การใช้กรดไขมันดิสทิลเลตจากน้ำมันรำข้าวเป็นสารกระตุ้นร่วมหรือโพรเซสซิงเอดในยาง
คอมพาวนด์

นายชลัชเมต เอกพันธ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

UTILIZATION OF RICE BRAN OIL FATTY ACID DISTILLATE AS

CO-ACTIVATOR OR PROCESSING AID IN RUBBER COMPOUNDS

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Field of Study	Petrochemistry and Polymer Science
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ชลัชเมต เอกพันธ์ : การใช้กรดไขมันดิสทิลเลตจากน้ำมันรำข้าวเป็นสารกระตุ้นร่วมหรือโพรเซสซิงเอดใน
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กรดไขมันดิสทิลเลตจากน้ำมันรำข้าว (RFAD) เป็นผลิตภัณฑ์ข้างเคียงที่ได้จากกระบวนการกลั่นน้ำมันรำ
ข้าวเป็นทรัพยากรหมุนเวียนที่มีมูลค่าต่ำ ในการศึกษานี้ได้พยายามศึกษาการใช้ประโยชน์ของกรดไขมันดิสทิลเลต
จากน้ำมันรำข้าวเป็นสารกระตุ้นร่วมหรือโพรเซสซิงเอดในยางธรรมชาติหรือยางอะคริโลไนไตรล์-บิวทาไดอีน สาร
กระตุ้นร่วมสังเคราะห์ได้โดยปฏิกิริยาอิพอกซิเดชันและไฮโดรจิเนชันเป็นอิพอกซิเดชันของกรดไขมันดิสทิลเลต
(EFAD) และไฮโดรจิเนชันของกรดไขมันดิสทิลเลต (HFAD) ได้ผสมสารทั้งสองชนิดกับยางธรรมชาติและยางอะคริโล
ไนไตรล์-บิวทาไดอีนในปริมาณ 2 ส่วนในร้อยส่วนและเปรียบเทียบกับกรดสเตียริก (STA) ซึ่งเป็นสารกระตุ้นร่วม
ทางการค้า สมบัติเชิงกลของยางวัลคาร์ไนซ์ของยางทั้งสองชนิดกับ RFAD มีค่าต่ำกว่าการใช้ STA เป็นสารกระตุ้น
ร่วม การใช้ EFAD ในยางอะคริโลไนไตรล์-บิวทาไดอีนจะเพิ่มความสามารถในการผลิต ขณะที่สมบัติเชิงกลเช่น
ความต้านทานแรงดึง มอดูลัสและความต้านทานแรงฉีกขาดของยางวัลคาร์ไนซ์ที่มีการใช้ HFAD และ STA เป็นสาร
กระตุ้นร่วมมีค่าใกล้เคียงกัน สำหรับโพรเซสซิงเอดสังเคราะห์ได้รับจากปฏิกิริยาเอสเทอริฟิเคชันกับแอลกอฮอล์ที่
เลือกใช้และปรับปรุงเพิ่มเติมโดยปฏิกิริยาอิพอกซิเดชันและไฮโดรจิเนชัน ความหนืดมูนนีและการทดสอบการไหล
ของยางธรรมชาติคอมพาวนด์กับกรดไขมันไซโคลเฮกซิลเอสเทอร์ (FChE) มีค่าที่ต่ำกว่าโพรเซสซิงเอดทางการค้า
Struktol WB16 ในขณะที่สมบัติเชิงกลจะมีค่าที่ต่ำกว่ายางธรรมชาติวัลคาร์ไนซ์ที่มีการใช้ Struktol WB16 เป็น
โพรเซสซิงเอดเล็กน้อย ดังนั้น FChE มีความเป็นไปได้ในการใช้แทน Struktol WB16 ในยางธรรมชาติ สำหรับยาง
อะคริโลไนไตรล์-บิวทาไดอีนการใช้อิพอกซิไดซ์ของกรดไขมันเมทิลเอสเทอร์ (EFME) เป็นโพรเซสซิงเอดที่มีความ
เหมาะสม ซึ่งช่วยเพิ่มความสามารถในการไหลและลดความหนืดมูนนีของยางคอมพาวนด์เมื่อเปรียบเทียบกับ
Struktol WB212 นอกจากนี้การใช้ EFME เป็นโพรเซสซิงเอดยังช่วยเร่งปฏิกิริยาวัลคาร์ไนซ์เซชันในระบบวัลคาร์
ไนซ์โดยใช้ซัลเฟอของยางโดยการลดเวลาในการเคียว สำหรับความต้านทานแรงดึง มอดูลัสและความต้านทานแรง
ฉีกขาดซึ่งสัมพันธ์กับความหนาแน่นเชื่อมขวางของยางวัลคาร์ไนซ์ของยางอะคริโลไนไตรล์-บิวทาไดอีนที่มีการเติม
EFME มีค่าต่ำกว่ายางอะคริโลไนไตรล์-บิวทาไดอีนวัลคาร์ไนซ์ที่มีการใช้ Struktol WB212 เป็นโพรเซสซิงเอดทาง
การค้าเล็กน้อย

สาขาวิชา   ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์   ลายมือชื่อนิสิต ....
ปีการศึกษา 2559   ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

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CHALACHMAT EKAPAN: UTILIZATION OF RICE BRAN OIL FATTY ACID DISTILLATE AS CO-ACTIVATOR OR PROCESSING AID IN RUBBER COMPOUNDS. ADVISOR: ASST. PROF. WARINTHORN CHAVASIRI, Ph.D., 84 pp.

Rice bran oil fatty acid distillate (RFAD), a by-product from refinery process of rice bran oil, is low-value renewable resource. The present study was attempted to utilize RFAD as co-activator or processing aid in NR or NBR compounds. The co-activators were fruitfully synthesized by epoxidation and hydrogenation furnishing epoxidizied rice bran oil fatty acid distillate (EFAD) and hydrogenated rice bran oil fatty acid distillate (HFAD). The two latter were compounded with NR and NBR as co-activator at 2 phr loading, and compared with commercial stearic acid (STA) co-activator. The mechanical properties of both NR and NBR with RFAD were lower than those with STA. EFAD improved processability in NBR compound, while the mechanical properties such as tensile strength, modulus and tear strength of HFAD and STA with both NR and NBR were similar. Synthesized processing aids were obtained by esterification with selected alcohols and further modified by epoxidation and hydrogenation. The Mooney viscosity and flowability test of compounded NR with fatty acid cyclohexyl ester (FChE) were better than those of Struktol WB16 commercial processing aid, while the mechanical properties of NR-FChE exhibited slightly lower than those of vulcanized NR with WB16. Therefore, FChE was possible to replace the commercial processing aid in NR compounds. For NBR compounding, epoxidized fatty acid methyl ester (EFME) was appropriate processing aid which improved the flowability and decreased Mooney viscosity compared with commercial processing aid. Moreover, EFME in NBR compound enhanced the sulfur vulcanization system by reducing cure time. However, the tensile strength, modulus, tear strength which related to the crosslink density of vulcanized NBR-EFME revealed slightly lower than NBR-WB212 commercial processing aid.

Field of Study:	Petrochemistry and Polymer	Student's Signature	....
	Science	Advisor's Signature	....
Academic Year:	2016		

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LIST OF ABBREVIATIONS

ASTM	American society for testing and materials
Et_2O	diethyl ether
°C	degree Celsius
CBS	n-cyclohexyl-2-benzothiazole sulfonamide
$CDCl_3$	deuterated chloroform
cm^{-1}	unit of wavelength
g	gram(s)
GC	gas chromatography
h	hour(s)
HCOOH	formic acid
H_2O_2	hydrogen peroxide
H_2SO_4	sulfuric acid
I.V.	iodine value
KI	potassium iodide
kN/m	kilonewton per meter
L	liter(s)
lbf-inc	pound force inch
m	meter
M	molar
min	minute(s)
mm	millimeter
mol	mole
mol/cm^3	mole per cubic centimeters
MPa	mega Pascal
N	normality
Na_2CO_3	sodium carbonate
Na_2SO_4	sodium sulfate

$Na_2S_2O_3$	sodium thiosulfate
NBR	acrylonitrile butadiene rubber
NR	natural rubber
phr	parts per hundred of resin
TMTD	tetramethylthiuram disulfide
%w/w	percentages of weight
ZnO	zinc oxide
δ	chemical shift

CHAPTER I

INTRODUCTION

1.1 Introduction

Rice bran oil fatty acid distillate (RFAD), one of by-products of rice bran oil industry is obtained from refinery process of crude rice bran oil. It is low value renewable resource. The major composition of RFAD is free fatty acid such as stearic, oleic, linoleic and palmitic acids. Normally, it has been used in animal feed, soap industries and as raw materials in biodiesel and oleochemical industries. RFAD is inexpensive, thus is suitable to modify as additives in plastic and rubber industries [1, 2].

Co-activator and processing aids are both important additives in rubber compounds that can be directly utilized from fatty acid. Stearic acid or a mixture of saturated fatty acids (stearic, lauric and palmitic acids) are usually used as co-activator for sulfur vulcanization which co-operated with metal oxide (such as ZnO) for activating accelerator during vulcanization of rubber [3]. In addition, long chain paraffinic end of fatty acid provides the lubricating effect of rubber while carboxylic acid group facilitates to absorb on the surface of filler or pigment. This eventually increases the dispersion and wettability of the filler on rubber matrixes [4].

Processing aids are chemicals or additives used mainly for improving processability of elastomer during processing, taking less time and allowing for more trouble-free operations such as extrusion, injection and calendaring process, and reducing energy during processing. Normally, they have the least effect on the properties. There are several types of processing aids depending on types of polymer

or rubber used, but mainly composes of fatty acids, fatty acid esters, fatty acid amides or fatty alcohols [5].

The aim of this work is to enhance the value of RFAD as industrial waste by modifying them as co-activator and processing aid for NR or NBR rubber compounds. For co-activator, RFAD was synthesized by epoxidation and hydrogenation to reduce double bond and used as co-activator in NR or NBR compounds. For the other, RFAD was esterified with selected alcohols and further modified by epoxidation and hydrogenation to achieve appropriate processing aids. The curing characteristics, Mooney viscosity, mechanical properties and crosslink density of NR or NBR with modified RFAD as either co-activator or processing aids will be investigated. Moreover, the effect of processing aids on flowability of rubber compounds will also be investigated by spider mold flow ability test.

1.2 Rice bran oil fatty acid distillate (RFAD)

RFAD (Figure 1.1) typically composes of fatty acids (majority of oleic, linoleic and palmitic acids). It is light pink semi solid with slightly smell at room temperature and can be melt into orange liquid at 40 °C. The specification of RFAD is shown in Table 1.1. RFAD can be used in wide application as animal feeds, raw materials for biodiesel production, oleochemical industries and utilized as additive in plastic and rubber industries [6, 7].

Figure 1.1 RFAD at room temperature

Table 1.1 Specification of RFAD

Parameters	Value
Acid value (mg KOH/g oil)	Min. 185
Color	Light pink
Form at room temperature	Semi solid
Moisture and volatile matter (% w/w)	Max. 1
Iodine value	Min. 85
Saponification value	Min.190

1.3 Elastomers

Rubbers are obtained from both rubber tree (natural rubber) and chemical synthesis by polymerization of diene monomer (synthetic rubber). Elastomers are received from crosslinking of rubber chain, long chain polymers which are elastic, generally having rather low Young's modulus and very large reversible elongations (500-1000%) at relative low stress compared with other materials. This requires that the polymer be completely or almost completely amorphous with low glass transition temperature as to obtain high polymer chain mobility. The initial mechanical properties of elastomers should be low but some elastomers undergo small amount of crystallization during elongation (stress induced crystallization). This acts as additional tensile strength and modulus.

1.3.1 Natural rubber (NR)

Natural rubber is one the most important natural products of Thailand. NR is organic elastic material obtained from the latex of rubber trees. The rubber latex is the colloid solution containing spherical rubber particles and contains a few percents of non-rubber constituents such as resin, protein, sugar and fatty acid which can

function as weak antioxidant, antiozonant and accelerator. The main composition of NR particle has the chemical structure as *cis*-1,4-polyisoprene (Figure 1.2) with its molecular weight in the range of 100,000–1,000,000. NR is usually compounded with carbon black, ZnO, stearic acid, accelerator and sulfur crosslinking agent for vulcanizing to thermoset materials. Peroxides and isocyanates can also be used. Main properties of vulcanized NR are excellent elasticity, high tensile strength, modulus, elongation at break, abrasion resistance, tear resistance, wear resistance and resistance to absorb amount of water but easy to swell in all usual solvents and poor in weather and ozone that cause double bond in their structures easy to react with ultraviolet light, oxygen and ozone. The vulcanized NR is widely used to various products as tire, components in cars, rubber grove and seal [8, 9].
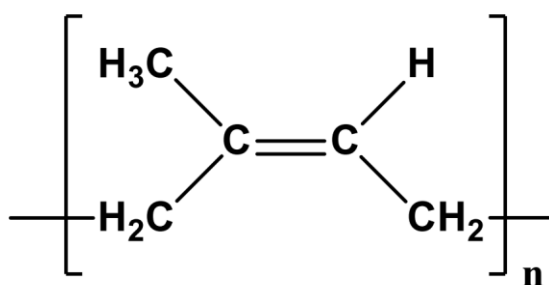
Figure 1.2 Chemical structure of cis-1,4-polyisoprene

1.3.2 Acrylonitrile butadiene rubber (NBR)

Acrylonitrile butadiene rubber or nitrile rubber (Figure 1.3) are copolymer of butadiene and acrylonitrile monomers which produced by radical copolymerization in emulsion system. In general, the chemical resistance of NBR depends on amount acrylonitrile content (18-20% in very low nitrile grade, 28-29% in low nitrile grade, 33-34% in medium nitrile grade and 38-39% in high nitrile grade and 45-48% in very high nitrile grade). The high acrylonitrile contents are used in application areas requiring good oil, fuel and chemical resistance. Moreover, other properties of NBR vulcanizates

are directly to the proportion of nitrile content (Table 1.2). However, like NR, NBR rubbers containing double bonds have limited resistance to oxidation and ozonization. NBR vulcanizates were obtained from both sulfur or peroxide crosslinking system. However, thermal resistant vulcanizates are also obtained during peroxide or phenolformaldehyde resin vulcanization [10].

NBR is cured by both sulfur or peroxide for enhancing physical properties. It can be mixed with reinforcing filler as carbon, silica or calcium carbonate. NBR compounds required phthalate ester type of plasticizers as aids for processing and can be mixed in kneaders, banbury, intermixes and two roll mills.

The vulcanized NBR can be used in wide variety of application or product requiring resistance to petroleum oils or chemicals such as flue hoses, wiper, cable jacketing, seals and belt. In automotive applications, NBR is used in water handling, in fuel and oil handling hoses with temperature range of -40 to 125 $^{\circ}$C [8].

$$\left[CH_2-CH=CH-CH_2 \right]_x \left[CH_2-CH \atop \substack{| \\ C \\ ||| \\ N} \right]_y$$
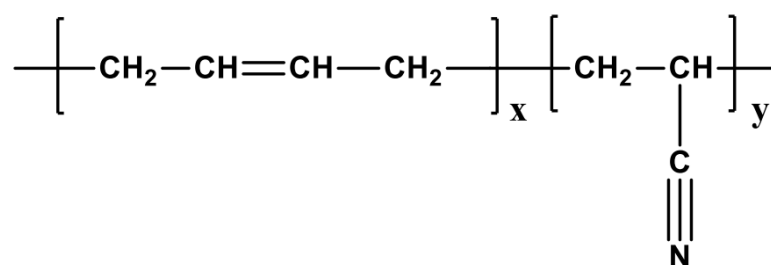
Figure 1.3 Chemical structure of NBR

Table 1.2 Property of NBR vulcanizates when nitrile content increases [11]

	Properties
Increase	Petroleum fluids and hydrocarbon fuels resistance
	Chemical resistance
	Heat resistance
	Ozone resistance
	Abrasion resistance
	Tensile strength
	Hardness
	Density
Decrease	Gas permeability
	Rebound resilience
	Low-temperature flexibility

1.4 Co-activators

Co-activator is used to accelerate vulcanization of rubber in the presence of ZnO, forming zinc stearate *in situ* (Figure 1.4). The most widely known co-activator of sulfur vulcanization reaction is stearic acid. Practically, it is always used in combination with suitable saturated fatty acid, the most frequently stearic or lauric acid. Activation effect of ZnO and stearic acid is ascribed mostly to its ability to create zinc stearate complex and generating curing sulfuric fragments with sulfur and accelerators. The participating acid increases the solubility of these complexes in rubber matrix which improve dispersive capacity of powder additive in compounds and sometimes also prolong induction initial of the vulcanization. Moreover, the paraffinic and acid group of stearic acids provide the lubricating effect, increase absorption on the surface of the pigments and increase the wettability of the filler. However, stearic acid has

comparatively lower solubility in elastomer and therefore higher dose may have adverse effect in the blooming and hence loss of rubber vulcanizates surface.
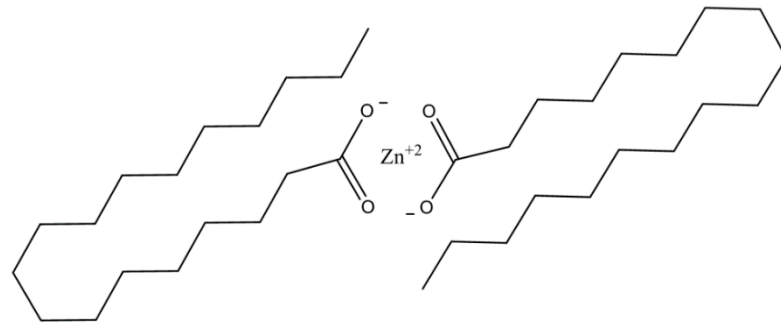
Figure 1.4 Chemical structure of zinc stearate [3]

1.5 Processing aids

Processing aids are chemicals or additives which improve the processability of elastomers, taking less time, and allowing for more trouble-free operations in mixing and subsequent operations, such as extrusion, injection and calendaring process. The function of processing aids is used as extender by decreasing the elastomer, allowed higher doses of filler to be incorporated, reduced energy during processing, hardness of vulcanizates, improved rubber flow and filler dispersion, and improved low temperature flexibility. However, processing aids are generally used not at higher doses, this may be having adverse effect in blooming on the surface of product and loss of rubber tactility. The processing aids are of 6 categories.

1. Fatty acid derivatives: mixtures derived from naturally occurring long chain saturated or unsaturated carboxylic acids such as stearic, palmitic, oleic or linoleic acids. Moreover, the fatty acid esters, fatty acid amides, fatty alcohols and derivatives are also included.

2. Natural synthetic resins: mostly defined products from thermal polymerization of side products, residue of the petroleum or coal industries. These include aliphatic, naphthenic and aromatic resins.

3. Polar surfactants: mostly comprising a mixture of metal salts and metal soaps such as barium salt of tall oil bound to inorganic filler, calcium salt of natural oil in organic filler. These include polar surfactants on high activity silica and processing lubricants with surfactant activity.

4. Low molecular weight polymers: by products from polymerization process or as specific low molecular weight polymerization products such as saturated polyethylene, polypropylene, polybutene and unsaturated polybutadiene, polyisoprene.

5. Fluorinated product: mostly used for polytetrafluoroethylene (PTFE) or other fluorine containing polymers.

6. Miscellaneous products: not appear into previous categories such as zinc methacrylate, sulfonic acid and sodium alkyl sulfates [12].

1.6 The mechanism of processing aids or plasticizer affecting on the polymer [3, 13, 14].

Plasticizer, processing aid, processing oil, lubricating agent and other additives are small molecules adding to soften polymer by lowering its glass transition temperature or reducing its crystallinity or melting temperature and improving processability of rubber compound without or less affecting its mechanical properties, as long as only small quantity are added to rubber compounds. Mostly, they are added to rubber compounds to aid the processing operation such as mixing, extrusion, injection, calendaring or molding.

Four major theories are explained how a processing aid or plasticizer affects to polymer in both internal and external plasticization. Some theories involve detailed analysis of polarity, solubility and interaction parameter and thermodynamics of polymer behavior, whereas others treat plasticization as a simple lubrication of chains of polymer from each other. An understanding of the plasticization process can be obtained by combining ideas from each theory, and an overall theory of plasticization must include all these aspects

1.6.1 Lubricating theory

This theory explains the effect of an external plasticizer on a polymer in terms of lubrication. Polymer without plasticizer, is mainly rigid properties because friction force exists between nearby polymer chains, binding them into network. When the polymer contained plasticizer, the binding is weakened and the small molecules of plasticizer are able to lubricate in between polymer chains. Figure 1.5 shows plasticizer molecules and polymer response based on lubricity theory.
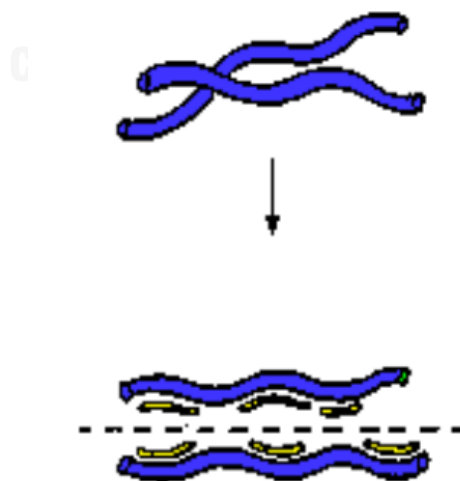
Figure 1.5 Plasticizer and polymer response based on lubricity theory

1.6.2 Gel theory

This theory extends the lubrication theory by having the plasticizer break the interaction between polymer chains which interacted by Van der waals force, hydrogen bonding or crystalline structure of a three-dimension gel structure. This point of gels is close together, thus permitting little movement and preventing their reformation. This gel site can interact with plasticizer and formed by loose attachments occurring at intervals along the polymer chain, thus separating a gel site of the nearby polymer chains. The plasticizer by its presence separates the polymer chains, allowing the polymer molecules to move more freely. This facilitates the movement of plasticizer molecule, thus imparting flexibility (Figure 1.6).
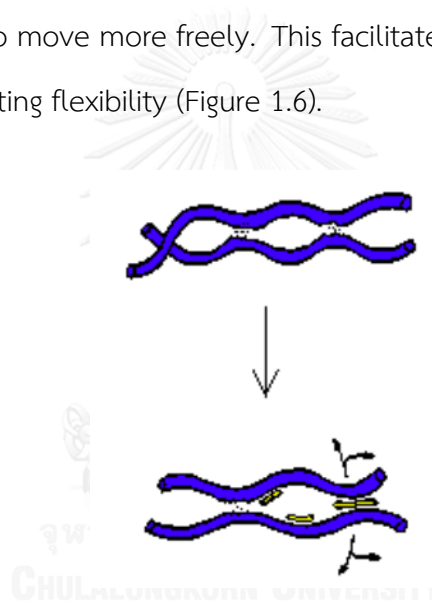
Figure 1.6 Plasticizer and polymer chains response based on gel theory

1.6.3 The free volume theory

The free volume theory is an extension of the lubricity and gel theories and can be used to explain both external and internal lubricating agent or plasticizers. In general, free volume of polymer matrix is estimated the internal space available for the movement of polymer chains, which provided flexibility to those resins. For the resin containing plasticizer, the small molecules were introduced to increase free volume of polymer matrix providing is more free space between them than between

polymer molecules. Thus, free volume can emerge from motion of the chain end, side chain, or the main chain. The fact that free volume increases with molecular motion is useful in explaining internal plasticization achieved by side chain addition, where each side chain acts as a small molecule and free volume of the system is increased.

1.6.4 Mechanistic theory

The mechanistic theory of plasticization (also referred to as solvation-desolvation equilibrium) can be depicted as having some resemblance to gel theory. The essential difference is that in the gel theory, the plasticizer stays attached to a site along the polymer chain, where the mechanistic theory states the plasticizer can move from one polymer location to another (Figure 1.7).
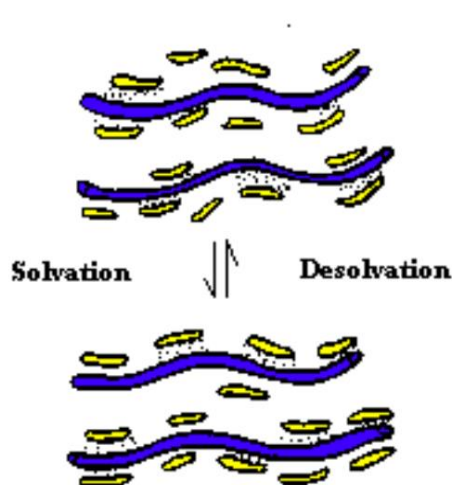
Figure 1.7 Plasticizer and polymer chains response based on mechanistic theory

1.7 Literature review on the use of fatty acid distillate as co-activator in rubber compounds

Fatty acid is one of the most useful raw materials as additive in plastic and rubber industries. Especially, the use as co- activator in rubber compounds which

always co-operated with metal oxide as ZnO. These complexes activated the process of crosslinking formation and could delay initial vulcanization. Normally, the most widely co-activator in sulfur vulcanization is stearic acid or combination of saturated fatty acid such as stearic, palmitic and lauric acids. Recently, fatty acid distillate of natural oil such as palm and rice bran oils, consisting of a mixture of free fatty acids, has been introduced as co-activator to reduce costs because of its inexpensiveness.

In 1993, Kuriakose and Rajendran [4] reported that rice bran oil could be used as co-activator and processing oil compounding ingredients in sulfur vulcanization of natural rubber, compared with stearic acid commercial co-activator. The free fatty acids of rice bran oil could be replaced by stearic acid in sulfur vulcanization of NR system without much affecting on the cure characteristics of the compound and mechanical properties of vulcanizates. Moreover, the low-cost product would be helpful in saving energy during mixing acting similar to less toxic lubricating agents.

In 1997, Ismail and Rahaizat [15] reported the effect of the concentration of palm oil fatty acid on curing and mechanical properties of $CaCO_3$ filled natural rubber compounds. The scorch and vulcanization time of NR filled $CaCO_3$ increased with increasing of palm oil fatty acid concentration indicated that palm oil fatty acid was retarded the vulcanization reaction. The maximum torque of NR compounds was increased to the maximum value at 3 phr of fatty acid and slightly decreased with increasing concentration. This result showed that palm oil fatty acid in excess acted as processing aid. The concentration effect of palm oil fatty acid on tensile strength and 300%modulus was increased up to 3 phr and then decreased with further addition of organic acid. When co-activator was used more than 3 phr, the excess fatty acid would act as plasticizer that affected on decreasing of degree of crosslinking and mechanical properties. Moreover, increasing of palm oil fatty acid improved the resistance to reversion indicating the stable mono or di sulfidic crosslinking.

In 1998, Ismail and Ruhaizat [16] reported the palm oil fatty acid as an activator in natural rubber gum compounds compared with stearic acid. The scorch and cure time of NR compounds with different co-activators were not much different at the same concentration. However, increasing the concentration of both acids slowed down vulcanization rate. The maximum and minimum torque of NR compounds with palm oil fatty acid were lower than stearic acid at every concentration indicating good plasticizing effect.

For the physical properties and crosslink density of NR vulcanizates, every concentration of palm oil fatty acid in NR exhibited tensile strength, 300% modulus, hardness and crosslink density lower than NR with stearic acid. However, the maximum mechanical properties of NR with palm oil fatty acid appeared at 3 phr.

In the same year, Ismail and Anuar [17] reported that palm oil fatty acid as an activator in carbon black filled NR compounds on dynamic properties, curing characteristic, reversion and fatigue. The scorch and cure time were increased with increasing of palm oil fatty acid concentration. For dynamic properties, the viscous torque or loss modulus and tan delta were decreased with increasing acid concentration. At similar palm oil fatty acid concentration, NR with 50 phr of carbon black showed the highest viscous torque and tan delta. Whereas reversion of NR vulcanizates decreased with increasing palm oil fatty acid concentration. For all carbon black concentrations, fatigue life increased with increasing acid concentration.

In 1999, Ismail and Salmiah [18] reported about palm oil fatty acid as an activator in carbon black filler in epoxidized natural rubber (ENR) and NR compounds. The scorch and cure time of ENR with palm oil fatty acid showed the shortest than NR at every concentration. For all rubbers studied, scorch time, cure time, mechanical properties as tensile strength, modulus and hardness of ENR and NR increased with increasing fatty acid contents.

In 2000, Kamal and colleagues [19] reported the comparison effect of palm oil fatty acid and stearic acid as activator on dynamic properties, curing characteristics and mechanical properties of carbon black filled ENR compounds. Scorch time of ENR with palm oil fatty acid was found to be lower than stearic acid indicating that stearic acid co-activator had process safety. While the cure time of ENR with palm oil fatty acid was faster at every concentration. The maximum elastic torque of ENR with palm oil fatty acid was lower than stearic indicating its action as processing aid in ENR.

The mechanical properties of ENR vulcanizates increased with increasing both fatty acid concentrations. ENR vulcanizates with stearic acid exhibited better tensile, modulus and hardness than palm oil fatty acid at same concentrations. However, the tensile, tear strength and crosslink density of ENR of both acids increased to the maximum value at 5 phr and then decreased.

1.8 Literature review on the use of fatty acid distillates and their derivatives as processing aid in rubber compounds

The processing aids and processing oils are multifunction additives for improving some properties of rubber compounds, without negative effect to physical properties of rubber vulcanizates. Moreover, it can be resolved high stickiness which is one of the properties of rubber compounds, this may be affect to the incompleteness of rubber product including negative impact to mechanical properties.

In 1999, Kuriakose and Varghese reported [5] that the compounding of nitrile and polychloroprene rubber with rice bran oil as multifunction additives in terms of processing aid, co-activator and antioxidant. In cure time values of both NBR and CR, they were lower than DOP or aromatic oil processing aid indicating that natural oil demonstrated cure acceleration in both mixtures. For the mechanical properties after heat aging of vulcanized NBR and CR, rice bran oil with both vulcanized compounds

exhibited resistance to heat aging than DOP or aromatic oil. Thus, the rice bran oil could replace conventional processing oil, co-activator and antioxidant in NBR and CR compounds.

In 2003, Kuriakose and Varghese [20] reported the use of RBO and ERBO in carbon black-filled NR and polychloroprene blends. Optimum cure time of RBO and ERBO in NR/CR blend were lower than aromatic oil indicating cure accelerating effect of fatty acid in natural oils. The maximum and minimum torque and compound viscosity values of NR/CR with ERBO was lower than conventional aromatic oil indicating softening effect. Mechanical properties of RBO and ERBO containing in NR/CR blend were not different conventional processing aid, this implied that both RBO and ERBO could replace aromatic oil in NR/CR blend.

In 2009, Jayewardhana and colleagues [21] reported that natural oil (palm oil, soy bean oil and sunflower oil) as alternative processing aids and activators compared with aromatic oil in carbon black filled NR. The NR contained three natural oils displayed higher scorch time than aromatic oil indicating better process safety and it could be used as a co-activator. The highest maximum torque values were given by NR with soybean oil related with amount of crosslink density in their vulcanizates which were effective to the highest mechanical properties as 300% modulus, hardness and resilience while sunflower oil also showed the highest tensile, tear strength and abrasion resistance. In addition, sunflower and palm oils presented the better physical properties after heat aging than aromatic oil.

Epoxidized vegetable oils as synthesized oil derived from natural products have become attractive candidates as processing aid to replace aromatic oil in rubber compounds due to their low toxicity. In 2011, Chandrasekara and colleagues [22] studied three epoxidized vegetable oils (soybean oil, palm oil and sunflower oil) as processing aids and activator in carbon black filled natural rubber compounds compared with aromatic oil. Epoxidized vegetable oils were obtained in 85-91 %yield.

When those vegetable oils were used as processing aid and co-activator in NR, the scorch time and cure rate index values were slightly lower than NR compounds with aromatic oil. Mechanical properties as tensile strength, modulus and tear strength of NR contained epoxidized palm oil vulcanizates showed higher than aromatic oils and other natural oils. While, ESFO had lesser. This was probably by the presence of polysulfidic linkages.

In 2015, Khalaf and colleagues [23] reported the effect of olive and orange oils compared with dioctyl adipate (DOA), a normal plasticizer in NBR on processability, mechanical properties, morphology and thermal stability of their vulcanizates. The minimum torque values of NBR prepared with olive and orange oils were lower than control mixtures. This was clearly indicated that the improvement of processability. The tensile strength, modulus, hardness and crosslink density of both vegetable oils prepared with NBR were higher than DOP containing high compatible of both high polar oils. The morphology results of NBR vulcanizates were also confirmed (Figure 1.8).
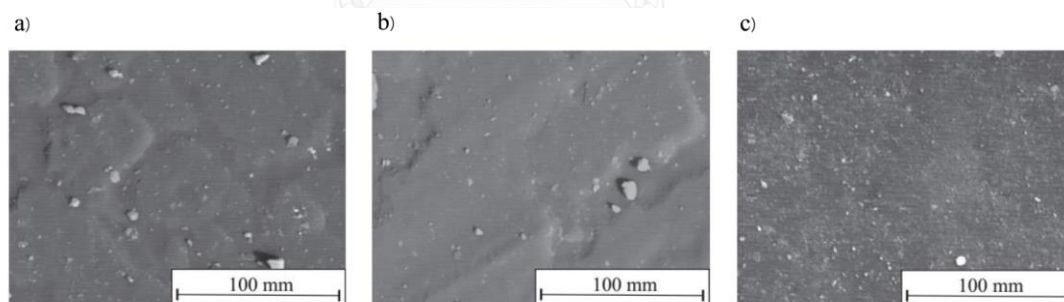
Figure 1.8 Morphology of NBR with a) DOA, b) olive oil and c) orange oil

In the same year, Boontawee and colleagues [24] reported the synthesis of benzyl esters of three vegetable oils (benzyl ester of coconut (CBE), palm (PBE) and soybean oils (SBE)) as processing oil in carbon black filled styrene butadiene (SBR) and studied on chemical modification, cure characterization, mechanical properties and morphology compared with aromatic oil. All benzyl ester oils were obtained at

maximized %yield (96% for PBO), by using the molar ration of fatty acid in vegetable oil/benzyl alcohol at 1.5:1 and 1%wt of H_2SO_4 as catalyst at 100 $^{\circ}$C for 3 h.

The SBR compounding with benzyl ester oils had low scorch time, low cure time and high cure rate index than SBR compounding with those aromatic oils. Moreover, three-benzyl ester oils showed low energy in vulcanizing process. However, SBR vulcanizates with those benzyl ester oils displayed lower hardness, tensile strength, modulus and high elongation at break than without oil. The morphology (Figure 1.9) of all SBR vulcanizes with processing oils gave smaller agglomeration of dispersed carbon black.
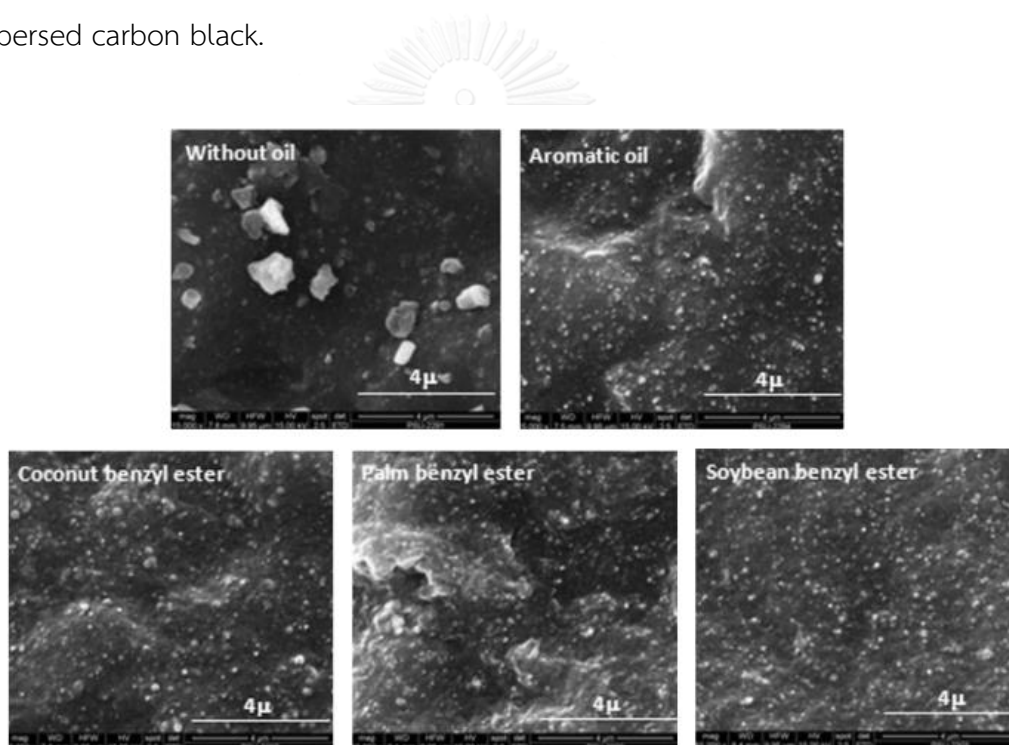
Figure 1.9 SEM micrographs of carbon black filled SBR with and without various processing oils.

In 2015, Thithithammawong and colleagues [25] reported the influence of *N*-phenyl-*p*-phenylenediamine in modified epoxidized palm oils (m-EPO) as processing oils compared with palm oil (PO), epoxidized palm oil (EPO) and petroleum based white oil (WO) on properties of ENR/PP TPVs. ENR/PP with m-EPO displayed the shortest scorch time and cure time. This result suggested that an oxirane ring or amine

group on m-EPO enhanced activity of vulcanizing agents during vulcanization. Moreover, the presence of high polar group as oxirane ring and amine in m-EPO promoted compatibility between ENR matrix and processing oils. These results confirmed by the highest difference torque (M_H-M_L) of ENR/PP contained m-EPO and SEM micrographs (Figure 1.10).

(A) WO   (B) PO   (C) EPO   (D) m-EPO
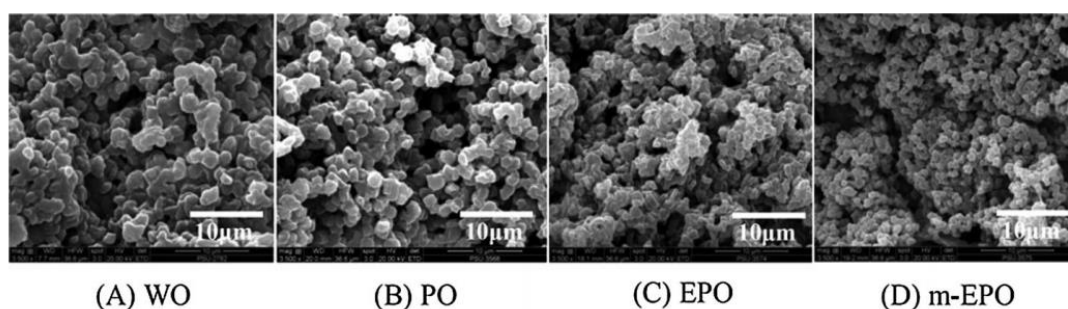
Figure 1.10 SEM micrographs of ENR/PP TPVs with several types processing oils at 20 phr

Recently, Pakhathirathien and colleagues [26] reported the synthesis of stearyl aromatic esters as processing aids in NR compounds compared with aromatic oil. Four stearyl esters namely, stearyl benzoate (SB), distearyl phthalate (SP), biphenyl-4-carboxylate (SBC) and stearyl naphthoate (SN) were prepared by the reaction of stearyl alcohol and benzoic acid, phthalic acid, biphenyl-4-carboxylic acid and 1-naphthoic acid, respectively, with H_2SO_4 at desired condition. Ester products were obtained in 87-90 %yield and used as processing oils in NR compounds. The aromatic esters enhanced curing characteristic by increasing scorch time and increasing cure rate index in a similar trend to the aromatic oil. NR compounded with SN oils showed the lowest Mooney viscosity at 100 ^{o}C and the lowest mixing energy. Moreover, the aromatic ester could slightly improve mechanical properties after aging the vulcanizates as tear strength, compression set and thermal stability.

1.9 The goal of this research

The goal of this research can be summarized as

1. To modify RFAD as co- activator and processing aid in NR or NBR compounds.

2. To study the effects of modified RFAD co-activators and processing aids on properties of NR or NBR compounds.

1.10 The scope of this research

The first part of this research involves the utilization of RFAD as co-activator in NR and NBR compounds compared with commercial stearic acid. Moreover, RFAD was modified by epoxidation and hydrogenation and used as co- activators in both compounded NR and NBR. The curing characteristic, Mooney viscosity, mechanical properties and crosslink density were investigated.

In the second part, RFAD was modified by esterification with selected alcohols (methanol, ethanol, *n*-butanol, 1-hexanol, cyclohexanol and benzyl alcohol) and used as processing aids for both NR and NBR compounds, compared with commercial processing aids. The fatty acid alkyl esters were further modified by epoxidation and hydrogenation to improve plasticization and to reduce double bond in their structures. Moreover, the appropriate quantity of processing aids were studied. The curing characteristic, Mooney viscosity, spider mold flow ability, mechanical properties and crosslink density of NR and NBR with different processing aids were investigated.

CHAPTER II

EXPERIMENTAL

This chapter concerns with the experimental to modify rice bran oil fatty acid distillate (RFAD) as co-activator or processing aid for two rubber compounds (natural rubber (NR) or acrylonitrile butadiene rubber (NBR)). The chapter consists of four sections: materials, chemicals, and instrument and equipment in section 2.1, the compounding molding and testing in section 2.2, the modified RFAD as co-activator and processing aids in rubber compounds in sections 2.3 and 2.4, respectively.

2.1 Materials, chemicals and instruments

2.1.1 Raw materials

The raw material, RFAD-by products from refinery process of rice bran oil was obtained from Thai Edible Oil Co., Ltd., Ayutthaya, Thailand in January 2016. RFAD was preheated at 100 $^{\circ}$C for 30 min to eliminate moisture. The quantity of fatty acid content of RFAD was analyzed by GC *via* fatty acid methyl ester.

2.1.2 Chemical reagents

All solvents used in this research were purified prior to use by standard methodology except for those which were reagent grades. The reagents for synthesizing co-activator and processing aids were purchased from Aldrich or otherwise stated and were used without further purification.

2.1.3 Instruments and equipment

FT- IR spectra were obtained on a Nicolet Fourier transform infrared spectrophotometer model Impact 410. Solid samples were incorporated to potassium bromide to form pellet. Liquid samples were dropped in sample holder.

The ^{1}H NMR spectra of synthetic products were performed in $CDCl_3$ which operated at 399.84 MHz nuclei. The chemical shifts were assigned by comparison with residue solvent protons.

Iodine value (I.V.) was defined as the mass of iodine in g consumed by 100 g of chemical substance relative amount of unsaturation. About 0.3-0.5 g of sample was dissolved in 20 mL chloroform then added 25 mL Wijs solution and kept in dark for 1 h. After specified, added 20 mL of 10%KI solution follow by distilled water and shaked vigorously. Titrated the mixer with 0.1 N of $Na_2S_2O_3$ solution until the yellow color has almost disappeared, 2 mL of starch soluble as indicator and continued the titration until the blue color has just disapperared. The procedure for determination of iodine value was calculated by equation as [27]:

$$I.V. = \frac{1.27 \times (B - A)}{W}$$

when   A = volume of 0.1N $Na_2S_2O_3$ (mL) when titration with sample

B = volume of 0.1N $Na_2S_2O_3$ (mL) when titration with blank

W = weight of sample (g)

2.2 Compounding, molding and testing

2.2.1 Compounding and molding

All rubbers and chemicals were obtained from Chemical Innovation Co., Ltd. The rubber compounds (NR and NBR) were prepared by kneader internal mixer 1.75 L

capacity, and two roll mill. The modified RFAD was used as either co-activator or processing aids.

For the mixing step, NR or NBR resin (TTR5L or Krynac 3345F, respectively) was masticated in kneader internal mixer for about 3 min. Carbon black N330, processing oil (paraffinic oil for NR and dioctyl adipate for NBR) and processing aid were added and milled to the mixer until compound torque was constant. Zinc oxide (ZnO) and co-activator were added and continued mixing for 3 min. After mixing, the compounds were cooled and created sheet by two roll mill external mixer. After cooled, sulfur, TMTD (tetramethylthiuran disulfide) and CBS (n-cyclohexyl-2-benzothiazole sulfenamide) were added and continued mixing about 3 min by kneader internal mixer. Finally, rubber sheets were created by two-roll mill external mixer. The rubber compounds were kept at room temperature for 24 h before testing and molding. The summarized procedure for the preparation of NR or NBR compounds with various co-activators or processing aids and experimental process are shown in Schemes 2.1 and 2.2, respectively.

The rubber vulcanized sheets were obtained by hydraulic compression machine with slap sheet of 2 mm thickness and molded 160 $^\circ$C, 10 MPa and $t_{c90}+1$ as vulcanization time for each compound. After completed, the vulcanized sheets were cooled by air for 15 min and kept at room temperature for 24 h before testing.

2.2.2 Curing characteristics Mooney viscosity and spider mold flow ability test

2.2.2.1 Curing characteristics

The curing properties were measured by rotorless viscometer (EKTRON-2000p) at 160 $^\circ$C for 10 min according to ASTM D5289. The minimum torque (M_L), maximum torque (M_H), different torque (delta(M_H-M_L)) scorch time (t_{s2}) and cure time (t_{c90}) were obtained [10].
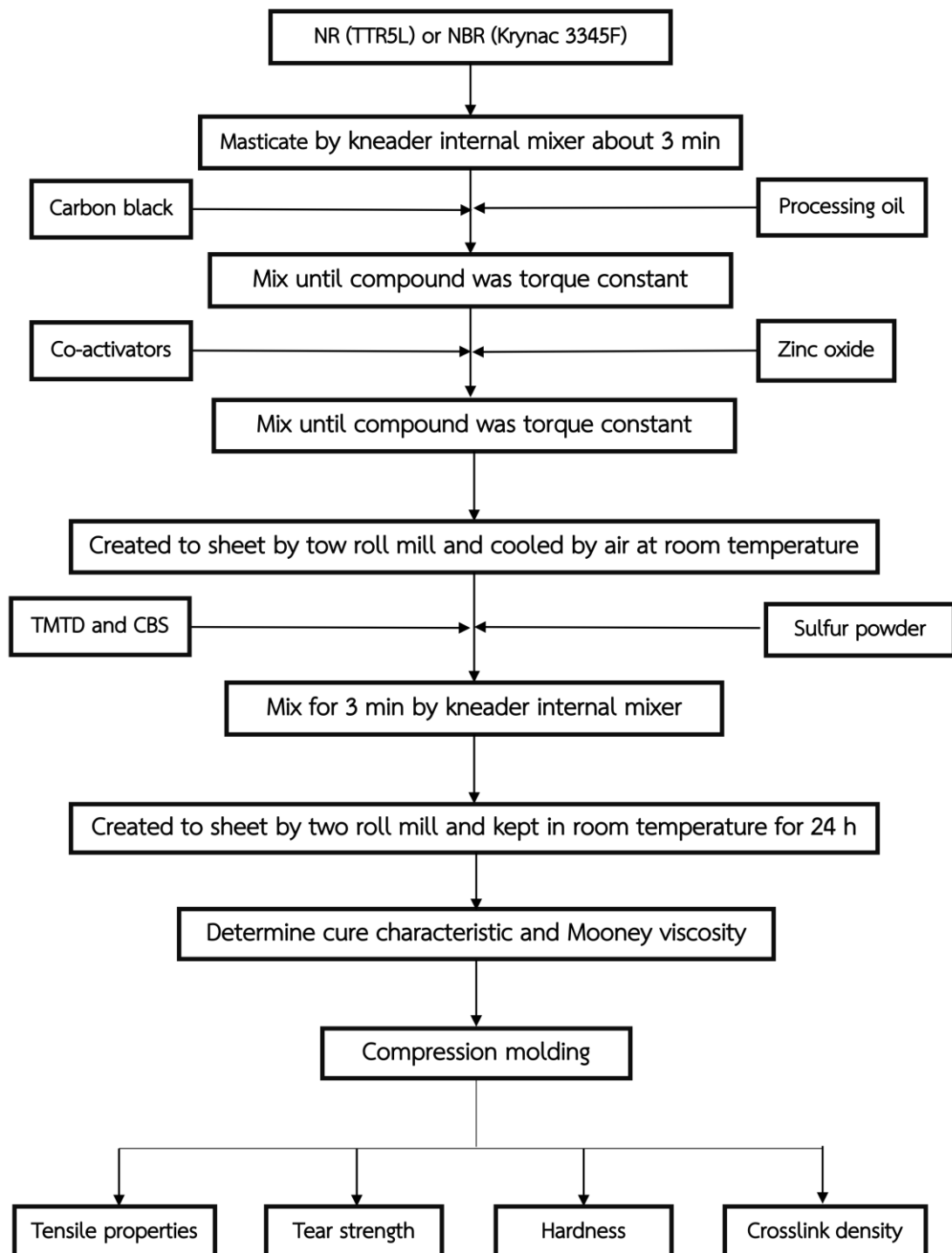
Scheme 2.1 The overall experiment process for NR or NBR with various co-activators

```
┌─────────────────────────────────────────┐
│     NR (TTR5L) or NBR (Krynac 3345F)     │
└─────────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────────────────┐
│   Masticate by kneader internal mixer about 3 min │
└─────────────────────────────────────────────────┘
```

┌──────────────┐   ┌──────────────────────┐
│ Carbon black │ ─────────────► ◄───────────────── │   Processing   │
└──────────────┘   │ oil/processing aid   │
                                                    └──────────────────────┘
```
                    │
                    ▼
┌─────────────────────────────────────────┐
│  Mix until compound was torque constant  │
└─────────────────────────────────────────┘
```

┌──────────────┐   ┌──────────────┐
│ Stearic acid │ ──────────────► ◄───────────────── │ Zinc oxide │
└──────────────┘   └──────────────┘
```
                    │
                    ▼
┌─────────────────────────────────────────┐
│  Mix until compound was torque constant  │
└─────────────────────────────────────────┘
                    │
                    ▼
┌───────────────────────────────────────────────────────────────┐
│ Created to sheet by tow roll mill and cooled by air at room    │
│ temperature                                                    │
└───────────────────────────────────────────────────────────────┘
```

┌──────────────┐   ┌────────────────┐
│ TMTD and CBS │ ──────────────► ◄───────────────── │ Sulfur powder │
└──────────────┘   └────────────────┘
```
                    │
                    ▼
┌─────────────────────────────────────────┐
│   Mix for 3 min by kneader internal mixer │
└─────────────────────────────────────────┘
                    │
                    ▼
┌───────────────────────────────────────────────────────────────┐
│ Created to sheet by two roll mill and kept in room temperature │
│ for 24 h                                                       │
└───────────────────────────────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────────────────┐
│  Determine cure characteristic and Mooney viscosity │
└─────────────────────────────────────────────────┘
                    │
          ┌─────────┴──────────┐
          ▼                    ▼
┌──────────────────────┐  ┌──────────────────────────┐
│ Compression molding  │  │ Spider mold flow ability │
│                      │  │          test            │
└──────────────────────┘  └──────────────────────────┘
          │
  ┌───────┼────────┬──────────┐
  ▼       ▼        ▼          ▼
┌──────┐ ┌──────┐ ┌────────┐ ┌──────────┐
│Tensile│ │ Tear │ │Hardness│ │Crosslink │
│proper.│ │streng│ │        │ │ density  │
└──────┘ └──────┘ └────────┘ └──────────┘
```

Scheme 2.2 The overall experiment process for NR or NBR with various processing aids

2.2.2.2 Mooney viscosity

The Mooney viscosity was measured by Mooney viscometer (Monsanto MV-2000) according to ASTM D1646. Two pieces of 12 g of rubber compounds were articulated with large rotor and tested at 125 $^{\circ}$C for 30 min. The Mooney viscosity was reported in ML(1+4)@125 $^{\circ}$C format [9].

when   M is designated as viscosity in Mooney units

L is designated as using a large rotor

1 is designated as preheating time of compound before starting rotor (min)

4 is designated as testing time after starting rotor (min)

125 $^{\circ}$C is designated as testing temperature ($^{\circ}$C)

2.2.2.3 Spider mold flow ability test

Spider mold flow ability test is one technique for determining flow ability of rubber compound. Rubber compound was allowed to flow and vulcanize in spider mold tester (Figure 2.1) at desired conditions. The spider mold flow ability test was measured by hot press hydraulic compression machine with spider mold tester at 160 $^{\circ}$C, 10 MPa and t_{c90} as vulcanization time for 9 g of selected compound. The spider mold flow specimen was obtained and cooled to room temperature for 24 h, then weighed.

Figure 2.1 Spider mold tester

2.2.3 Mechanical properties and crosslink density

The vulcanized rubber sheets were obtained by thin sheet compression molding using hydraulic press at 160 $^{\circ}$C, 10 MPa and t_{c90}+1 as vulcanization time. After 24 h at room temperature, the vulcanized sheets were cut by rubber die cut into dumb-bell shape type C shape, respectively [11].

2.2.3.1 Hardness testing

The hardness value was obtained by shore A durometer tester according to ASTM D2240. The thickness of test specimens was at least 6 mm. The conditions of testing were followed by 25 $^{\circ}$C and 50% relative humidity.

2.2.3.2 Tensile properties

The rubber vulcanized sheets were cut into dumb-bell shape with 3.3 cm of gage length, 2 mm thickness length by die cut according to ASTM D412 (Figure 2.2). Tensile strength, elongation at break, 50, 100, 200 and 300 %modulus were obtained

by universal testing machine (Tensile tech III) with 500 mm/min crosshead speed. The test conditions were followed by 25 $^{\circ}$C and 50 % relative humidity.
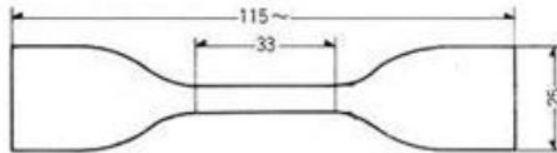
Figure 2.2 A schematic of the specimen for tensile test [11]

2.2.3.3 Tear strength

The rubber vulcanized sheets were cut into tear strength type C (Figure 2.3) shape according to ASTM D624. The sample thickness was 2.00 mm. Tear strength values were obtained by universal testing machine with 500 mm/min crosshead speed. The tear strength conditions were followed by 25 $^{\circ}$C and 50% relative humidity.
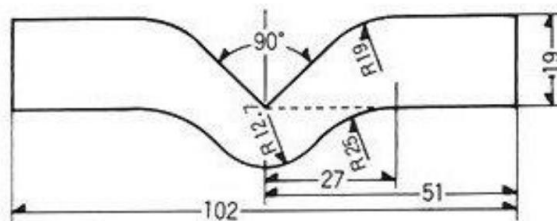
Figure 2.3 A schematic of the specimen for tear test (Die C) [11]

2.2.3.4 Specific gravity

The vulcanized specimen was cut to 2x3 cm and weighed in air and distilled water at standard condition by using specific gravity balancing kit. The specific gravity (SG) were obtained.

2.2.3.5 Crosslink density

Crosslink density was measured by swollen technique. The rubber vulcanizates were cut to 20 x 20 x 2 mm and weighed (m_0). The specimens were kept to swell in close bottles containing toluene at room temperature for 48 h. After completion, the swollen samples were instantly reweighed (m_1) and left for 24 h before aging at 80 $^{\circ}$C for 48 h and weighted again (m_2). The crosslink density of rubber vulcanizate was determined by Flory-Rehner equation [24].

2.3 Modified RFAD as co-activator

RFAD was modified by epoxidation and hydrogenation. The synthetic compounds were used as co-activator in NR and NBR compounds at 2 phr compared with commercial co-activator (stearic acid commercial grade).

2.3.1 The preparation of epoxidized fatty acid distillate (EFAD)

Preheated 50 g RFAD at 70 $^{\circ}$C for 30 min to eliminate the moisture then added to the two-necked round bottom flask attached with thermometer, mechanical stirrer on a hot plate and reflux condenser completed set up. Added about 0.5 mole of HCOOH per 1 mole of RFAD double bond, H_2SO_4 (conc) about 3% w/w of RFAD into the reactor and heated to 55 $^{\circ}$C for 15 min then slowly dropped with constant rate 2 moles of 30% solution of H_2O_2 per 1 mole of RFAD double bond. The addition was completed in 30 min and the reaction was continued for 3 h. After reaction completed, the mixture was dissolved in Et_2O and washed with distill water until pH 7.0 to eliminate free acid. The organic layer was obtained from upper layer. After that, dried the organic layer with anhydrous Na_2SO_4, then filtered. Finally, the residue Et_2O was removed by rotatory evaporator and the yellow wax solid was obtained [28, 29] and analyzed for iodine value, ^{1}H NMR and FT-IR.

2.3.2 The preparation of hydrogenated fatty acid distillate (HFAD).

RFAD 10 g in 50 mL round bottom flask was added hexane. After that, 3%w/w of Pd/C was added to the mixture. The reaction was continued stirring at room temperature for 24 h by balloon filled with H_2. After the reaction completed, Pd/C was filtered off. Finally, hexane was removed by rotatory evaporator. The white powder was obtained as product and analyzed by iodine value, ^{1}H NMR and FT-IR [30, 31].

After characterization, the synthetic co-activators were compounded with NR or NBR as presented in Table 2.1 and properties were tested.

Table 2.1 NR or NBR formulations with different co-activator

Ingredient	Quantity (phr)	
	NR	NBR
Rubber	100	100
Carbon black N330	55	50
Co-activator*	2	2
Zine oxide	5	5
Processing oil	4	4
Sulfur powder	1.8	0.5
TMTD	0.1	1.5
CBS	1.8	1.5

*various STA/RFAD/EFAD/HFAD

2.4 Modified RFAD as processing aid

The RFAD was modified by esterification with selected alcohols (methanol, ethanol, *n*-butanol, 1-hexanol, cyclohexanol and benzyl alcohol). The synthetic compounds were used as processing aid in NR or NBR compounds at 2 phr compared with commercial processing aid (Struktol WB16 and Struktol WB212 for NR and NBR, respectively).

2.4.1 The preparation of fatty acid alkyl esters

The fatty acid alkyl esters were prepared by esterification of RFAD with selected alcohols (methanol, ethanol, *n*-butanol, 1-hexanol, cyclohexanol and benzyl alcohol). The semi solid RFAD was melted into flask at 100 $^{\circ}$C for 30 min to eliminate the moisture. The reaction was started by addition of selected alcohol (3:1 molar ratio of alcohol to RFAD) and H_2SO_4 (conc) (5% w/w of RFAD) to flask for 15 min at 100 $^{\circ}$C with stirring constantly. After that, added RFAD into the mixer and continued reacting for 3 h. The reaction mixer was cooled down, purified by deionize water, extracted with 5% Na_2CO_3, removed the excess alkyl alcohol by column chromatography. The fatty acid alkyl ester as light-yellow liquid product was obtained and analyzed by iodine value, ^{1}H NMR and FT-IR [24, 32].

For the fatty acid methyl ester (FME) and fatty acid cyclohexyl ester (FChE) were further modified by epoxidation and hydrogenation to reduce double bonds in their structures and to improve flow ability.

2.4.2 The preparation of epoxidized fatty acid methyl ester (EFME) or epoxidized fatty acid cyclohexyl ester (EFChE)

The synthesis of EFME and EFChE was started by FME and FChE, respectively. The epoxidized reactions were similar to that in Section 2.3.1. The epoxidized fatty acid alkyl ester as light-yellow liquid product was obtained and analyzed by iodine value, ^{1}H NMR and FT-IR.

2.4.3 The preparation of hydrogenated fatty acid methyl ester (HFME) or hydrogenated fatty acid cyclohexyl ester (HFChE)

The HFME and HFChE was synthesized by HFAD with methanol or cyclohexanol respectively. The stock of HFAD was prepared similar to that in Section 2.3.2 in hexane. The esterification of hydrogenated fatty acid distillate with methanol or cyclohexanol was

carried out according to the method in 2.4.1. The yellow liquid and yellow wax solid of HFME and HFChE were obtained and analyzed for iodine value, ^{1}H NMR and FT-IR.

All synthesized processing aids were compounded with NR or NBR (Table 2.2) and properties were tested.

Table 2.2 NR or NBR formulation with different processing aid

Ingredient	Quantity (phr)	
	NR	NBR
Rubber	100	100
Carbon black N330	55	50
Stearic acid	2	1
Zinc Oxide	5	5
Processing oil	4	4
Processing aid*	2	2
Sulfur powder	1.8	0.5
TMTD	0.1	1.5
CBS	1.8	1.5

* Various Struktol@WB16/FME/FEE/FHE/FChE/FBE/EFChE/HFChE for NR.

Various Struktol@WB212/FME/FEE/FHE/FCHE/FBE/EFME/HFME for NBR.

2.4.4 Study on the optimum amount of processing aid on properties of NR and NBR

The appropriate amount of processing aids for NR and NBR was studied by varying the amount as 0, 2 and 4 phr. NR and NBR formulated with different processing aids contents are given in Table 2.3.

The summarized chart of the utilization and modification of RFAD as co-activators and processing aids are illustrated in Scheme 2.3.

When co is substances for using as co-activator

pa is substances for using as processing aid.

Table 2.3 NR or NBR formulation with different amount of appropriate processing aid

Ingredient	Quantity (phr)	
	NR	NBR
Rubber	100	100
Carbon black N330	55	50
Stearic acid	2	1
Zinc Oxide	5	5
Processing oil	4	4
Processing aid*	0,2,4	0,2,4
Sulfur powder	1.8	0.5
TMTD	0.1	1.5
CBS	1.8	1.5

* Appropriated processing aids from experiment 2.4.3
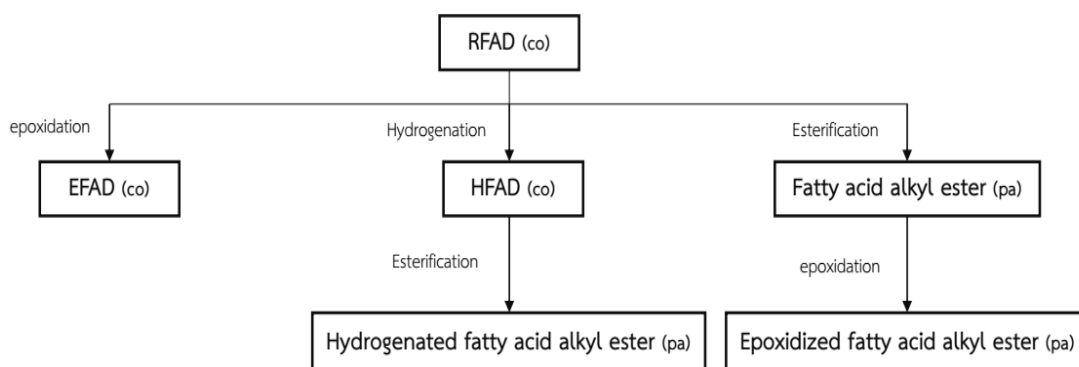
Scheme 2.3 Summarized chart of the utilization and the modification of RFAD

CHAPTER III

RESULTS AND DISCUSSION

3.1 Characterization of rice bran oil fatty acid distillate (RFAD)

RFAD as by-product from refinery process of rice bran oil was pink semi solid at room temperature and melted into light orange liquid at about 40 ^{o}C. The fatty acid composition of RFAD was analyzed as its methyl esters by GC as reported in Table 3.1.

Table 3.1 The composition of RFAD

Fatty acid		%w/w
Saturated fatty acid		
Palmitic acid	16:00	29.2
Stearic acid	18:00	1.7
Unsaturated fatty acid		
Palmitoleic acid	16:01	0.3
Oleic acid	18:01	38.1
Linoleic acid	18:02	28.2
Linolenic acid	18:03	0.9

The main fatty acid compositions of RFAD were unsaturated fatty acids (67.5%: 38.1% oleic acid, 28.2% linoleic acid, 0.9% linolenic acid and 0.3% palmitoleic acid) and 30.9% saturated fatty acids (29.2% palmitic acid and 1.7% stearic acid). The high content of double bonds in RFAD was confirmed by iodine value as reported in Table 3.2.

3.2 Synthesis of co-activators and their uses in NR or NBR

3.2.1 Characterization of epoxidized fatty acid distillate (EFAD) and hydrogenated fatty acid distillate (HFAD)

EFAD and HFAD were prepared by either epoxidation of fatty acid distillate with H_2O_2 or hydrogenation with H_2 in the presence of Pd/C to transform double bond to epoxide and saturated compound analogues with the aim to alter mechanical properties of vulcanized rubbers. The percent yield, iodine value and characteristics of commercial stearic acid (STA), RFAD, EFAD and HFAD are collected in Table 3.2.

Table 3.2 %Yield and iodine value and characteristics of synthesized co-activators

Co-activator	%yield	Iodine value (gl_2/100g)	Characteristics
STA	-	14.72	White powder
RFAD	-	94.55	Pink-orange semi solid
EFAD	88.56	10.82	Yellow wax solid
HFAD	92.72	6.82	White powder

The optimized conditions for EFAD were 1:0.5:2 molar ratio of double bond in fatty acid: HCOOH: H_2O_2 in the presence of 3% w/w H_2SO_4 at 55 ^{o}C for 3 h. In case of HFAD, optimized conditions were performed by hydrogenation with H_2 balloon at room temperature for 24 h in the presence of 3%w/w Pd/C. EFAD and HFAD were successfully synthesized with 89 and 93 % yield, respectively. Neat RFAD showed the highest iodine value (94.55 gl_2/100g) while both synthetic co-activators presented lower values (10.82 and 6.82 gl_2/100g for EFAD and HFAD, respectively). This indicated that the unsaturated portions in fatty acid disappeared either by oxirane ring formation or hydrogenation process. STA, commercial co-activator showed 14.72 gl_2/100g.

Synthesized co-activators were characterized by FT-IR and ^{1}H NMR spectroscopy. The summary of IR spectral assignment is displayed in Table 3.3. The IR spectra of each co-activator (Figures A.1-4) are shown separately in Appendix A.

All co-activators exhibited the C-H stretching peak at 2848 and 2915 cm^{-1} of aliphatic chain in fatty acid, the C=O peak of carboxylic group at 1698-1702 cm^{-1}, C-H bending at 1460-1472 cm^{-1} and C-O stretching of carboxylic group at 1295-1310 cm^{-1}. In addition, the C-O in epoxy ring could be observed at 1073 cm^{-1} [20]. However, the decreasing of double bond in epoxidized and hydrogenated products were not clearly seen in only IR spectra. Therefore, their ^{1}H NMR spectra were recorded to confirm those structures (Figure 3.1).

Table 3.3 IR spectral assignment of synthesized co-activators

Co-activator	IR peak assignment (cm^{-1})				
	C-H stretching, aliphatic	C=O stretching	C-H bending	C-O stretching	C-O alkyl ether
STA	2848, 2915	1698	1462	1295	-
RFAD	2848, 2916	1706	1459	1228	-
EFAD	2848, 2915	1702	1466	1285	1073
HFAD	2848, 2915	1698	1460	1293	-

Figure 3.1 reveals the ^{1}H NMR spectra of commercial STA, RFAD, EFAD and HFAD. The ^{1}H NMR spectrum of RFAD showed three signals of vinylic protons (-C**H**=C**H**-) at δ_H 5.4 ppm, the protons attached to *bis* allylic carbon (-CH=CH-C**H$_2$**-CH=CH-) at δ_H 2.8 ppm and unsaturated protons (-CH=CH-C**H$_2$**-) at δ_H 2.0 ppm. Nonetheless, the disappearance of these protons in EFAD, HFAD and STA confirmed the completion of epoxidation and hydrogenation. These observations were in good agreement with the

results from iodine value (Table 3.2). Moreover, the new signals of -C**H₂**-CH-O- (δ_H 1.4-1.5 ppm) and -C**H**-O-C**H**- (δ_H 2.9-3.5 ppm) were detected instead which were the characteristic signals of EFAD [22, 28].
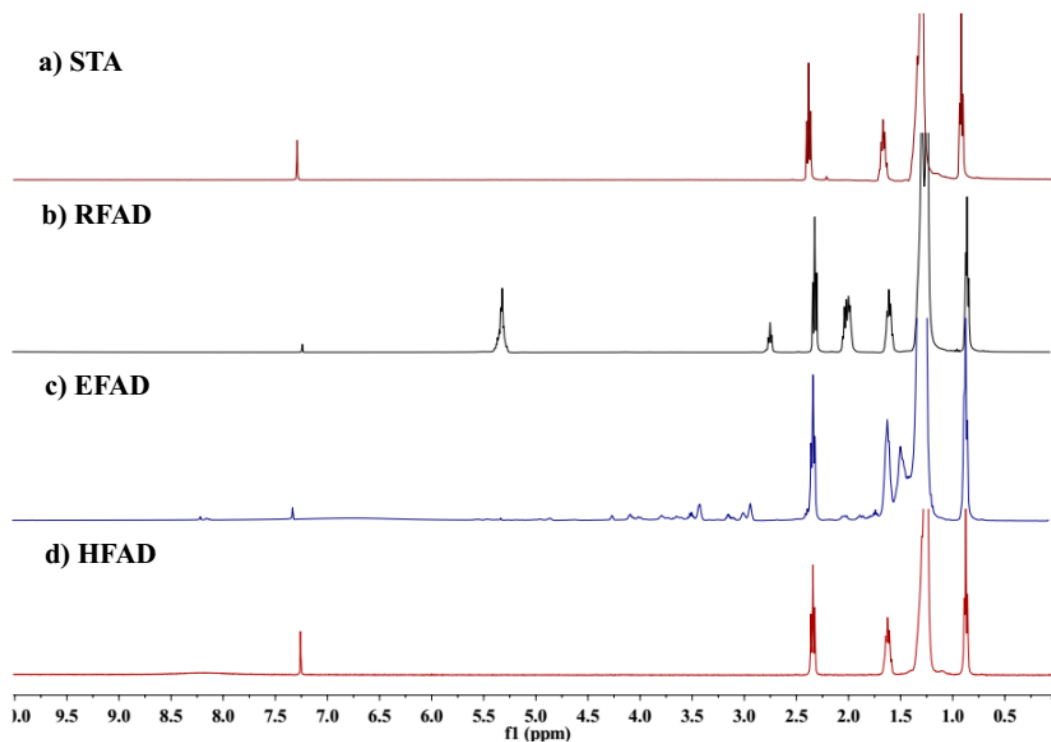
Figure 3.1 The ^{1}H NMR spectra of a) STA b) RFAD, c) EFAD and d) HFAD

3.2.2 Study on the effect of co-activator on NR vulcanizates

The effects of RFAD, EFAD and HFAD on NR compared with commercial STA at 2 phr, prepared by kneader internal mixer, were investigated by determining curing characteristic, Mooney viscosity, mechanical properties and crosslink density.

3.2.2.1 Effect of co-activator on curing characteristics and Mooney viscosity of NR compounds

The curing characteristics and Mooney viscosity of carbon black filled NR compound with various co-activators are displayed in Table 3.4. Various co-activators were compared at 2 phr loading. Both of NR-HFAD and NR-STA compounds exhibited

the highest maximum torque (M_H) indicating the highest elastic modulus which related the highest crosslink density. Moreover, NR-EFAD represented the highest Mooney viscosity (ML(1+4@125°C) at 111.84 MU, this could be explained that the poor lubricity and compatibility between high polar co-activator with NR non-polar matrix. While, Mooney viscosity of NR-STA and NR-HFAD behaved similarly.

The scorch time (t_{s2}) and cure time (t_{c90}) of carbon black filled NR with different co-activators did not obviously change, but t_{c90} of NR-RFAD slightly increased causing from double bond of unsaturated fatty acid retarding vulcanization rate by decreasing the concentration of vulcanizing agent, sulfur or sulfur donor. The NR with EFAD co-activator showed slightly lowest t_{s2} because the decomposition of oxirane ring was directly proportional with vulcanization which led to problem of scorching [22].

Table 3.4 Effect of co-activator on curing characteristics and Mooney viscosity of NR

Curing characteristics	NR-STA	NR-RFAD	NR-EFAD	NR-HFAD
Minimum torque (M_L); lbf-in	13.95	13.44	12.60	16.98
Maximum torque (M_H); lbf-in	33.14	31.89	31.43	32.49
Delta(M_H-M_L); lbf-in	19.19	18.45	18.83	15.15
Scorch time (t_{s2}); min:sec	1:44	1:44	1:38	1:44
Cure time (t_{c90}); min:sec	2:19	2:22	2:15	2:14
ML(1+4@125°C); MU	107.82	109.78	111.84	107.36

3.2.2.2 Effect of co-activator on mechanical properties and crosslink density of NR vulcanizates.

The tensile properties, hardness, tear strength, crosslink density and specific gravity of the carbon black filled NR vulcanizates with different co-activators at 2 phr loading are presented in Table 3.5. Vulcanized NR with RFAD showed tensile strength, modulus and tear strength lower than that with commercial STA at 25.63, 2.22, 4.14,

10.30, 18.05 MPa, and 59.87 kN/m, respectively. This should be affected from double bonds in RFAD which retarded vulcanization by reduction of sulfur and vulcanizing agent. This reason was confirmed by the amount of crosslink density of vulcanized NR-RFAD which was the lowest at 1.853×10^{-4} mol/cm^3 [16]. Meanwhile, NR-EFAD also showed the lowest tensile strength, 200, 300% modulus and tear strength at 24.76, 10.07, 17.41 MPa and 57.35 kN/m, respectively. Although it did not have any effect by double bond, the high polarity of oxirane ring in EFAD had poor compatibility with NR non-polar matrix. The mechanical properties and crosslink density of NR-HFAD were not much different with vulcanized NR-STA due to both co-activators being mainly saturated fatty acids. Therefore, HFAD could be used to replace commercial STA co-activator in NR.

Table 3.5. Effect of co-activator on mechanical properties and crosslink density of NR

Properties	NR-STA	NR-RFAD	NR-EFAD	NR-HFAD
Hardness; shore A	70.3 ± 0.6	68.0	70.0	69.0
Tensile strength; MPa	26.26 ± 0.30	25.63 ± 0.59	24.76 ± 0.56	27.34 ± 0.64
Elongation at break; %	371.8 ± 9.5	396.9 ± 11.9	398.9 ± 8.1	364.7 ± 9.8
50%modulus; MPa	2.67 ± 0.06	2.22 ± 0.05	2.29 ± 0.03	2.38 ± 0.09
100%modulus; MPa	5.13 ± 0.12	4.14 ± 0.12	4.17 ± 0.08	4.75 ± 0.18
200%modulus; MPa	12.47 ± 0.28	10.30 ± 0.32	10.07 ± 0.20	12.87 ± 0.71
300%modulus; MPa	20.76 ± 0.41	18.05 ± 0.65	17.41 ± 0.29	21.88 ± 0.77
Tear strength; kN/m	66.86 ± 1.83	59.87 ± 3.00	57.35 ± 6.80	66.93 ± 6.55
Specific gravity	1.12903	1.12870	1.1288	1.12947
Crosslink density; *10^{-4} mol/cm^3	2.079 ± 0.087	1.853 ± 0.024	1.900 ± 0.059	1.999 ± 0.041

3.2.3 Study on the effect of co-activator on NBR vulcanizates

The effect of RFAD, EFAD and HFAD co-activator with carbon black filled NBR compared with commercial STA at 2 phr, prepared by kneader internal mixer, was investigated by determining curing characteristic, Mooney viscosity, mechanical properties and crosslink density.

3.2.3.1 Effect of co-activator on curing characteristics and Mooney viscosity of NBR compounds

The curing characteristics and Mooney viscosity of carbon black filled NBR with various co-activators compared with commercial STA at 2 phr loading are presented in Table 3.6. The M_L and M_H and delta(M_H-M_L) of NBR compounds were not clearly different. However, the NBR with RFAD showed the highest M_L and M_H which may be due to the semi solid of RFAD as poor lubricating agent in NBR [19]. This result was confirmed by the highest Mooney viscosity (ML(1+4@125°C) of NR-RFAD at 56.54 MU. In addition, the lowest Mooney viscosity that had the positive effect on rheological of rubber compounds was with EFAD as co-activator at 50.32 MU. The high polarity of oxirane ring in EFAD increased the compatibility and acted as lubricating agent. This effect would increase the free volume of NBR chains [25]

The scorch time and cure time of NBR with different co-activators did not obviously change. The t_{s2} of EFAD in NBR was slightly the lowest because of the oxirane ring having the effect like in EFAD in NR. For the NBR-HFAD, the t_{s2} was the highest. This is positive effect to the rubber processing by delaying scorch resistance to allow forming of rubber vulcanizate. The t_{c90} of NBR compound with STA and HFAD showed similarly while NBR with RFAD was the highest. This result illustrated that the double bonds of fatty acid which retarded the vulcanization rate by decreasing the concentration of vulcanizing agent.

Table 3.6 Effect of co-activator on curing characteristics and Mooney viscosity of NBR

Curing characteristics	NBR-STA	NBR-RFAD	NBR-EFAD	NBR-HFAD
Minimum torque (M_L); lbf-in	15.56	17.23	15.36	15.72
Maximum torque (M_H); lbf-in	30.89	32.88	31.32	32.21
Delta(M_H-M_L); lbf-in	15.33	15.65	15.96	16.49
Scorch time (t_{s2}); min:sec	1:57	2:01	1:54	2:24
Cure time (t_{c90}); min:sec	4:18	4:53	4:27	4:20
ML(1+4@125°C); MU	55.07	56.54	50.32	55.80

3.2.3.2 Effect of co-activator on mechanical properties and crosslink density of NBR vulcanizates.

Tensile strength, elongation at break, 50, 100, 200, 300%modulus, tear strength, crosslink density and specific gravity of carbon black filled vulcanized NBR with various co-activators at 2 phr loading are presented in Table 3.7. The NBR with RFAD showed the lowest 50, 100, 200, 300% modulus and tear strength at 2.38, 4.36, 9.39, 15.55 MPa and 33.86 kN/m, respectively. These are related to the lowest crosslink density of NBR-RFAD at 2.679×10^{-4} mol/cm^3, the double bonds in RFAD typically caused decreasing of crosslink density and related to other properties [19]. For EFAD as co-activator, the lowest tensile strength at 23.53 MPa was observed. This might be because of the more plasticizing effect of high polar co-activator with polar NBR rubber. However, the modulus and tear strength of NBR-EFAD were founded at high values indicating high crosslink density at 2.710×10^{-4} mol/cm^3. The oxirane ring in EFAD enhanced the vulcanization by increasing the formation of a highly active sulfurating agent in NBR [25]. In addition, the mechanical properties and crosslink density of vulcanized NBR with HFAD was not much different to the vulcanized NBR-STA.

Table 3.7 Effect of co-activator on mechanical properties and crosslink density of NBR

Properties	NBR-STA	NBR-RFAD	NBR-EFAD	NBR-HFAD
Hardness; shore A	69.0 ± 1.0	68.3 ± 0.6	70.0	68.9 ± 0.6
Tensile strength; MPa	24.54 ± 1.10	24.88 ± 0.53	23.53 ± 1.04	24.25 ± 0.43
Elongation at break; %	434.0 ± 16.1	467.24 ± 14.68	418.14 ± 22.73	416.8 ± 10.3
50%modulus; MPa	2.63 ± 0.13	2.38 ± 0.07	2.40 ± 0.20	2.56 ± 0.06
100%modulus; MPa	4.83 ± 0.27	4.36 ± 0.14	4.47 ± 0.45	4.57 ± 0.16
200%modulus; MPa	10.40 ± 0.36	9.39 ± 0.14	10.05 ± 1.04	10.34 ± 0.47
300%modulus; MPa	16.80 ± 0.40	15.55 ± 0.24	16.55 ± 1.33	17.07 ± 0.30
Tear strength; kN/m	37.44 ± 2.77	33.86 ± 3.84	36.24 ± 2.25	35.56 ± 2.32
Specific gravity	1.17640	1.17670	1.17620	1.17627
Crosslink density; $*10^{-4}$ mol/cm^3	2.764 ± 0.058	2.679 ± 0.013	2.710 ± 0.011	2.751 ± 0.031

3.3 Synthesis of processing aids and their uses in NR or NBR

3.3.1 Characterization of fatty acid alkyl esters

Fatty acid alkyl esters were prepared by esterification of RFAD with selected alcohols (methanol, ethanol, *n*-butanol, 1-hexanol, cyclohexanol and benzyl alcohol). The conditions of esterification were operated at 100 °C for 3 h. %Yield, iodine value and characteristics of fatty acid alkyl esters namely fatty acid methyl ester (FME), fatty acid ethyl ester (FEE), fatty acid butyl ester (FBuE), fatty acid hexyl ester (FHE), fatty acid cyclohexyl ester (FChE) and fatty acid benzyl ester (FBE) are reported in Table 3.8. All fatty acid alkyl esters were obtained in high yield (79-85 %) as light-yellow liquid except for FChE and FBE as yellow viscous liquid. The iodine values of all fatty

acid alkyl esters were in the range of 80-91 gI_2/100g indicating the high double bond proportion.

Table 3.8 %Yield and iodine value of synthetic fatty acid alkyl esters

Synthetic processing aid	%yield	Iodine value (gI_2/100g)	Characteristics
FME	84.42	91.08	Clear light-yellow liquid
FEE	85.07	89.52	Clear light-yellow liquid
FBuE	79.24	81.54	Clear light-yellow liquid
FHE	82.97	82.01	Clear yellow liquid
FChE	81.06	80.80	Yellow viscous liquid
FBE	81.91	89.17	Yellow viscous liquid

The structures of synthesized fatty acid alkyl esters were elucidated by FT-IR and ^{1}H NMR. The FT-IR spectral assignments are displayed in Table 3.9. The spectra of fatty acid alkyl esters (Figures A.5-10) are presented separately in Appendix A.

From Table 3.9, IR spectra of fatty acid alkyl esters illustrated that no absorption band of O-H stretching group of alkyl alcohols was present in raw starting materials at about 3300 cm^{-1}. The absorption bands of the C-H stretching peak at 2853 and 2921 cm^{-1} of aliphatic chain in fatty acid, C-H bending at 1435-1462 cm^{-1} and C-O stretching at 1161-1178 cm^{-1} were detected. Moreover, the major absorption bands of C=O stretching of alkyl ester were displayed at 1731-1742 cm^{-1} which were shifted form 1698 cm^{-1} of C=O stretching of carboxylic acid in RFAD (Table 3.3) [26, 33]. The ^{1}H NMR analysis was carried out to confirm the accomplishment of this synthesis as presented in Figure 3.2.

Table 3.9 IR spectral assignment of synthesized fatty acid alkyl esters

Fatty acid alkyl ester	IR peak assignment (cm^{-1})			
	C-H stretching, aliphatic	C=O stretching	C-H bending	C-O stretching
FME	2922, 2853	1741	1435	1170
FEE	2922, 2853	1737	1463	1178
FBuE	2921, 2853	1737	1462	1174
FHE	2922, 2854	1737	1463	1172
FChE	2922,2853	1732	1453	1177
FBE	2923,2853	1738	1454	1161

For ^{1}H NMR spectra (Figures 3.2a-f), all fatty acid alkyl esters exhibited three methyl protons (-CH$_3$) at δ_H 0.86-0.90 ppm and two methylene protons (-CH$_2$-) at δ_H 1.25-1.30 ppm. The ^{1}H NMR spectrum of FME (Figure 3.2a) reveals three methoxy (-O-CH$_3$) at δ_H 3.55-3.65 ppm. Two oxymethylene protons (-O-CH$_2$-) could be assigned at δ_H 4.00-4.20 ppm of FEE, FBuE and FHE (Figures 3.2b-d). For FChE (Figure 3.2e), the presence of -O-C**H**< proton was detected at δ_H 4.76 ppm whereas for that of FBE (Figure 3.2f), the two protons of -O-C**H$_2$**-CH$_2$-Ph were observed at δ_H 5.20 ppm and aromatic protons could be assigned at δ_H 7.39-7.42 ppm. All synthetic processing aids showed three signals of unsaturation as vinylic protons (-C**H**=C**H**-) at δ_H 5.25-5.41 ppm, protons attached to *bis* allylic carbon (-CH=CH-C**H$_2$**-CH=CH-) at δ_H 2.75-2.82 ppm and allylic protons (-CH=CH-C**H$_2$**-) at δ_H 2.05-2.20 ppm. These ^{1}H NMR spectra were clearly confirmed their identities as fatty acid alkyl esters [24, 33, 34].
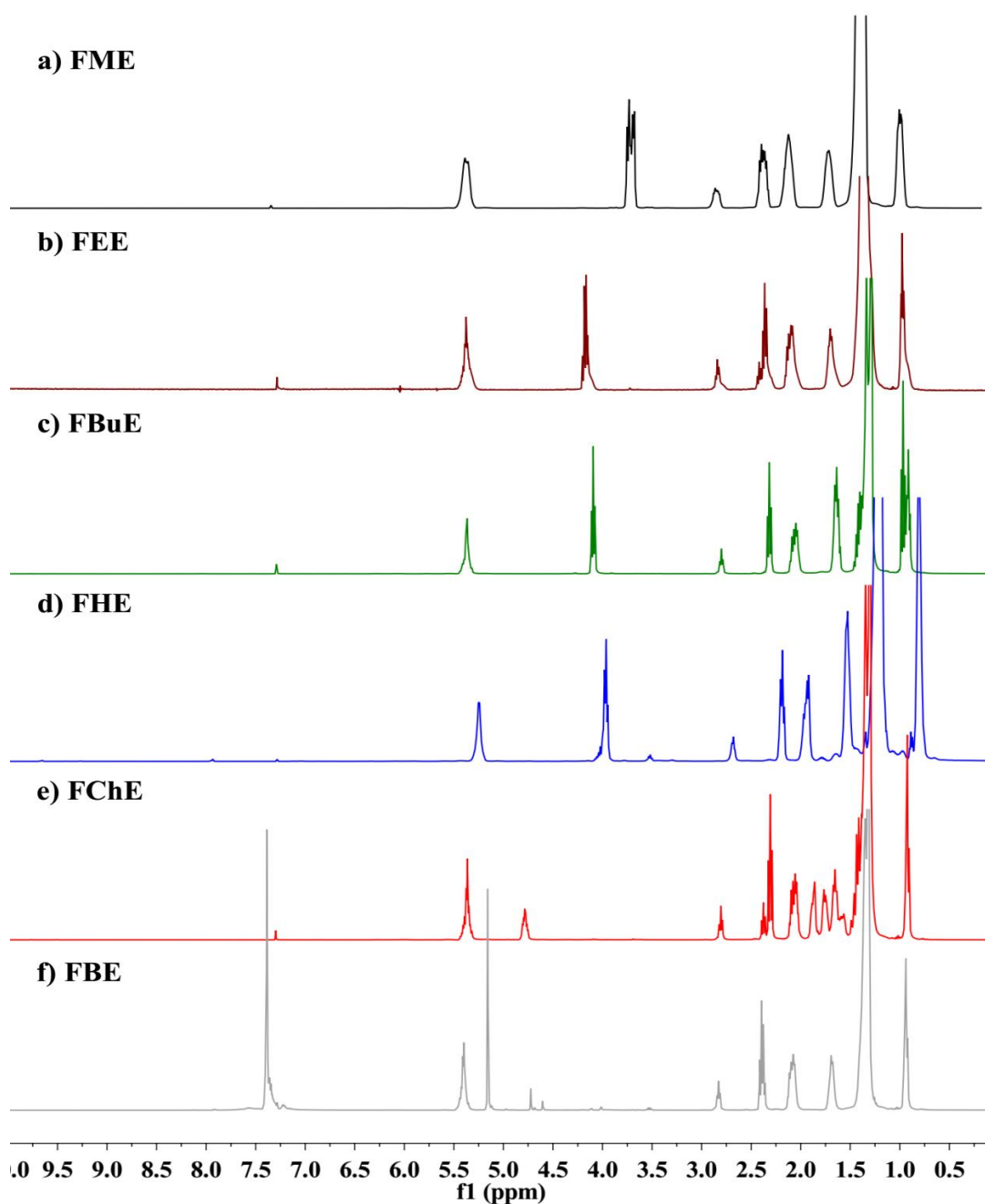
Figure 3.2 The ^{1}H NMR spectra of a) FME, b) FEE, c) FBuE, d) FHE, e) FChE and f) FBE

3.3.2 Characterization of modified fatty acid alkyl esters

FME and FChE were further modified by epoxidation with H_2O_2 and hydrogenation with H_2 in the presence of Pd/C to improve processability and reduce double bond which affected on mechanical properties of vulcanized rubber. The

structures of epoxidized fatty acid methyl ester (EFME), hydrogenated fatty acid methyl ester (HFME), epoxidized fatty acid cyclohexyl ester (EFChE) and hydrogenated fatty acid cyclohexyl ester (HFChE) were characterized by iodine value, FT-IR and ^{1}H NMR. % Yield, iodine value and characteristics of EFME, HFME, EFChE and HFChE are presented in Table 3.10.

Table 3.10 exhibits %yield, iodine value and characteristics of modified FME and HFME. The epoxidized products of both FME and FChE were obtained as yellow and brown viscous liquid, respectively. In the case of hydrogenated products, HFME was obtained as light-yellow liquid while HFChE as yellow wax solid. In case of %yield, all modified fatty acid methyl and cyclohexyl esters were obtained in high yield (83-88 %). The iodine values of EFME, HFME, EFChE and HFChE were low indicating that the epoxidation and hydrogenation reduced double bonds in fatty acid alkyl ester structures. These results were confirmed by FT-IR and ^{1}H NMR spectra in Table 3.11 and Figure 3.3, respectively.

Table 3.10 %Yield and iodine value of EFME, HFME, EFChE and HFChE

Synthetic processing aid	%yield	Iodine value (gI$_2$/100g)	Characteristics
FME	84.42	91.08	Clear light-yellow liquid
EFME	88.03	10.09	Yellow viscous liquid
HFME	86.04	9.13	Clear yellow liquid
FChE	81.06	80.80	Yellow viscous liquid
EFChE	88.24	9.50	Brown viscous liquid
HFChE	83.11	8.39	Yellow wax solid

Table 3.11 displays the spectral assignment of IR spectra of modified fatty acid methyl and cyclohexyl esters products. The absorption band of O-H stretching group

of methyl and cyclohexyl ester were not appeared. All modified fatty acid alkyl esters exhibited the absorption band of C-H stretching peak at 2849-2853 and 2916-2922 cm^{-1} of aliphatic chain of fatty acid, C-H bending at 1435-1453 cm^{-1} and C-O stretching at 1161-1186 cm^{-1}. Moreover, the absorption band of C=O stretching of alkyl ester was visualized at 1702-1742 cm^{-1} which was shifted form 1698 cm^{-1} of C=O stretching vibration of carboxylic acid in RFAD (Table 3.3). For EFME and EFChE, the absorption bands of C-O of epoxy ring at 1067 cm^{-1} were detected. However, the decreasing of double bond in epoxidation and hydrogenation were not clearly seen in only IR spectra. Therefore, ^{1}H NMR analysis was carried out as presented in Figure 3.3.

Table 3.11 IR spectral assignment of modified fatty acid methyl and cyclohexyl esters

Co-activator	IR peak assignment (cm^{-1})				
	C-H stretching, aliphatic	C=O stretching	C-H bending	C-O stretching	C-O alkyl ether
FME	2922, 2853	1741	1435	1168	-
EFME	2922, 2853	1739	1463	1170	1067
HFME	2922, 2852	1742	1435	1168	-
FChE	2922, 2853	1732	1453	1177	-
EFChE	2922, 2853	1731	1455	1177	1067
HFChE	2916, 2849	1702	1462	1186	-

Figure 3.3 shows the ^{1}H NMR spectra of EFME, HFME, EFChE and HFChE which were derived from the epoxidation and hydrogenation of FME and FChE, respectively. Figures 3.3a and 3.3b reveal three methoxy protons (-O-C**H**$_3$) at δ_H 3.55-3.65 ppm of EFME and HFME. On the other hand, Figures 3.3c and 3.3d display the ^{1}H NMR spectra

of EFChE and HFChE, which revealed a proton of -O-C**H**< at δ_H 4.76 ppm of cyclohexyl ester. Moreover, both epoxidized fatty acid alkyl esters showed the presence of epoxy protons in the region of δ_H 2.80-3.20 ppm. Furthermore, all modified fatty acid alkyl esters represented the disappearance or decreasing of double bond signals of vinylic protons (-C**H**=C**H**-) at δ_H 5.4 ppm, protons attached to *bis* allylic carbon (-CH=CH-C**H₂**-CH=CH-) at δ_H 2.8 ppm and allylic protons (-CH=CH-C**H₂**-) at δ_H 2.0 ppm (Figures 3.6a-d). Nonetheless, these protons were disappeared in EFME, HFME, EFChE and HFCHE that confirmed the completion of epoxidation and hydrogenation [28, 35]. These observations were in good agreement with the results from iodine value (Table 3.10).
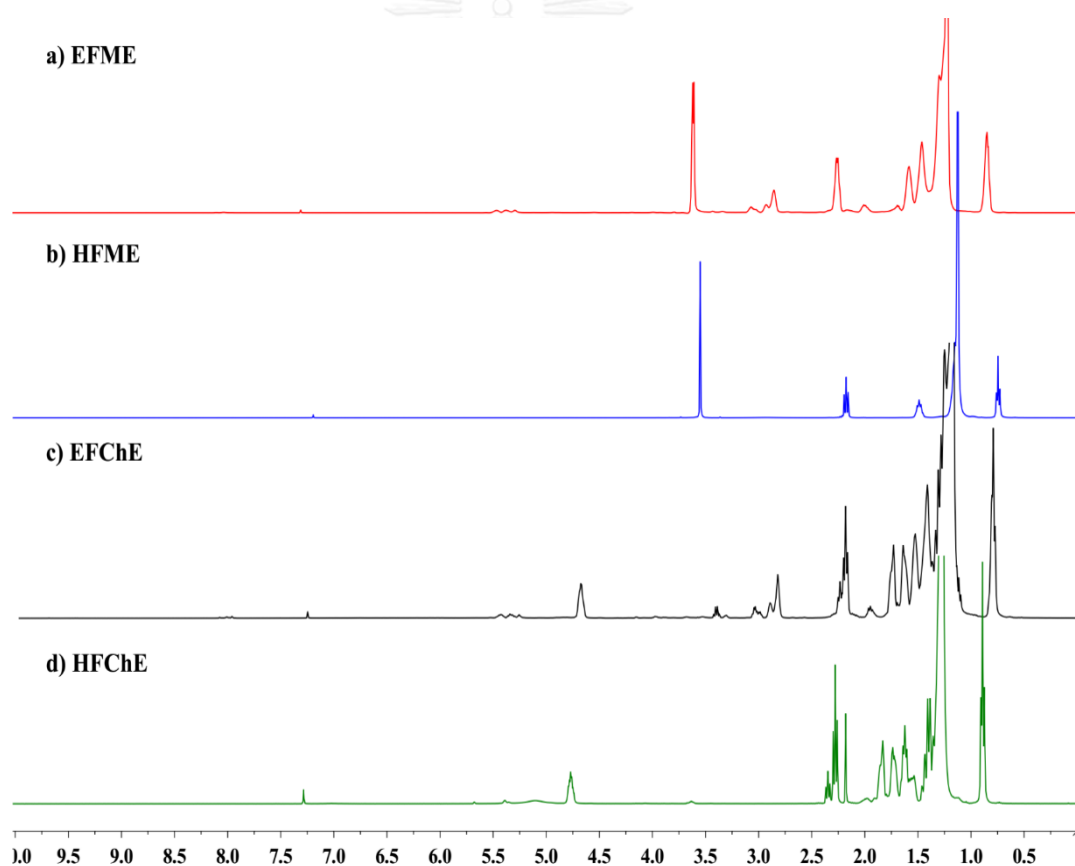
Figure 3.3 The ^{1}H NMR spectra of a) EFME, b) HFME, c) EFChE and d) HFChE

3.3.3 Study on the effects of processing aid on NR compounds

3.3.3.1 Effect of fatty acid alkyl esters as processing aid on the properties of NR compounds

The effect of synthesized fatty acid alkyl esters on the properties of NR compounds at 2 phr was investigated compared that with Struktol WB16, a commercial processing aid. The curing characteristics, Mooney viscosity, spider mold flow ability test and their vulcanizates properties were demonstrated. Moreover, modified FChE, EFChE and HFChE were also compounded with NR and investigated their properties.

3.3.3.1.1 Effect of synthesized processing aid on curing characteristics, Mooney viscosity and spider mold flowability test of NR compounds.

The curing characteristics and Mooney viscosity of compounded NR with various synthesized fatty acid alkyl esters and modified fatty acid cyclohexyl ester are displayed in Table 3.12. The t_{s2} and t_{c90} of compounded NR with all fatty acid alkyl esters (entries 1-7) were slower than that with Struktol WB16 commercial processing aid that cause higher sulfur dilution effect due to interaction between double bond that presented in the fatty acid molecules and sulfur. Therefore, the higher t_{s2} and t_{c90} were observed [24]. In case of FChE and FBuE, t_{s2} was decreased that led to problem of scorching.

The torque difference (delta(M_H-M_L) of all fatty acid alkyl esters were closely similar to commercial processing aid, NR-WB16. While, the M_H of NR with fatty acid alkyl ester except for FME and FBE was increased when compared that with Struktol WB16 indicating high elastic modulus. However, the Mooney viscosity (ML (1+4@125 °C) of NR-FChE revealed the lowest value at 82.97 MU. This result indicated that cyclohexyl ester improved the mixing performance and decreased the consumption of energy due to processing [26]

Table 3.12 Curing characteristics and Mooney viscosity of NR compounded with synthetic processing aid

Entry/Curing characteristic	1	2	3	4	5	6	7	8	9
	NR-WB16	NR-FME	NR-FEE	NR-FBuE	NR-FHE	NR-FChE	NR-FBE	NR-EFChE	NR-HFChE
Minimum torque (M_L); lbf-in	17.86	17.97	19.83	21.74	20.53	22.72	17.49	21.51	19.51
Maximum torque (M_H); lbf-in	32.97	33.97	37.29	37.73	37.84	39.59	32.27	39.77	35.20
Delta(M_H-M_L); lbf-in	15.11	16.00	17.46	15.99	17.31	16.87	14.78	18.26	15.69
Scorch time (t_{s2}); min:sec	1:38	1:47	1:44	1:31	1:38	1:28	1:48	1:48	1:51
Cure time (t_{c90}); min:sec	2:31	2:50	3:03	2:42	3:27	3:03	2:37	3:08	2:38
ML(1+4@125°C); MU	89.12	93.35	96.27	86.22	94.91	82.97	92.56	97.15	97.57

Table 3.12 (entries 6, 8 and 9) shows the curing characteristic and Mooney viscosity of NR-FChE, NR-EFChE and NR-HFChE, respectively. The t_{s2} of NR contained EFChE and HFChE increased when compared that with FChE. This is beneficial to the rubber process. There must be sufficient delay or scorch resistance to allow shaping or forming in the mold. In case of t_{c90}, NR contained EFChE and FChE were similar. While, that of NR-HFChE decreased when compared that with FChE. This might be to the disappeared of unsaturated proportion by hydrogenation with H_2 of HFChE. The M_H and Mooney viscosity of NR-EFChE were significant over values indicating higher elastic modulus when compared with NR-FChE at 2 phr. This could be explained by the fact that the polarity of EFChE was higher than that of NR matrix which could not be incorporated and lubricated between rubber chains. In case of HFChE, high Mooney viscosity was observed. HFChE processing aid with low content of double bond could not brake agglomerated carbon black which increased hard segments and decreased the free volume, leading to high viscosity in NR matrix [24].

The spider mold specimens and their average weight of NR with different fatty acid alkyl esters are displayed in Figures 3.4 (a-g). This test was determined the flowability of rubber compounds by measuring average weight output and observed the details and appearance of spider mold specimen. The spider mold specimen and their average weights of NR-FChE revealed the highest detail with the weight at 5.2845 g related to the lowest Mooney viscosity. The highest detail, completeness and the smoothest surface of spider mold specimen of NR-FChE associated with non-polar processing aid of FChE were high absorbed and dispersed by NR non-polar matrix. This was due to the increment of free volume between NR rubber chain. Moreover, FChE processing aids were decreased the aggregation of carbon black with stearic effect of bulky cyclohexyl ester group and double bond in their structures [24]. Therefore, FChE was the suitable processing aid for carbon black filled NR compound.

$W_{NR\text{-}WB16} = 4.8634$ g

a) NR-WB16

$W_{NR\text{-}FME} = 4.3711$ g

b) NR-FME

$W_{NR\text{-}FEE} = 4.3535$ g

c) NR-FEE

$W_{NR\text{-}FBuE} = 4.5230$ g

d) NR-FBuE

$W_{NR\text{-}FHE} = 4.8992$ g

e) NR-FHE

$W_{NR\text{-}FChE} = 5.2845$ g

f) NR-FChE

$W_{NR\text{-}FBE} = 4.5372$ g

g) NR-FBE

$W_{NR\text{-}EFChE} = 4.4110$ g

h) NR-EFChE

$W_{NR\text{-}HFChE} = 4.8105$ g

i) NR-HFChE

Figure 3.4 Spider mold specimens and their average weight of a) NR-WB16, b) NR-FME, c) NR-FEE, d) NR-FBuE, e) NR-FHE, f) NR-FChE g) NR-FBE, h) NR-EFChE and i) NR-HFChE

For Figures 3.4f, h and i, the spider mold specimens and average weight of NR-FChE, NR-EFChE and NR-HFChE were demonstrated. Spider mold specimens and average weight of NR-FChE were higher than other modified fatty acid cyclohexyl esters. The smooth surface and completeness detail could be observed upon the

addition of FChE in NR spider mold specimen. This result could be confirmed by the lowest Mooney viscosity. In the case of EFChE in compounded NR, the less detail and weight of spider mold specimens resulted from the difference in high polarity between oxirane ring in EFChE with NR matrix. This provided the less dispersion and distribution of processing aid, and the rough surface in spider mold specimens. In case of HFChE, the detail and average weight output were lower than NR-FChE, this result confirmed the effect of double bond on the increment of the dispersion of carbon black in NR matrix which increased the soft segment and flowability in NR-FChE [36]. Therefore, according to Mooney viscosity and spider mold flow ability of NR with fatty acid alkyl esters, FChE disclosed to be the most suitable processing aid for NR compounds.

3.3.3.1.2 Effect of synthesized processing aid on the mechanical properties and crosslink density of vulcanized NR

The mechanical properties and crosslink density of vulcanized NR with different typse of fatty acid alkyl esters and commercial processing aid are summarized in Table 3.13 (entries 1-7). The tensile strength, 50, 100, 200, 300%modulus and tear strength of vulcanized NR-WB16 exhibited the high values at 26.42, 2.74, 5.40, 13.72, 22.95 MPa, and 69.43 kN/m and low elongation at break related to the highest crosslink density, compared that with other processing aid types. However, some properties as tensile strength and 50, 100, 200 and 300% modulus of NR-FEE were higher than NR-WB16 but low tear strength because the high polarity of FEE could not conduct the disperse of carbon black and not incorporated with NR chains as observed from poor Mooney viscosity and spider mold flow ability test. Moreover, the short chain fatty acid alkyl esters as FEE and FME were possible to migrate on the NR surface. For NR-FChE, 50, 100, 200 and 300% modulus and crosslink density showed lower values than NR with commercial processing aid, resulting from the higher effective of plasticizing effect than

those for Struktol WB16, which increased the free volume in rubber matrix. Moreover, FChE consisted of double bond which retarded the amount of crosslink affecting on the improvement of flexibility properties [3].

The mechanical properties of vulcanized NR with modified fatty acid cyclohexyl ester are displayed in Table 3.13 (entries 6, 8 and 9). The comparison of mechanical properties of vulcanized NR with FChE, EFChE and HFChE were not much different. However, tensile strength, 200 and 300%modulus of EFChE and HFChE showed slightly higher than FChE as processing aid although crosslink density of vulcanized NR of both modified FChE were clearly higher than FChE. This may be explained by the double bond in FChE could improve free volume between rubber matrix. Moreover, FChE improved the dispersion and broke the agglomeration of carbon black. This phenomenon was also observed from previous literatures that more double bonds present in fatty acid benzyl ester led to the increment of the lubricity in non-polar rubber [24]

Table 3.13 Mechanical properties and crosslink density of NR vulcanized with various fatty acid alkyl ester as processing aid

Entry/	1	2	3	4	5	6	7	8	9
Mechanical properties	NR-WB16	NR-FME	NR-FEE	NR-FBuE	NR-FHE	NR-FChE	NR-FBE	NR-EFChE	NR-HFChE
Hardness; shore A	69.7 ± 0.58	69.3 ± 0.58	71.0	70.7 ± 0.58	70.0	70.0	71.0	69.7 ± 0.58	69.7 ± 0.58
Tensile strength; MPa	26.42 ± 0.35	26.87 ± 0.38	27.09 ± 0.37	26.66 ± 0.59	25.75 ± 0.22	27.39 ± 0.30	26.78 ± 0.44	27.40 ± 0.36	27.45 ± 0.23
Elongation at break; %	341.9 ± 5.7	348.8 ± 5.9	345.4 ± 5.7	390.9 ± 4.5	388.7 ± 5.1	404.2 ± 7.6	392 ± 5.4	401.2 ± 6.6	397.8 ± 8.6
50%modulus; MPa	2.74 ± 0.04	2.65 ± 0.07	2.82 ± 0.07	2.33 ± 0.07	2.35 ± 0.05	2.38 ± 0.05	2.38 ± 0.04	2.28 ± 0.04	2.28 ± 0.09
100%modulus; MPa	5.40 ± 0.16	5.21 ± 0.16	5.53 ± 0.13	4.48 ± 0.12	4.48 ± 0.12	4.59 ± 0.08	4.65 ± 0.13	4.56 ± 0.06	4.54 ± 0.20
200%modulus; MPa	13.72 ± 0.48	13.46 ± 0.46	13.89 ± 0.17	11.65 ± 0.72	11.09 ± 0.34	11.62 ± 0.16	11.48 ± 0.34	11.90 ± 0.28	11.88 ± 0.32
300%modulus; MPa	22.95 ± 0.53	22.74 ± 0.51	23.22 ± 0.26	19.8 ± 0.59	19.3 ± 0.29	19.98 ± 0.48	19.61 ± 0.58	20.08 ± 0.50	20.19 ± 0.48
Tear strength; kN/m	69.43 ± 4.25	66.86 ± 5.92	60.22 ± 7.04	64.8 ± 3.75	63.62 ± 5.01	61.15 ± 5.92	62.76 ± 2.47	60.75 ± 6.93	64.92 ± 8.57
Specific gravity	1.12857	1.12940	1.12937	1.12767	1.12780	1.12783	1.12752	1.12793	1.12964
Crosslink density; $\times 10^{-4}$ mol/cm^3	1.863 ± 0.013	1.855 ± 0.010	1.856 ± 0.018	1.762 ± 0.024	1.818 ± 0.021	1.742 ± 0.023	1.731 ± 0.028	1.856 ± 0.015	1.797 ± 0.028

3.3.3.2 Effect of the amount of fatty acid cyclohexyl ester as processing aid on the properties of NR compounds

Three different amounts of FChE in NR compound (0, 2 and 4 phr) were examined to search for the optimum concentration in NR compound. The curing characteristics, Mooney viscosity, spider mold flow ability test and their vulcanizate properties of NR with different amount of FChE were demonstrated.

3.3.3.2.1 Effect of the amount of FChE on curing characteristics, Mooney viscosity and spider mold flowability test of NBR compounds.

The curing characteristic and Mooney viscosity of NR compounds with different amounts of FChE at 0, 2 and 4 phr are summarized in Table 3.14.

Table 3.14 Curing characteristics and Mooney viscosity of NR compounded with different amount of FChE

Entry/	1	2	3
Curing characteristic	NR-noPa	NR-2FChE	NR-4FChE
Minimum torque (M_L); lbf-in	13.95	22.72	16.3
Maximum torque (H_H); lbf-in	33.14	39.59	30.02
Delta(MH-ML); ibf-in	19.19	16.87	13.72
Scorch time (t_{s2}); min:sec	1:44	1:28	2:07
Cure time (t_{c90}); min:sec	2:19	3:03	4:35
ML(1+4@125°C); MU	107.82	82.97	83.21

It can be seen that the cure time of NR with processing aids were slower than without, and the increasing amount of processing aid also increased cure time. This effect should be derived from plasticizing effect which increased the free volume in NR matrix. Moreover, FChE contained high content of double bond was sensitive to

decrease the concentration of sulfur or sulfur donor crosslinking agents. The torque difference (delta(M_H-M_L)) was decreased with the increasing amount of FChE indicating the decreasing of crosslink density of those vulcanizates. In addition, the Mooney viscosity of NR with 4 phr (Table 3.14, entry 3) of FChE was lower than NR without processing aid, but slightly higher at 2 phr. This should be plasticizing effect which increased soft segment and free volume and easily to slip between polymer chain when processing [3]

The spider mold specimens and average weight output of NR with various amounts of FChE at 0, 2 and 4 phr are shown in Figure 3.5.

$W_{NR-noPa}$ = 3.7298 g $W_{NR-2FChE}$ = 5.2845 g $W_{NR-4FChE}$ = 6.3423 g

a) NR-noPa   **b) NR-2FChE**   **c) NR-4FChE**

Figure 3.5 Spider mold specimens and their average weight of a) NR-noPa, b) NR-2FChE and c) NR-4FChE

The spider mold specimens of NR with 4 phr of FChE (Figure 3.5c) illustrated the highest detail, completeness, and their average weight than 2 and 0 phr (Figures 3.5a and 3.5b) at 3.7298, 5.2845 and 6.3423 g, respectively. This indicated the highest flow ability of NR compounds although the higher Mooney viscosity was observed than that at 2 phr. The increased concentration of FChE was due to the free volume in NR matrix, which was direct improved the flowability of rubber compound by acting as internal plasticizer.

3.3.3.2.2 Effect of the amount of FChE on the mechanical properties and crosslink density of vulcanized NR

The mechanical properties of vulcanized NR with and without FChE are summarized in Table 3.15. The mechanical properties of vulcanized NR with and without FChE are summarized in Table 3.15. The addition and increasing amount of FChE into NR compound resulted in the decrease of the hardness, tensile strength, 50, 100, 200, 300% modulus, tear strength and specific gravity but increased the elongation at break. Those mechanical properties were relative to the amount of crosslink density of vulcanized NR. Therefore, the mechanical properties and crosslink density of vulcanized NR with 4 phr of FChE were the lowest. High amount of processing aid affected on the increment of free volume in NR matrix. Moreover, high double bond content of FChE had a possibility to decrease the crosslink density of vulcanized NR.

Table 3.15 Mechanical properties and crosslink density of vulcanized NR with different amount of FChE

Entry/ Mechanical properties	1 NR-noPa	2 NR-2FChE	3 NR-4FChE
Hardness; shore A	70.3 ± 0.57	70.0	68.3 ± 0.58
Tensile strength; MPa	26.26 ± 0.30	27.39 ± 0.30	25.89 ± 0.38
Elongation at break; %	371.8 ± 9.5	404.2 ± 7.6	418.9 ± 4.1
50%modulus; MPa	2.67 ± 0.06	2.38 ± 0.05	1.81 ± 0.06
100%modulus; MPa	5.13 ± 0.12	4.59 ± 0.08	3.59 ± 0.14
200%modulus; MPa	12.47 ± 0.28	11.62 ± 0.16	9.68 ± 0.30
300%modulus; MPa	20.76 ± 0.41	19.98 ± 0.48	17.36 ± 0.30
Tear strength; kN/m	66.86 ± 1.83	61.15 ± 5.92	59.21 ± 5.48
Specific gravity	1.12903	1.12783	1.12053
Crosslink density; $*10^{-4}$ mol/cm^3	2.079 ± 0.087	1.742 ± 0.023	1.64 ± 0.035

3.3.4 Study on the effect of processing aids on NBR compounds

3.3.4.1 Effect of fatty acid alkyl esters as processing aid on properties of NBR compounds

The effect of synthesized fatty acid alkyl esters with NBR compounds at 2 phr was examined compared with Struktol WB212 commercial processing aid. The curing characteristics, Mooney viscosity, spider mold flow ability test, mechanical properties and crosslink density were determined. Moreover, the further modification to reduce double bonds of FME by epoxidation and hydrogenation (EFME and HFME) were conducted and used to compound with NBR, and investigated the properties of blended products.

3.3.4.1.1 Effect of synthesized processing aid on curing characteristics, Mooney viscosity and spider mold flowability test of NBR compounds.

The curing characteristics and Mooney viscosity of compounded NBR with different fatty acid alkyl esters are summarized in Table 3.16. The t_{c90} of NBR with all types of fatty acid alkyl esters except for FChE were faster than that of Struktol WB212 probably because fatty acid alkyl esters could undergo reversed hydrolysis to fatty acids. The cure activator in sulfur vulcanization system could be possible to react with ZnO to form zinc stearate by dehydration. Zinc stearate then reacted with sulfur, cure accelerator or sulfur donor accelerator to form zinc complex. This complex accelerated the vulcanization reaction so that cure time became lower [18]. In addition, the Mooney viscosity, ML(1+4@125°C) of NBR with FME, FEE and FBE (Table 3.16, entries 2, 3 and 7) displayed lower than that with commercial processing aid at 47.73, 47.26 and 45.45 MU, respectively. This result indicated the low M_H values of these compounds which were suitable and greater to replace commercial processing aid for NBR. The torque difference of NBR-WB 212 exhibited the highest indicated the highest crosslink density.

Table 3.16 Curing characteristics and Mooney viscosity of NBR compounded with synthetic processing aid

Entry/ Curing characteristic	1 NBR-WB212	2 NBR-FME	3 NBR-FEE	4 NBR-FBuE	5 NBR-FHE	6 NBR-FChE	7 NBR-FBE	8 NBR-EFME	9 NBR-HFME
Minimum torque (M_L); lbf-in	13.68	12.69	13.29	15.28	18.52	15.25	11.72	12.73	15.95
Maximum torque (H_H); lbf-in	29.16	27.34	28.26	30.45	35.16	30.43	24.8	27.65	31.33
Delta(M_H-M_L); lbf-in	15.48	14.65	14.97	15.17	16.64	15.18	13.08	14.92	15.48
Scorch time (t_{s2}); min:sec	2:01	2:01	2:07	2:04	2:04	2:04	2:07	1:57	1:54
Cure time (t_{c90}); min:sec	5:04	4:30	4:14	4:44	4:49	5:34	4:05	3:47	3:49
ML(1+4@125°C); MU	50.28	47.73	47.26	50.39	55.43	55.22	45.45	43.18	53.23

Table 3.16 (entries 2, 8 and 9) shows the curing characteristics and Mooney viscosity of compounded NR with FME and modified fatty acid methyl esters (EFME and HFME), respectively. The t_{c90} of both EFME and HFME in compounded NR were lower than that with FME. This is affected from decreasing of double bond by epoxidation and hydrogenation reaction. Moreover, the oxirane ring in EFME enhanced soluble of sulfur in NBE matrix and also increased the formation of a highly active sulfurating agent [37]. The Mooney viscosity, ML(1+4@125°C) of EFME (Table 3.16, entry 8) shows the lowest value at 43.18 MU. The high polarity of oxirane group and methyl ester in fatty acid chain led to flexibility and more compatible with high polarity of acrylonitrile group in NBR chain by increasing the free volume between those rubber chains [25].

The spider mold flow specimens and their average weight of NBR with different processing aids are shown in Figures 3.6

For Figures 3.6a-g, the spider mold specimens and their average weights of NBR with fatty acid alkyl esters compared with Struktol WB212 at 2 phr were presented. The spider mold specimens of NBR contained FME, FEE and FBE (Figures 3.8b, c and g) showed the higher detail and completeness than commercial processing aid. Moreover, the spider mold average weight output of FME, FEE and FBE were observed in the same trend at 6.7507, 6.5745 and 6.6117 g, respectively. This might be that the high polarity of short alkyl chain for FME and FEE or high steric effect of aromatic bulky group in FBE had more compatibility with acrylonitrile group of NBR. While the fatty acid chain could be easily blended with butadiene part. However, the spider mold specimens and their average weight of FME showed better than others. Therefore, FME was suitable processing aid for NBR compounds.

$W_{NBR-WB212}$ = 6.4768 g

a) NBR-WB212

$W_{NBR-FME}$ = 6.7507 g

b) NBR-FME

$W_{NBR-FEE}$ = 6.5747 g

c) NBR-FEE

$W_{NBR-FBuE}$ = 6.1871 g

d) NBR-FBuE

$W_{NBR-FHE}$ = 6.0297 g

e) NBR-FHE

$W_{NBR-FChE}$ = 6.1041 g

f) NBR-FChE

$W_{NBR-FBE}$ = 6.6117 g

g) NBR-FBE

$W_{NBR-EFME}$ = 6.9513 g

h) NBR-EFME

$W_{NBR-HFME}$ = 6.6611g

i) NBR-HFME

Figure 3.6 Spider mold specimens and their average weight of a) NBR-WB212, b) NBR-FME, c) NBR-FEE, d) NBR-FBuE, e) NBR-FHE, f) NBR-FChE g) NBR-FBE, h) NBR-EFME and i) NBR-HFME

The spider mold specimens and average weight of NBR-FME, NBR-EFME and NBR-HFME are shown in Figures 3.6b, h and i, respectively. For the spider mold flow ability test, NBR with EFME displayed the highest flowability which measured by spider mold flow tester. The average weight output of spider mold specimens of NBR-EFME being the highest at 6.9513 g indicated the lowest Mooney viscosity. It was clear that the oxirane ring in EFME improved the compatibility and lubricity of EFME with NBR matrix which increased the free volume between NBR chain. The high polarity of oxirane ring could interact properly with the carbon black surface and acrylonitrile group, which consisted of active polar group while non-polar fatty acid chain interacted with butadiene group [5]. Therefore, EFME showed the greater lubricity than FME in NBR compounds.

3.3.4.1.2 Effect of synthesized processing aid on the mechanical properties and crosslink density of vulcanized NBR

The mechanical properties and crosslink density of NBR with different fatty acid alkyl esters were compared that with Struktol WB212 and summarized in Table 3.17 (entries 1-7). The tensile strength: 50, 100, 200, 300%modulus and tear strength of NBR with FME, FEE and FBE were rather lower than NBR-WB212. This may be due to the effect of better plasticizing which affected on the crosslink density and related to their low mechanical properties. The double bonds in fatty acid were affected to lower the amount of crosslink density by decreasing the concentration of vulcanizing agent. For long chain fatty acid alkyl esters as FBuE, FHE and FChE (entries 4, 5 and 6), the mechanical properties as 50, 100, 200 and 300%modulus were higher than others. That was because low polar processing aids were incompatible with NBR matrix. This result confirmed by the lowest tear strength was obtained at 38.64, 34.45 and 39.39 for FBuE, FHE and FChE, respectively. The low tear strength implied the generated agglomeration of carbon black in NBR matrix, which was initiated the defect when tested.

Table 3.17 Mechanical properties and crosslink density of NBR with various synthetics processing aid

Entry/	1	2	3	4	5	6	7	8	9
Mechanical properties	NBR-WB212	NBR-FME	NBR-FEE	NBR-FBuE	NBR-FHE	NBR-FChE	NBR-FBE	NBR-EFME	NBR-HFME
Hardness; shore A	70.0	68.0	68.7 ± 0.6	69.0	69.0	69.0	68.3 ± 0.6	70.0	69.0
Tensile strength; MPa	25.44 ± 1.30	24.00 ± 1.11	24.17 ± 0.35	24.06 ± 0.80	23.93 ± 0.35	24.39 ± 0.23	23.98 ± 1.06	24.12 ± 0.75	24.28 ± 0.66
Elongation at break; %	431.3 ± 17.3	440.6 ± 20.6	440.7 ± 6.1	418.9 ± 18.4	431.1 ± 6.2	422.9 ± 9.5	408.6 ± 10.3	422.7 ± 7.2	425.8 ± 15.9
50%modulus; MPa	2.35 ± 0.06	2.33 ± 0.07	2.17 ± 0.10	2.66 ± 0.26	2.23 ± 0.06	2.80 ± 0.23	2.21 ± 0.03	2.32 ± 0.09	2.49 ± 0.09
100%modulus; MPa	4.26 ± 0.15	4.30 ± 0.16	3.95 ± 0.25	4.92 ± 0.31	4.17 ± 0.10	5.1 ± 0.25	4.02 ± 0.08	4.29 ± 0.19	4.60 ± 0.16
200%modulus; MPa	10.34 ± 0.09	9.81 ± 0.20	9.46 ± 0.48	10.86 ± 0.30	9.57 ± 0.18	10.91 ± 0.32	9.93 ± 0.32	10.14 ± 0.30	10.32 ± 0.25
300%modulus; MPa	17.11 ± 0.05	15.84 ± 0.21	15.71 ± 0.53	17.13 ± 0.30	16.18 ± 0.22	17.16 ± 0.36	16.86 ± 0.48	16.55 ± 0.34	16.67 ± 0.26
Tear strength; kN/m	48.58 ± 5.49	41.68 ± 0.55	41.78 ± 4.43	38.64 ± 1.03	34.45 ± 4.31	39.39 ± 3.30	45.5 ± 2.04	43.21 ± 3.07	41.81 ± 3.89
Specific gravity	1.17480	1.17307	1.17520	1.17350	1.17320	1.17590	1.17367	1.72733	1.17300
Crosslink density; $*10^{-4}$ mol/cm^3	2.679 ± 0.01	2.571 ± 0.04	2.485 ± 0.03	2.525 ± 0.04	2.563 ± 0.01	2.501 ± 0.03	2.48 ± 0.01	2.605 ± 0.01	2.673 ± 0.03

For Table 3.17 (entries 2, 8 and 9), the mechanical properties and crosslink density of NBR with EFME and HFME were summarized and compared with unmodified FME. Tensile strength, modulus and tear strength of NBR with EFME and HFME were slightly higher than NBR-FME. Moreover, it was observed that the crosslink density of both modified FME were also increased. This implied that the reducing of double bond of fatty acid could improve the tensile strength, modulus and crosslink density of vulcanized NBR.

According to curing characteristics, Mooney viscosity, spider mold flow ability, mechanical properties and crosslink density, EFME was the most suitable processing aid for NBR due to high lubricity effect and the slightest negative impact to mechanical properties and crosslink density.

3.3.4.2 Effect of the amount of epoxidized fatty acid methyl ester as processing aid on the properties of NBR compounds

The effect of the amount of EFME at 0.2 and 4 phr in NBR compound was examined to observe the optimum concentration on NBR compound. The curing characteristics, Mooney viscosity, spider mold flow ability test, physical properties and crosslink density were determined.

3.3.4.2.1 Effect of the amount of EFME on curing characteristics, Mooney viscosity and spider mold flowability test of NBR compounds.

The effect of the amount of EFME with NBR compound on curing characteristic and Mooney viscosity are summarized in Table 3.18. The t_{c90} of NBR compound with processing aid was slower than without. The increasing amount of EFME from 2 to 4 phr was also increased the cure time. This was affected from plasticizing effect which increased the free volume in NBR matrix [20]. Moreover, the scorch time of NBR with

4 phr of EFME was found to be increased which was a positive effect in rubber process. There must be sufficient delay scorch resistance to allow shaping or forming in the mold. For Mooney viscosity, NBR with 2 phr of EFME presented the lowest viscosity. However, this result was confirmed by spider mold flow ability.

Table 3.18 Curing characteristics and Mooney viscosity of NBR with different amount of EFME

Entry/	1	2	3
Curing characteristic	NBR-noPa	NBR-2EFME	NBR-4EFME
Minimum torque (M_L); lbf-in	18.57	12.73	15.14
Maximum torque (H_H); lbf-in	30.70	27.65	23.68
Delta(M_H-M_L); lbf-in	12.13	14.92	8.54
Scorch time (t_{s2}); min:sec	1:57	1:57	3:19
Cure time (t_{c90}); min:sec	3:28	3:47	6:08
ML(1+4@125°C); MU	56.99	43.18	47.23

The effect of the concentration of EFME compounded with NBR on spider mold specimens and their average weight are displayed in Figure 3.7. The spider mold specimens and their average weight of NBR with 2 phr of EFME (Figure 3.7b) exhibited the highest detail and their average weight output at 6.9513 g, which was related with Mooney viscosity. Therefore, 2 phr of EFME was optimized amount of processing aid for NBR compounding.
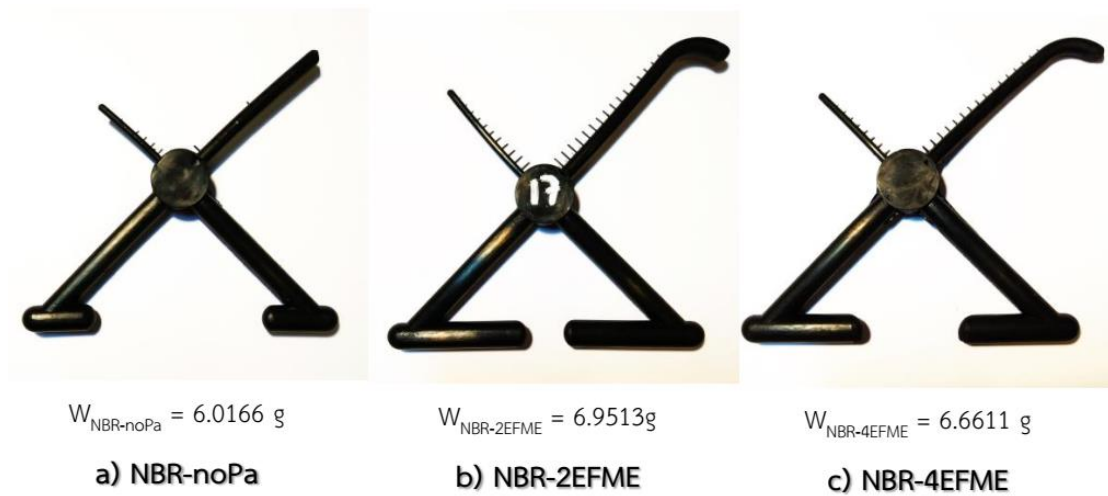
$W_{NBR-noPa} = 6.0166$ g $\quad\quad W_{NBR-2EFME} = 6.9513$ g $\quad\quad W_{NBR-4EFME} = 6.6611$ g

a) NBR-noPa **b) NBR-2EFME** **c) NBR-4EFME**

Figure 3. 7 Spider mold specimens and their average weight of a) NBR- noPa, b) NBR-2EFME and c) NBR-4EFME

3.3.4.2.2 Effect of the amount of EFME on the mechanical properties and crosslink density of vulcanized NBR

The results of mechanical properties and crosslink density of vulcanized NBR with increasing the concentration of EFME at 0, 2 and 4 phr are summarized in Table 3.19. The addition of EFME into NBR compounds decreased the tensile strength, 50, 100, 200, and 300%modulus. The 4 phr loading of EFME displayed the lowest crosslink density which affected to other related properties as hardness, tensile strength, 50, 100, 200, 300% modulus and tear strength. While elongation at break at 4 phr loading revealed the highest. This result indicated that the increasing of processing aid affected on decreasing of mechanical properties.

Table 3. 19 Mechanical properties and crosslink density of vulcanized NBR with different amount of EFME

Entry/ Mechanical properties	1 NBR-noPa	2 NBR-EFME	3 NBR-4EFME
Hardness; shore A	70.0	70.0	67.0
Tensile strength; MPa	24.61 ± 0.46	24.12 ± 0.75	23.51 ± 0.92
Elongation at break; %	406.4 ± 8.5	422.7 ± 7.2	455.02 ± 21.0
50%modulus; MPa	2.71 ± 0.05	2.32 ± 0.09	2.05 ± 0.07
100%modulus; MPa	5.02 ± 0.07	4.29 ± 0.19	3.64 ± 0.20
200%modulus; MPa	11.34 ± 0.08	10.14 ± 0.30	8.64 ± 0.41
300%modulus; MPa	17.99 ± 0.07	16.55 ± 0.34	14.82 ± 0.54
Tear strength; kN/m	36.52 ± 3.81	43.21 ± 3.07	39.33 ± 3.93
Specific gravity	1.17867	1.72733	1.17013
Crosslink density; $*10^{-4}$ mol/cm^3	3.341 ± 0.12	2.605 ± 0.01	2.458 ± 0.06

CHAPTER IV

CONCLUSION

The aim of this research was to utilize RFAD for two purposes as co-activator and processing aid for NR and NBR compounds. Those synthesized additives were carried out fruitfully and well characterized by FT-IR, ^{1}H NMR spectroscopy and iodine values. Both synthesized products were further compounded with NR and NBR compared with commercial additive used. Curing characteristics, Mooney viscosity, spider mold flowability, mechanical properties and crosslink density were investigated and compared.

4.1 Utilization of RFAD as co-activators

The synthesized co-activators were prepared by epoxidation and hydrogenation in high yield. Their structures were confirmed by IR, ^{1}H NMR and iodine values indicating the presence of less double bonds. The use of RFAD and synthesized co-activators (EFAD and HFAD) compared with commercial co-activator in NR and NBR compounds was performed, RFAD was retarded the vulcanization rate and slightly decreased crosslink density which related to mechanical properties in both NR and NBR. For EFAD, the processability in NBR compound was improved, but could not incorporate in NR. Vulcanized properties and crosslink density of NR or NBR with HFAD were similar that with STA commercial co-activator.

4.2 Utilization of RFAD as processing aids

The synthesized processing aids were prepared by esterification of RFAD with selected alcohol (methanol, ethanol, *n*-butanol, 1-hexanol, cyclohexanol and benzyl alcohol). For the appropriate fatty acid alkyl ester for either NR or NBR, further

modification by epoxidation and hydrogenation were conducted to improve the lubricating property. These synthesized processing aids were compounded with NR and NBR and compared with commercial processing aid.

For NR compounds, the addition of FChE at 2 phr loading displayed the lowest Mooney viscosity and the highest flowability compared with other processing aids. However, the mechanical properties and crosslink density of NR-FChE were slightly lower than those of NR-WB16. Moreover, the increasing of FChE concentrations improved the flowability of NR compound. Therefore, FChE was possible to replace the commercial processing aid in NR compounds.

For NBR compounds, the addition of EFME illustrated the lowest Mooney viscosity and the highest flowability compared with other processing aids. EFME was improved the curing characteristic acting as co-activator to generate vulcanization rate. However, mechanical properties of NBR-EFME were slightly lower than commercial processing aid at equal concentration. The optimum concentration of EFME was observed at 2 phr with the highest flowability.

4.3 Suggestions for future works

This research has developed a new processing aid from RFAD for NR or NBR compound. The outcome of flowability displayed that FChE and EFME were possible to replace commercial processing aid for NR or NBR, respectively. The future work should be focused on other properties of NR and NBR containing those processing aid as blooming, morphology, heat aging properties, oil resistance, compression set and dynamic mechanical properties. Those obtained results will confirm the appropriability and prevent other negative impact from those processing aid in NR or NBR.

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APPENDIX A

IR SPECTRA OF SYNTHETIC PRODUCTS

1.1 IR spectra of co-activator
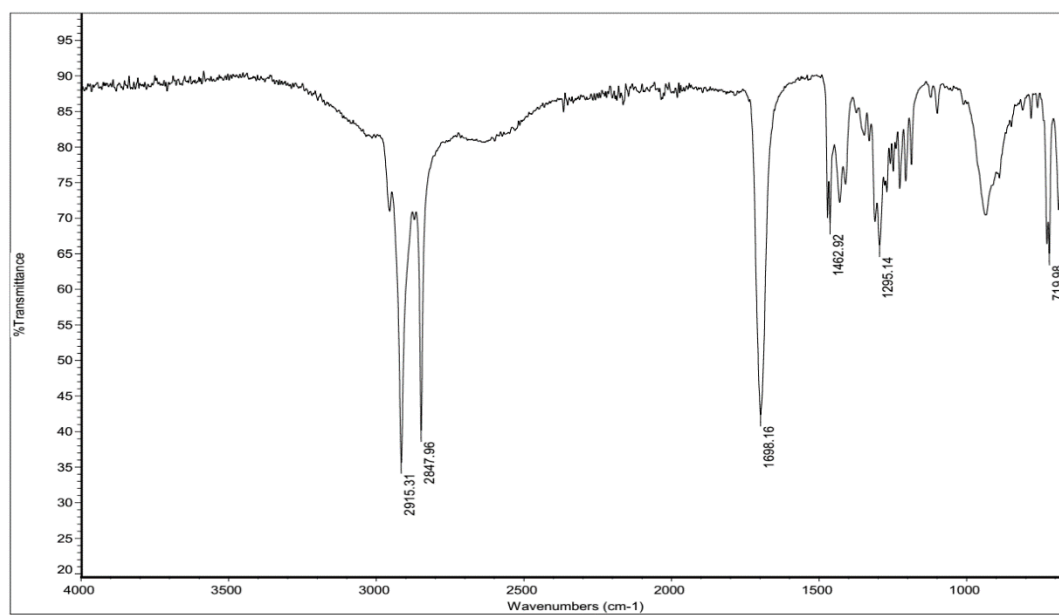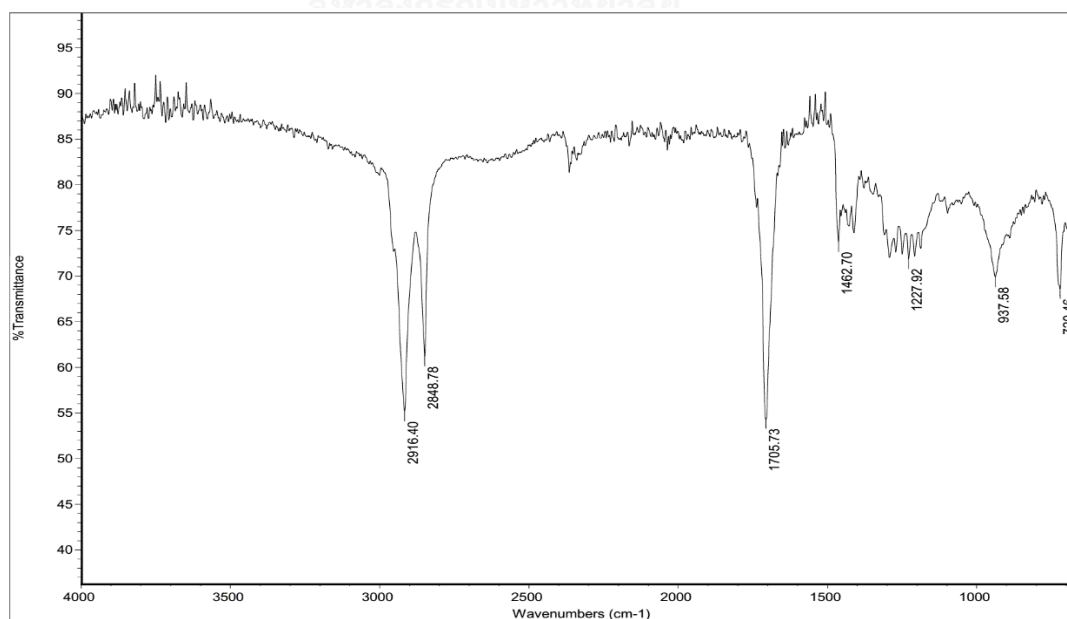

Figure A.1 IR spectra of stearic acid (STA)

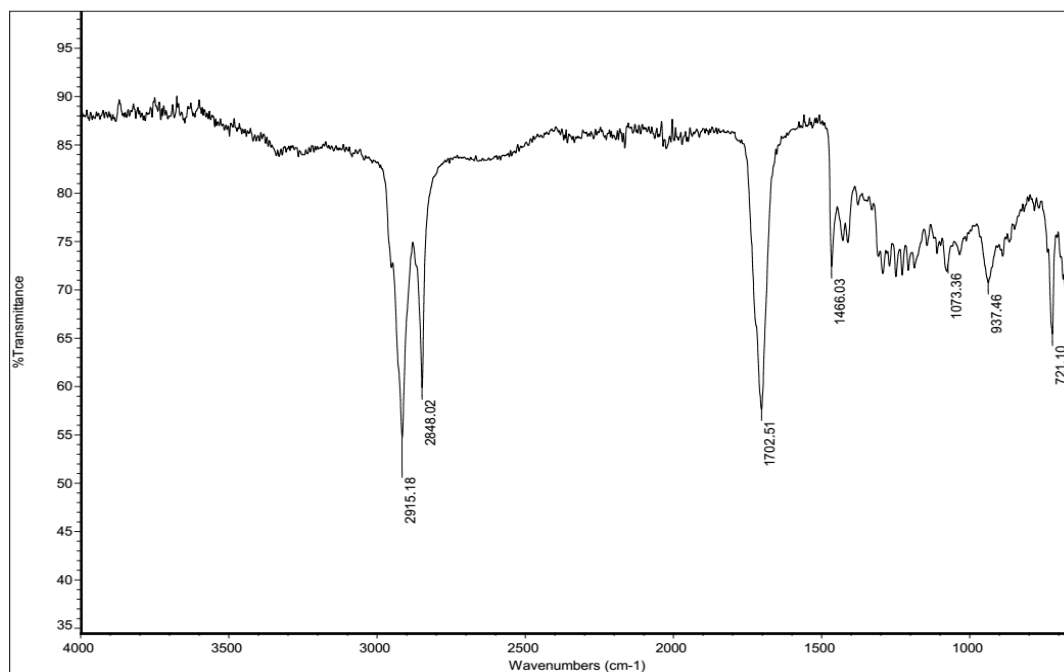**Figure A.2** IR spectra of rice bran oil fatty acid distillate (RFAD)

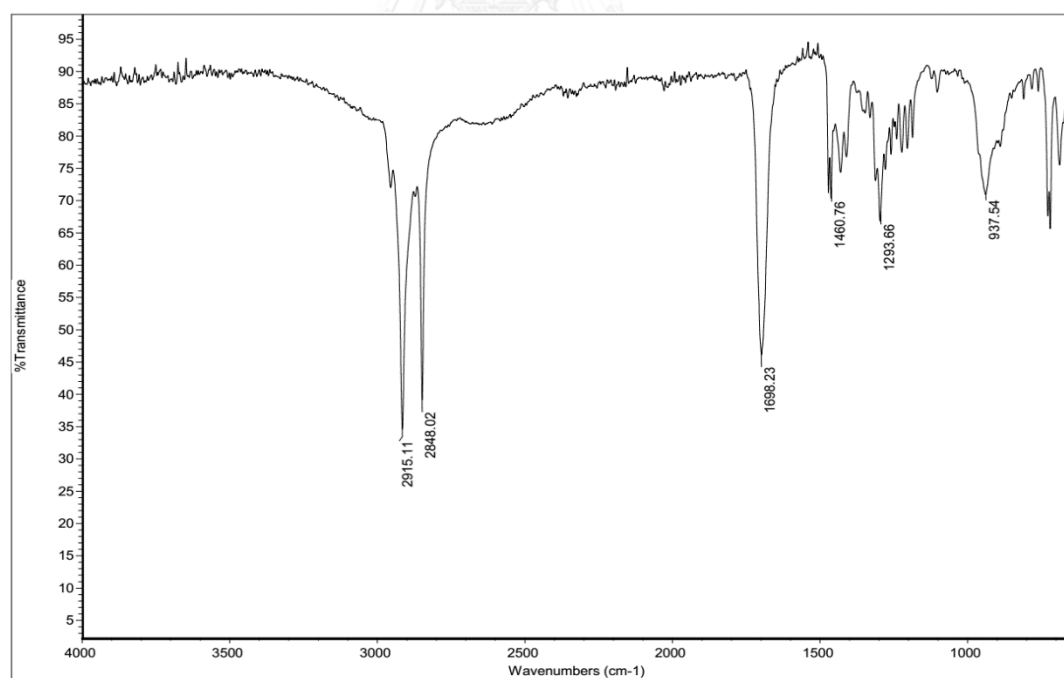**Figure A.3** IR spectra of epoxidized fatty acid distillate (EFAD**)**

Figure A.4 IR spectra of hydrogenated fatty acid distillate (HFAD
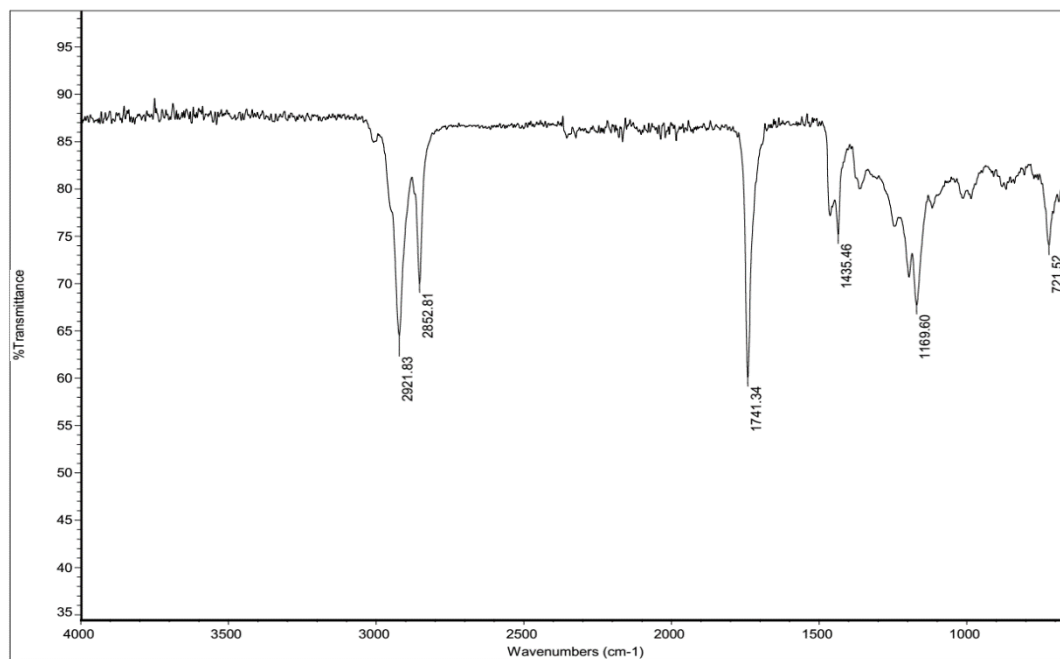
1.2 IR spectra of synthesized processing aid
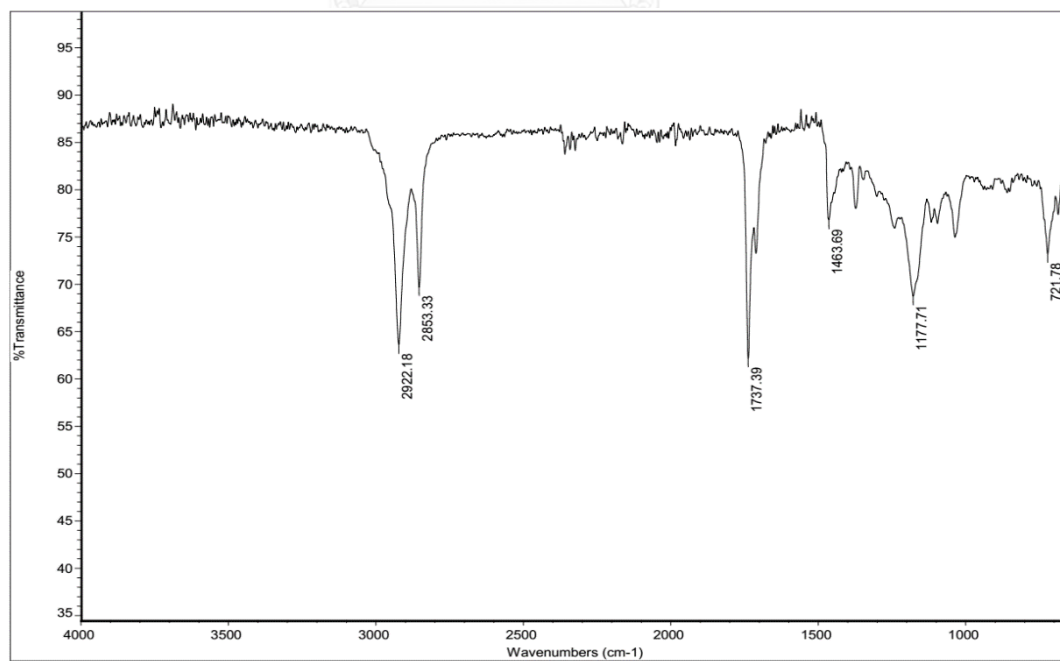

Figure A.5 IR spectra of fatty acid methyl ester (FME)

Figure A.6 IR spectra of fatty acid ethyl ester (FEE)
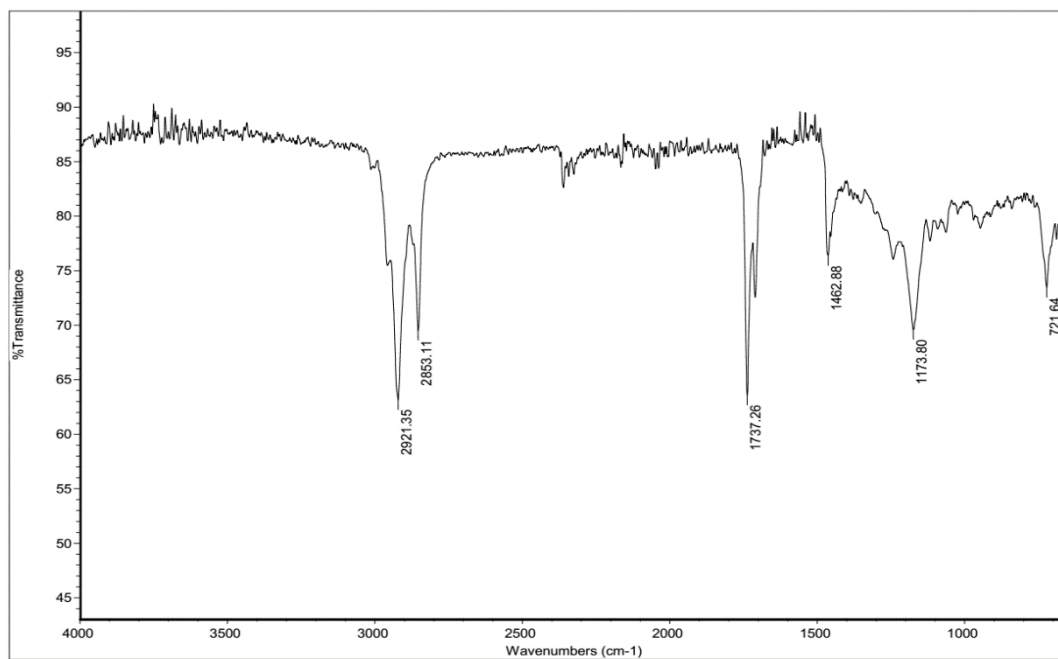
Figure A.7 IR spectra of fatty acid butyl ester (FBuE)
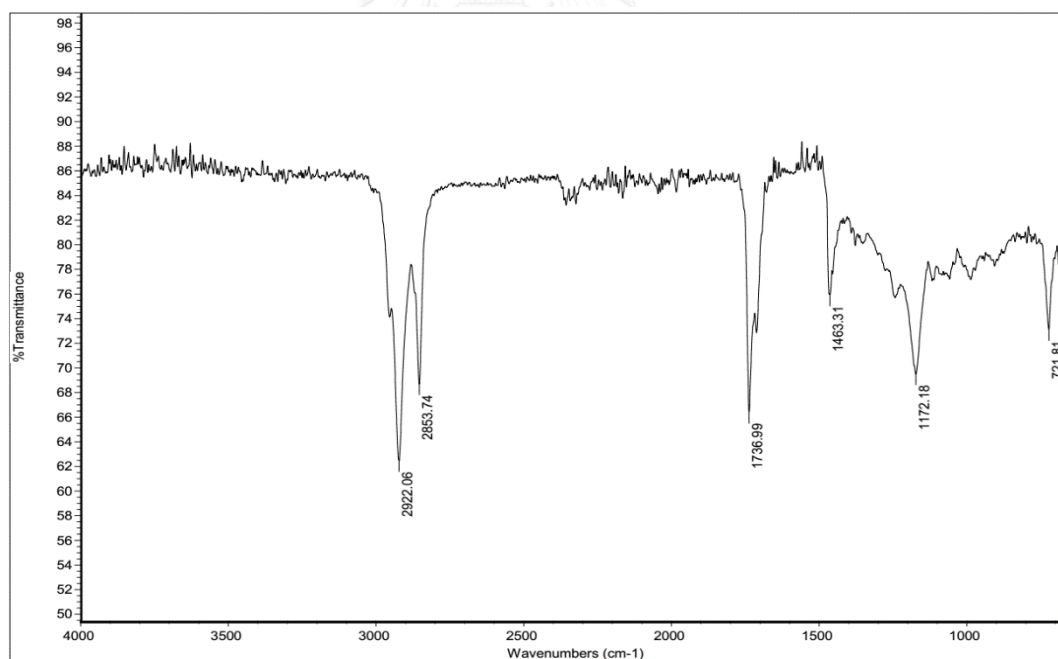
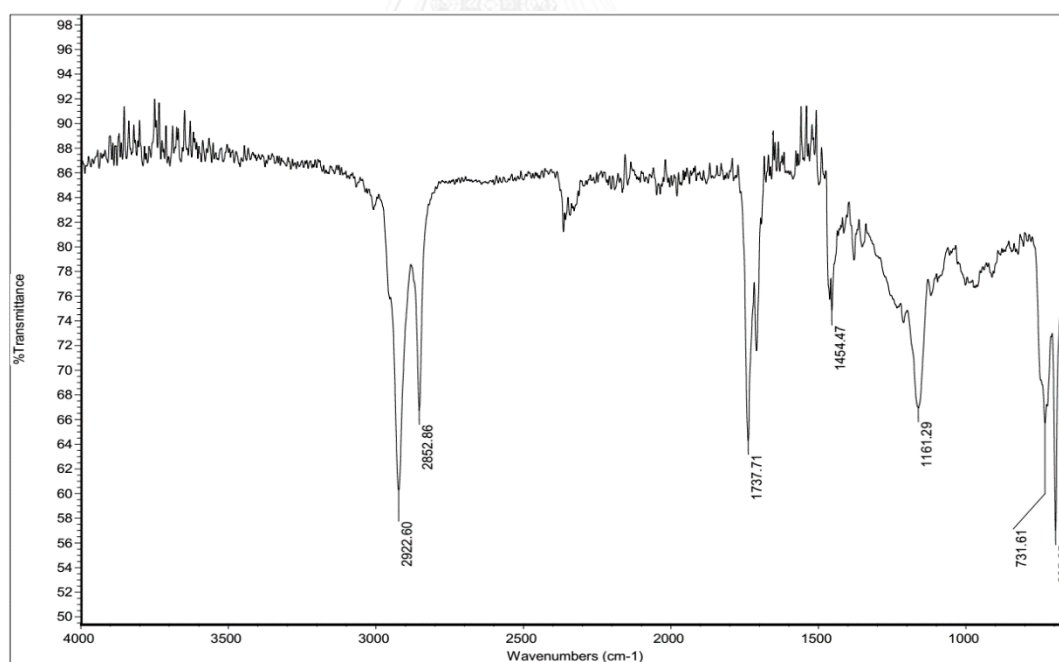
Figure A.8 IR spectra of fatty acid hexyl ester (FHE)
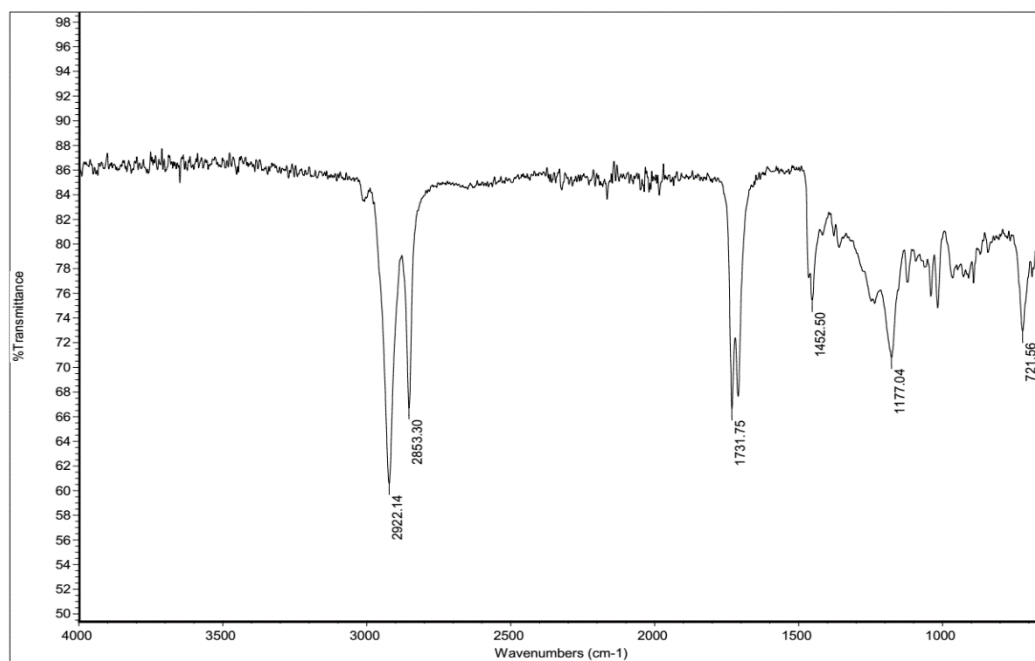
Figure A.9 IR spectra of fatty acid cyclohexyl ester (FChE)

Figure A.10 IR spectra of fatty acid benzyl ester (FBE)
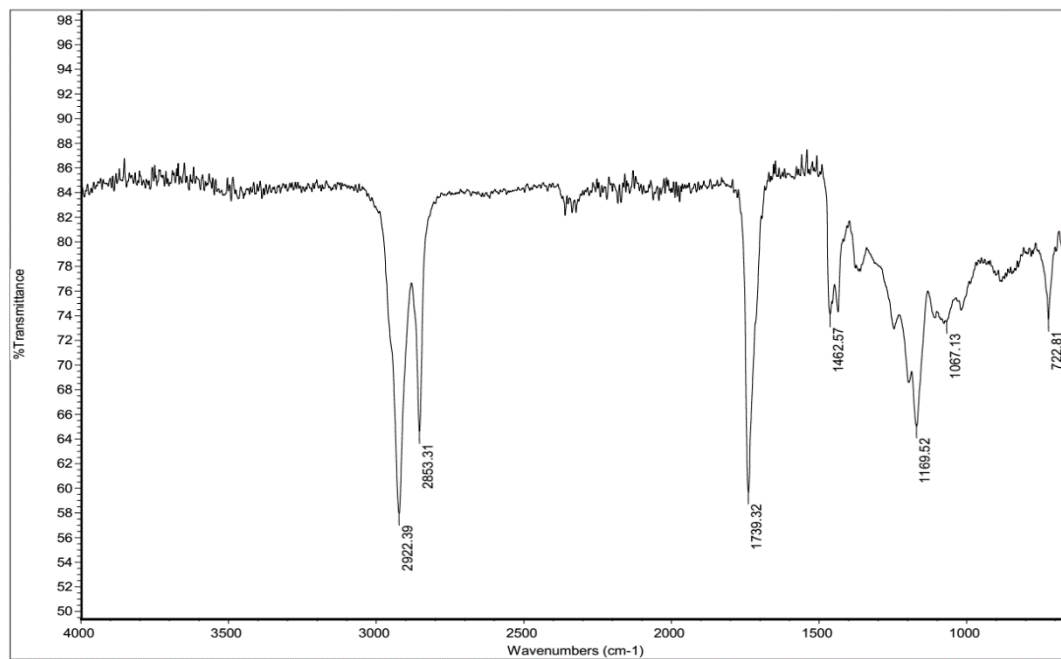
1.3 IR spectra of further modified FME and FChE

Figure A.11 IR spectra of epoxidized fatty acid methyl ester (EFME)
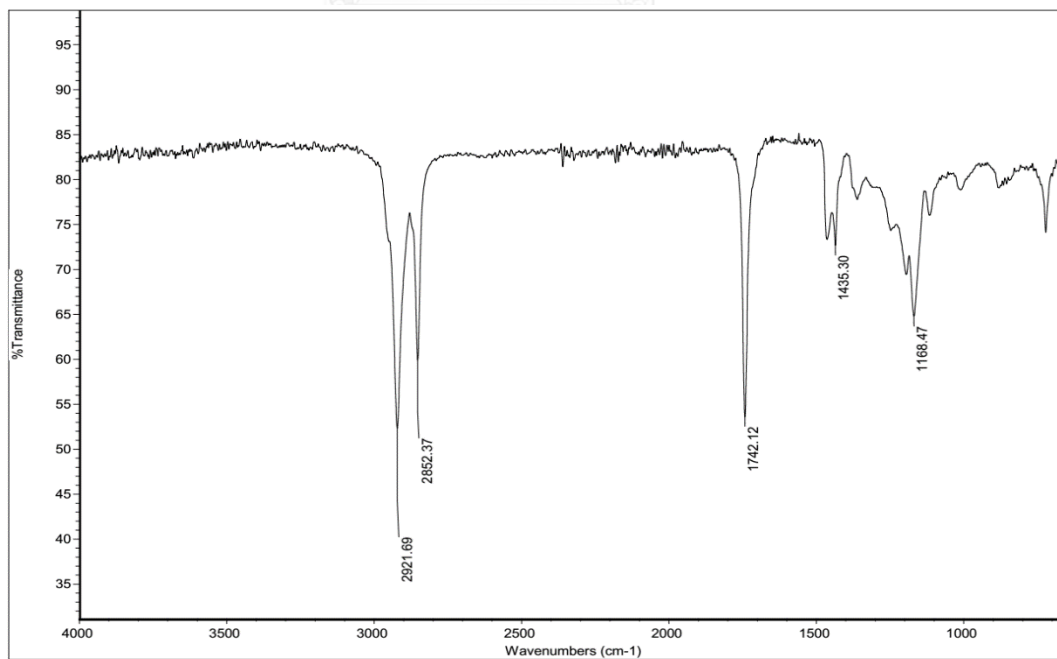

Figure A.12 IR spectra of hydrogenated fatty acid methyl ester (HFME)
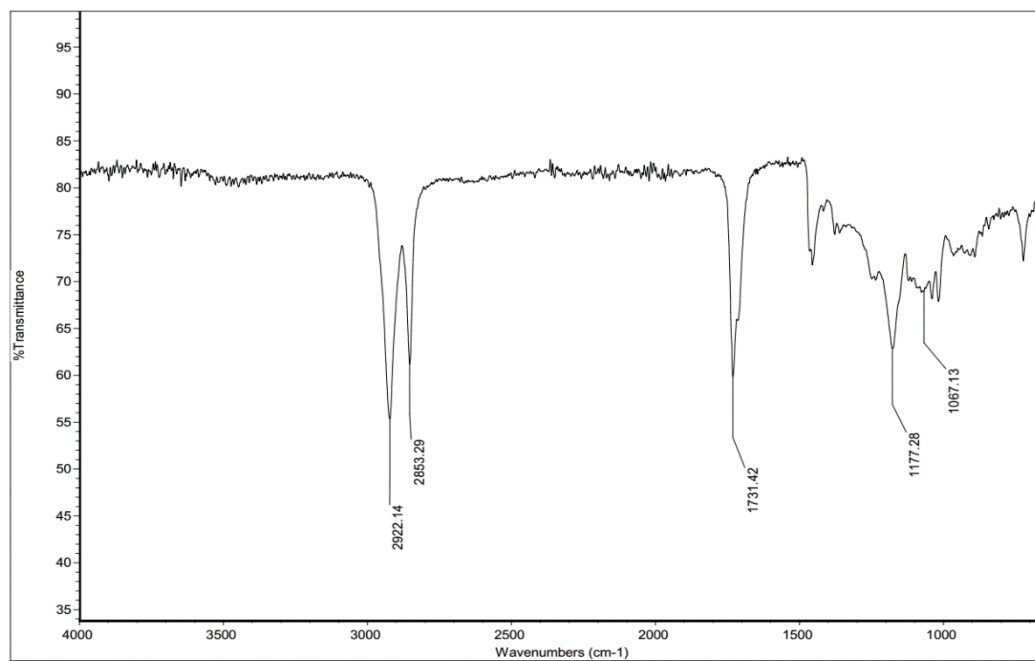
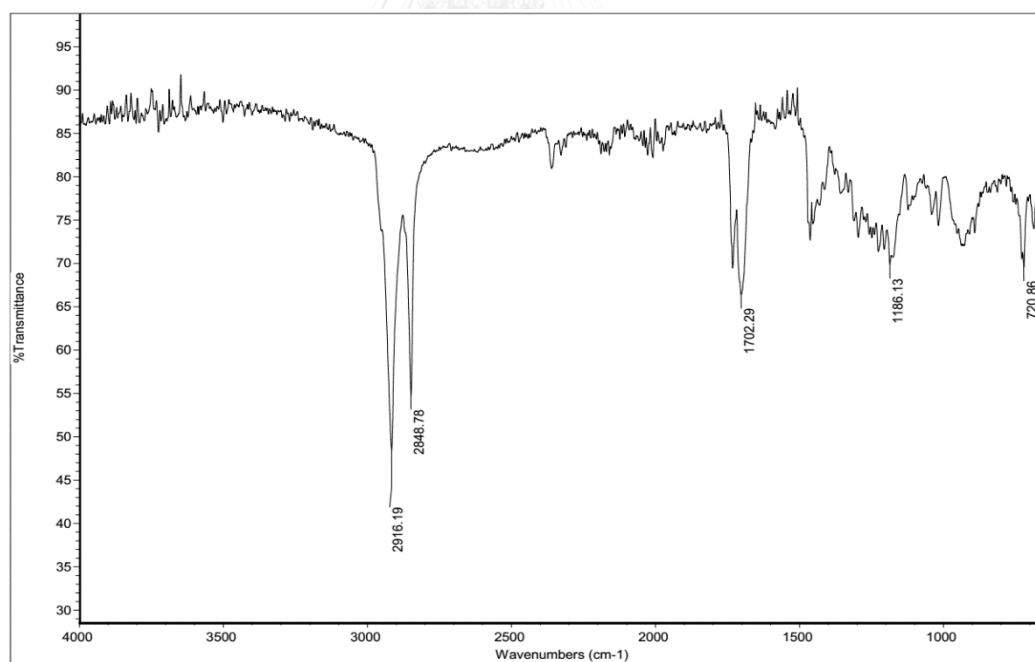**Figure A.**13 IR spectra of epoxidized fatty acid cyclohexyl ester (EFChE)

Figure A.14 IR spectra of hydrogenated fatty acid cyclohexyl ester (HFChE)

APPENDIX B

CALCULATION

1.Calculation of Iodine value

Iodine value is a measure of the unsaturation of fat or oil and is expressed in term of gram of iodine adsorbed per one hundred grams of sample. The iodine value was calculated as follows Eq. B.1:

$$I.V. = \frac{1.27 \times (B - A)}{W}$$

(B.1)

when   A = volume of 0.1N $Na_2S_2O_3$ (mL) when titration with sample

B = volume of 0.1N $Na_2S_2O_3$ (mL) when titration with blank

W = Weight of sample (g)

Example:

$$I.V. \text{ of RFAD} = \frac{1.27 \times (51.6 - 25.15)}{0.3852}$$

I.V. of RFAD = 95.21 gI_2/100g

2. Calculation of crosslink density [38, 39]

The crosslink density (**V**) of NR and NBR were calculated according to Flory-Rehner equation (Eq. B.2).

$$v = -\frac{\ln(1 - Vr) + Vr + \chi\, Vr^2}{Vs\,(Vr^{1/3} - Vr/2)}$$

(B.2)

when V_s is the molar volume of the swelling solvent (106.3 cm^3/mol for

toluene)

χ is the Flory-Huggins interaction parameter of rubber network-solvent

(0.393 and 0.435 for NR and NBR in toluene systems).

V_r is the volume fraction of polymer in the swollen in solvent. It was

calculated by followed equation (Eq B.3):

$$V_r = \frac{\dfrac{m_0\phi(1-\alpha)}{\rho_r}}{\left[\dfrac{m_0\phi(1-\alpha)}{\rho_r} + \dfrac{(m_1-m_2)}{\rho_s}\right]}$$

(B.3)

when m_0 is weight of vulcanized rubber before swollen.

m_1 is weight of vulcanized rubber after swollen in toluene

m_2 is weight of vulcanizaed rubber after aging at 80 ^{o}C for 48 h. (Dry

rubber)

ϕ is mass fraction of rubber matrix per rubber compound (phr of

rubber/total phr)

α is weight loss of vulcanized rubber after aging, calculated by α =

$(m_0-m_2)/m_0$

ρ_r is density of vulcanized rubber (kg/m^3)

ρ_s is density of toluene (0.87 kg/m^3)

Table B.1 Weights and parameter of NBR-EFME

Entry	ρ_r (kg/m^3)	m_0 (g)	m_1 (g)	m_2 (g)	α (m_0-m_2/m_0)	ϕ
1	1.17197	0.9742	2.0123	0.9316	0.04373	0.6039
2	1.17197	0.9842	2.0281	0.9407	0.04420	0.6039
3	1.17197	0.9632	1.9911	0.9209	0.04392	0.6039

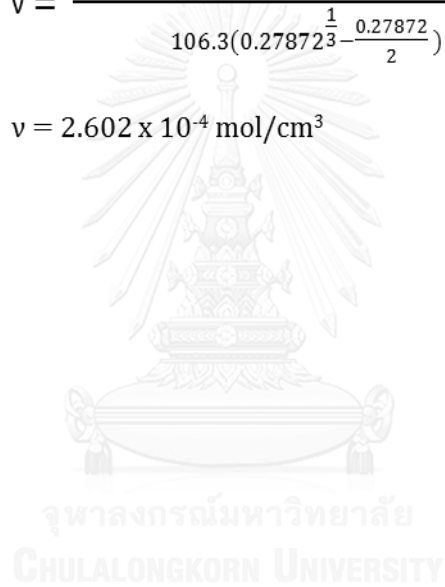From Entry 1, Subtituting the know value to Eq. B.3 for calculated V_r

$$V_r = \frac{\frac{0.9742 \times 0.6039 \times (1-0.04373)}{1.17197}}{\left[\frac{0.9742 \times 0.6039 \times (1-0.04373)}{1.17197} + \frac{(2.0123-0.9316)}{0.87}\right]}$$

$V_r = 0.27872$

Thus, Subtituting Vr = 0.27872 in Eq B.2 for calculated the crosslink density of NBR-EFME (Entry1).

$$v = \frac{\ln(1-0.27872) + 0.27872 + (0.435 \times 0.27872^2)}{106.3(0.27872^{\frac{1}{3}} - \frac{0.27872}{2})}$$

$v = 2.602 \times 10^{-4} \text{ mol/cm}^3$

VITA

Mr. Chalachmat Ekapan was born on November 16, 1991 in Songkhla, Thailand. He graduated with Bachelor's Degree of Petrochemical and Polymeric Materials from Faculty of Engineering and Industrial Technology, Silpakorn University in 2013. He continued study Master Degree in Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University 2014 and completed in 2016. He has also attended the Pure and Applied Chemistry International Conference 2017 (PACCON 2017). His present address is 28 Romjai road, Sadao, Songkhla, 90120, Thailand.