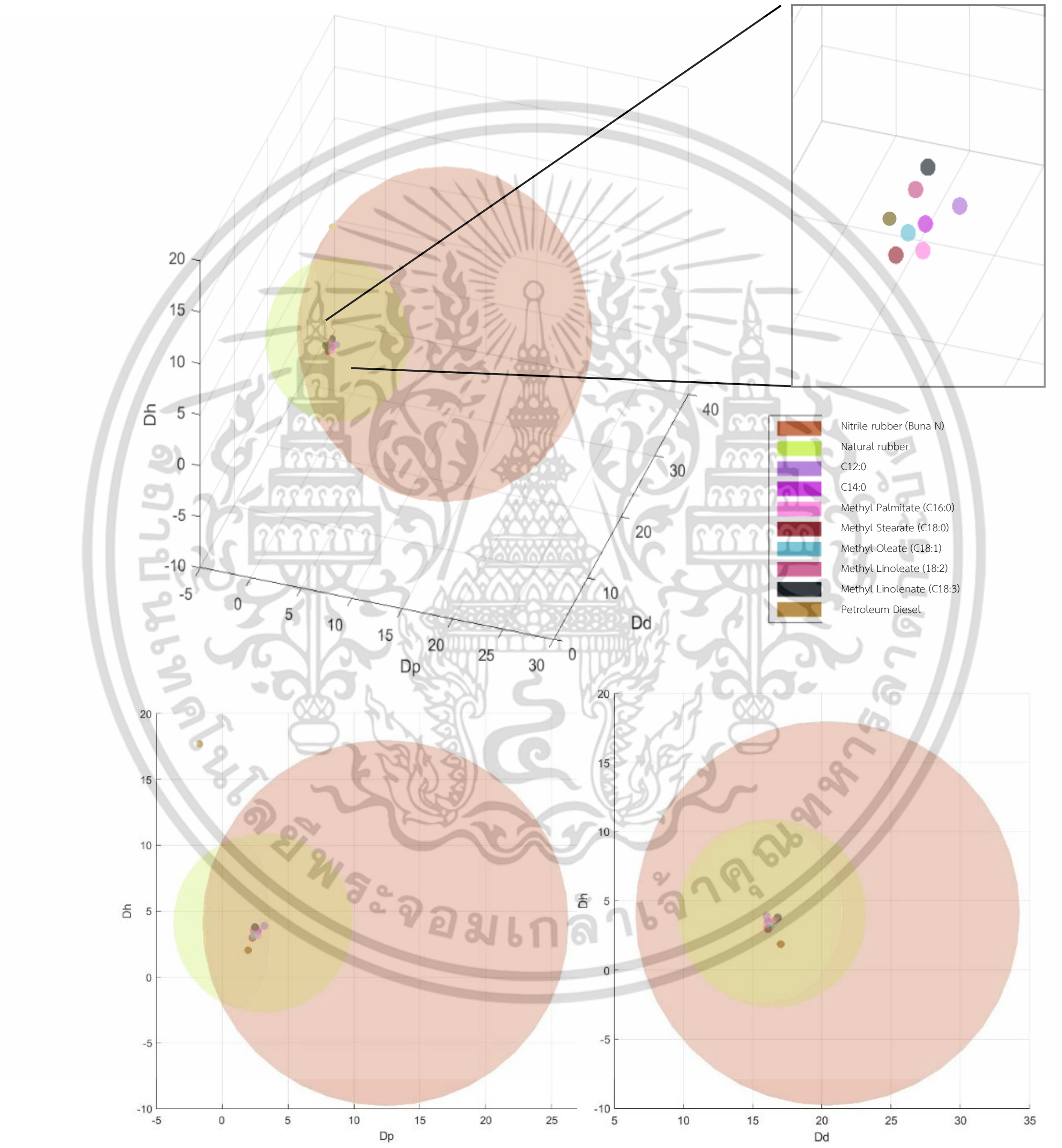


Figure 4.5 The Hansen solubility parameter sphere of Nitrile rubber, Natural rubber and common compositions of FAME in biodiesel.

Figure 4.5 shows the Hansen solubility parameters sphere of Nitrile rubber, Natural rubber [5] and common compositions of FAME in biodiesel [23], reveals the affinity parameters between the rubbers and FAME composition. Distance between center of natural rubber solubility sphere and FAME composition is shorter than center of nitrile rubber sphere even longer interaction radius sphere. As shows in Figure 4.5, the nitrile rubber has different polar parameter from the others materials due to nitrile triple bond from acrylonitrile in the polymers, made the nitrile rubber has resistance to swelling of fuel when contact with non-polar liquid such as neat diesel. Even the compositions of FAME have similarity with nitrile rubber than neat diesel, the distance between center of sphere still further than the center of natural rubber and the others fuel, causing the high swelling and low compatibility behavior of materials.

4.1.3 Determination of Composition of FAMEs in Palm Biodiesel and Partially Hydrogenated Biodiesel

Through partial hydrogenation process, the composition of FAME in biodiesel has been changed, the compositions and contents has been determined by using gas chromatography. Each composition has different of HSP value, effects to the material compatibility as mention in [10]. The result in Table 4.1 shows the amount of all of unsaturated fatty acid ester contents in biodiesel. The base both biodiesels derived from palm oil.

The result of biodiesel after partially hydrogenation process reveal decreased of both polyunsaturated and monounsaturated contents, hence increasing the amount of saturated FAME content. Due to higher oxidation stability of saturated fatty acid, the oxidation stability of partially hydrogenated biodiesel enhanced from conventional biodiesel at 10.43 up to 42.89 hours according to EN15751 oxidation stability test method. Figure 4.6 shows bar charts of composition of conventional palm biodiesel and partially hydrogenated biodiesel plot with RED value between each composition and nitrile rubber (Buna N). The composition of palm biodiesel seem to has lower RED value such as methyl linoleate (C18:2) much more than partially hydrogenated biodiesel, result in the higher fuel absorption by the rubber due to higher affinities of solubility parameters.

Table 4.1 The composition of FAME in palm biodiesel and partially hydrogenated FAME determined by GC analysis.

FAME	Percentage content of FAME (%)	
	Palm Biodiesel B100	Partially hydrogenated biodiesel
C12:0	0.31	0.73
C14:0	0.99	1.13
C16:0	43.29	45.41
C16:1	0.29	0.12
C18:0	4.42	10.28
Trans-C18:1	0.09	0.15
Cis-C18:1	40.21	39.17
C18:2	9.21	0.54
C18:3	0.37	0.10
C20	0.42	0.35
Others	0.82	2.37

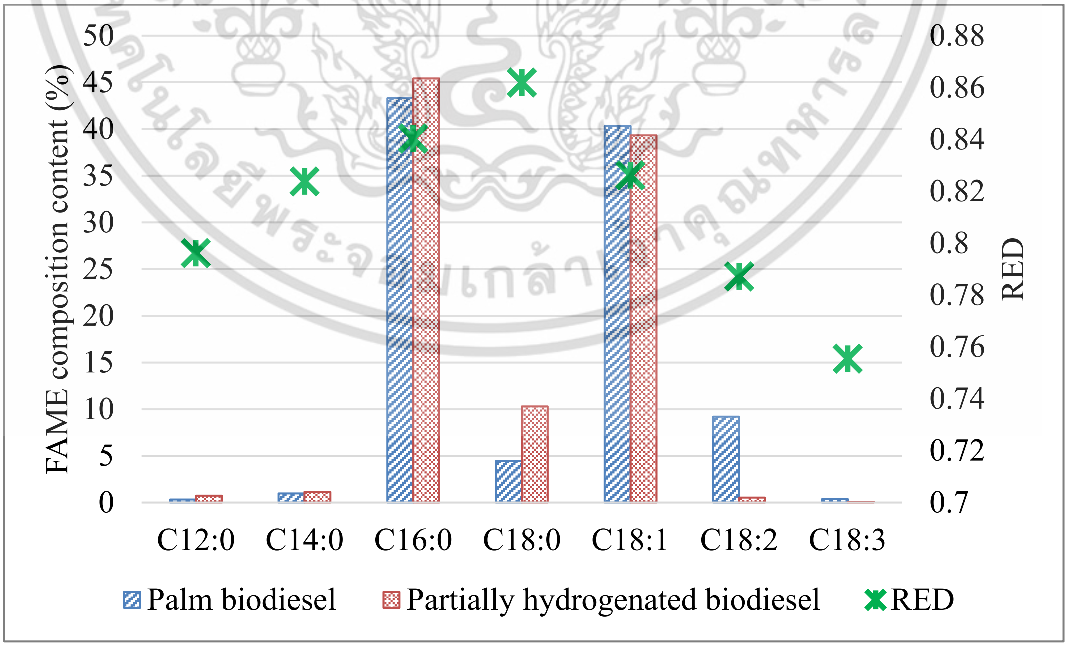


Figure 4.6 the compositions and contents in palm biodiesel and partially hydrogenated biodiesel and Relative energy distance between each composition with nitrile rubber

However, the swelling of rubber with varied materials composition does not considered the degradation of materials. Many research [6], [14], [24], [25] revealed the biodiesels are easily deteriorated by environments such as light accelerated the photo-oxidation, oxygen in air and heat exposure. Partially hydrogenation process is one of the most considering method use to enhance stability of biodiesel by reduced polyunsaturated fatty acid to minimize the easily degraded structure. The chemical degradation of both biodiesels and how it affected the rubber is discussed in next section.

4.2 Degradation of Biodiesels and Nitrile Rubber

The partially hydrogenated biodiesel has different properties from conventional biodiesel due to different certain compositions and contents of fatty acid. The composition of FAME solubility has been several studied separately. However, the different solubility between palm biodiesel and partially hydrogenated biodiesel has not been studied widely. The different stability of both fuels is significantly different according to research [2], which degradation products apparently effects the solubility parameters of solvents. In additions, several degradation products such as organics acid or peroxide can attack the chemicals structure of nitrile rubber. Therefore, the degradation of biodiesels has been studied and test its compatibility with high acrylonitrile content rubber sample.

4.2.1 Degradation of Palm Biodiesel and Partially Hydrogenated Biodiesel in Accelerated Aging Condition

A show the concentration of peroxide and acid content in both biodiesels at 85°C with bubbling 5 liters per hour of air zero. The peroxide contents in palm biodiesel increased rapidly since the first three days after testing, then reach its maximum points at 7 days after the test. After reaching highest point, peroxide content is decreasing continuously due to decomposition through test period and form into acid formation. In contrast, the peroxide contents in partially hydrogenated biodiesel is stable for the first 3 weeks and slightly increased at the week later. Then the peroxide contents suddenly increased after 4 weeks reaching highest point and then slightly decreased, as same as palm biodiesel. The trend lines of acid contents in the same figure reveals that the acid product is an after production of peroxide product. In the Figure 4.7B, The peroxide contents and acid value in partially hydrogenated biodiesel and palm biodiesel were heated at 85°C but with sealing cap were shown. The slightly decreased of peroxide value and slightly increased of acid value with increasing of exporsure time due to deformation of peroxide.

Figure 4.8 represents to IR spectra of partially hydrogenated biodiesel and palm biodiesel heat at 85°C and bubbling air zero 5 l/h. The degradation product of the biodiesel does not form as fast as air bubbling method. The peak area under between 1850-1600 cm^{-1} is representative of quantity of C=O group from ester function in biodiesel and degradation products such as aldehydes, ketones or carboxylic acids. Figure 4.9 show the correlate between acid value of biodiesel and the peak area under 1850-1600 cm^{-1} to estimate the degradation of biodiesel by determine the IR spectra. These correlations presume the degradation product mostly form in carbonyl acid structure.

The appearance of biodiesel ageing tested show in the Figure 4.10 including accelerate ageing partially hydrogenated biodiesel, partially hydrogenated biodiesel, accelerate ageing palm biodiesel and palm biodiesel. Once the acid value of biodiesel increased, the color of biodiesel become lighter, due to absence of carotenoid pigment from oxidative reaction [26].

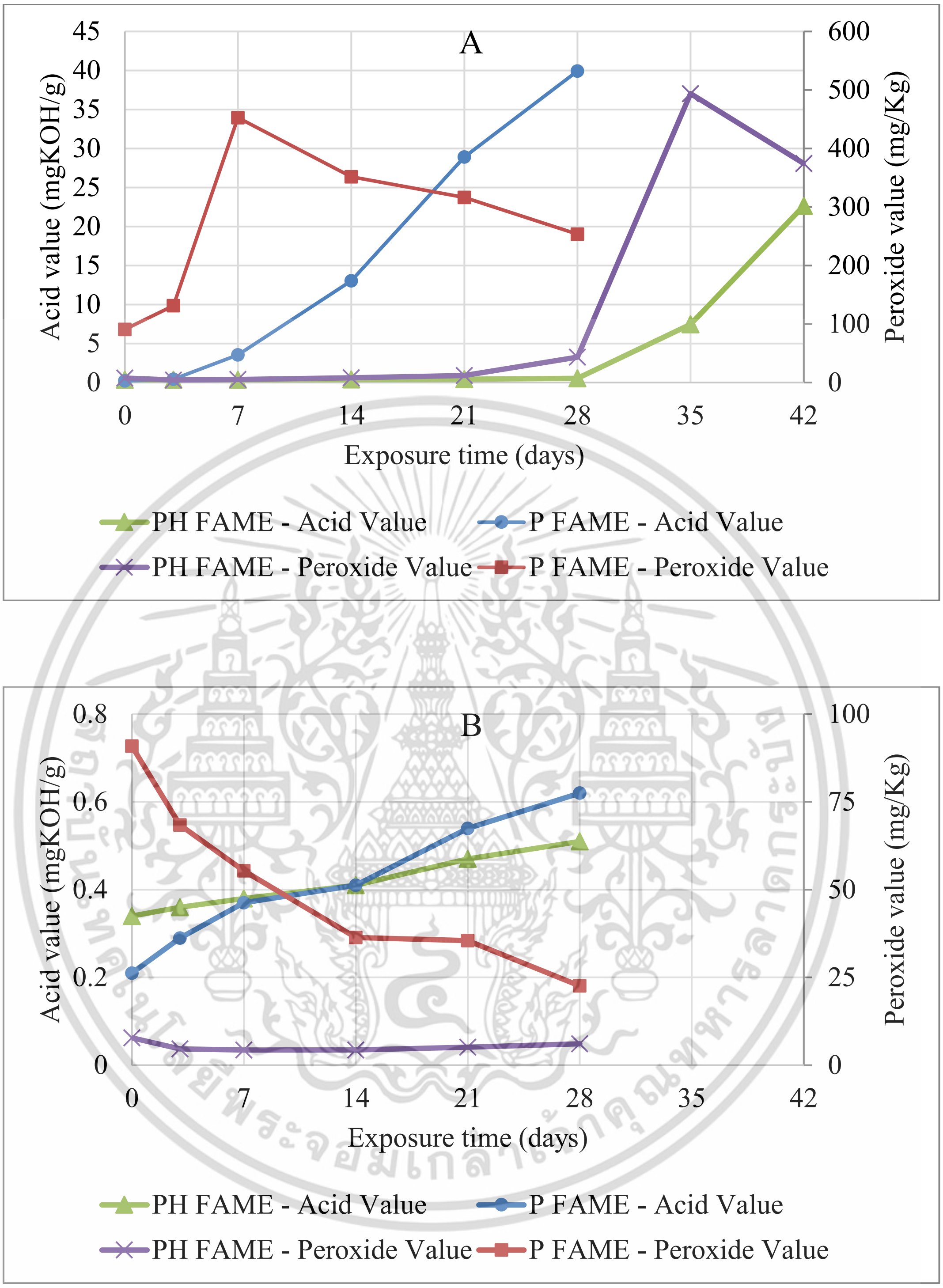


Figure 4.7 The concentration of degradation products in biodiesel heat at 85°C as function of ageing time including peroxide contents and acid contents in, A) bubbling 5 liters per hour of air zero and B) limit air contacted by sealing cap

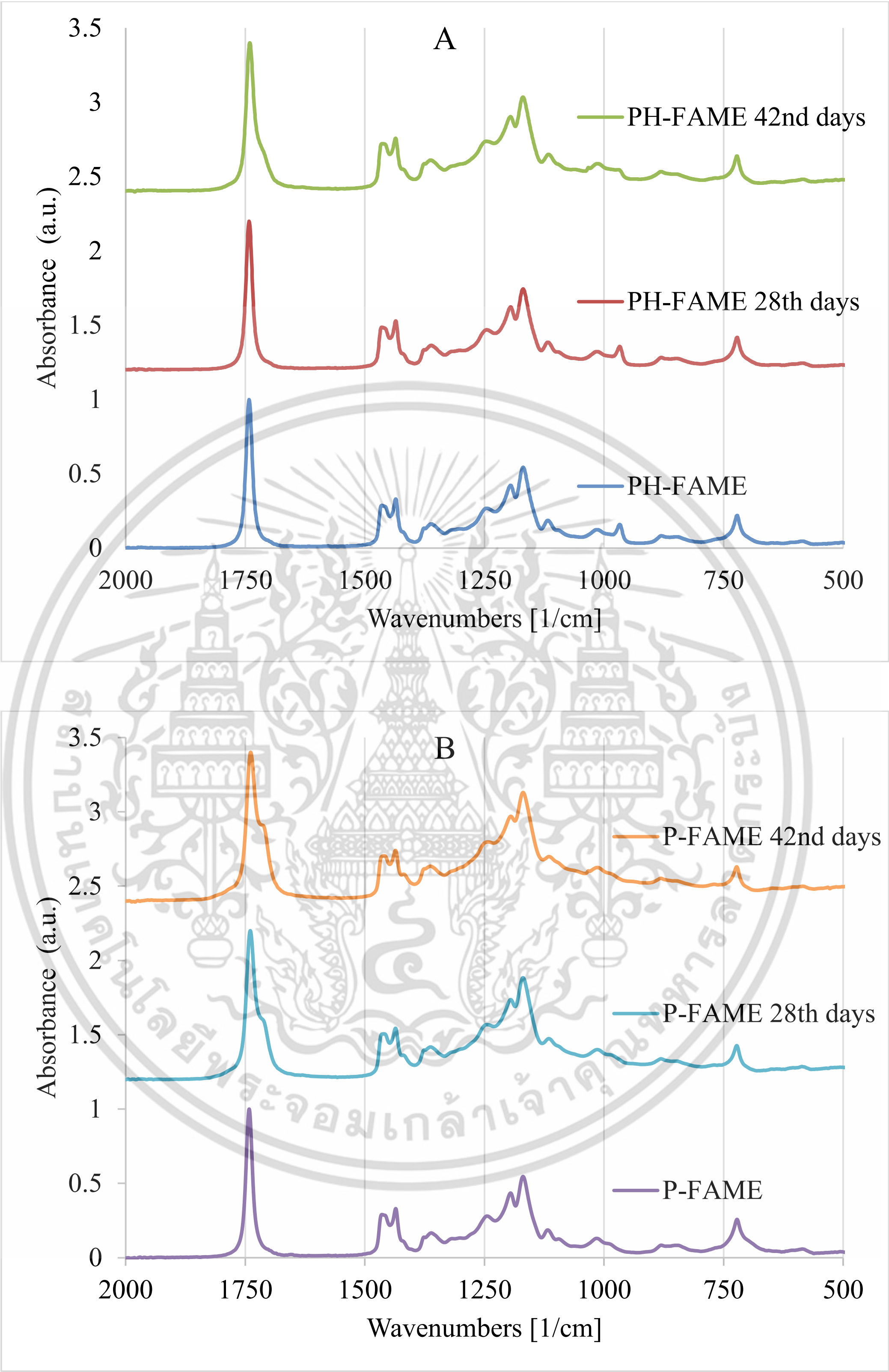


Figure 4.8 IR spectra of accelerated ageing A) partially hydrogenated biodiesel, B) palm biodiesel for 42 days.

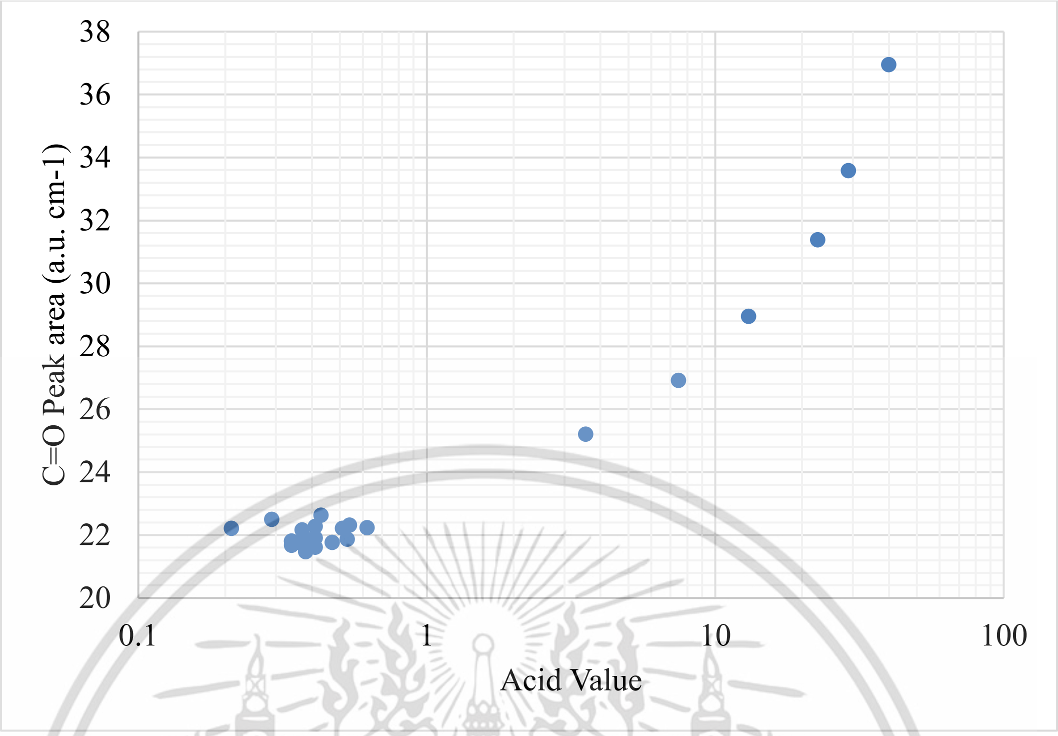


Figure 4.9 Peak area under C=O band between 1850-1600 cm-1 of IR spectra plot in function of Acid Value contents.

4.2.1 Degradation of The Biodiesel Used in Immersion Test

The biodiesel degradation when has NBR2 immersed cannot be determined the degradation product such as peroxide and acid value as same as 4.2.1 which required large amount of biodiesel to determined. The degradation of biodiesel with rubber immersed has been determined by using IR spectra as can be considered as mention in 4.2.1 instead due to low amount of biodiesel required. The area under carbonyl band between 1850-1600 cm^{-1} of accelerated ageing condition of both biodiesel with and without rubber immersed are show in the Figure 4.11.

For the partially hydrogenated biodiesel without rubber immersed, the degradation occurred after passed 28 days of exposure, however with rubber immersed the degradation was not occurred. In the other hands, the palm biodiesel with rubber immersed has degraded after passed 3 days of exposure as same as no rubber immersed in the same condition. The rising of carbonyl peak area of palm biodiesel with rubber immersed was lower than without rubber immersed.

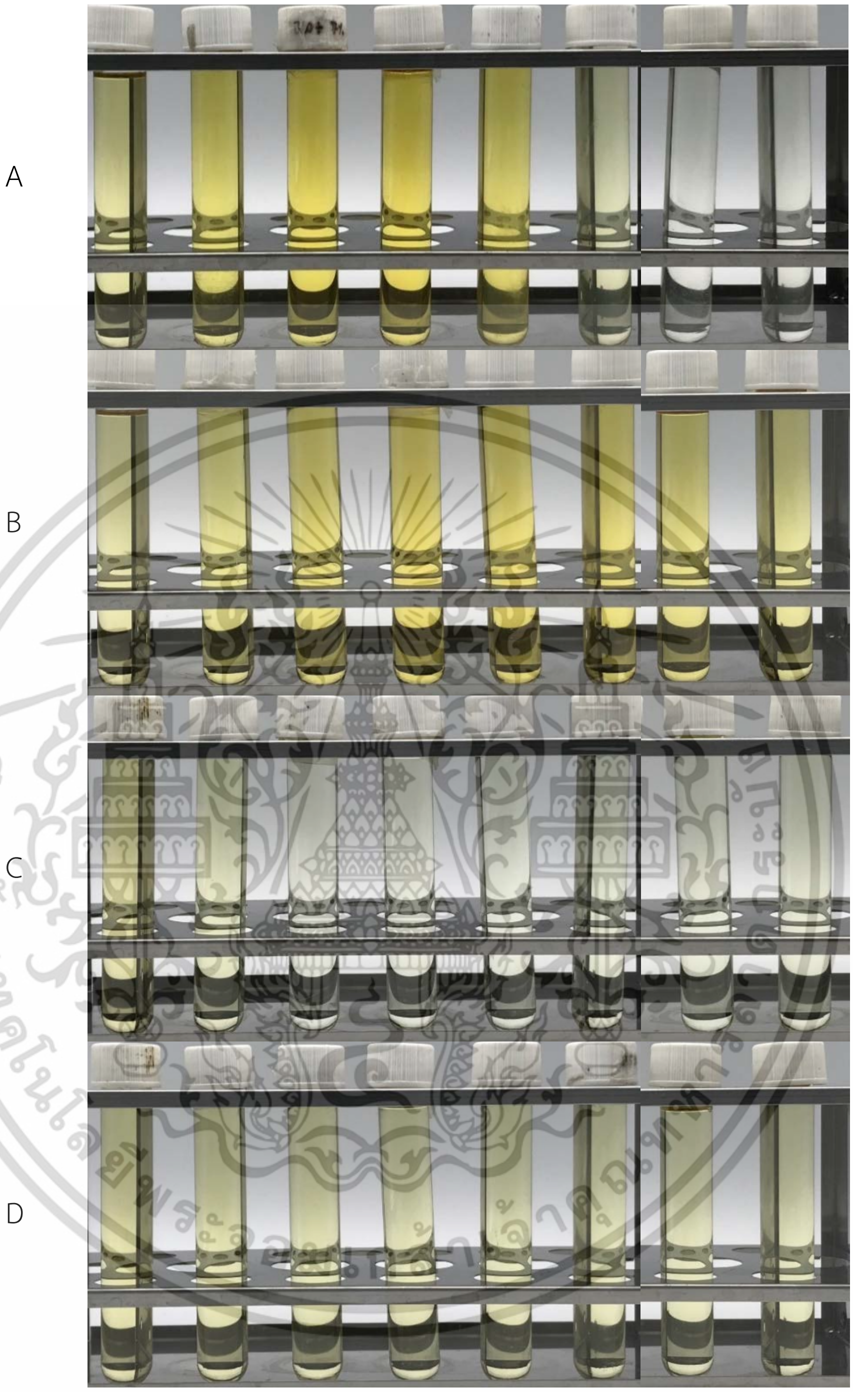


Figure 4.10 The appearance of A) accelerated ageing of partially hydrogenated biodiesel, B) partially hydrogenated biodiesel, C) accelerated ageing of palm biodiesel and D) palm biodiesel before heat and heat for 3, 7, 14, 21, 28, 35 and 42 days in 85 ℃

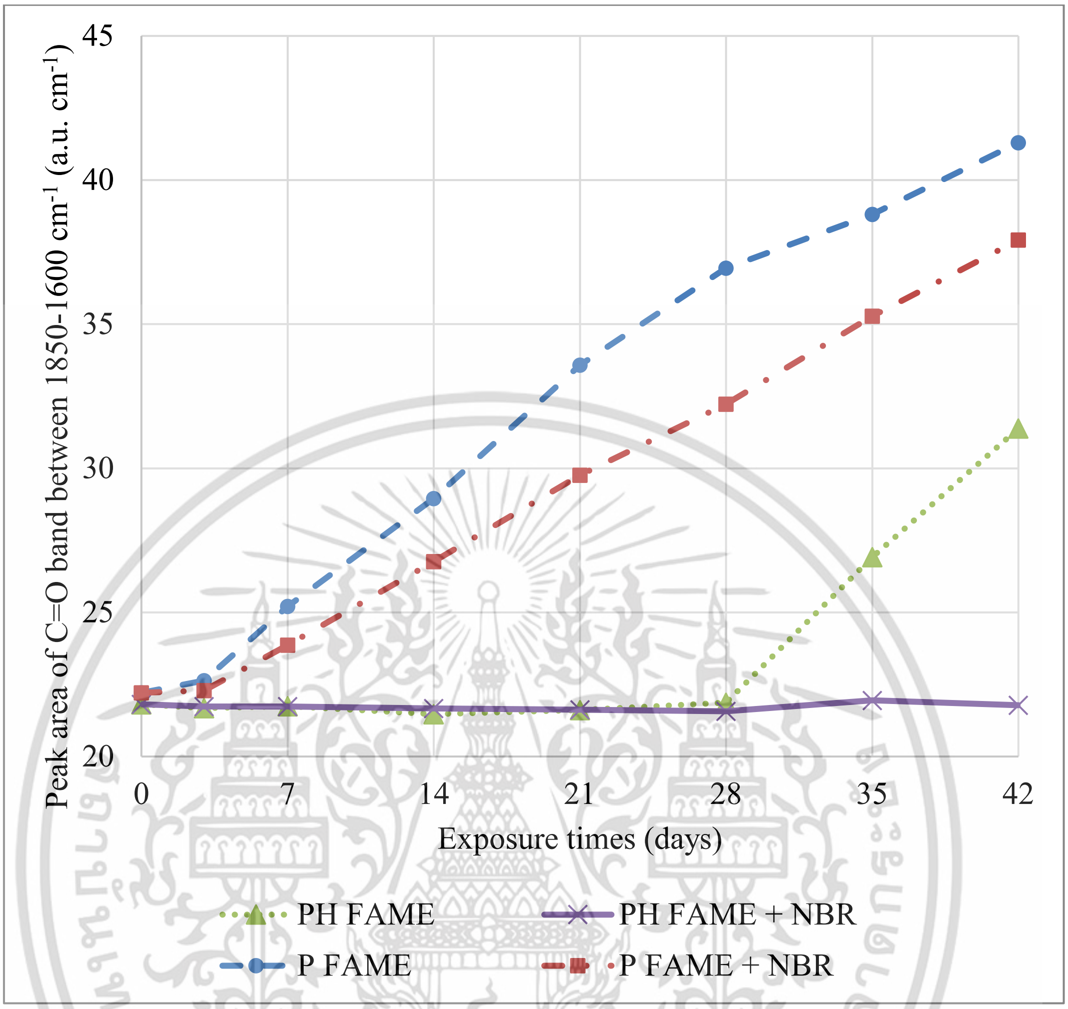


Figure 4.11 Peak area under C=O band between 1850-1600 cm^{-1} of IR spectra of biodiesel with and without contacted with NBR2

The appearance of biodiesel after immersion tests are shows in the Figure 4.12. Once the acid value of biodiesel increased, the color of biodiesel become lighter [26]

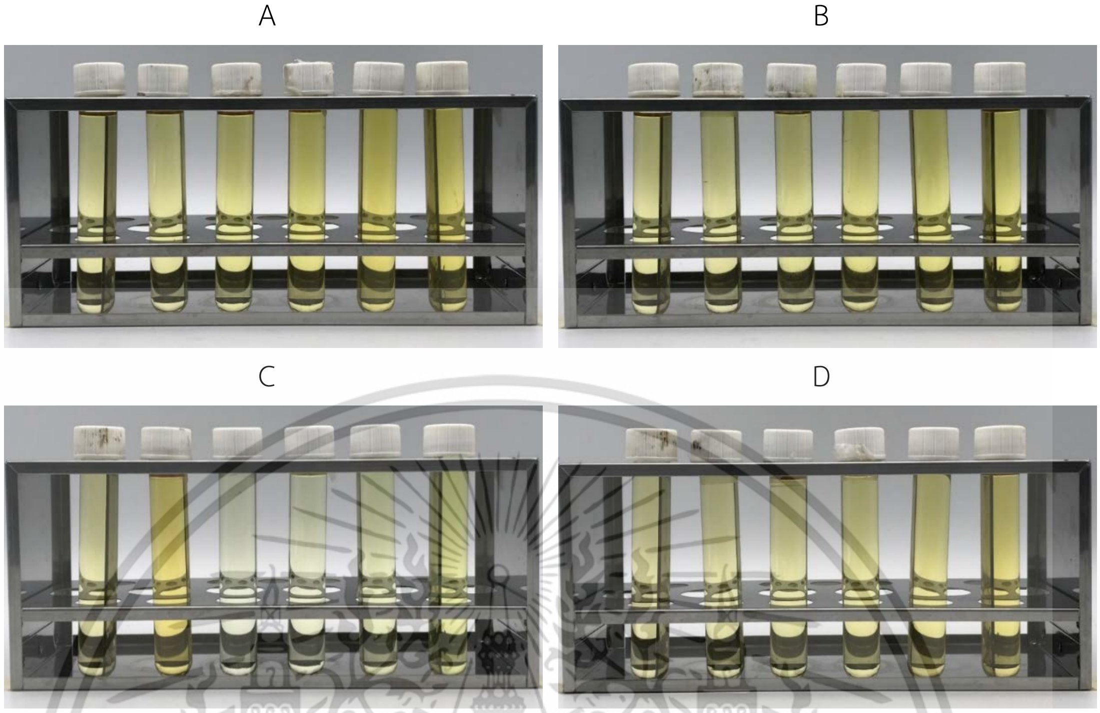


Figure 4.12 The appearance of A) accelerated ageing of partially hydrogenated biodiesel, B) partially hydrogenated biodiesel, C) accelerated ageing of palm biodiesel and D) palm biodiesel before heat and heat for 3, 7, 14, 21 and 28 days in 85 °C with NBR2 immersed

4.2.2 Swelling of Palm Biodiesel and Partially Hydrogenated Biodiesel in NBR at Different Aging Condition

The change in mass of the NBR2 samples were shows in the Figure 4.13. The mass increased of the NBR2 immersed fuel shows fast uptake during earliest stage, then the mass increased is nearly steady after 3 days except for the samples immersed into the accelerate ageing palm biodiesel condition, then the mass of the sample slowing increased then steady between days 7 to days 14 of test period. Finally, the mass increased of the samples were different for each condition and test fuel. The mass increased of the sample test with accelerated ageing partially hydrogenated biodiesel was the lowest for all of four test fuel. The sample uptake fuel fast at first 3 days and slower rate up to 7 days, then the mass of sample reduced. The sample test with sealing bottle of partially hydrogenated biodiesel has higher fuel uptake as the same trends as accelerate ageing partially hydrogenated biodiesel during first 7 days, then the mass continuing increased instead. For palm biodiesel, the mass change of the samples test with sealing bottle of palm biodiesel has been increased highest for all of four condition in the 3rd days, then the mass slighter increased to 7th days. After steady between 7 and 14 days, the mass then increased again until 28th days. The mass samples test with accelerate ageing palm biodiesel increased lower than the mass increased of the samples immersed in sealing bottle of palm biodiesel. Later, the mass of sample continued to increase implicitly instead of steady increase like the others.

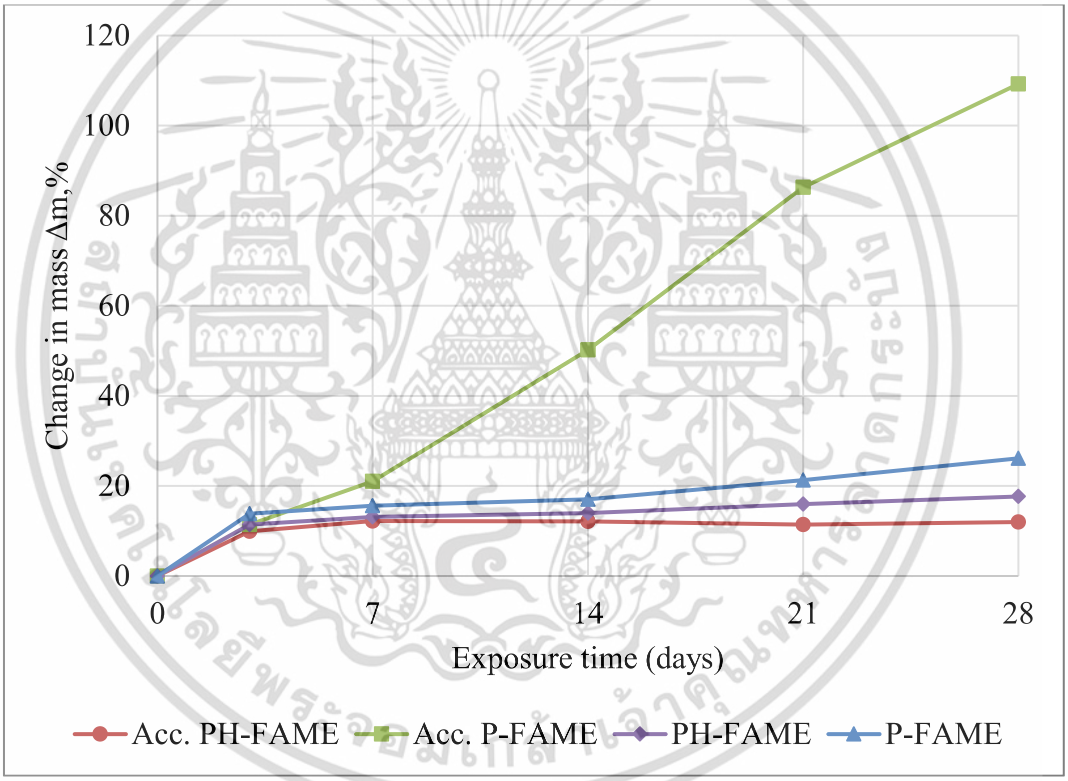


Figure 4.13 The percentage of mass change of NBR2 on exposure to partially hydrogenated biodiesel and palm biodiesel with and without accelerated ageing condition

The ratio between increased mass of samples and increased volume of samples was calculated from equation (4.1). This ratio was stated to compared with the density of fuel to understand the behavior of sample swelling.

$$\text{Ratio of increased mass–volume} = (m_1 - m_0)/(v_1 - v_0) \tag{4.1}$$

Where m_0 and v_0 is the initial mass and volume of the samples, m_1 and v_1 is the mass and the volume after immersion test. Figure 4.14 shows the mass-volume increased ratio is higher than the density of both biodiesels. Assuming the biodiesel were absorbed into the rubber matrix meanwhile the rubber could contain its shape and not expanded its volume.

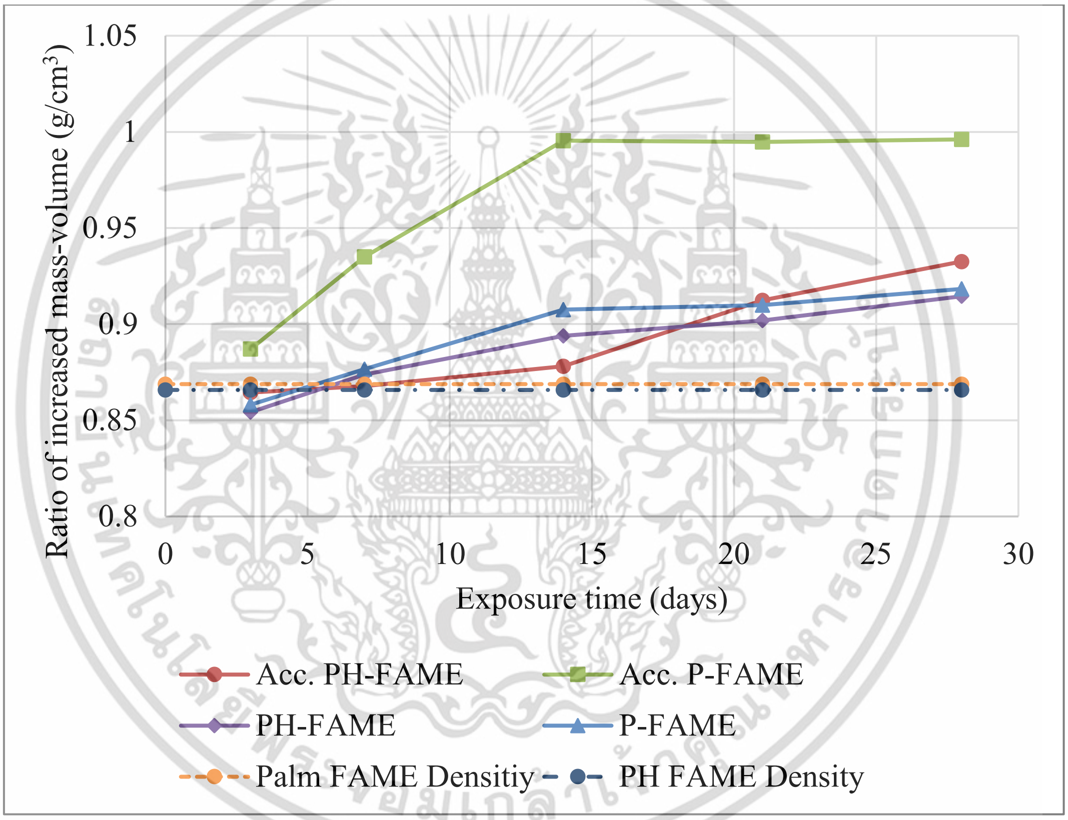


Figure 4.14 the Mass-Volume ratio of the samples and the density of both biodiesels

4.2.3 Structure Degradation of Nitrile Rubber

During the immersion test, the biodiesel has high reactive bonding of oxygen in the structure which can react and conduct degradation to the rubber. In this section, the result will be divided into 2 dimensions. Firstly, the crosslink density of the sample, which has important role to mechanical performance of rubber. And the chemicals bonding of the rubber, which could describe the degradation mechanism and predict the life-time service of the rubber, is discussed in another dimension.

Figure 4.15 show the relative change of crosslink density of sample after immersion test for 7 and 28 days. The crosslink density of the sample has been increased more than pretest samples from oxidative hardening reaction. After 7 days of immersion test, NBR2 test with sealing bottle of partially hydrogenated biodiesel show least change of crosslink density for all of tests fuel due to high stability and less oxygen in environment contact. And highest change of crosslink density of the sample is the sample test with accelerate ageing partially hydrogenated biodiesel because of high oxygen exposure, meanwhile the accelerated ageing palm biodiesel is already degraded as reveal in Figure 4.8 and does not cause oxidative crosslinking of the rubber anymore. After immersion for 28 days, the both condition of rubber test with partially hydrogenated biodiesel show highest increased of crosslink density to the rubber and accelerate ageing palm biodiesel shows least change of crosslink density.

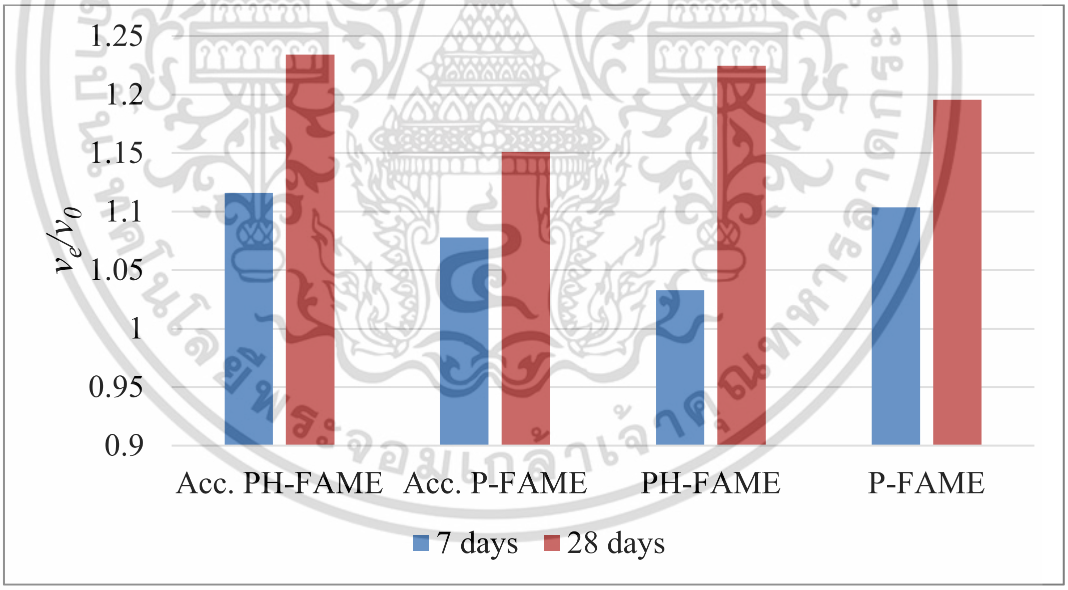


Figure 4.15 Relative change in crosslink density of NBR2 after immersed in accelerated ageing partially hydrogenated biodiesel, partially hydrogenated biodiesel, accelerated ageing palm biodiesel and palm biodiesel for 7 days and 28 days.

Figure 4.17 shows the IR spectra of the rubbers before and after immersed test and cleaned by benzene. The NBR2 test with accelerate ageing palm biodiesel shows large area of carbonyl group between 1800-1650 cm^{-1}, meanwhile the peak area of rubber test with palm biodiesel show slighly increased and the rubber test with partially hydrogenation biodiesel for both condition is neglect. Function group of carbon double bond at 950 cm^{-1} refering to butadiene group and nitrile group at 2230 cm^{-1}, has loss in the rubber test with accelerate ageing biodiesel.

Figure 4.18A shows the ratio of nitrile group per butadiene group[27] of the sample after immersion test. The result show that the sampel test with accelerate ageing palm biodiesel reduce the nitrile function group of the rubber more than the others fuel, which reduce compatibility of the polymer matrix cause its absorb more fuel. And Figure 4.18B represent the carbonyl groupe expressed as $A_{C=O}/A_{CH2}$ (the ratio of IR absorbance at 1760 cm−1 to that at 2950 cm−1). The carbonyl index of the NBR2 test with accerlated ageing palm biodiesel has been increased fast during first 14 days, then increased as slower rate. Meanwhile the rubber test with both partially hydrogenated biodiesel reveal less increrased even than sealing palm biodiesel. The conduction of increasing carbonyl index group has colerate to degradation of biodiesel more than biodiesel itself react with the rubber.

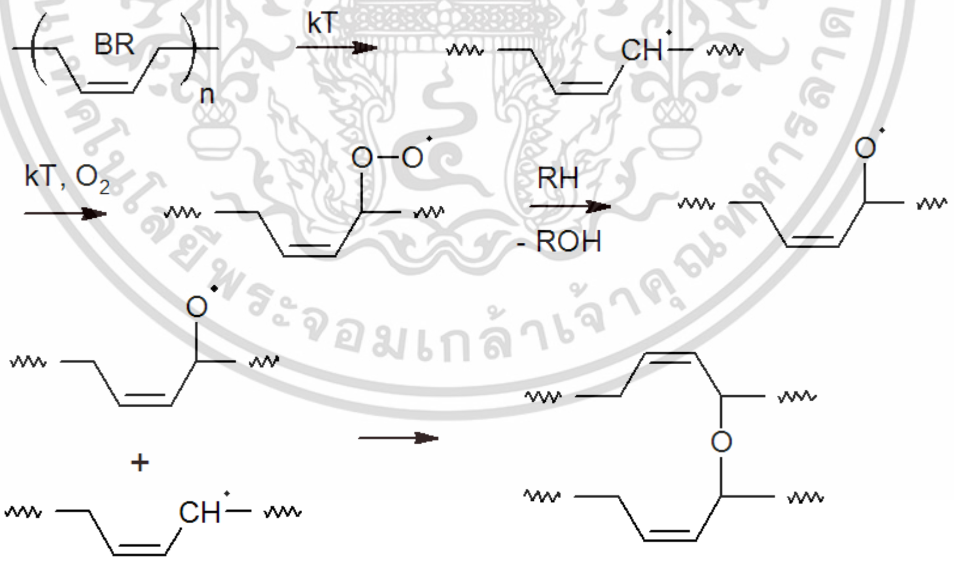


Figure 4.16 Oxidative hardening in the rubber pathway

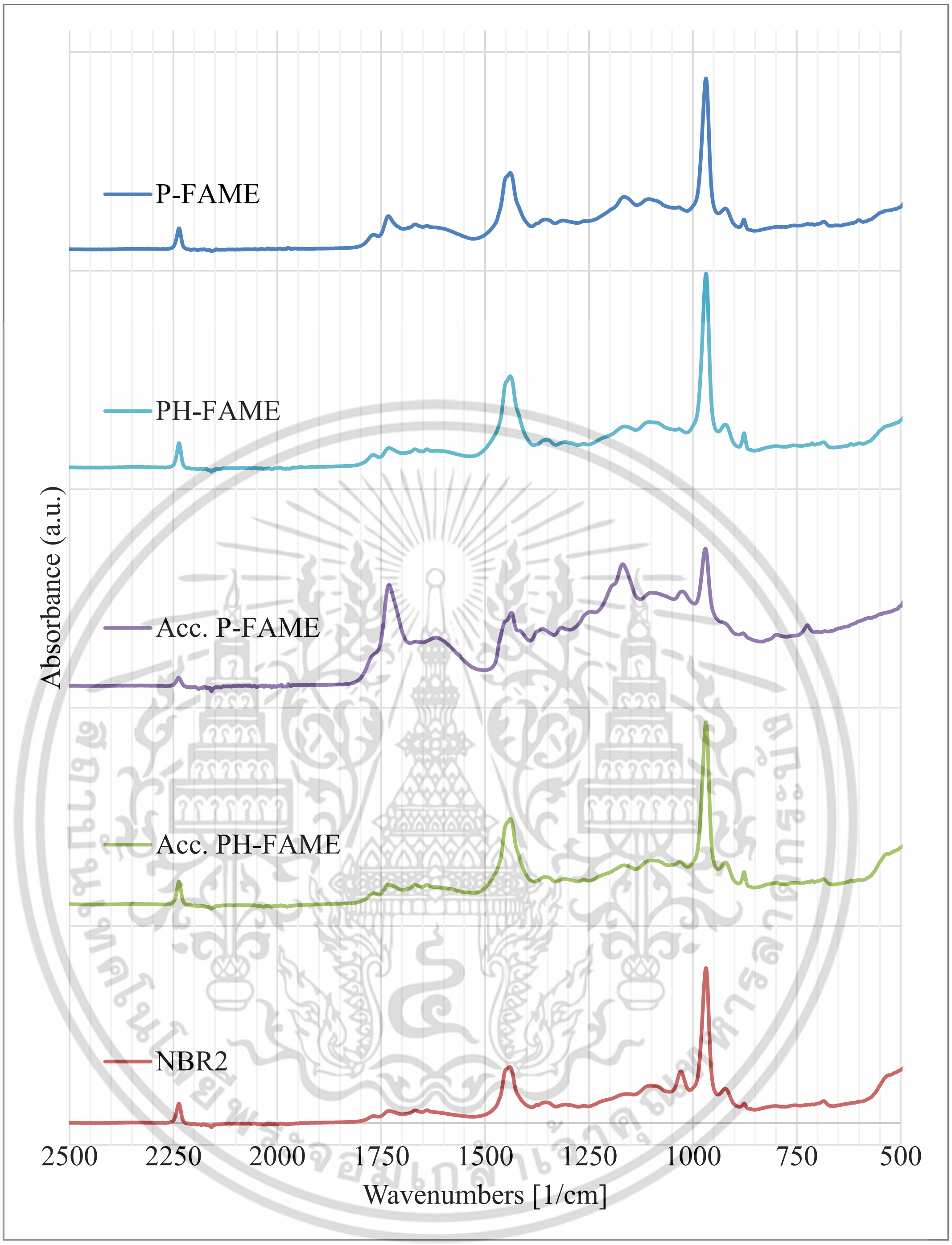


Figure 4.17 IR spectra of rubber before and after immersed in accelerated ageing partially hydrogenated biodiesel, accelerated ageing palm bioidesel, partially hydrogenated biodiesel and palm biodiesel for 28 days

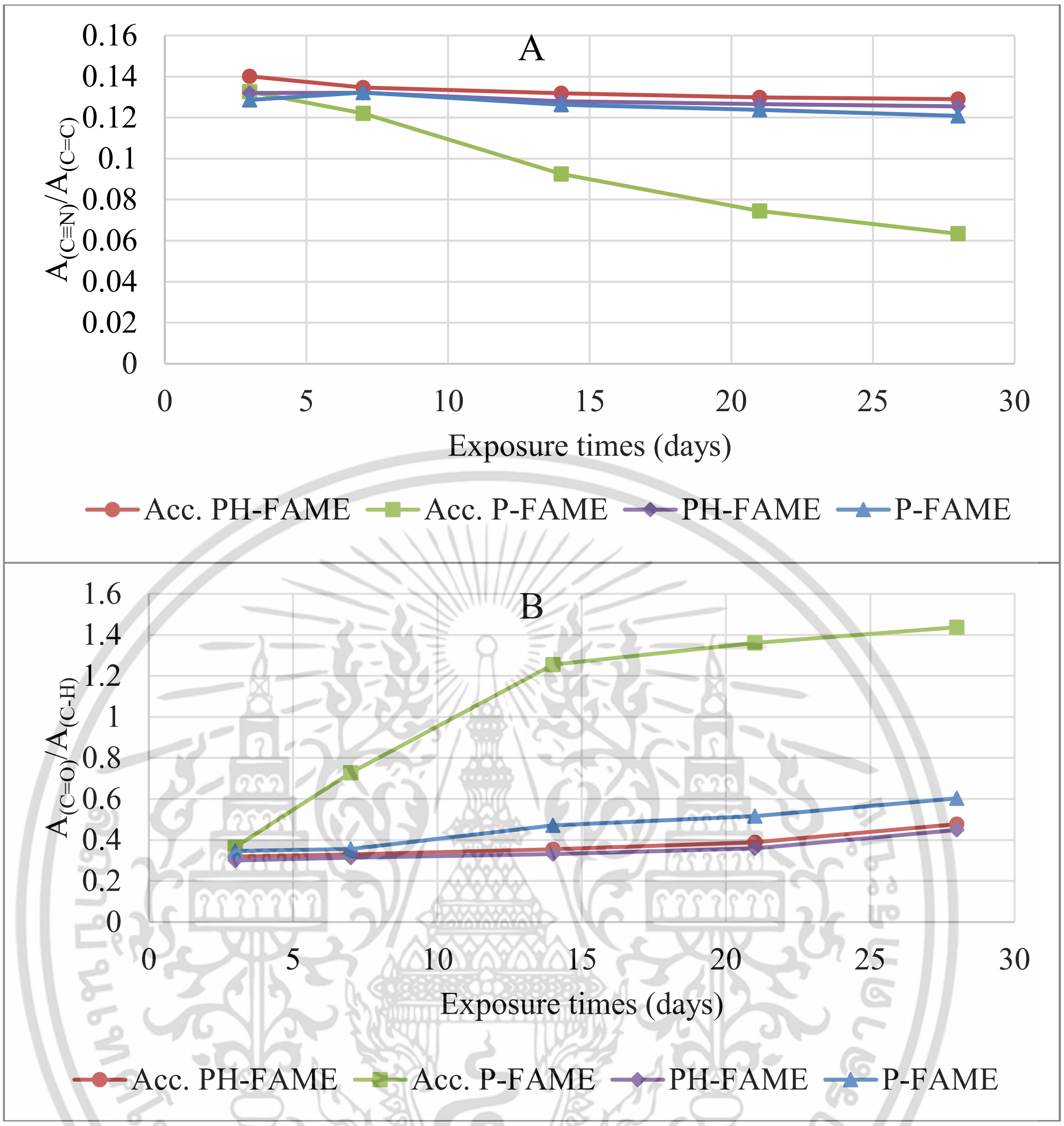


Figure 4.18 A) Ratio of IR spectra of nitrile group per carbon double bond according to butadiene function and B) carbonyl index of NBR2 test with accelerated ageing partially hydrogenated biodiesel, accelerated ageing palm bioidesel, partially hydrogenated biodiesel and palm biodiesel for 28 days

4.2.4 Morphology and Compositions After Exposed to Palm Biodiesel and Partially Hydrogenated Biodiesel

Figure 4.19 show the appearance of the rubber after immersion in accelerate ageing partially hydrogenated biodiesel, accelerate ageing palm biodiesel, partially hydrogenated biodiesel and palm biodiesel from left to right by order. After immersion test, the rubber become darker when increased the exposure times. And the rubber immersed in accelerate ageing palm biodiesel show significantly change after 14 days. After immersion for 28 days, the rubber shows pocket-like appearance of the surface and deep into the rubber matrix as show in Figure 4.20. The SEM image of this pocket shows in Figure 4.23 reveals it is a crack and erode through the surface of the rubbers, and the edge of crack has a plenty of small hole.

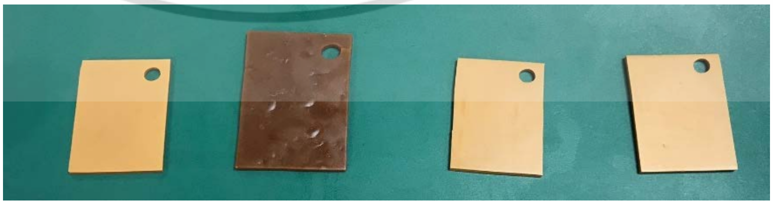
Exposure times	Samples
3rd days	
7th days	
14th days	
21st days	
28th days	

Figure 4.19 The appearance of NBR2 after immersion test with accelerated ageing partially hydrogenated biodiesel, accelerated ageing palm bioidesel, partially hydrogenated biodiesel and palm biodiesel from left to right.

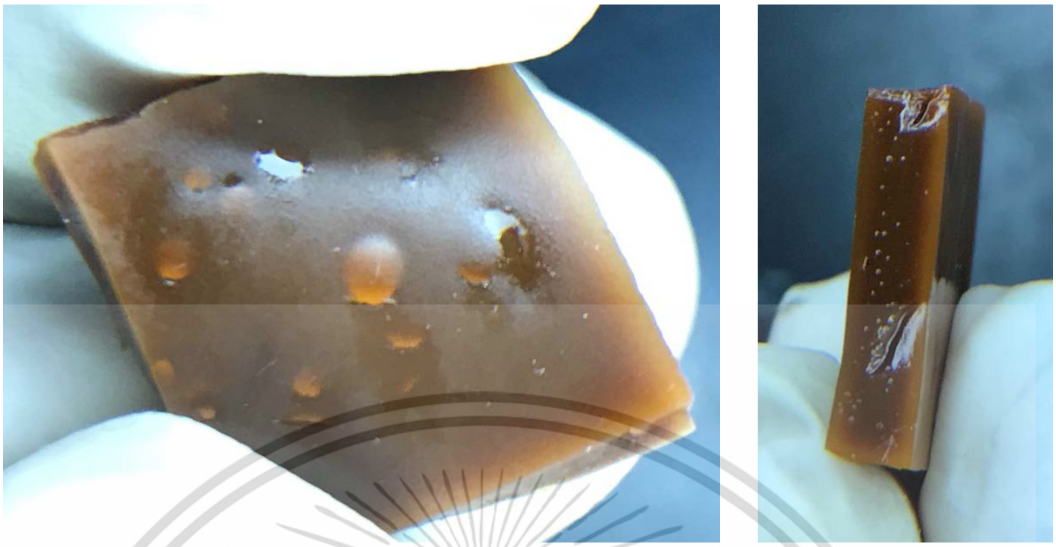


Figure 4.20 Surface (left) and cross section (right) of NBR2 immersed in accelerated ageing palm biodiesel for 28 days

Figure 4.21 shows SEM image of NBR2 before and after immersion for 28 days. A pretest NBR2 show smooth surface, contained a white reflecting particle refers to zinc oxide. After immersion test, the NBR2 test with accelerate ageing partially hydrogenated biodiesel show mild roughly surface, less zinc oxide and small crack as show in Figure 4.22. Appearance of NBR2 immersed in accelerate ageing biodiesel was the roughest, zinc oxide seems to disappear and fully with small hole on the surface. The surface of NBR2 immersed in partially hydrogenated biodiesel is mild rough and has small crack on the surface as same as accelerate ageing condition as show in the Figure 4.22B. And the surface of NBR immersed in palm biodiesel is same as partially hydrogenated biodiesel but not have small crack on the surface. The zinc oxide on the rubber surface immersed in sealing cap of biodiesel seems not to reduce as much as the accelerate ageing condition due to less degraded of biodiesel [11].

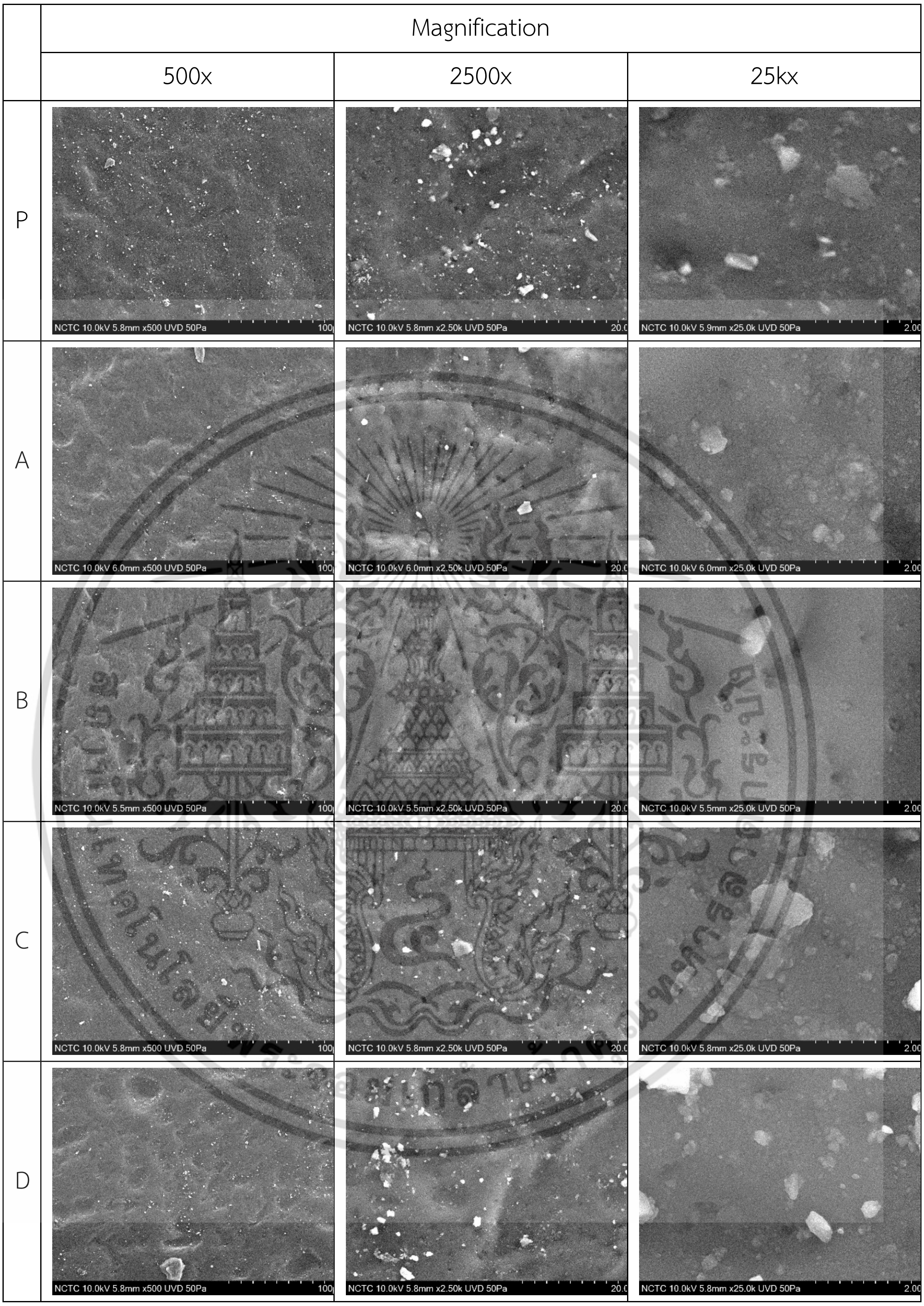


Figure 4.21 Scanning electron microscope image of NBR2 after immersion test in P) Pretest, A) accelerated ageing partially hydrogenated biodiesel, B) accelerated ageing palm bioidesel, C)partially hydrogenated biodiesel and D) palm biodiesel

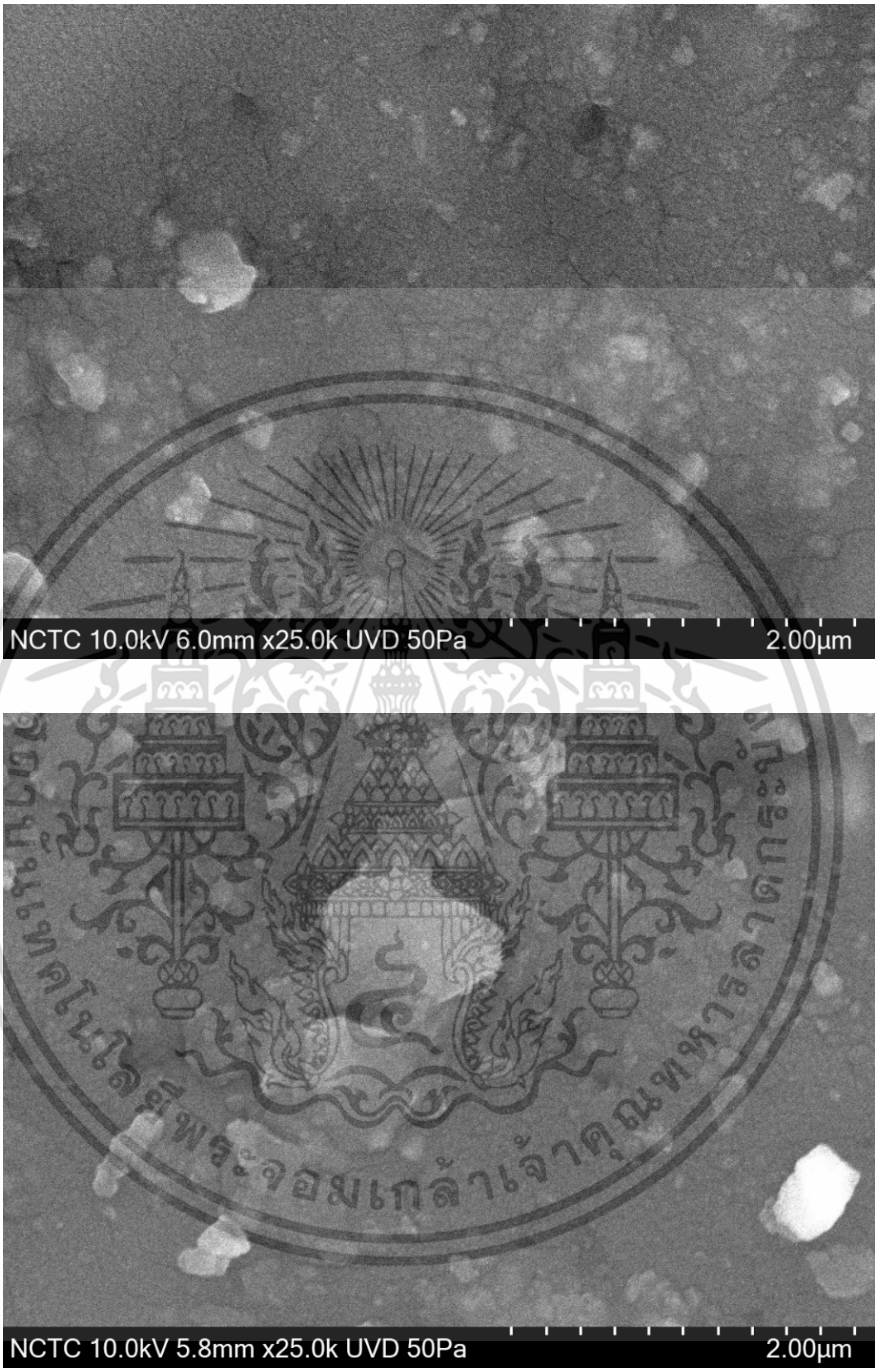


Figure 4.22 SEM image show small crack on the surface of NBR2 after immersed in A) Accelerate ageing partially hydrogenated biodiesel and B) partially hydrogenated biodiesel

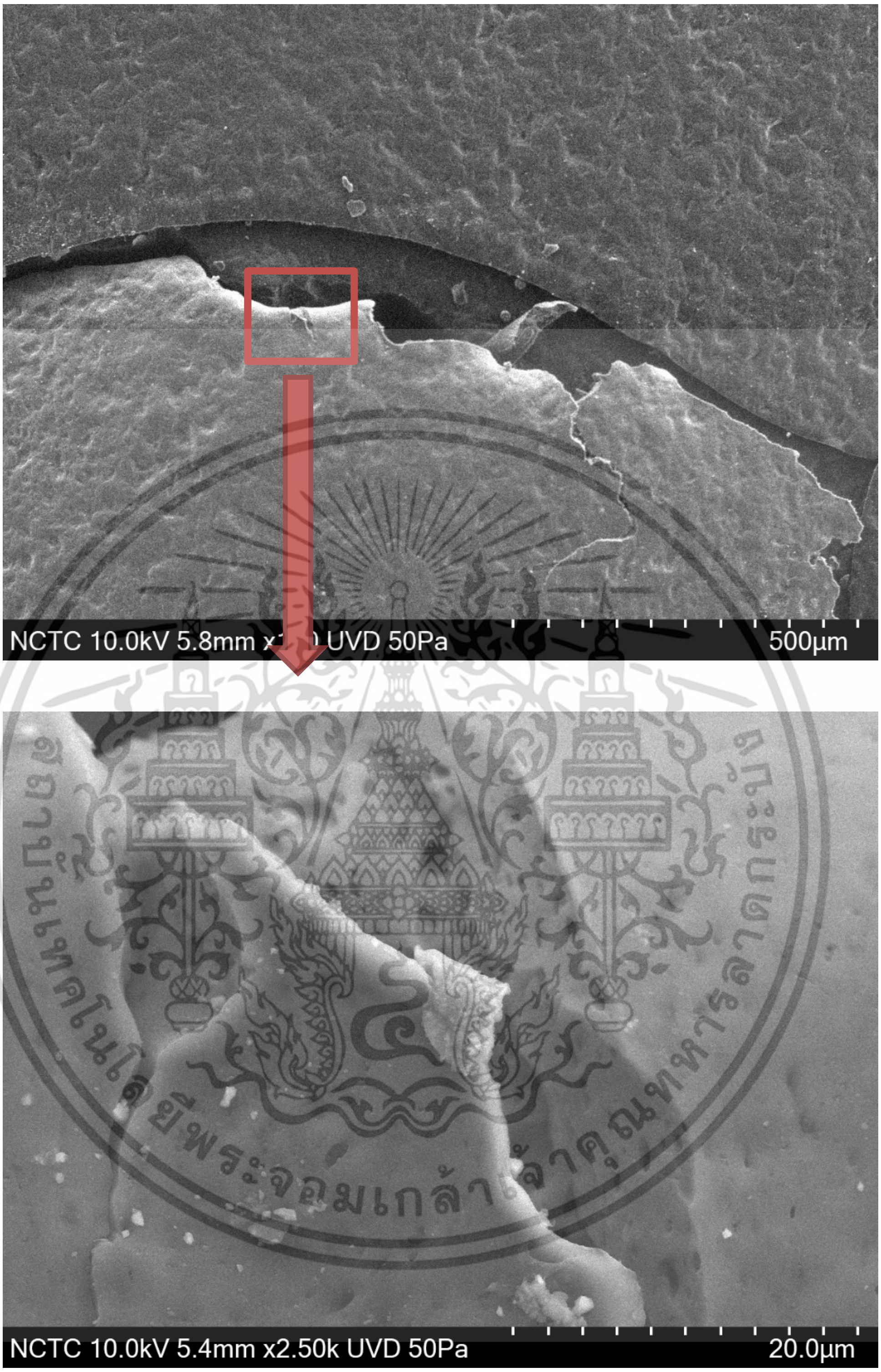


Figure 4.23 SEM image of Pocket-like appearance on the surface of NBR2 immersed in accelerate ageing palm biodiesel

TGA result of NBR2 before and after immersion test for 28 days shows in the Figure 4.24. The absence of weight between 200-300°C is from the vaporize of biodiesel from boiling point, and the absence between 400-600°C is due to vaporize of polymers. As show in the figure, the composition after the test of NBR2 test with accelerate ageing palm biodiesel has most contained of biodiesel in the rubber matrix and has least polymer composition.

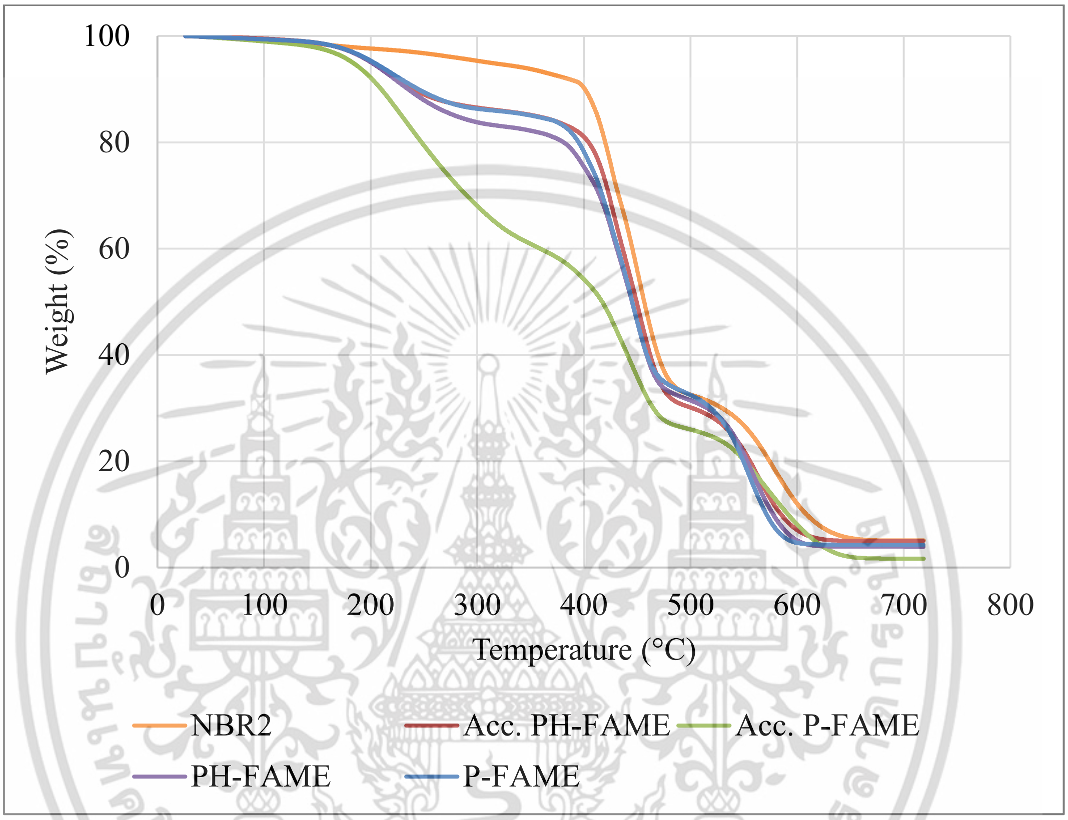


Figure 4.24 TGA of NBR2 before and after immersion test with partially hydrogenated biodiesel and palm biodiesel

In conclusion, the accelerated ageing of palm biodiesel not only destroy the chemical bonding of nitrile rubber, but also dissolve and penetrate deep into the inner matrix of the rubber as reveal from SEM image.

4.2.5 Mechanical Performance of NBR After Exposed to Palm Biodiesel and Partially Hydrogenated Biodiesel

Figure 4.25 show the result of relative change of tensile strength of the tested samples after immersed in fuel for 3 days, 7 days and 28 days. The tensile strength of the samples after 3rd is reduced from pretest samples but not large different between each ageing and fuel condition except the samples immersed in palm biodiesel without accelerate ageing due to highest fuel uptake as mention in 4.2.2. After pass 7 days of immersion, the change in tensile strength of the samples is slightly increased from day 3 for each test condition except for the samples immersed in accelerated ageing palm biodiesel. Finally, at 28th days of immersion, the tensile strength of the samples for each condition shows clearly different characters. The tensile strength of the samples immersed in accelerated ageing partially hydrogenated biodiesel is increasing higher than the others due to the sample was occupied as observed from mass-volume ratio from Figure 4.14 meanwhile mass of the rubber was not increasing. The samples immersed in accelerated ageing palm biodiesel is fully destroyed from the immersion test, the tensile strength and elongation after tested for 28 days was neglect. The samples test with sealing bottle of partially hydrogenated biodiesel show a slightly change of tensile strength between days 3, 7 and 28 of immersion test. And the samples test with sealing bottle of palm biodiesel, the tensile strength of the samples was reduced more than samples immersed in partially hydrogenated biodiesel.

Figure 4.26 shows the elongation of the NBR2 after 3,7 and 28 days of immersion test with accelerate ageing and sealing bottle of both partially hydrogenated biodiesel and palm biodiesel. As mention before, the samples immersed in accelerate ageing palm biodiesel is the most degraded samples, the elongation reduced by immersion times and completely loss its performance after immersion test for 28 days. For the others test fuels, the elongation of the samples after immersion test for 3 days, slighly reduced from pretest sample similarly. After 7 days of immersion, the elongation of the samples slighly increased for each conditionn except the samples test with partially hydrogeanated biodiesel, according to crosslink density of the samples has lowest increased than the others. After immersion for 28 days, the elongation of all samples reduced from 7th days immersion test.The samples test with partially hydrogenated biodiesel, both accelerate ageing and not, has similar elongation performance according to crosslink density of both rubber is change with the same trend. And the elongation of the samples test with palm biodiesel is poor than partially hydrogenated biodiesel according to lower crosslink density of the rubber.

Figure 4.27 shows the relative hardness change compared with the pretest sample. The hardness of the materials is considered as the factor to sealing performance of the products such as gaskets. The change of hardness of materials represent to the degradation of the rubber causing shorter service life time and fuel could be able to penetrate through the rubber. The hardness of samples in every fuel exposure condition have the same behavior. After tested for 3 days, the samples hardness slightly change, then reduce after 7 days and finally increased after tested for 28 days. However, the hardness of the samples test with accelerate ageing of palm biodiesel decresed in fuction of increasing biodiesel exposure times.

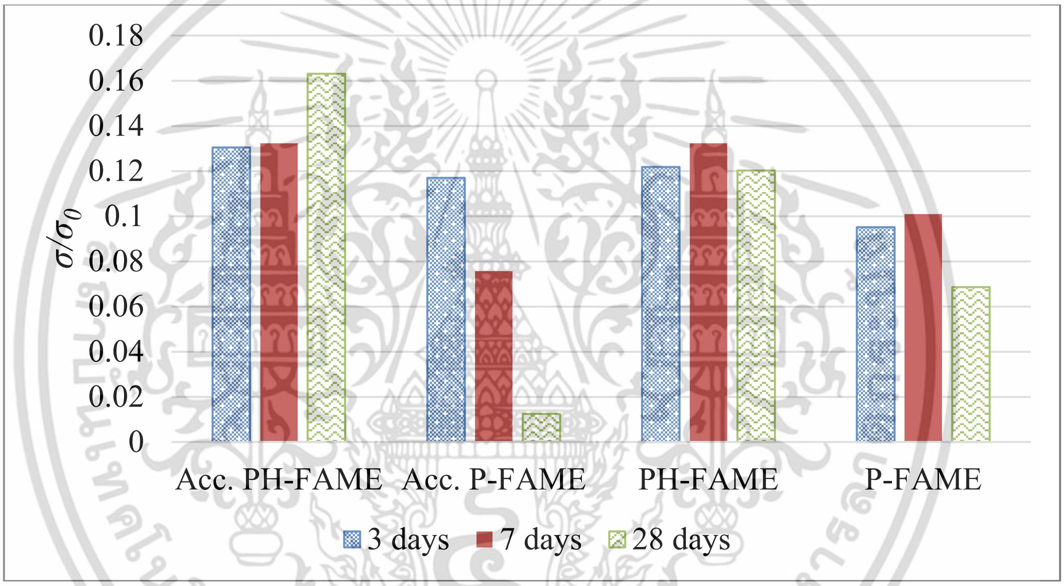


Figure 4.25 Relative tensile strength change of NBR2 after immersed in accelerated ageing partially hydrogenated biodiesel, partially hydrogenated biodiesel, accelerated ageing palm biodiesel and palm biodiesel.

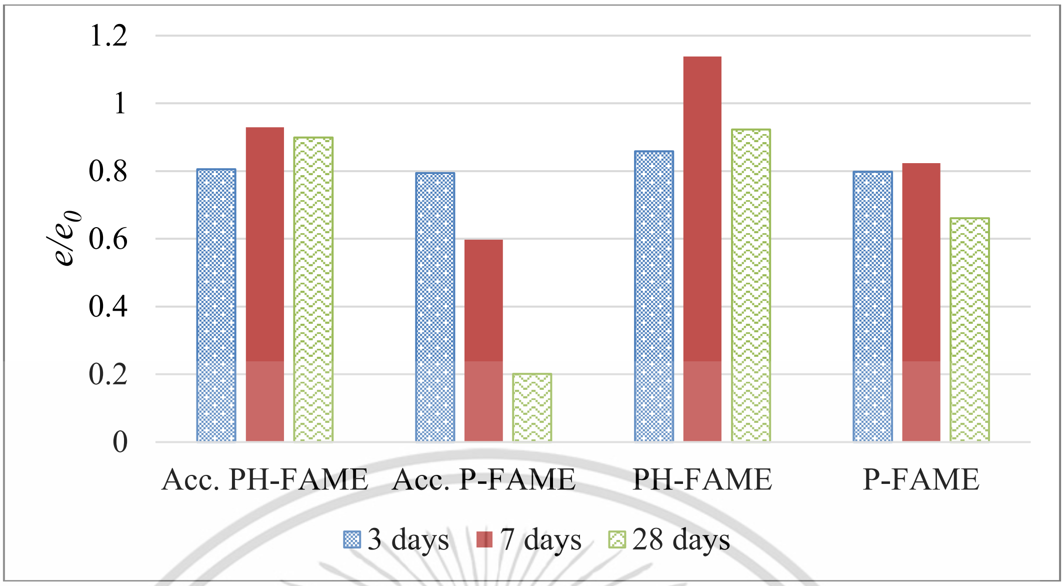


Figure 4.26 Relative elongation change of NBR2 after immersed in accelerated ageing partially hydrogenated biodiesel, partially hydrogenated biodiesel, accelerated ageing palm biodiesel and palm biodiesel

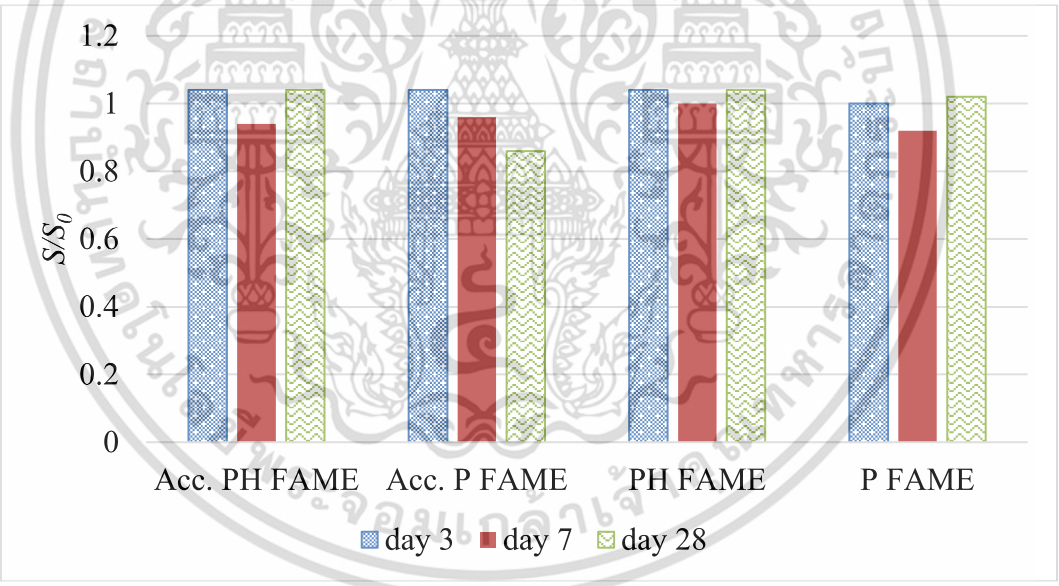


Figure 4.27 Relative Hardness (Shore A) change of the NBR2 after immersed in accelerated ageing partially hydrogenated biodiesel, partially hydrogenated biodiesel, accelerated ageing palm biodiesel and palm biodiesel.

4.3 Evaluation of Commercial Nitrile Rubber in Biodiesel and Petroleum Diesel in Different Refresh Fuel Condition

The behaviors of users influence the degradation of biodiesel. For example, biodiesel stored in a tank of a rarely used vehicle can be degraded and attacks the rubber composition in the fuel system, as discussed in 4.2. On the other hands, the new fresh fuels are always refilled in the regular used vehicles and may rapidly degrade the materials like the results in section 4.1 during the first three day. Notwithstanding, the effect of refilling the new fresh fuel on the rubber change has not been widely studied. Therefore, this part has investigated and compared the effect of the fresh fuel and degradation fuel to simulate the real condition when using the vehicle. After the fuel run out, the fuel system will contact the new fresh fuel filled in the vehicle. But the vehicle is parked for the long period, the fuel system always contacts with the degraded fuel. For the real application, NBR1 the commercial black NBR rubber sheet, was used as the specimens in the immersion tests. The rubber contains plasticizer, rubbers, carbon black, calcium carbonate and other additives as revealed by the thermogravimetric analysis.

4.3.1 Swelling of NBR in Biodiesel and Petroleum Diesel

Because the compositions and contents in the NBR1 are not available and informed by the supplier, the preliminary test to verify the behavior of NBR1 immersed under biodiesel was firstly investigated. As applied in the real condition, biodiesel blended diesel was selected as the test fuel in the preliminary test like in section 4.1.2. However, the concentration used in this study is 7, 10 and 20 % which are the percentage used in many countries. In addition, 50, 80 and 100 % biodiesel (pure biodiesel) are included in the experiment. The immersed rubbers were weighted after immersion started for day 1 (rapidly change), 7 (equilibrium condition) and 28 (the last degradation).

Figure 4.28 shows the mass change of the immersed rubber in biodiesel blended fuel. The result reveals that biodiesel increased the weight of the rubber for all immersion period, hence rubber swelling. When the immersion period was lengthened, the weight gradually increased, in particularly, the high percentage of biodiesel. However, not pure biodiesel but the blend with 50 and 80 % of biodiesel results in the highest mass change. The rubber exposed to 7% biodiesel (commercial diesel in Thailand) gained the lowest weight. The behaviors of NBR1 degradation corresponds well with the RED of natural rubber in Figure 4.2. This implies that the NBR1 specimens may contain a large amount of natural rubber or it is natural based rubber.

The NBR1 specimens may contained natural rubber blended due to low compatibility with mixed blended diesel, according to low compatibility as show in Figure 4.2, high density and stronger mechanical strength also are the properties of natural rubbers and additive such as $CaCO_3$ to reducing cost.

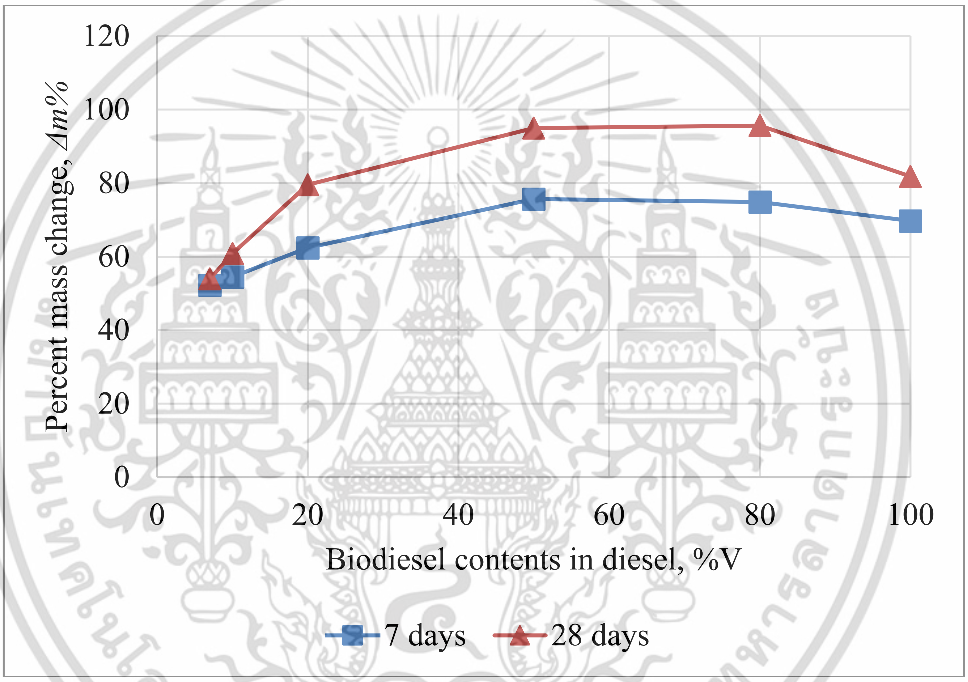


Figure 4.28 The mass change of NBR1 for 7 days and 28 days of immersion test at 55°C

The behavior of material degradation from the preliminary test in section 4.1. indicated that all test fuels resulted in the same way in which the rubber is swelled but not dissolved. Therefore, only neat fuels will be used as the test fuel in this section. The rubber compatibility with diesel, palm biodiesel and partially hydrogenated biodiesel have been conducted with different refreshing fuel conditions. The refresh condition has been conducted by changing the fuel for immersion every day during the first three days and then once a week later. For the degraded fuel conditions, the rubbers were soaked in the same fuel filled from the beginning until finishing the immersion test. Figure 1.8 presents the mass change of the rubber when exposed to the fresh and degraded diesel (Figure 4.28A), biodiesel (Figure 4.28B), and partially hydrogenated biodiesel (Figure 4.28C), respectively.

The results show that for all test conditions the mass of fuel uptake into the rubber can be divided into two phases; the fast and slow uptake phase, consequently. The rubber immersed in petroleum diesel without refilling increased the mass with a higher rate during after day 1 and then the weight slightly increased after day 1 to day 28. Compared with the unchanged fuels, the rubber in the refilled condition has the lower increase mass during the first three days and the mass slightly decreased from day 3 to day 7. Hence, the dissolving process dominated the absorption. After day 7, the rate of increased mass is higher than that of unchanged fuel condition. As the result, the mass of rubber immersed under fresh diesel fuel is higher than the degraded diesel at the last stage.

In Figure 4.28B, the mass increased of the rubber immersed in biodiesel in both conditions shows the higher rate than those exposed to diesel and partially hydrogenated biodiesel. Firstly, the mass rapidly increased for the first three days for both conditions. In addition, the refreshing condition has significantly affected on the mass increased higher than no refreshing condition, which opposites with the rubber immersed in the petroleum diesel. Subsequently, the mass of rubber for both conditions is continuously increased with the higher rate of refreshing condition until finishing the test

For the rubber immersed in partially hydrogenated biodiesel, the mass increased for the first three days was lesser than the rubber immersed in palm biodiesel, but higher than the ones immersed in diesel condition. While diesel and biodiesel show the different trend of mass increased during the first three days between refreshing and no refreshing conditions, the rubber immersed in partially hydrogenated biodiesel shows no different. Like the palm biodiesel, the refilling of the fresh fuel resulted in the higher increased mass of the rubber than that of the degraded partially hydrogenated biodiesel after day 3 until finishing the test.

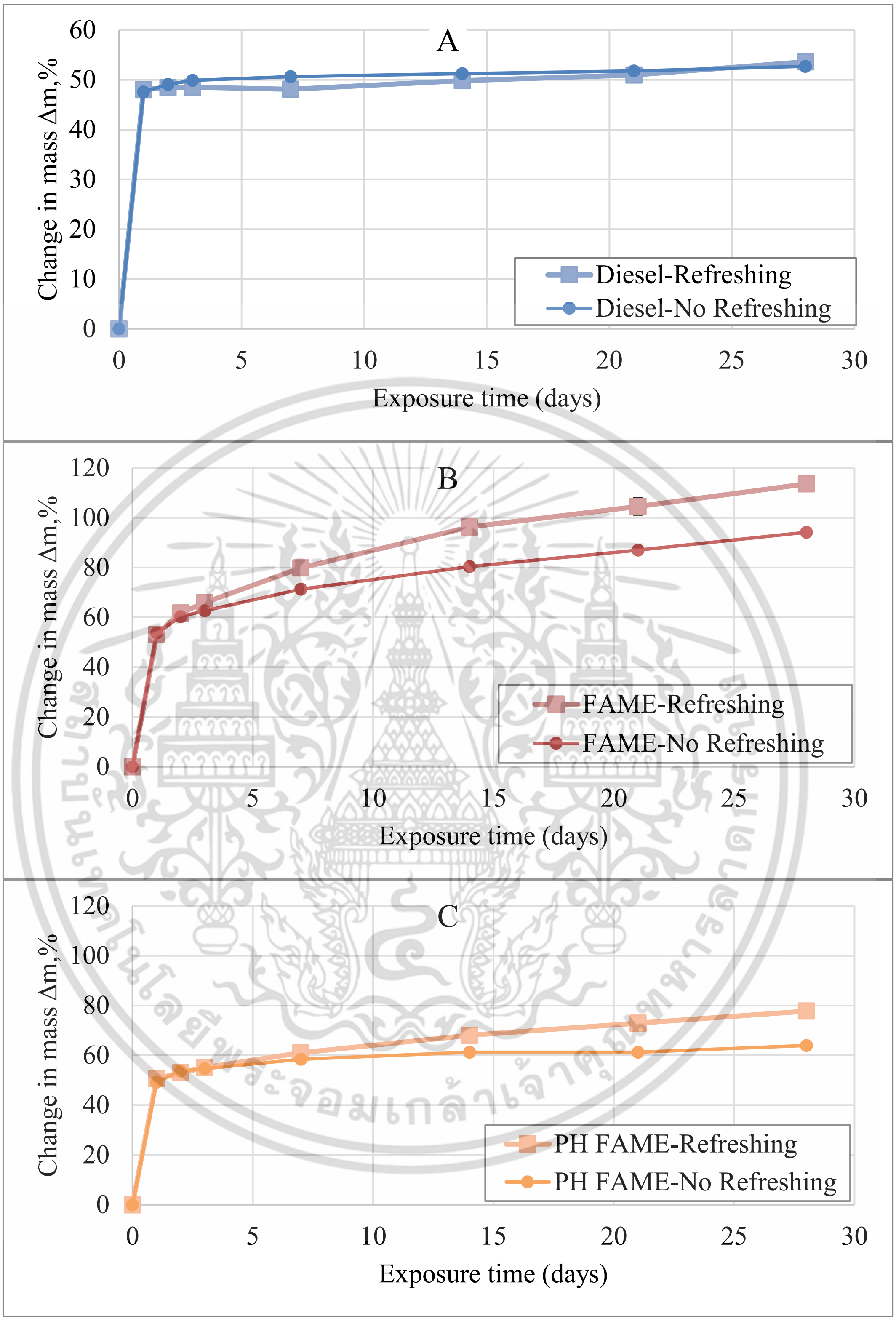


Figure 4.29 The percentage of mass change of NBR1 immersion into A) petroleum diesel, B) palm biodiesel and C) partially hydrogenated biodiesel

To clarify the different behavior of the rubber degradation when immersed under the fresh and degraded fuel, the mass-volume increased ratio of the rubber after immersed in the fuel has been calculated in equation (4.1), the result of calculation shows in Figure 4.30. In addition, the density of all three test fuels are included in the figure. After immersed in the fuel, all of rubbers have the mass-volume ratio lower than density of fuel to which the rubber exposed. Hence, the rate of mass change is lower than the rate of volume change when compare to the density of exposed fuel. The rubbers immersed in diesel fuel for both conditions yield the higher volume change per mass change than the rubbers immersed in the other fuels. The volume change per mass change of the rubbers continuously increased when the exposure times increased thus decreasing the ratio. The rubber immersed with the refresh fuel condition has the higher volume increase than no refreshing condition, assuming to loosening of polymer structure. After 14 days of immersion, the mass increase per volume increase of the rubber has become stable for both conditions although there is fuel uptake happen in this period.

Unlike exposing to the diesel, the rubber immersed in the palm biodiesel showed the higher mass change than the volume change when the exposure time was lengthened, and the ratio is higher when increasing of exposure time. Refilling with the fresh fuel, the rubbers has the mass change higher than the volume change when compared with no refreshing fuel. The ratio of the rubber immersed in partially hydrogenated biodiesel has the lower value than the rubber immersed in palm biodiesel. The ratio between both conditions have the same trends for the first half of immersions, but then the rubbers in no refreshing conditions has become less increased than the refreshing condition.

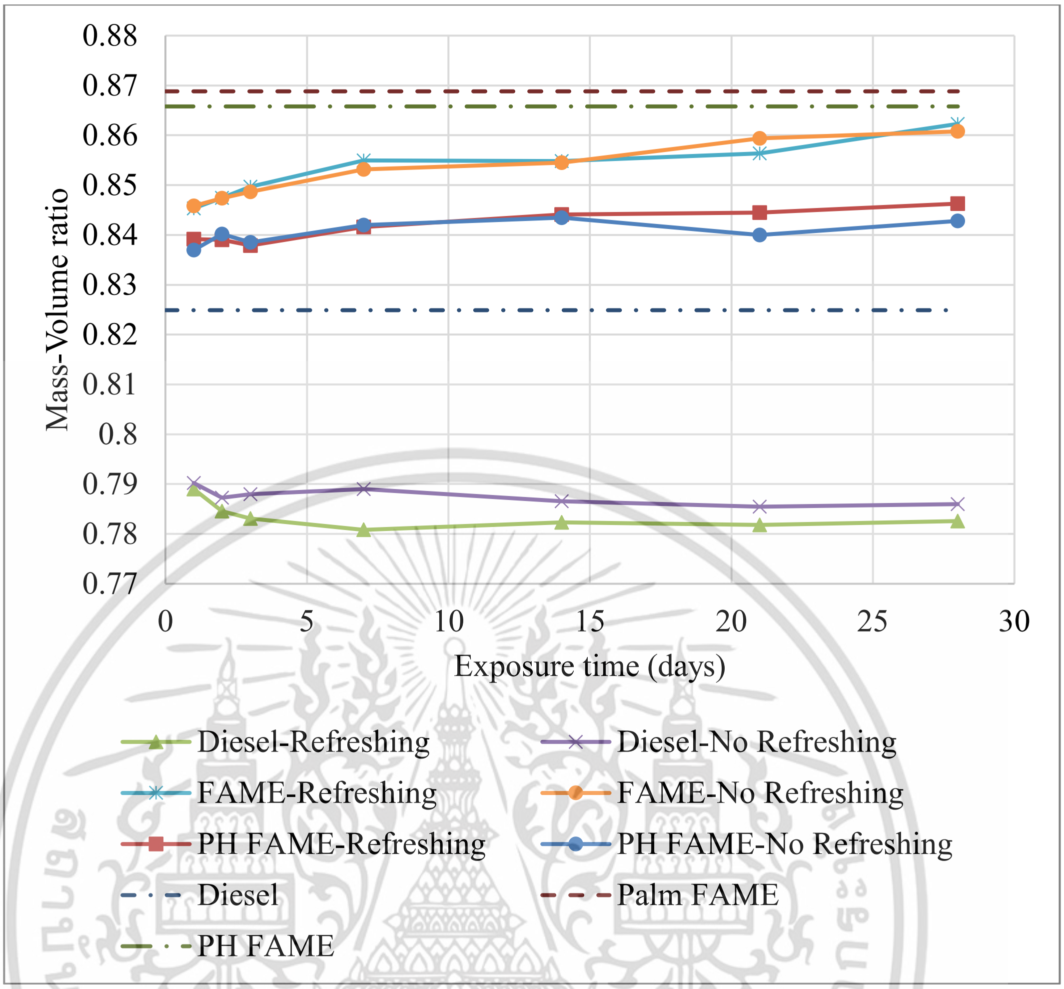


Figure 4.30 Swelling density of rubber in function of exposure times and density of fuel

The process called solvation-unfolding-swelling was happen when polymer is added to solvent liquid such as fuel. The chain structure or the rubber absorbs the solvent and increases the volume of the polymer matrix while loosening out from their shape. If on the contrary, the polymer-solvent interactions are still strongly enough, the process will continue until all segments are solvated. Thus, the whole loosen coil will diffuse out of the swollen polymer, dispersing into a solution. As shows in Figure 4.30, the rubbers only absorb a limited of petroleum diesel might not loosen coil segment enough to diffuse out to the solvent, while the rubbers immersed in biodiesel has higher biodiesel uptake along with immersion time. The rubbers matrix become loosening and even absorb more fuel into the matrix, giving a swollen gel as a result.

The appearance of the fuels before (one in the left) and after the immersion tests (two in the middle) as well as the aged fuels (two in the last) at the same condition are represented in

Figure 4.31. After ageing the fuel without the immersed rubber, the appearance of all test fuels has no change. However, the colors of the fuels with immersed rubber were changed after immersion test. The colors of petroleum diesel and partially hydrogenated biodiesel with the immersed rubbers shows no different when the immersion test was conducted for 7 and 28 days as shown in

Figure 4.31A and B, respectively. In contrast, the color of the palm biodiesel with immersed rubber is significantly changed between days 7 and 28 of immersion test. The color of fuels is turned to darker when the immersion test is lengthened because the rubber is dissolved into the fuel.

4.3.2 Mechanical Degradation

The mechanical properties of the rubber after immersed in the test fuel were determined by tensile test after immersed for 7 days and 28 days. Figure 4.32A show the relative change of tensile strength (the rubber after immersion test – the fresh rubber) of the rubber immersed in all test fuels. After immersed for 7 days, the tensile strength of rubbers immersed in refreshing biodiesel has reduced more than rubber immersed in no refreshing biodiesel. In contrast to biodiesel, the rubber immersed in petroleum diesel showed the opposite trends of decreased tensile strength between fresh and degraded fuel. After immersed for 28 days, the tensile strength of the rubbers immersed in the refreshing fuel decreased higher than that of no refreshing condition for all test fuels. Moreover, the rubbers immersed in both biodiesels have completely degraded and cannot apply the force to the rubbers while the rubbers immersed in no changing fuel were slightly degraded from days 7.When compared among each test fuel, petroleum diesel yielded the lowest change of tensile strength, followed with partially hydrogenated biodiesel and palm biodiesel, respectively.

Figure 4.31 The color before test, 7, 28 days after immersion test and 7, 28 heats fuel without immersion test of A) Petroleum diesel, B) Palm biodiesel and C) Partially hydrogenated biodiesel

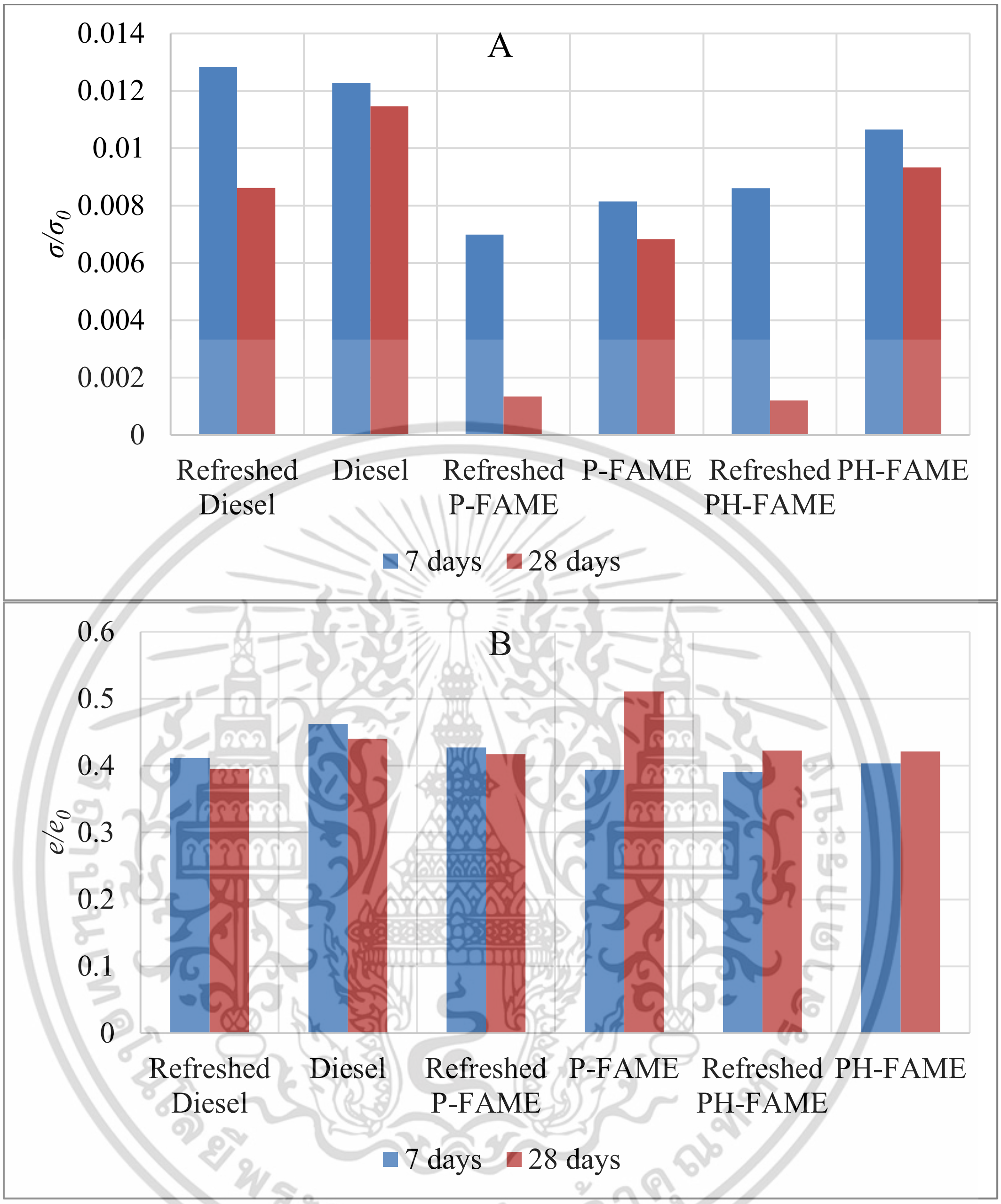


Figure 4.32 The relative change of A) tensile strength and B) elongation of the rubbers after immersion for 7 days and 28 days

The relative change of elongation of the rubbers after exposed to each test fuels is shown in Figure 4.32B. The elongation of the rubbers immersed in diesel for both conditions decreased over immersion times. In contrast, the elongation of the rubbers immersed in partially hydrogenated biodiesel increased when the exposed time increased. The rubbers immersed in palm biodiesel shows the different trend of the elongation change. The elongation of the rubbers in refreshing condition slightly decreased, but significantly increased with the highest value in no refreshing condition after finishing the immersion test.

After finish the immersion test at day 28, the hardness of immersed rubbers was tested and shown in Figure 4.33, The results are consistent with tensile strength of the rubbers. The hardness of the rubbers immersed in the refreshing fuels decreased higher than those in the degraded fuels. Diesel resulted in the lowest hardness change. The rubber immersed in the fresh palm biodiesel is completely destroyed and turned to be the pulpy matter, but the rubbers tested with fresh partially hydrogenated biodiesel still contained its shape. However, the rubbers immersed in conventional palm biodiesel has better hardness properties than the samples immersed in partially hydrogenated biodiesel.

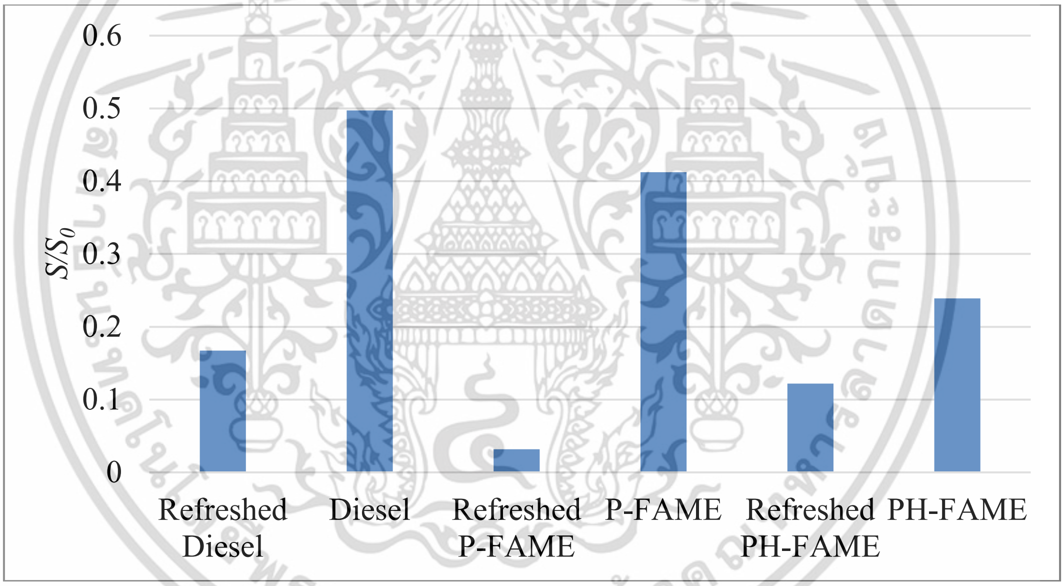


Figure 4.33 The relative change of Shore A scale hardness of the rubber after immersion for and 28 days

Tensile strength and hardness of the rubbers immersed in refreshing fuels are decreased from the fresh rubber higher than those of the rubber immersed in no refreshing fuels. But the elongations of the rubbers are not altered as the same trend with the tensile strength and hardness.

All of the rubbers absorbed the fuel and rubbers performance change according to solubility of both materials are different, the fuel refreshing conditions has corelate to the degradation of rubber structure and some additive in the rubber composition. So, the crosslink density of the rubber and rubber compositions has been determined and discussed in the next section.

4.3.3 Structure and Composition Degradation

The relative change of crosslink density of the rubbers is shown in Figure 4.34. The crosslink density of the samples decreased with the increased immersion time. Palm biodiesel and partially hydrogenated biodiesel have the similar trends to decrease the crosslink density of the rubbers with the higher extent when exposed to the fresh fuel. Partially hydrogenated biodiesel showed the less effect to decrease the crosslink of the rubber than that of conventional biodiesel. On the other hand, the crosslink density of the rubber in diesel shows no difference when immersed with the fresh and degraded fuel.

As discussed in 4.3.1, NBR1 contained many compositions including natural rubber to enhance rubber sheet mechanical performance. The natural rubber has the lower compatibility with fuel than high polar nitrile rubber. Also, natural rubber is bulky side groups undergo softening due to radical recombination reactions are less likely to occur due to steric hindrance. Then, the rubber degraded by chain scission mechanism attacked by the fuel as show in the Figure 4.35

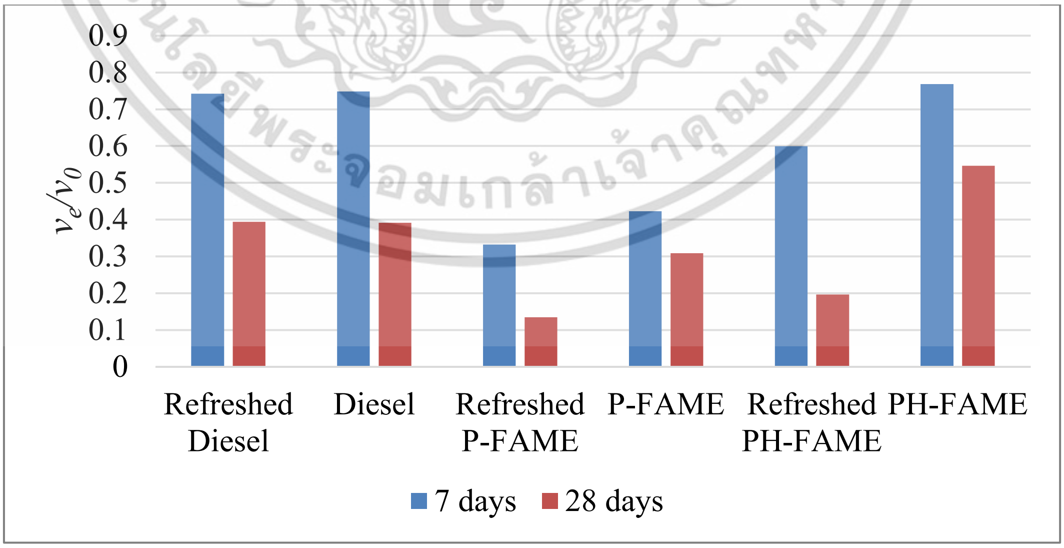


Figure 4.34 The relative change of crosslink density of the rubbers after immersion for 7 days and 28 days

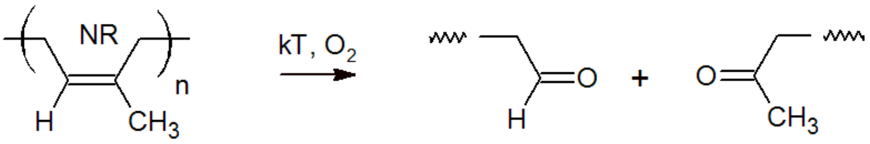


Figure 4.35 Oxidative softening (Chain scission) pathway

Figure 4.36 shows the IR spectra of pretest and after immersion test rubber samples. A change of the absorbance intensity is noticed in the range of vibrations 1545–1580 cm^{-1} which corresponds to the bonds C=N, S-S-C=N, R-CH= N-R’. These functional groups are recognized as crosslinks of the rubber [28]. The sulfur crosslinks of the rubber has been absented from the rubber immersed in refreshing of diesel and palm biodiesel, in contrast, the rubber immersed in partially hydrogenated biodiesel has no effect for both refreshing condition and not refreshing one. However, the IR spectra is measured by ATR method which measure from the surface of rubber only, this might not represent to overall crosslink of the rubber as same as calculated from Flory-Rehner equation.

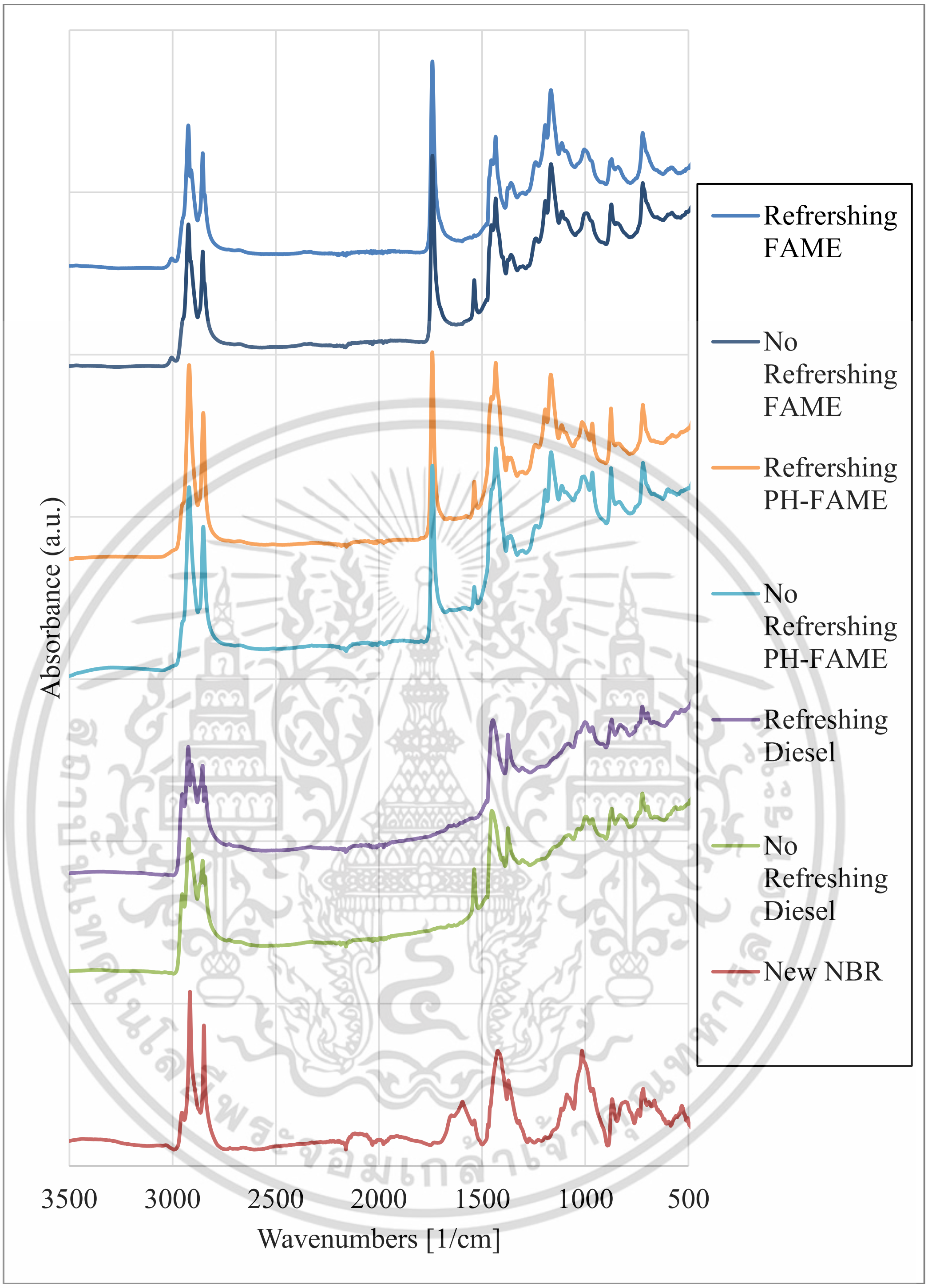


Figure 4.36 The FTIR spectra for optimum loading of OPA, silica, and carbon black filled natural rubber vulcanizates (a) Before aging, and (b) After aging.

The relations between the percentage of mass increase and the change of crosslink density is shown in Figure 4.37A while Figure 4.37B presents the correlation between the relative tensile change in function of the relative crosslink density change.

Shown in Figure 4.37A, the mass increase due to fuel uptake is higher when the change in crosslink density of the rubber decreases as predicted by the equilibrium swelling theory of Flory and Rehner [29]. Meanwhile the relative change of tensile strength was decreased when the crosslink density decreased after the test. Moreover, the rubbers immersed refreshing of both palm and partially hydrogenated biodiesel after 28 days were spoiled than the other rubbers.

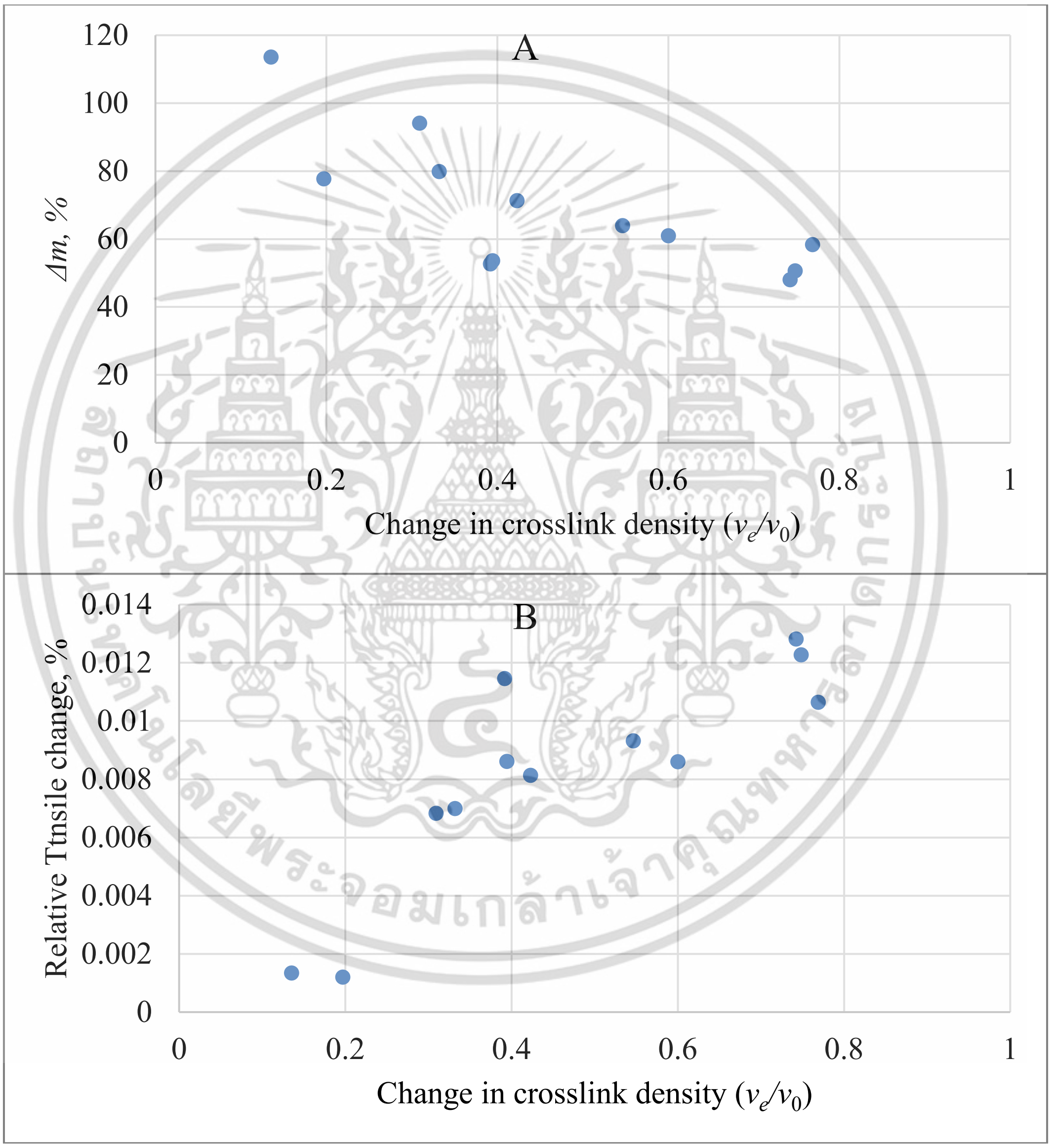


Figure 4.37 Correlation between A) the percentage mass increased and B) the relative change of tensile strength in the fucntion of relative change of crosslink density.

Figure 4.38 shows the compositions of the rubber after immersed in the test fuels, which characterized by thermogravimetry analysis, the rubbers immersed in the refreshing and degraded petroleum diesel has the similar compositions. For both types of biodiesel, the polymer contents in the rubbers was reduced higher when the rubber immersed in the fresh fuel than those in the degraded condition.

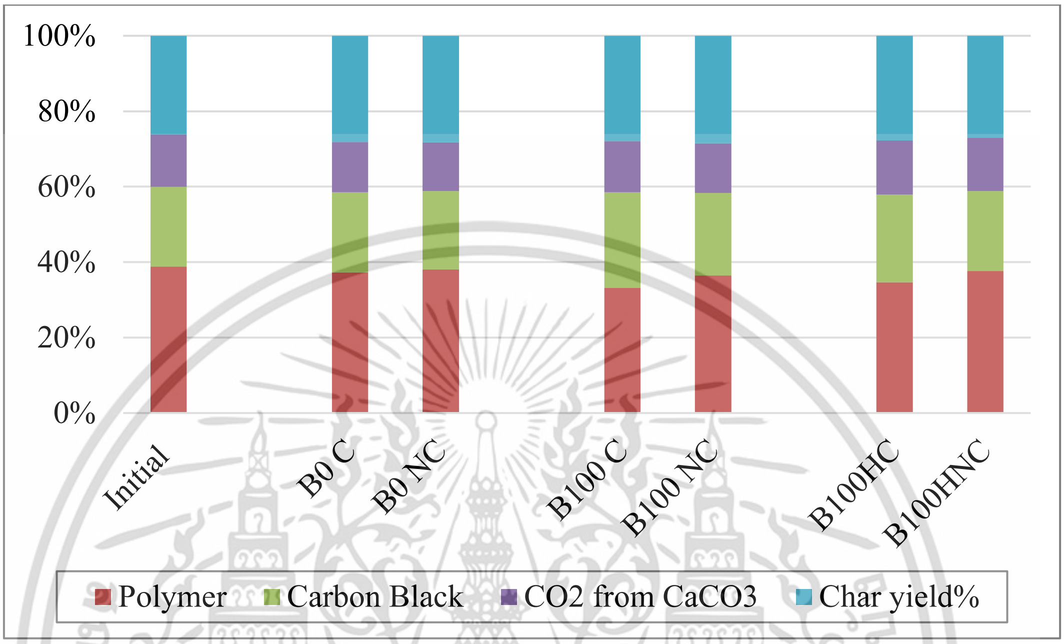


Figure 4.38 The compositions of the NBR1 without volatile composition, analyze by TG analysis

In conclusion, the mechanism of degradation and swollen rubber immersed in diesel has been affected by the solubility parameters between materials, the refreshing condition of fuel and the structure degradation. The behavior of absorbing rubber could be considered by the solubility parameters of the fuel. The rubber could readily absorb high solubility fuel. After rubber absorbed fuel for a while, the rubber chain segment is dissolved into the fuel. This mechanism is affected by refreshing condition of the rubber. Finally, as discussed in the 4.2, the oxygen contained in biodiesel influences to the degradation of rubber structure and causes the crosslink scissor chain mechanism, then result in poor mechanical properties after fuel immersion.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

In conclusion, the compatibility of biodiesel or any biodiesel blended with nitrile rubber depending on both factors of materials. The composition of biodiesel and amount of content has different compatibility with different materials. In the experiments, the HSPs for each composition were used as describe to rubber absorption behavior. The high affinity of composition such as ester groups in biodiesel and nitrile group in acrylonitrile has high polar structure and cause “like dissolve like” into both materials, resulting in high swelling of the rubber in biodiesel than the none polar fuel such as petroleum diesel. And the composition such as acrylonitrile also has important roles to describe the performance to oil resistance of the rubber. The high acrylonitrile content in the rubber not also effect to the swelling behavior of the rubber, but also reduce the rubber dissolving into the fuel either.

The partially hydrogenation process enhance the conventional palm biodiesel by reduce the amount of polyunsaturated fatty acid in palm biodiesel, result in increasing of oxidation stability and resisted to degraded overtime when exposed to heat and oxygen. After the immersion test of rubber in both biodiesel with and without accelerate ageing the degradation, the biodiesel degradation is slower and retard the oxidation phase of biodiesel in both palm and partially hydrogenated biodiesel by absorb some of oxidation product into the polymer matrix and suspend the further decompose or inter-react to form other oxidation product. The rubber immersed in degraded biodiesel show evidently degrading behavior, the appearance color of the rubber is darker, it absorbed more fuel and dissolve more than the other immersed in not degraded fuel according to thermogravimetry analysis. The structure of nitrile rubber also change, carbonyl functional group has been increased and the oxidative crosslink is not increased as the rubber immersed in other fuel. However, the rubber immersed in the biodiesels without accelerated ageing has slightly different effect to the rubber. The partially hydrogenated biodiesel shows less solubility than palm biodiesel evidently such as, the lower RED value of composition and contents, lower fuel uptake in the rubber. The amount of fuel penetrates to the rubber matrix less in rubber immersed in partially hydrogenated biodiesel, result in less effect to the rubber change in both structure and mechanical performance.

The user behavior of refilling fresh fuel influence to the degradation of the rubber more than retain the same fuel in the system with commercial nitrile rubber for whole period of the test. The swelling of rubbers in refreshing fuel are higher in the rubbers immersed in both biodiesels, however the rubber immersed in petroleum diesel has no or slightly effect of refreshing fuel. The refreshing biodiesels cause the commercial nitrile rubber high swelling of fuel and decreased of mechanical performance. In conclusion, the degradation of biodiesels in for 4 weeks is not effects as much as the refreshing fuel exposed to the rubber.

In summary, the compatibility of biodiesel with basic materials such as nitrile rubber has many factors to concerned. The composition of biodiesel and nitrile rubber must concern its solubility between each material, and easiest way to predict the swelling-dissolving of materials is using HSP. When both nitrile rubber and biodiesel are in contacted, the degradation behavior of both material exposed to high heat and air can be retard due to the oxidation pathway of both materials are similar and the rubber can absorb the primary product of biodiesel. However, the degradation of biodiesel is no effect as much as the refreshing fuel exposed to the rubber. The composition and structure have been washed out during immersion in refreshing fuel more, result in poor mechanical performance and cannot retain the shape after immersion.

To produce the vehicle parts from nitrile rubber to use for fuel system, higher of acrylonitrile contents of base materials is recommended. However, nitrile rubber alone is still not suited to use with directly exposure to high polar molecule of fuel such as biodiesel or partially hydrogenated biodiesel. The high compatibility materials with fuel such as Fluorocarbon (FKM) coated at the nitrile rubber surface still required.

For further study recommendation, the composition of biodiesel or different fuel material compatibility should be studied individually. Any type of rubber should also test the compatibility with partially hydrogenated biodiesel since the fuel compatibility is not widely studied yet. The ageing condition for biodiesel should varied more temperature and amount of air in contacted to see the effect of degradation.

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APPENDIX

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Effects of Unsaturated Fatty Acid in Biodiesel on Degradation of Acrylonitrile Butadiene Nitrile Rubber

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Abstract. Acrylonitrile Butadiene Rubber (NBR), mostly used as a sealing material in fuel systems, is compatible with most petroleum-based fuel but not with biodiesel which composed of a higher polar molecule. The different component of a fatty acid such as double bond in a carbon chain has the effects on biodiesel properties. This study has investigated the degradation mechanisms of NBR when exposed to different biodiesel. Biodiesel which has different amount of monounsaturated and polyunsaturated fatty acid is used as the test fuel. In addition, the conventional petroleum diesel is experimented as the reference. To accelerate the degradation rate of NBR and reduce the test period, the test rubbers soaked in the test fuel are kept in the oven at 55 °C. To clarify the degradation rate, the weight and volume change as well as mechanical properties are measured during the immersion period. Furthermore, the structure of the degraded rubber is analysed and compared with the fresh sample by Fourier-transform infrared spectroscopy (FTIR).

1. Introduction

Biodiesel, represent as successfully usable biofuel, is produced from vegetable oils and waste cooking oil from food industries. Biodiesel has important role nowadays in fuel consumption widely because of its many benefits. Benefits from using biodiesel is carbon reduction, better emission from combusting characteristic[1], support local agriculture and energy secure for national economy. But recently, biodiesel usage in Thailand has been limited to blended with petroleum diesel only 7% v/v due to its chemical properties. Biodiesel, refers to Fatty Acid Methyl Ester (FAME), is easily to oxidize with oxygen in atmosphere[2]. Moreover, its chemical structure show polarity of its molecule with opposite with conventional diesel which non-polar molecule structure.

An improvement of conventional FAME called H-FAME has been introduced. H-FAME derived from conventional FAME by partially hydrogenation process to reduce polyunsaturated carbon chain in fatty acid becoming monoene-rich FAME[3]. The oxidation stability of palm H-FAME has increased when compare with conventional palm FAME. The biodiesel can be storage in longer time before use as it will not oxidize with the oxygen in the atmosphere easily.

The effect of using H-FAME in a vehicle test and performance of combustion has been studied. The H-FAME can be use without or least effect to the performance of the engine[4–6]. Different feedstock of biodiesels have been studied its compatibility[7][8], however the material compatibility of H-FAME with the other materials in vehicle parts still lack of studied. Especially the degradation mechanism of easily degraded material such as NBR when immersed into H-FAME still not been study yet[6]. The characterize of the NBR after degradation and the effect of degraded are not be clearing understand.

This study is focused on degradation of acrylonitrile butadiene rubber, which mostly used as sealing material in automotive part. The test samples processed from commercial NBR sheet were characterize before and after immersion test. The immersion test held at 55°C ± 2°C for 4 weeks in the cap closed bottle to seal the oxygen in the air react with the rubber and the fuel. the test fuels are including conventional B100 palm biodiesel, partially hydrogenation B100 palm H-FAME and conventional diesel B0 as reference.

2. Experimental

2.1. Materials

2.1.1. Test fuel

Palm biodiesel was supplied from Global Green Chemicals Public Co., Ltd., Thailand. The partially hydrogenation called H-FAME. was processed at Thailand Institute of Scientific and Technological Research (TISTR) derived from different palm biodiesel feedstock.

Both fuels were examined by gas chromatography to separating the different components of fatty acid methyl ester (FAME) in each fuel. The result of FAME content in the table 1 shows the significant reduction of linoleic acid (C18:2) of Palm H-FAME when compared to conventional palm biodiesel.

For the reference, B0 supplied from Bangchak Corporation Public Co., Ltd uses as reference fuel. The NBR degradation was compare between each.

Table 1. Fatty acid methyl ester profiles of test biodiesels

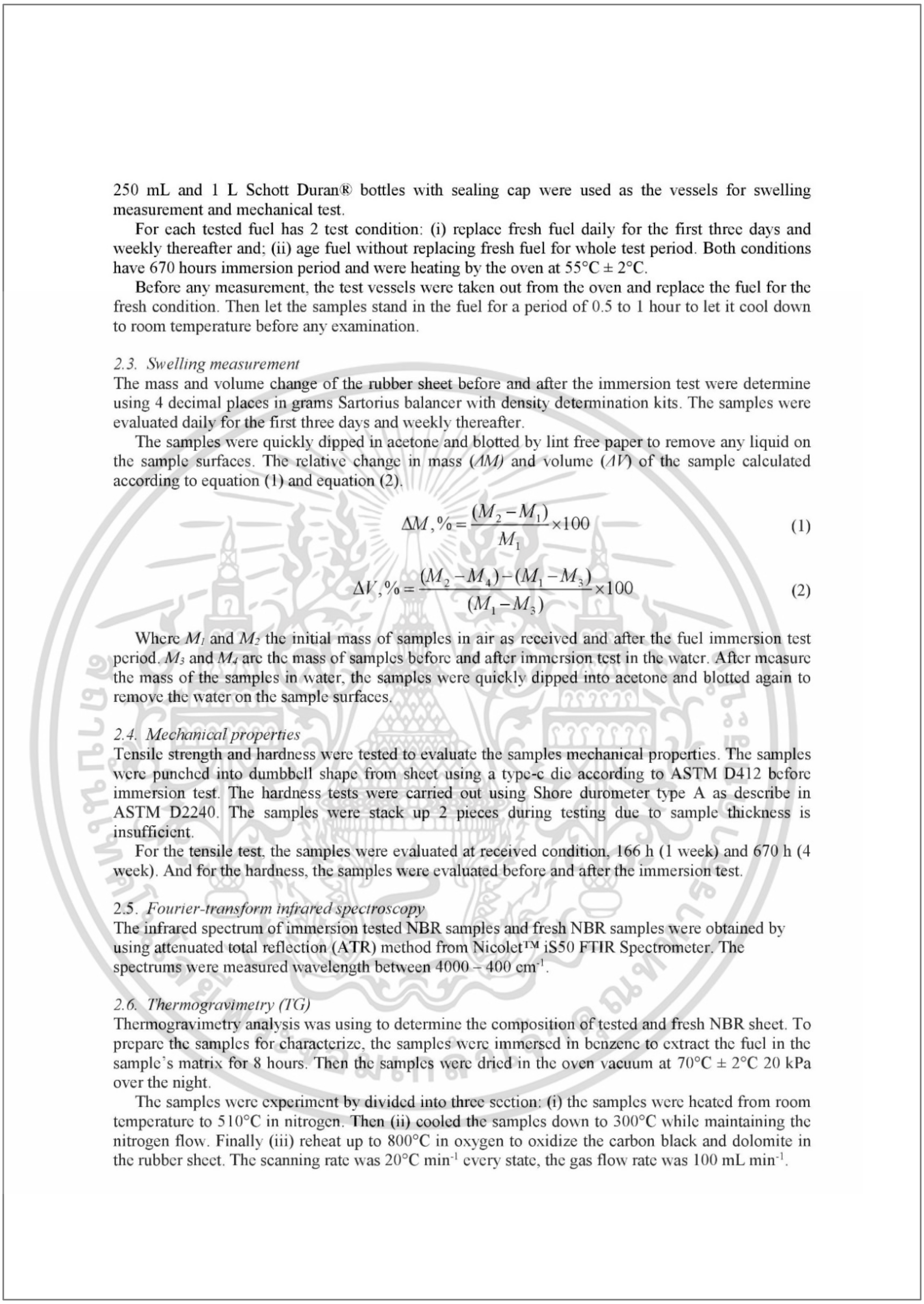
	Percentage content of FAME	
FAME	Palm Biodiesel B100	Palm H-FAME
C16:0	43.29	45.41
C18:0	4.39	10.28
C18:1	49.18	38.74
C18:2	8.97	0.52
Others	3.14	5.57

2.1.2. Acrylonitrile butadiene rubber

Acrylonitrile butadiene rubber sheet with 2 mm thickness supplied from Masterpac-Asia Co., Ltd. The rubber was examined by thermogravimetry analysis, revealing the rubber contained 38 wt.% of polymer, 20 wt.% of carbon black, 2.5 wt.% of volatile compounds and 39 wt.% of ash (containing calcium carbonate revealed by IR and EDS)

2.2. Testing Condition

The test samples were cut from rubber sheet into rectangular shape (4×3 mm) and punch a hole at the corner to hang the sample on stainless steel wires to split the sample when immersed in the fuel. The



250 mL and 1 L Schott Duran® bottles with sealing cap were used as the vessels for swelling measurement and mechanical test.

For each tested fuel has 2 test condition: (i) replace fresh fuel daily for the first three days and weekly thereafter and; (ii) age fuel without replacing fresh fuel for whole test period. Both conditions have 670 hours immersion period and were heating by the oven at 55°C ± 2°C.

Before any measurement, the test vessels were taken out from the oven and replace the fuel for the fresh condition. Then let the samples stand in the fuel for a period of 0.5 to 1 hour to let it cool down to room temperature before any examination.

2.3. Swelling measurement

The mass and volume change of the rubber sheet before and after the immersion test were determine using 4 decimal places in grams Sartorius balancer with density determination kits. The samples were evaluated daily for the first three days and weekly thereafter.

The samples were quickly dipped in acetone and blotted by lint free paper to remove any liquid on the sample surfaces. The relative change in mass (*ΔM*) and volume (*ΔV*) of the sample calculated according to equation (1) and equation (2).

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

$$\Delta V,\% = \frac{(M_2 - M_4) - (M_1 - M_3)}{(M_1 - M_3)} \times 100 \tag{2}$$

Where M_1 and M_2 the initial mass of samples in air as received and after the fuel immersion test period. M_3 and M_4 are the mass of samples before and after immersion test in the water. After measure the mass of the samples in water, the samples were quickly dipped into acetone and blotted again to remove the water on the sample surfaces.

2.4. Mechanical properties

Tensile strength and hardness were tested to evaluate the samples mechanical properties. The samples were punched into dumbbell shape from sheet using a type-c die according to ASTM D412 before immersion test. The hardness tests were carried out using Shore durometer type A as describe in ASTM D2240. The samples were stack up 2 pieces during testing due to sample thickness is insufficient.

For the tensile test, the samples were evaluated at received condition, 166 h (1 week) and 670 h (4 week). And for the hardness, the samples were evaluated before and after the immersion test.

2.5. Fourier-transform infrared spectroscopy

The infrared spectrum of immersion tested NBR samples and fresh NBR samples were obtained by using attenuated total reflection (ATR) method from Nicolet™ iS50 FTIR Spectrometer. The spectrums were measured wavelength between 4000 – 400 cm^{-1}.

2.6. Thermogravimetry (TG)

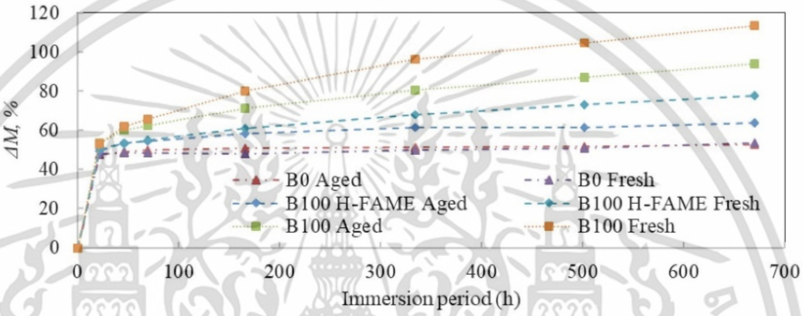
Thermogravimetry analysis was using to determine the composition of tested and fresh NBR sheet. To prepare the samples for characterize, the samples were immersed in benzene to extract the fuel in the sample's matrix for 8 hours. Then the samples were dried in the oven vacuum at 70°C ± 2°C 20 kPa over the night.

The samples were experiment by divided into three section: (i) the samples were heated from room temperature to 510°C in nitrogen. Then (ii) cooled the samples down to 300°C while maintaining the nitrogen flow. Finally (iii) reheat up to 800°C in oxygen to oxidize the carbon black and dolomite in the rubber sheet. The scanning rate was 20°C min^{-1} every state, the gas flow rate was 100 mL min^{-1}.

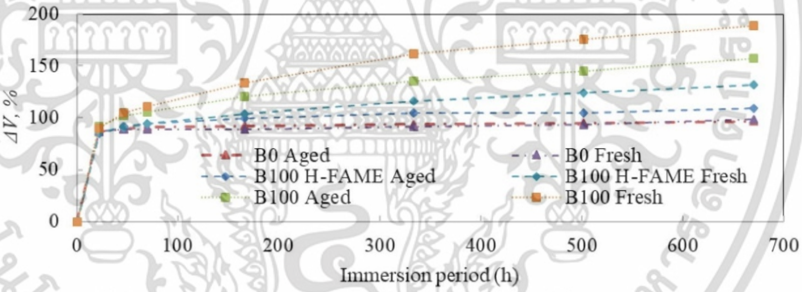
3. Results and Discussion

3.1. *Rubber Swelling behavior*

Figure 1 shows the change in mass of the NBR samples upon exposure in aged fuels and fresh fuel conditions. The swelling rate is high during the first three days in every test fuel. The samples exposure to the conventional diesel (B0) have swelling rate almost the same both aged and fresh condition of fuel. The swelling rate of NBR in B0 has reach its equilibrium point since a week after immersion test started. The NBR swelling much more when expose in conventional palm B100 than partially hydrogenated B100 (H-FAME). Moreover, both biodiesels have been absorbed into the sample better when replace fresh fuel during test period. The samples swelling in fresh B100 more than in aged B100 19.4% and in fresh H-FAME more than aged fuel 13.8%.



(a) Change in mass, %



(b) Change in volume, %

Figure 1. Swelling rate of NBR during exposed to the fuel

Similar trends are found for the change in volume. figure 1b, shows the change in volume of the samples when exposure in the different fuel and condition. The volume change in sample is much larger than the mass change, which means low density fuel absorbing into the rubber. The swollen rate of B100 is much higher than H-FAME. The samples immersed in the conventional diesel show the lowest change in volume and seems to be reached its equilibrium swollen of the samples.

Many study explain the swelling of elastomer in biodiesel by using "like dissolves like" principle. The NBR rubber contain a complex mixture of polymer, additive and filler[9]. The high polar substances in NBR cause its compatiblity with most petrolium fuels which are non – polar substances. A polar part presented in esters in biodiesel can interact with the high polar acrylonitrile in nitrile rubber, causes it higher swell.

The other principle explain the swelling behavior of the samples is Hansen solubility parameter (HSP). In HSP, not only the polar substances include in solubility parameter, hydrogen bonding force and molecular dispersion also including for calculated the solubility of 2 materials[10]. According to Lei Zhu at el's work[7], the lower amount of double bonds of fatty acid methyl ester is compatiblity (low swelling behavior) more than the higher double bonds.

3.2. Mechanical properties

Figure 2-4 shows the tensile strength, Young's modulus and hardness of NBR after immersion in test fuel for 166 (1 week) and 670 (4 weeks) in both fresh and aged condition. When compare with the received NBR which has tensile strength at 4.68 MPa, Young's modulus at 7.14 MPa and hardness at 65 scale shore A, all tested samples were decreased. Tensile strength of tested sample in aged fuel condition are seemed to be stable even the further immersion period. The tested samples in B0 are less degraded than the both tested biodiesels. The fresh fuel condition degraded the NBR samples significantly in every test fuel. Both biodiesels cause degradation dramatically when compare with conventional diesel. The hardness of the test samples in biodiesel are significantly more degraded than H-FAME.

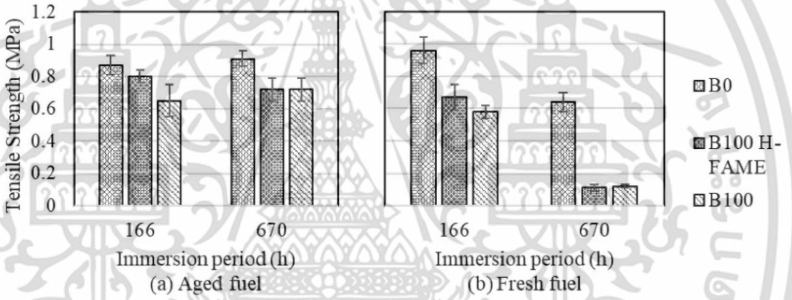


Figure 2. Change in tensile strength of elastomers after immersion test for 166 h and 670 hours

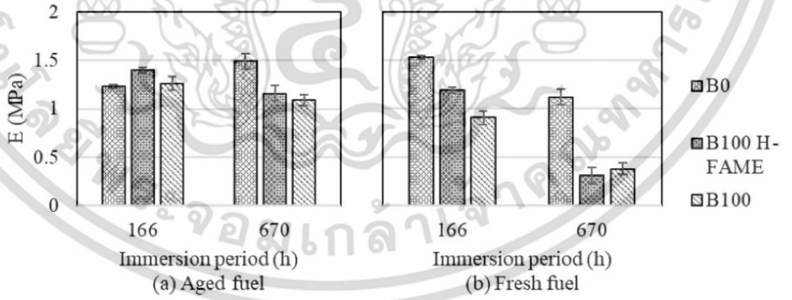


Figure 3. Changes in Young's modulus of elastomers after immersion test for 166 h and 670 hours in

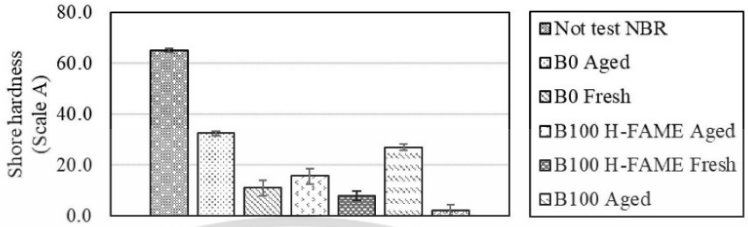


Figure 4. Hardness of NBR before and after exposure to the test fuel in aged and fresh fuel condition

The change in mechanical properties are causing to the chemical reaction between the crosslink and the test fuel. The reduction of crosslink in the rubber can occur be occurred due to chain scission or introduction of polar oxygen groups into elastomers[11]. The swollen behavior of test samples is also affecting the mechanical properties due to reducing the density of polymer chain[12].

3.3. Material characterization

To characterize the NBR samples to examined degradation occurs in the materials matrix, the infrared spectroscopy was used to characterize the chemical bonding of the samples. In the figure *5*, the infrared absorbance spectra of fresh and tested NBR samples. The spectra of fresh NBR sample has been corrected baseline due to matt black color can absorb the infrared spectra well. The tested samples immersed in both biodiesels shows peak at 1730 cm^{-1} of carbonyl bonds of ester groups[13]. The peak at 1530 cm^{-1} correspond to amide II due to C-N stretching vibrations in combination with N-H bending[8]. In B0 and B100, the peak of amide II is decreased when replace fuel during the test period. The reduction of amide II in the sample's matrix causing the samples are vulnerable to the chemical attack of the test fuel.

However, the samples immersed in the H-FAME does not show the reduction at peak 1530 cm^{-1} in both condition[14]. In addition, the peak of spectra at 1460 cm^{-1}, suggest the formation of C=C aromatic compounds[8], seems to be increased the most when comparing to the samples immersed in the others fuel.

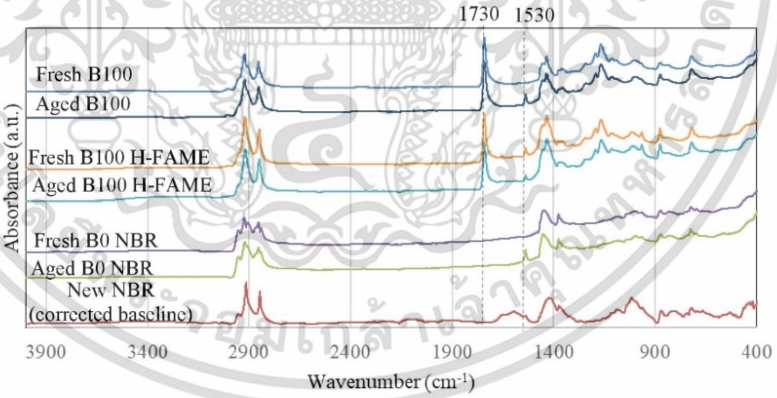


Figure 5. Infrared spectra received NBR rubber and immersion tested NBR samples

The reduction of calcium carbonate was observed by using thermogravimetry analysis to find out the content in the rubber sheet. The result shows in table *2*. The carbon black in the rubber is known as the stable substance materials which does not react with acidic or basic media[15]. If calculated each content and compare with the carbon black, the reduction of %wt polymer and calcium carbonate are reduce the most in test sample in B100 fresh condition and least at B0 aged condition.

Table 2. Result of thermogravimetric analysis when calculated in term of $\%wt_{contents}/\%wt_{carbon\ black}$

Contents	New NBR	B0		B100 H-FAME		B100	
		Aged	Fresh	Aged	Fresh	Aged	Fresh
Polymer	1.84	1.83	1.77	1.77	1.49	1.67	1.31
$CaCO_3$	0.66	0.62	0.63	0.67	0.62	0.60	0.53
Residue	1.24	1.36	1.33	1.27	1.20	1.31	1.10

4. Conclusions

The materials compatibility between acrylonitrile butadiene rubber and different type of diesel fuel have been studied. After immersed the tests samples in B0, B100 palm diesel and partially hydrotreated B100 palm diesel in different condition of replacing fuel, the test samples have been examined. The change in mass, volume and mechanical properties are indicate the partially hydrotreated biodiesel process can improve the materials compatibility between biodiesel and the high polar elastomer such as NBR test subject. However, the hydrotreated fuel still less compatibility with NBR when compare to non-polar neat diesel.

When comparing the tests result, the material compatibility of H-FAME is between conventional biodiesel and petroleum diesel in every examined method. This is reasonable to conclude that if blend the H-FAME with petroleum diesel instead of palm biodiesel at a same ratio, the materials compatibility of H-FAME blend will be better than the conventional diesel as Manida et al. studied[6].

When characterize of the test samples, the result shows different kind of degradation occurred in the test samples. The amide II part is not disappeared when even replace fresh fuel weekly. The degradation mechanism of both NBR and biodiesel need to be study further. However, reduce the effect of rubber additive and filler in the rubber to accurate the result is necessary to be considered.

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