สมบัติการปรับค่าดัชนีความหนืดของพอลิไอโซพรีนน้ำหนักโมเลกุลต่ำจากยางธรรมชาติในสารหล่อลื่น

นาย รักษ์เผ่า พลรัตน์

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VISCOSITY INDEX IMPROVING PROPERTY OF LOW MOLECULAR WEIGHT POLYISOPRENE FROM NATURAL RUBBER IN LUBRICANT

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A Thesis Submitted in Partial Fulfillment of the Requirements

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รักษ์เผ่า พลรัตน์ : สมบัติการปรับค่าดัชนีความหนืดของพอลิไอโซพรีนน้ำหนักโมเลกุลต่ำจากยางธรรมชาติในสารหล่อลื่น (VISCOSITY INDEX IMPROVING PROPERTY OF LOW MOLECULAR WEIGHT POLYISOPRENE FROM NATURAL RUBBER IN LUBRICANT) อ.ที่ปรึกษา: รศ. ดร.อมร เพชรสม, 97 หน้า.

ยางธรรมชาติน้ำหนักโมเลกุลต่ำถูกนำมาผสมกับกับน้ำมันพื้นฐานที่ปัจจุบันใช้ในกระบวนการผลิตน้ำมันหล่อลื่นของเชลล์ เพื่อให้ยางธรรมชาติแสดงสมบัติการปรับค่าดัชนีความหนืดในน้ำมันหล่อลื่น โดยศึกษาสมบัติการละลายและค่าดัชนีความหนืดในน้ำมันพื้นฐานในหลายๆสภาวะทั้งเวลาในการผสมและอุณหภูมิการละลายเปรียบเทียบกับโอซีพีโคพอลิเมอร์ จากการทดลองเมื่อวัดค่าดัชนีความหนืดและค่าความหนาแน่นในของผสมพบว่ายางธรรมชาติส่งผลในการปรับค่าดัชนีความหนืดของน้ำมันพื้นฐานอยู่ในเกณฑ์ที่ดี แต่ยังคงต่ำกว่าเมื่อเปรียบเทียบกับโอเลฟินโคพอลิเมอร์โดยประมาณค่าเฉลี่ย 10.84 % และพบว่าอุณหภูมิที่พอลิเมอร์ ทั้งสองเริ่มละลายได้ดีคือ 90 องศาเซลเซียส และละลายได้สมบูรณ์ที่ 120 องศาเซลเซียส สำหรับเวลาในการผสมที่ทำให้พอลิเมอร์ละลายหมดสำหรับยางธรรมชาติคือ 120 นาที และ 240 นาที สำหรับโอซีพีโคพอลิเมอร์

สำหรับการผสมยางธรรมชาติน้ำหนักโมเลกุลต่ำเพื่อทำหน้าที่ปรับค่าดัชนีความหนืดในน้ำมันหล่อลื่น SEA 15W-40 ตามส่วนผสมจริงที่ใช้งานการผลิตด้วยการเปรียบเทียบตามคุณสมบัติทางกายภาพที่ใช้ในการควบคุมคุณภาพการผลิต พบว่ายางธรรมชาติสามารถปรับค่าดัชนีความหนืดให้ค่าสูงสุดคือ 156 แต่ยังมีค่าต่ำกว่าเมื่อเปรียบเทียบกับโอเลฟินโคพอลิเมอร์ประมาณ 12.29% ที่สภาวะเดียวกัน และพบว่าเวลาและอุณหภูมิในการผสมไม่มีผลในการเปลี่ยนแปลงดัชนีความหนืดรวมทั้งสมบัติทางกายภาพ เมื่อผสมยางธรรมชาติในน้ำมันเครื่องเกรดต่ำพบว่าค่าความเสถียรในการเกิดปฏิกิริยาออกซิเดชั่นลดลงเล็กน้อยและเมื่อนำน้ำมันเครื่องที่ได้นี้ไปทดสอบใช้งานกับการทำงานจริงในเครื่องยนต์พบว่าไม่ส่งผลกระทบต่อการทำงานของเครื่องยนต์

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ .... ลายมือชื่อนิสิต..
ปีการศึกษา ....2550.................................. ลายมือชื่ออาจารย์ที่ปรึกษา........................

4773412723: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORD: VISCOSITY INDEX IMPROVER / NATURAL RUBBER / LUBRICANT

RAKPAO PONERATTANA: VISCOSSITY INDEX IMPROVING PROPERTY OF LOW MOLECULAR WEIGHT POLYISOPRENE FROM NATURAL RUBBER IN LUBRICANT. THESIS ADVISOR: ASSOC. PROF. AMORN PETSOM, Ph.D., 97pp.

Low molecular weight natural rubber was blended with base oil currently used in Shell's lubricant production in order to improve the viscosity index of lubricating oil. The solubility and viscosity index of natural rubber blended lubricant were studied at various mixing time and temperature and the data were compared with those of OCP copolymer. It was found that viscosity index of natural rubber blended lubricating oil was improved but still 10.84 % lower than those of OCP copolymer. It was also found that both natural rubber and OCP copolymer started soluble at 90°C. and their complete dissolution temperature was 120°C. The times of mixtures to completely dissolve were 120, and 240 minutes for NR and copolymer respectively.

The low molecular weight natural rubber was then blended into 15W-40 lubricating oil following the current formulation and quality control. The maximum viscosity index was found to be 156, but it was approximately 12.29 % lower than that of OCP at the same blending condition. It was also found that various blending times and temperatures have no influence to viscosity index and physical properties. Low-grade engine oils had also been formulated with natural rubber and found that the oxidation stability of natural rubber blended oil was slight drop. When low-grade natural rubber blended engine oil was tested with engine operation it showed no effect on engine performance.

Field of Study: Petrochemistry and Polymer Science.. Student's Signature:..................
Academic Year: …2007.. Advisor's Signature:..................

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Finally, I would like to affectionately give all my gratitude to my parents for their love, understanding, encouragement and support throughout my entire study. Without them, I would never be able to achieve this goal.

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LIST OF ABBREVIATIONS

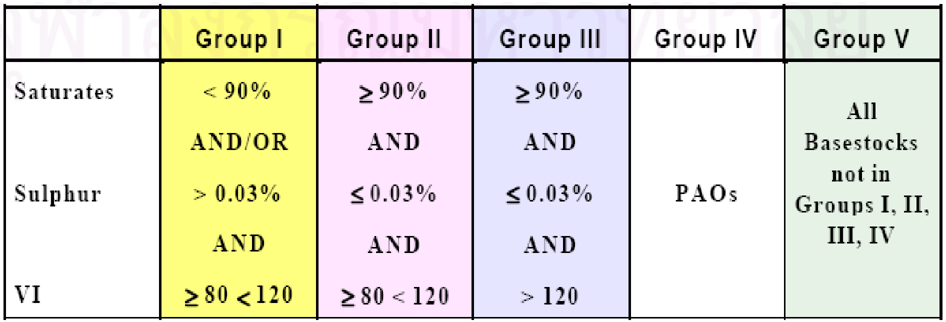
^{o}C	degree Celsius
Conc.	concentration
Kg	kilogram
L	liter
OCP	olefin copolymer
NR	natural rubber
VI	viscosity index
VII	viscosity index improver
ASTM	American Society for Testing and Material
@	at
Conc.	concentration
min	minute
cST	centistokes
%	percentage
BET	Brunauer-Emmett-Teller method
UOM	unit of measurement
Min	minimum
Max	maximum
Typ	typical
CCS	cold cranking simulation
VK	viscosity
NBR	Acrylonitrile butadiene rubber

CHAPTER I

INTRODUCTION

In the world today, the technology of motor vehicles and industry machines has been rapidly changed and developed along with high marketing competition as can be observed in highly efficient cars with higher speed and more powerful road transportation or high-tech robot machines. High-tech machines require very good lubrication to make them last longer or increase availability to perform heavy working. Machines or cars, particularly when they have been functional for example moving or rotating parts require high quality lubrication to perform smooth working with fully expected efficiency. Lubricating oil improvement technology is becoming important as well since undeniably two surfaces moving against each other need very good lubrication to accommodate movement and protect those materials at the same time. Additives were added into the refinery lubricating base oil in order to increase oil efficiency and fulfill non-basic property that required by movement condition such as heat reduction and rush protection.

Table 1.1 API Base stock classifications



	Group I	Group II	Group III	Group IV	Group V
Saturates	< 90%	≥ 90%	≥ 90%	PAOs	All Basestocks not in Groups I, II, III, IV
	AND/OR	AND	AND		
Sulphur	> 0.03%	≤ 0.03%	≤ 0.03%		
	AND	AND	AND		
VI	≥ 80 < 120	≥ 80 < 120	> 120		

Table 1.1 shows the importance of viscosity index property in lubricant base oil since viscosity index has been applied as a major factor to classify the quality of base oils. Base oil has been classified into 5 groups by considering number of saturated, sulphur and viscosity index.

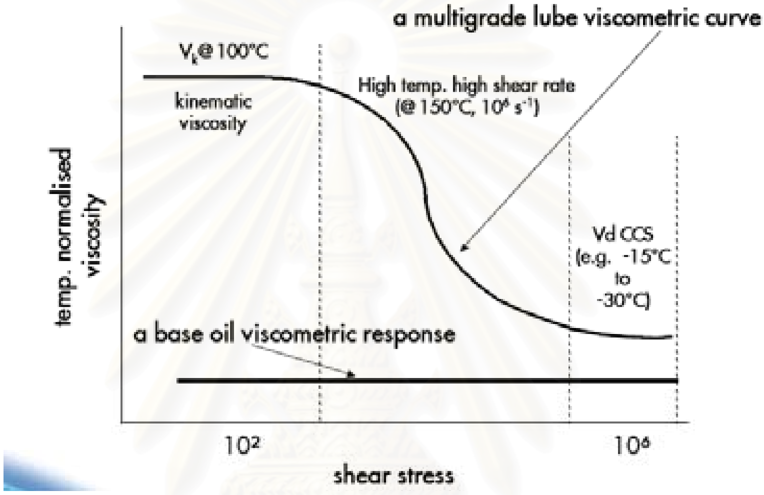


Figure 1.1 Lubricant viscometric curve

Figure 1.1 shows that viscosity of lubricating oil is directly related to shear stress in temperature difference. The viscosity index is highly important, particularly in multi-grade oils, to provide lubricating oil compositions with a much flatter viscosity-temperature curve than the unmodified oil. It is especially vital that the lubricating oil compositions exhibit specified maximum viscosities at relatively low temperatures and specified minimum viscosities at relatively elevated temperatures.

1.1 Viscosity index improver in lubricating oil blending

Typical lubricating oil composition has two basic components as mineral base oil and additive in several formulations depending on lubricating condition required and purposes. Mineral base oils can be modified by a vast array of additives for purposes of improving viscosity index, thermal stability, oxidation stability, detergency, and other properties. The viscosity index is highly important especially in multi-grade oils, to provide lubricating oil compositions with much flatter viscosity-temperature curve than the unmodified oil. It is especially vital that the lubricating oil compositions exhibit specified maximum viscosities at relatively low temperatures and specified minimum viscosities at relatively elevated temperatures. The viscosity index of mineral lubricants are altered by the presence of high molecular weight polymeric additives such as polymethacrylates polyisobutylene, olefin copolymer.

In this study hydrogenated olefin copolymer polystyrene-polyisoprene (which is current using as commercial composition) was chosen to compare the effect of viscosity index property improving in lubricating oil blending against low molecular weight natural rubber which is the studied material of this research.

Table 1.2 Standard SAE 15W-40 lubricant oil blending formulation

Component	% By weight
Base oil (high viscosity index 60)	51.66 %
Viscosity index improver 4%	35.00 %
Other lubes additives	13.34%
Total	100.00 %

Table 1.2 shows the amount of viscosity index improver in lubricant oil composition that higher when compare to another component, it can be identified that viscosity index is major lubricating oil's property required.

1.2 Natural rubber using for viscosity index improver in lubricant

Basically the viscosity index improver has an objective to minimize viscosity changed by temperature difference and increase stability of viscosity of lubricating oil in high shear stress working condition. The rubbery and plastic characteristics in the polymer chain are major qualifications that could make base oil preserve their shear stress and shear rate ratio by moving chain when temperature has been changed instead of liquid shear rate loss.

Considering at present viscosity index improvers polymer and olefin copolymer are become widely and most used in lubricant production such as VI improver of Infeneum or Lubrizol company that are worldwide lubricant additives providers whereas OCP is used as VI improver. The reference lubricating oil production that this study has chosen for comparison is Shell lubricant oil, where hydrogenated copolymer polyethylene -polyisoprene has been applied as viscosity index improver.

Regarding OCP, which is used in current lubricating oil blending, it has the composition of a polymer called polyisoprene that is commonly found in most natural rubber structures. Polyisoprene in natural rubber was raised to determine the possibility of applying it as a viscosity index modifier in the lubricating oil blending process since polyisoprene's dominant property appears in OCP as one the of major components. The rubbery and elongating characteristic of polyisoprene could perform viscosity stability whilst the temperature changes. However the size of polyisoprene in natural rubber looks like bigger than expected. The original average molecular weight can be up to 1,000,000 which would not be miscible in mineral base oil blending. The expecting molecular weight of polyisoprene has been recommended for blending is around 15,000 – 200,000, so low molecular weight natural was studied in order to make better solubility and get compatibility with mineral base oil on lubricant blending process.

1.3 Low molecular weight natural rubber

Considering existing material, it is essential for the copolymers that they have to be compatible with the mineral lubricating oils blending. For this purpose it is necessary to carefully select the molecular weights and type of polymer which in the entire structure of the copolymer will be compatible with the lubricating oil.

Typical block copolymers that are being used hydrogenated polystyrene-polyisoprene and they are limited to average molecular weights of polystyrene between about 5,000 and 50,000 (preferably 9,000 and 35,000) while polyisoprene is limited to average molecular weights between about 10,000 and 1,000,000, (preferably 15,000 and 200,000). Natural rubber has a majority composition of polyisoprene and has original average molecular weight of 1,000,000. This is too high and not compatible with mineral oil blending, thus modified natural rubber with lower molecular weight that comply with compatible range has to be looked for.

Low molecular weight natural rubber can be created via two methods. The first method is by masticating dry rubber in a two-roll mill. Adding chemicals in fresh field latex before coagulation and drying is another method. The commonly used chemicals can be summarized as hydrogen peroxide, sodium nitrite potassium persulphate, peptizing agent and nitrobenzene.

Today there is a local company that has a production line with low molecular weight natural rubber for commercial scale and this is widely used in several manufacturing areas.

1.4 Low molecular weight natural rubber advantage

Thailand is the biggest planter and provider of natural rubber to the world market. Natural rubber is a convenience and is widely applied in many of industrial areas and likely contributes from government for various applications and value added.

To increase natural rubber value, modifying rubber to another form would be preferable rather than rib rubber form, and low molecular weight natural rubber was considered to be an option to create initiative with this research.

Cost reduction on lubricating oil blending was expected by using local material that could lower operating cost.

For natural rubber, the value added in the future will be realized and could increase national earning.

Since natural rubber is biodegradable it will not effect the environment and reduce the degree of industrial waste.

1.5 Objectives of the research

Main objective of this research is comprised of 3 studying areas:

1. To observe solubility characteristic of low molecular weight natural rubber in mineral oil under various conditions and parameters, closely related to actual manufacturing practice.
2. To investigate viscosity index improving property of low molecular weight natural rubber.
3. To apply low molecular weight natural rubber to actual lubricants oil blending process.

1.6 Scope of the research

In order to meet objectives of the research, initial study was on the solubility of low molecular weight natural rubber in mineral base oil compared to olefin copolymer that is the currently used material. Mixing equipment was installed with similar design to the actual blending unit, but minimized blending vessel size intended to get close to the condition of industrial production. The temperature and mixing time were varied and physical properties were measured to evaluate the effect of each polymer and blending parameter following polymer blended at 2%, 4%, 8% and 10%, temperature of mixing was set 30, 60, 90 and 120 ˚C, mixing time was varied at 30, 45, 60, 90, 120 and 240 minutes. The physical properties, viscosity index and density of blended product were measure regarding to American Society of Testing and Materials (ASTM) D 4052 “Density and relative density of liquids by digital density Meter”, D 445 “Kinematics viscosity of transparent and opaque liquids (and calculation of dynamic viscosity) “, D-2270 “ viscosity index”.

In the second step, viscosity index improving property of natural rubber was studied with actual components of lubricant oil blending SAE 15W-40. The physical property of commercial lubricant oil using OCP was used for comparison. The experiment was performed with varying concentration of polymer at 2%, 4%, 8% and 10%, mixing temperature at 30, 45 and 60 ˚C mixing time at 10, 20 and 30 min. The 50/50 OCP and natural rubber was also performed with the same mixing status. The physical viscosity index has been measured with the objective of understanding the effect of natural rubber in lubricating oil in terms of physical properties compared to the real lubricant currently in use. Lubricating oil’s physical properties that were applied in quality control system for industrial production have been measured to ensure quality product will be performed according to American Society of Testing and Materials (ASTM) D 4052 “Density and relative density of liquids by digital density meter”, D 445 “Kinematics viscosity of transparent and opaque liquids (and calculation of dynamic viscosity)”, D 5293 “Apparent viscosity test “, D 97 “Pour point test “and ISO16140 method SMS 2798 “Metal content“.

The last experiment was to study the effect of the engine when low grade engine oil formulated with natural rubber was used instead of OCP in the real engine working for 6 weeks at 4 hour / day.

CHAPTER II

THEORY AND LITERATURE REVIEWS

The viscosity index in lubricating oil is one of the most important properties for lubrication to create a high stability of viscosity in oil, since the fluid flow is directly related to the viscosity and temperature, as well as the working temperature changing, which has been considered for the oil properties impact. The viscosity index is an indicator that could represent the viscosity steadiness while temperature is changing. For the present technology of the viscosity index adjustment in the term of microstructure, the long chain polymers were selected as the specific additive to increase the viscosity consistency. Many types of copolymer have been used to modify the viscosity index and isoprene copolymer is one of them. This experiment studied the possibility of using isoprene polymer in the natural rubber for adjusting the viscosity index in lubricating oil.

2.1 Lubricating oil

A lubricant is a substance introduced between two moving surfaces in order to reduce the friction and wear between them. The lubricant provides a protective film that allows for two touching surfaces to be separated, thus lessening the friction between them.

Since the Roman era, there were many liquids, including water, that have been used as the lubricants to minimize friction, heat and wear between mechanical parts in contact with each other. Currently, lubricating oil or lube oil is the most commonly used as a lubricant because of its wide range of possible applications. Two basic categories of lube oil are mineral and synthetic. Mineral oils are refined from naturally occurring petroleum, or crude oil. The synthetic oils are manufactured: the polyalphaolefins, which are the hydrocarbon-based polyglycols or ester oils.

Although there are many types of lube oils to select, the mineral oils are the most commonly used because the crude oil supply can be rendered inexpensively; moreover, the large body of data on their properties and use already exist. Another advantage of mineral-based lube oils is that they could be produced in a wide range of the viscosities referred to the substance resistance to flow for diverse applications. They range from the low-viscosity oils, which consist of hydrogen-carbon chains with molecular weights of around 200 atomic mass units (amu), to highly viscous lubricants with the molecular weights as high as 1,000 amu. The mineral-based oils with different viscosities could even be blended together to improve their performance in a given application. The common 10W-30 motor oil; for example, is a blend of low viscous oil (for easy starting at low temperature) and highly viscous oil (for better motor protection at normal running temperature). First used in the aerospace industry, the synthetic lubricants that are usually formulated are ill-suited for the specific application to mineral oils. For example, the synthetics are used where the extremely high operating temperatures are encountered or the lube oil must be burnt resistant. This article will focus on the mineral-based lube oil.

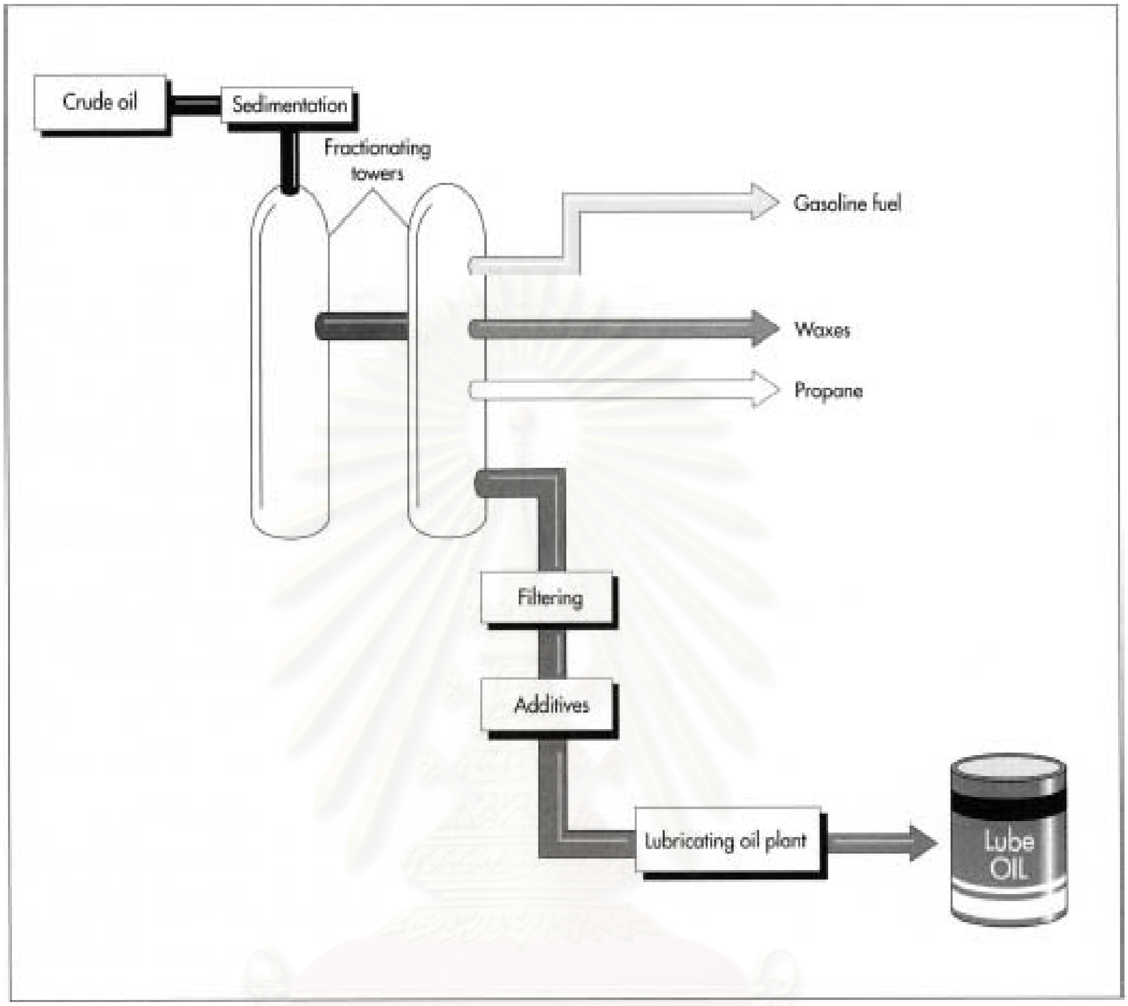


Figure 2.1 lubricating oil productions.

The basic functions of the lubricant are friction reduction, heat removal and suspension of contaminants. Designing the lubricant to perform these functions is a complicated task, involving the careful balance of properties in both base oil and performance enhancing additives.

The lubricating oil is a liquid lubricant that has been used in the engine for performing the following key functions.

1) To keep moving parts apart
2) To reduce friction
3) To transfer heat
4) To carry away contaminants & debris
5) To transmit power
6) To protect against wear
7) To prevent corrosion

A typical lubricating oil contains 90% base oil (most often petroleum fractions, called mineral oils) and less than 10% additives. Synthetic liquids such as the hydrogenated Polyolefin's, esters, silicone, fluorocarbons and many others are sometimes used as base oils. The additives can eliver reduced friction and wear, increased viscosity, improved viscosity index, resistance to corrosion and oxidation, aging or contamination, etc.

Mineral oil is used to encompass the lubricating base oil derived from crude oil. The API designates the several types of lubricant base oil identified as:

1. Group I - Saturates < 90% and/or sulfur >0.03% and viscosity index $\geq$ 80 to <120

2. Group II - Saturates ≥ 90% and sulfur ≤ 0.03% and viscosity index ≥ 80 to <120
3. Group III – Saturates ≥ 90% sulfur ≤ 0.03% and viscosity index ≥ 120
4. Group IV – Poly alpha olefins (PAO)
5. Group V – All others not included above

The lubricant industry commonly extends this group terminology to include:

1 Group I plus with a viscosity index of 103 - 108

2 Group II plus with a viscosity index of 113 - 119

3 Group III plus with a viscosity index of ≥ 140

For deep consideration into the properties required of the basic lubricant, particularly those which have been designed for being used in different temperatures climates (which is the most important property), is the viscosity index. Thus objective study would be related to the effect of viscosity index when the new polymer was applied as the viscosity index improver, such as a simpler natural polymer like rubber.

2.2 Lubricating oil blending process

The composition of lubricating oil blending was categorized into 2 major components: the base oil and the additive blend in various formulations depending on oil's application and requirement. The process of the oil blending can be carried out by many methods with typical parameters for the current blend which is considered on the ratio of oil component, mixing time, blending temperature and mixing method. The blending facility of this experiment has been simulated to reasonable the existing unit that is used in the lubricating oil blending plant of shell lubricants.

2.3 Lubricating oils properties and the role of additives

The main objective of the lubricating oils is to order and induce the required properties of lubricating for the effectiveness in engines and machines. The specific properties are required to be activated in oils both individually and functionally represented in oil. Then, several additive and types were used for affecting and representing its dominant potential, and they were categorized as the following: -

- Detergent
- Dispersant
- Polymeric Dispersants
- Oxidation and Bearing
- Anti wear additives
- Viscosity Modifiers
- Pour Point Depressants
- Miscellaneous Additives

Some of the most important properties necessary for the satisfactory lubricant performance are:

1. Low volatility under the operating conditions: The volatility characteristics are essentially inherent to the choice of base oil for the particular type of service; also, it could not be improved by the use of additive materials.

2. The satisfactory flow characteristics in the temperature range of use: The flow of characteristics largely depends on the choice of base oil; however, they could be improved through the use of pour point depressants and viscosity modifiers. The former can improve the low-temperature flow properties, while the latter can enhance the high-temperature viscosity characteristics.

3. The superior stability or the ability of desirable characteristics maintenance for a reasonable period of use: While these characteristics depend to some extent on the base oil, they are primarily associated with the additive materials, which enhanced the base fluid properties in this area. The environment in which it operates affects the lubricant stability. Such factors as temperature, oxidation potential and contamination with water, unburned fuel fragments, and corrosive acids limit the useful life of the lubricant. This is the area where the additives were made to be the major contribution for improving the performance characteristics and extending the useful life of the lubricants.

4. The compatibility with other materials in the system: The compatibility of the lubricants with seals, bearings, clutch plates, etc., may also be partially associated with the base oil. However, the additive chemistry could have the major influence on such characteristics.

Table 2.1 Lubricant additives.

Property required	Additives
Detergents (Metallic Dispersants)	Salicylates, Sulfonates, Phenates ,Sulfophenates
Ashless Dispersants	N-substituted long-chain alkenyl succinimides High-molecular-weight esters and polyesters Amine salts of high-molecular-weight organic acids Mannich base derived from high-molecular-weight alkylated phenols
Oxidation and Bearing Corrosion Inhibitors	Organic phosphates, Metal dithiocarbamates, Sulfurized olefins, Zinc dithiophosphates
Antioxidants	Phenolic compounds, Aromatic nitrogen compounds, Phosphosulfurized terpenes
Viscosity Modifiers / Improvers	Polymethacrylates, Ethylene-propylene copolymers (OCP), Styrene-isoprene copolymers (OCP), Styrene-ester copolymers
Antiwear Additives	Organic phosphates, Sulfurized olefins, Zinc dithiophosphates, Alkaline compounds as acid neutralizers
Pour Point Depressants	Wax alkylated naphthalene, Polymethacrylates, Crosslinked wax alkylated phenols, Vinyl acetate/fumaric-acid-ester copolymers, Vinyl acetate/vinyl-ether copolymers, Styrene-ester copolymers

2.4 Viscosity index

The viscosity index is a petroleum industry term. It is the lubricating oil quality indicator, or arbitrary measure, for the change of kinematical viscosity with temperature. The viscosity of liquids decreases as the temperature increases. The viscosity of the lubricant is closely related to its ability to reduce the friction. Generally the thinnest liquid/oil which still forces two moving surfaces apart is required. If the lubricant is too thick, it will require a lot of energy to move the surfaces in the same way, if it is too thin, the surfaces will rub and the friction will increase.

As stated above, the viscosity index highlights the lubricant viscosity changes with variations of temperature. Many lubricant applications require lubricant for performing across the wide range of conditions for example, in an engine. The automotive lubricants must reduce the friction between the engine components when it is started in the cold (~10˚C) as well as when it is running (up to 200˚C). The best oils (with the highest VI) will not vary much in the viscosity over such the temperature range. Therefore, the engine will perform well throughout.

The VI scale was established by the Society of Automotive Engineers (SAE). The temperatures selected the arbitrarily for the reference are 100 ˚F (40 ˚C) and 210 ˚F (100˚C). The original scale was only stretched between VI=0 (worst oil) and VI=100 (best oil), but since the conception of the scale better oils have also been produced, leading to VI>100.

The VI improver additives and higher quality base oils are widely used nowadays that increases the VI attainable beyond the value of 100. The Viscosity index of synthetic fluids is ranged from 80 to over 400.

2.5 Viscosity index improver

The viscosity index improver is the chemical additive that is added to finish the lubricants and improve the viscosity index. The lubricant additive, usually the high-molecular-weight polymer, reduces the tendency of oil to change the viscosity with temperature. The multi-grade oils provide effective lubrication over a broad temperature range, and usually contain VI improvers. While the viscosity index improvers could enhance the viscosity index (VI), they could break down under the shear or over time, resulting in diminished performance. Typically viscosity index improvers are long chain, high molecular weight polymers that function by increasing the relative viscosity of oil more at the high temperatures than at low temperatures.

The viscosity index improvers could be thought of as spring mechanisms as they coil at cold temperatures and uncoil as the temperature increases. The uncoiling makes the molecules larger, which increases the internal resistance within the thinning oil. It reduces the overall viscosity loss of the fluid. The loss of fluid viscosity could be also occur due to a condition known as the temporary shear. The temporary shear occurs when the long viscosity index improver molecules align themselves in the direction of the stress (flow). This alignment generates less resistance and allows the reduction in fluid viscosity. When the stress is removed, the molecules return to their random arrangement, and temporary loss in viscosity is recovered.

The long molecules in the viscosity index improvers (VII) could be subject to shearing in service, which reduces their ability to minimize fluid viscosity loss. A permanent shear occurs when the shear stress ruptures long molecules and converts them into shorter and lower weight molecules. The shortened molecules offer less resistance to flow and minimize their ability to maintain the viscosity. The permanent shearing of viscosity index improvers could result in the piston ring sticking (due to the deposit formation), increased oil consumption and accelerated equipment wear. It should be noted that some VII are more significantly in shear stable than others. Also, although the type of base stock used and intended the application determines the need for VII, many synthetic stocks may not require them at all. The typical viscosity index improvers are polymers and copolymers of olefins, methacrylates, dienes or alkylated styrenes.

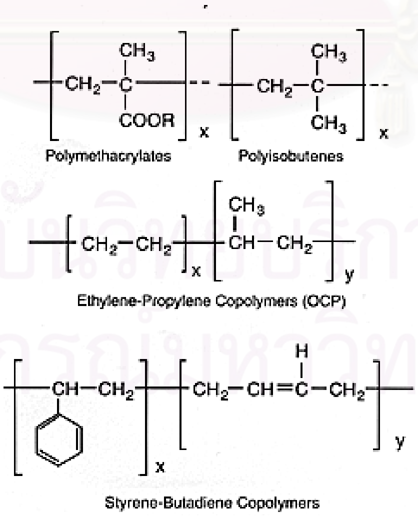


Figure 2.2 Viscosity index improvers.

A viscosity index improver is typically made up of oil soluble organic polymers with molecular weights ranging from about 10,000 to 1,000,000. The polymer's molecule in solution is swollen by the lubricant, and the volume of the swollen entity determines the degree to which the polymer increases the viscosity. At higher temperature, the larger volume and the greater thickening affect the polymer. Hence, the oil tends to thin less due to the increased temperature.

In addition, for viscosity improvement, the performance of these polymers also depends on the shear stability or resistance to mechanical shear and on their chemical and thermal stability. With a given polymer system, the shear stability decreases with the increase in molecular weight. The loss due to shear is reflected in the loss in the lubricant viscosity. On the other hand, the thickening power of the viscosity modifiers increase with the increase in molecular weight for a given polymer type. A performance balance must then be established which takes into the consideration shear stability and the viscosity needs as well as thermal and oxidative stability in actual engine operation.

The permanent shear occurs when the shear stress ruptures long molecules and converts them into shorter and lower weight molecules. The shortened molecules have offer less resistance to flow and their ability to maintain viscosity is minimized. The permanent shearing of viscosity index improvers could result in the piston ring sticking (due to the deposit formation), increased oil consumption and accelerated equipment wear. It should be noted that some VIIs are more significant in shear stable than others. Also, although the type of base stock used and the intended application determines the need for VII, many synthetic stocks may not require them at all.

2.6 Olefin copolymer currently used for viscosity index improver

The current viscosity index improvers, which are formulated with compositions for high performance in lubricating oil are star olefin copolymers. The star polymers have the tetra block copolymer arms of the hydrogenated polyisoprene - polyisoprene with a block of the polystyrene and provide the excellent low temperature performance in lubricating oils, exhibit good thickening efficiency, and finish as the polymer crumb

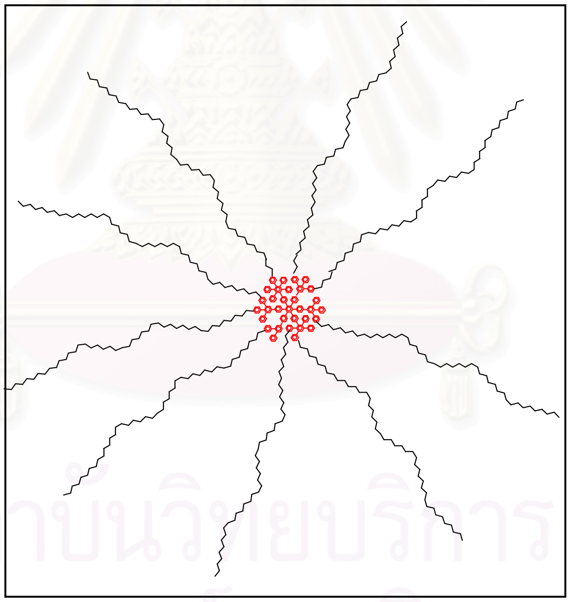


Figure 2.3 Hydrogenated star block copolymer styrene-isoprene structure.

Figure 2.4 Commercial hydrogenated star block copolymer styrene-isoprene.

2.7 Natural rubber structure and properties

Natural rubber (NR) is one of the most important commodities in Thailand, and in each year, it earns for Thailand almost 100,000 million baht from exporting of both raw materials and rubber products. Natural rubber (NR) is produced from the crop harvested from rubber plantations both in the latex form as well as in the field coagulum form. The major commercial source of natural latex used to create rubber is the Para rubber tree, Hevea brasiliensis (Euphorbiaceous).

The molecular structure of natural rubber is composed of carbon atoms and smaller hydrogen atoms. However, its amorphous mass of coiled and kinked chains readily allows the motion of its molecular chain making it extremely flexible. In its natural form, rubber that is too soft cannot be used for any useful purpose. Therefore, its properties have to be improved for using the special processing techniques.

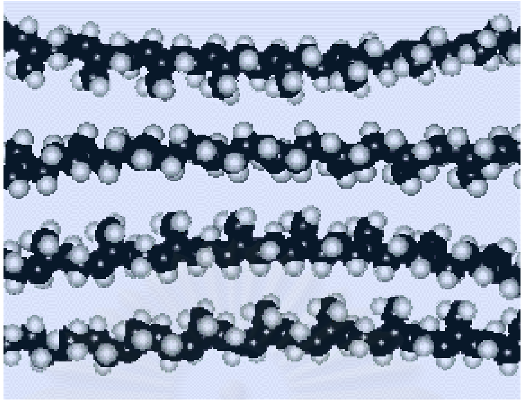


Figure 2.5 Natural rubber structure.

One of the most well known natural polymers is the polyisoprene, or the natural rubber. The ancient Mayans and Aztecs harvested it from the hevea tree and used it to make the waterproof boots and balls, which they used to play in a game similar to basketball. It is what we call an elastomer, that is it recovers its shape after being stretched or deformed. Normally, natural rubber is treated to give it crosslinks, which make it an even better elastomer.

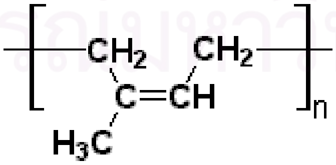
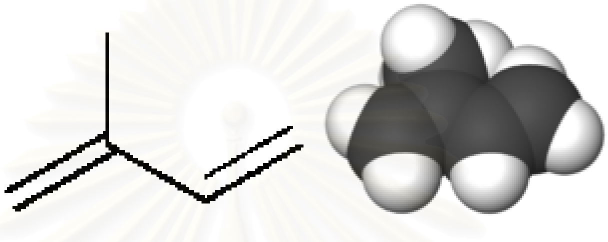


Figure 2.6 Polyisoprene.

Table 2.2 Isoprene structure and properties

Isoprene	
	
Chemical name	2-Methyl-1,3-butadiene
Other names	isoprene
Chemical formula	C_5H_8
Molecular mass	68.11 g/mol
CAS number	[78-79-5]
Density	0.681 g/cm³
Melting point	-145.95 °C
Boiling point	34.067 °C
SMILES	C=C(C)C=C

Polyisoprene is a diene polymer, which is the polymer made from a monomer containing two carbon-carbon double bonds. Like the most diene polymers, it has the carbon-carbon double bond in its backbone chain. The polyisoprene could be harvested from the sap of the heave tree, but it could be made by Ziegler-Natta polymerization.

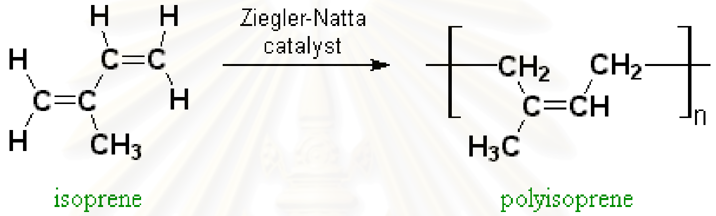


Figure 2.7 Synthesis of polyisoprene.

The property of rubber commercial crude or raw rubber is a tough, no crystalline elastic solid having a specific gravity of 0.911, and a refractive index of 1.5910. Its composition is varied in different latexes, according to the method of preparation on the plantation. A typical analysis is shown in Table 2.3.

Table 2.3 Composition of natural rubber

Component	Smoked Sheet	Pale Crepe
Moisture	0.6%	0.4%
Acetone-soluble material	2.9	2.9
Proteins	2.8	2.8
Ash	0.4	0.3
Water-soluble material	1.0	1.0
Esters insoluble in acetone	1.0	1.0
Rubber hydrocarbon	91.3	91.6 .
	100.0%	100.0%

Rubber does not dissolve in water, alcohol, or acetone, but it swells and disperses in benzene, toluene, gasoline, carbon bisulfate, turpentine, chloroform, carbon tetrachloride, and other halogen-containing solvents, producing viscous cements that find application as adhesives.

2.8 Low molecular weight natural rubber

The mineral lubricating oils that have been modified by the additives for purposes of improving viscosity index are highly important, especially in multi-grade oils, to provide the lubricating oil compositions with much flatter viscosity-temperature curve than the unmodified oil. It is essential for block copolymers to be compatible with mineral lubricating oils in which they are to be utilized if they are to be successful in the viscosity index improving additives. The block copolymer, according to current additive use, is a polystyrene block that has an average molecular weight between about 9,000 and 35,000 while the hydrogenated polyisoprene block has an average molecular weight between about 15,000 and 200,000 at least 80% of the double bonds of the polyisoprene block reduced by the hydrogenation. Therefore, the polyisoprene can be used for the low molecular weight as expected.

Reducing the molecular weight of natural rubber to the preferable level 15,000 - 200,000 was carried out by two methods. The first method was to masticate dry rubber in two-roll mill. Another method was by adding the chemicals in fresh field latex before coagulation and drying. This method used hydrogen peroxide and sodium nitrite or potassium persulphate or hydrogen peroxide and potassium persulphate of peptizing agent or nitrobenzene.

Hydroxylamine hydrochloride was also added as the viscosity stabilizer (for dry rubber) before coagulating latex by 1.5% of formic acid. The coagulant was then dried at 55 ^{o}C for 3-4 days. The prepared low molecular weight natural rubber obtained mooney viscosity ML 1+4 (100 ^{o}C) within the range of 50-60. The natural rubber molecular weight range is 100,000–200,000, equivalent with the mooney viscosity of 50–70, the reference to search the required natural rubber in this study.

Table 2.4 Low molecular weight natural rubber properties

Property	STR 5L
Dirt (retained on 44u aperture) %wt	0.04 max
Ash %wt	0.04 max
Volatile matter %wt.	0.80 max
Nitrogen %wt.	0.60 max
Initial wallace plasticity (Po)	35.0 min
Plasticity retention index (PRI)	80.0 min
ML (1+4) 100 C	60 (+7-5)
Color lovibond scale (individual value, max)	4.0

Figure 2.8 Low molecular weight natural rubber.

2.9 Natural rubber for viscosity index improving

More particularly, the invention related to the dispersants, dispersants with VI improving properties, and dispersant VI improvers from selectively hydrogenated copolymers has been prepared to use the conjugated dienes. The invention is additionally directed to the dispersants, dispersants with VI improving properties, and dispersant VI improvers from chemically modified derivatives of the above polymers.

Liquid elastomers are well known and used in various applications. For example, many functionally terminated polybutadiene liquid elastomers are known. These materials are generally highly unsaturated and frequently form the base polymer for polyurethane formulations. The preparation and application of hydroxyl-terminated polybutadiene is detailed by J. C. Broses et al. in Hydroxyl-terminated polymers obtained by free radical polymerization--Synthesis, characterization and applications.

Also, liquid polymers possessing acryl ate, car boxy- or mercapto-terminals are known. In addition to the butadiene, it is known to utilize the isoprene as the base monomer for the liquid elastomers. The liquid elastomers may contain the additional monomers, such as styrene or acrylonitrile, for controlling compatibility in blends with polar materials, such as epoxy resins.

Also known in the prior art is pure hydrocarbon, non-functionalized liquid rubbers. These liquids of elastomers would be contained in varied degrees of instauration for utilization in vulcanization. A typical example of highly unsaturated liquid elastomers is polybutadiene, e.g., that sold under the name of RICON by Ricon Resins, Inc. The liquid of polyisoprene that has been hydrogenated to saturate 90% of its original double bonds

is marketed as LIR-290 by Kuraray Isoprene Chemical Co. Ltd. still more highly saturated are liquid butyl rubbers available from Hardman Rubber Co., and Trilene, a liquid ethylene-propylene-diene rubber (EPDM) available from Uniroyal Chemical Co. The more highly saturated liquid elastomers exhibit good oxidation and ozone resistance properties.

2.10 Mooney viscosity property of natural rubber

Natural rubber (NR) is a product of biological origin. It gives, like many polymers of the natural origin, the particular complex and variable structure depending on the agronomic parameters. The main consequence is the substantial variability in NR properties, notably its process ability. Forecasting NR process ability remains a crucial problem for manufacturers. The heart of the problem, therefore, lies in identifying new quality attributes enabling more effective prediction of the NR process ability. To that end, we investigated the Mooney torque relaxation.

The mooney viscometer is an inexpensive instrument (cost and maintenance), that is easy to use and, above all, available in the great majority of factories producing natural rubber. The measurement of the NR mooney viscosity is governed by the international standard, ISO 289. This standard specifies the test temperature (100 ˚C), sample-preheating time before the start of shearing (1 min) and the shearing duration (4 min). It is conventionally written as ‘ML (1+4)100’ (‘L’ for ‘large’ rotor). When the natural rubber sample undergoes shearing in a Mooney viscometer at 2 rpm (1.6 s^{-1}), the torque increases for a few seconds to a maximum value (V_{max}). Then it decreases very rapidly to reach the minimum value (V_{min}) in many cases, and lastly rises again at varied speeds to the plateau (V_R or ML $(1+4)_{100}$) reached after 2–4 min depending on the sample. The Mooney viscosity could be linked to a composite measurement of the viscoelastic behavior of the elastomer, since it could not be used to distinguish between the elastic and viscous components. However, it is common to find two polymers with the same complex viscosity, with very different elastic and viscous components. The clearer distinction in such cases would thus mean separating the complex response into its constituent parts and studying each of them. The decay in Mooney torque once the rotor stops characterizes rubber relaxation, which makes it possible to evaluate the elastic and viscous components of the material

Natural rubber which has molecular weight ranging between 100,000–200,000 is equivalent to mooney viscosity of 50–70. Mooney viscosity is the other commonly cited criterion for defining the NBR. The mooney test is reported the arbitrary units, and it is the current standard measurement of polymer collective architectural and chemical composition. The Mooney viscosity provides data measured under narrowly defined conditions, with a specific instrument that is fixed at one shear rate. The mooney viscosity of polymers will normally relate to how they will be processed. Lower mooney viscosity materials (30 to 50) are used in injection molding, while the higher Mooney products (60 to 80) could be more highly extended and used in the extrusion and compression molding. More definitive polymer characterization could now be achieved by using the newer instruments and techniques that measure properties at shear rates pertinent to specific processing requirements. Using these newer instruments, such as the RPA2000, MDR2000, Capillary Die Rheometer and the newer Mooney machines, it is now possible to rheologically measure elastic, as well as the viscous characteristics. The RPA2000 and MDR2000 also measure the cure rates and cure states.

2.11 Related researches

US Patent 342896 , (1977) Hamrock, W.F. found certain hydrogenated block copolymers having at least 3 blocks are highly effective viscosity index improving additives for mineral oils and are especially effective at evaluated temperatures for instant Polystyrene - hydrogenated polyisoprene- polyisoprene , Polystyrene - hydrogenated polybutadiene- polyisoprene

US Patent 6034042, (2000) Rhodes, R. B. used star polymer as viscosity index improver for engine oil compositions. The polymer provide excellent low temperature performance in lubricating oil, and found that the average molecular weight of isoprene was between 15,000 – 200,000.

Tribology international “Mechanism of action of viscosity index improvers” Müller, H. G. experimentally studied at different shear rates ranging from $1000S^{-1}$ to $35,000S^{1}$ and at both VI reference at 40 ° C and 100 ° C. of several multigrade oils formulated with four different polymer-type VI. It was found that the viscosity loss with increasing shear rate is greater for hydrocarbon polymer types than for methacrylate and viscosity index is affected by the shear rate as well as by the type and concentration of polymer additive.

US Patent 6906126 Honeycutt T. et.al. test the natural latex rubber mixed into mineral oil and extracted to reduce protein levels prior to its vulcanization, Ideally, the mineral oil is characterized as having a density of approximately 0.818 to 0.880 and a viscosity of approximately 33.5 cf at 40° C.

Polymer testing, E. Ehabe´a, et.al. found better assessment of natural rubber (NR) quality and process ability, through the identification of new attributes in terms of Mooney torque relaxation, using the standardized ISO289 method (ML(1C4)100, and able to converse number into molecular weight of natural rubber as well.

In research of patent 342896 A block copolymer that is currently being usied as VI improver hydrogenated polyisoprene block has an average molecular weight between about 15,000 and 200,000.

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Lubricating oil blending formulation

Reference lubricating oil that was selected to be base line this study has been blended using the following formulation with varying on viscosity index improvers and blending conditions.

Table 3.1 Formulation of standard lubricating oil SEA 15W-40

Component	% By weight
High viscosity index base oil	41.666
Extra high viscosity index base oil	10.000
Olefin copolymer 4% (Viscosity index improver)	35.000
Lubad A	10.000
Lubad B	3.300
Other additives	0.034
	100.000

*** Lubad A is represented to anti oxidant additives.

*** Lubad B is represented to pour point, cleaning and rust inhibiting additives

3.1.2 Base oil

The high viscosity index (HVI) base oil from crude oil refinery process was supplied by Shell and it has been used as standard base oil for Shell lubricant blending process and applied to this experiment.

Figure 3.1 Base oil

Table 3.2 Base oil HVI 60 quality control

Property with UOM	Test Method	Inspection Criteria	Min	Target	Max	Typical	Spec. Val. Txt.
Acid Value (mg KOH/g)	ASTM D974	S			0.05		
Appearance	Visual	SBA					Clear and Bright.
Ash (%m)	ASTM D482	S			0.01		
Cloud Test (h)	SMS 2556	S	7				
Colour (ASTM Units)	ASTM D1500	SBA			1.5	1	
Colour stability increase (ASTM Units)	SMS 260	S			1	0.5	
Flash Point Closed (°C)	ASTM D93	SBA	204				
Kinematic Viscosity (mm²/s)	ASTM D445	SBA	4.4	4.65	4.9		
Pour Point (°C)	ASTM D97	SA			-12		
Viscosity Index (VI Units)	ASTM D2270	SA	95			120	
Water Separability (mins)	ASTM D1401	SA			20		
Noack Volatility loss (%m)	CEC L-40-T-87	S			20		

3.1.3 Viscosity index improver materials

The viscosity index improver materials used in this study were hydrogenated styrene-isoprene copolymer and low molecular weight natural rubber.

3.1.3.1 Olefin copolymer

Hydrogenated styrene-isoprene copolymer or star olefin copolymer was supplied by Infineum with commercial name Infineum SV150.

Figure 3.2 Hydrogenated styrene-isoprene copolymer.

Table 3.3 Infeneum SV 150 olefin copolymer specification

Property with UOM	State	Test Method	Min	Target	Max	Spec. Val. Txt.
Antioxidant (%m)		BAM 929	0.03		0.2	
Ash (%m)		BAM 908			0.2	
Chroma	Munsell Value 8.75	ASTM D1535			0	
Chroma	Munsell Value 9.0	ASTM D1535			0.5	
Chroma	Munsell Value 9.25	ASTM D1535			1	
Chroma	Munsell Value 9.5	ASTM D1535			1.5	
Haze		BAM 1203			2	
Iron Content (mg/kg)		BAM 1205			50	
Kinematic Viscosity (mm^2/s)	100°C	ASTM D445	15	16.5	18	
Nickel Content (mg/kg)		BAM 1205			60	
Particle matter index		BAM 1005				Max. D
Residual unsaturation (meq/g)		BAM 1207			0.12	
Total extractables (%)		BAM 1214			3	
Viscosity loss (%)		ASTM D6278			10.5	
Volatile matter (%m)		BAM 907			1	

3.1.3.2 Low molecular weight natural rubber

The commercial grade low macular weight natural rubber STR 5L was selected for this research since it has mooney viscosity 50-70 that meets the research's assumption required and expected regarding the size of polymer chains soluble in mineral oil. The natural rubber was selected for the experiment module and it was supplied by local maker name Chemical Innovation Co., Ltd.

Table 3.4 Low molecular weight natural rubber properties

Property	STR5L	STR5L Limit
Dirt (retained on 44u aperture) %wt	0.04 max	0.04 max
Ash %wt	0.04 max	0.04 max
Volatile matter %wt	0.80 max	0.80 max
Nitrogen %wt	0.60 max	0.60 max
Initial Wallace Plasticity (Po)	35.0 min	35.0 min
Plasticity Retention Index (PRI)	80.0 min	60.0 min
ML (1+4) 100 °**C**	60 (+7-5)	-
Color Lovibond Scale (individual value, max)	4.0	6.0

* Table does not mention amount of proteins content in LMNR

Figure 3.3 Low molecular weight natural rubber (LMNR).

3.2 Equipments and instruments

3.2.1 Motor and shear mixer : Silverson, UK

3.2.2 Heater 1,000 Watts : TTM H10C, Thailand

3.2.3 Thermo couple : Digicon DP, Thailand

3.2.4 Kinematic viscosity : Canon, USA

3.2.5 Cold cranking simulator CCS : Cannon CCS 2B, USA

3.2.6 Digital density analyzer : Anton Paar DMA 48, Austria

3.2.7 Metal content analyzer : ICP-OES, USA

3.2.8 Pour and cloud point analyzer : Herzog, USA

Figure 3.4 Motor and shear mixer.

Figure 3.5 Electrical heater.

Figure 3.6 Thermo couple meter.

3.3 Material mixing

The sequence and measurement of the required physical properties of the mixed material are the following.

3.3.1 The OCP and natural rubber has been blended into base oil with concentration of 2%, 4%, 8% and 10% by weight and varied temperature at 30, 60, 90 and 120 °C and the mixing time at 30, 45, 60, 90, 120 and 360 minutes. The observation of solubility behavior of all variance-mixing materials has been taken.

3.3.2 Lubricating oil SEA 15W-40 was blended by using both polymers as viscosity index improver and base oil concentration of 2%, 4%, 8% and 10% at temperature 30, 45 °C and mixing time for 10, 20 and 30 minutes.

3.3.3 Blending 2 low grade of engine oils marine and diesoline following to commercial formulation varying on NR and OCP to compare physical properties especially oxidation stability, and use blending oil that mix with NR to the real engine test to observe machine working condition and used oil after 6 weeks and 4 hour per day working status.

3.4 **Determination properties blended polymer with base oil, lubricating oils.**

3.4.1 Density (ASTM D 4052; Standard test method for density and relative density of liquids by digital density meter)

Figure 3.7 Digital density analyzer.

3.4.2 Apparent viscosity measurement for low temperature lubricant oil (ASTM D5293; Standard test method for apparent viscosity in range of temperature-5 °C. To -35 °C by cold cranking simulator)

Figure 3.8 Cold cranking simulator.

3.4.3 Zinc and calcium content in lubricating oil (ISO16140 method SMS 2798 Standard test for metal content in lubricating oil with ICP-OES instrument)

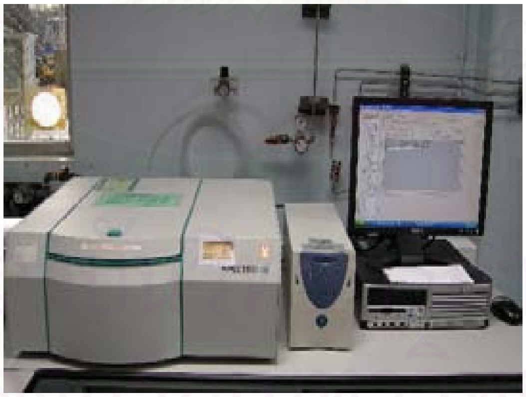


Figure 3.9 Metal content analyzer.

3.4.4 Pour point of lubricating oil (ASTM D 97; Standard test method for pour and cloudy point)

Figure 3.10 Pour point analyzer.

3.4.5 Kinematics viscosity (ASTM D 445; Standard test method for pour and cloudy point)

Figure 3.11 Kinematic viscosity.

3.4.6 Test the low grade blending oil with actual diesel engine operation for 6 weeks at 4 hours / day by applying lubrication to heavy duty pump as routine working condition.

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Lubricating oil 15W-40 quality control

The following blending formulation and control properties that are represented as in Table 3.1 and 3.2 were prepared by using the actual components as in the commercial blending process and formulated by Shell lubricant in production line with varying by NR and OCP. The specification and quality control items that are presented in Table 4.1 have been in order to ensure that the product would meet requirements and standard. It was used as the reference when the viscosity index improver was changed to another material.

Table 4.1 Lubricating oil 15W-40

Control property	Test Method	Unit	Minimum	Maximum	Target
Density @ 30 ˚C	ASTM D4052	Kg / l	0.7780	0.9520	0.8650
Appearance	Visual	None	1	0	1
Calcium content	SMS 2798	% mass	0.2660	0.3100	0.2880
Zinc content	SMS 2798	% mass	0.098	0.114	0.106
Pour point	D 97	Deg. C	-90	-30	-60
Kinematic viscosity 100 °C	ASTM D445	cST	18.10	20.00	19.05
Viscosity @ 20 °C	ASTM 5293	cST	0	70	35
Viscosity index	ASTM 2270	VI			152

4.2 Base oil and polymer blending

4.2.1 Solubility of polymer

Basically, the polymer will not suddenly dissolve into paraffin oil at ambient temperature and normal conditions. Both the olefin copolymer and low molecular weight natural rubber were initially swollen and gradually blended at higher temperatures in the high shear mixer. The experimental observation for both polymers has the initial stage of swollen at 90˚C. Also, the high concentration of both mixed polymeric materials gave more viscous material during mixing.

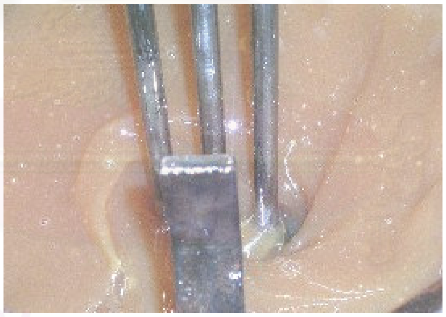


Figure 4.1 Low molecular weight natural rubber with high shear mixing stage.

Figure 4.2 shows base oil and natural rubber mixed together with high shear stirrer under temperature and concentration control. This Figure represents natural rubber at 2 % by weight concentration mixed with base oil at temperature of 90˚C to give rather viscous homogenous mixture. Thus high power shearing from mixer is required in order to obtain good mixing condition beside temperature and blending time.

Table 4.2 Solubility comparison chart of OCP and NR with various conditions at 4% concentration

Conc.	Temp (°C)	Time (Min)	Solubility NR	Solubility OCP
4%	30	30	No	No
4%	30	45	No	No
4%	30	60	No	No
4%	30	90	No	No
4%	30	120	No	No
4%	30	240	No	No
4%	60	30	No	No
4%	60	45	No	No
4%	60	60	No	No
4%	60	90	Slightly	Slightly
4%	60	120	Slightly	Slightly
4%	60	240	Slightly	Slightly
4%	90	30	No	No
4%	90	45	No	No
4%	90	60	Slightly	Slightly
4%	90	90	Slightly	Slightly
4%	90	120	Significant	Partially
4%	90	240	Significant	Significant
4%	120	30	No	No
4%	120	45	Slightly	Slightly
4%	120	60	Partially	Partially
4%	120	90	Significant	Significant
4%	120	120	Completely	Most
4%	120	240	Completely	Completely

* Remark; visual inspection result of partially has been assume as above 30% solid was dissolved into the oil, and for term of most solubility was meant by 80% and above.

Figure 4.2 Polymer completely blended with 2 % concentration at 120˚C, OCP 240 minutes mixing (left) and NR 120 minutes mixing (right).

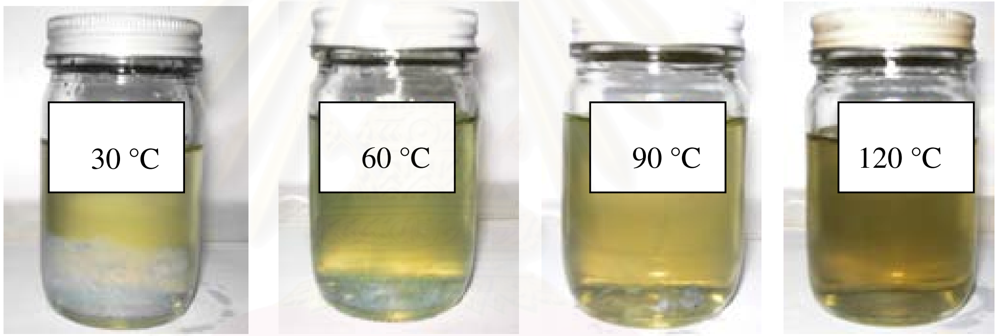


Figure 4.3 OCP (4%) blend tendency at various temperatures and 240 min. mixing.

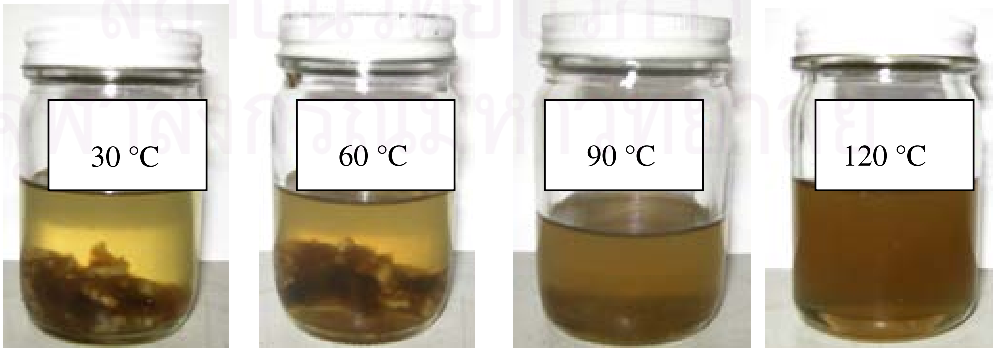


Figure 4.4 NR (4%) blend tendency at various temperatures and 120 min. mixing.

The polymer solubility in the base oil of two selected materials has similar blending behaviour as they started swelling at 90˚C, and they were gradually dissolved. The natural rubber had a little bit faster rate in blending than the OCP at swollen temperature and become obvious different when mixing time was 120 min which NR dissolved into base oil while OCP required 240 min to be completely dissolved.

4.2.2 The effect of polymers on viscosity index.

4.2.2.1 The effect viscosity index from concentration.

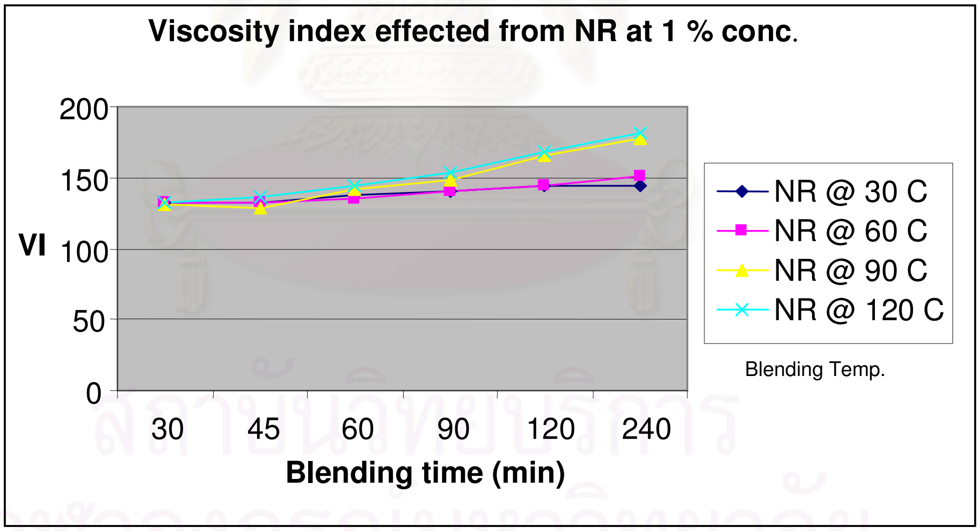


Figure 4.5 VI of natural rubber blended with oil blended for 1% NR varying on blending time.

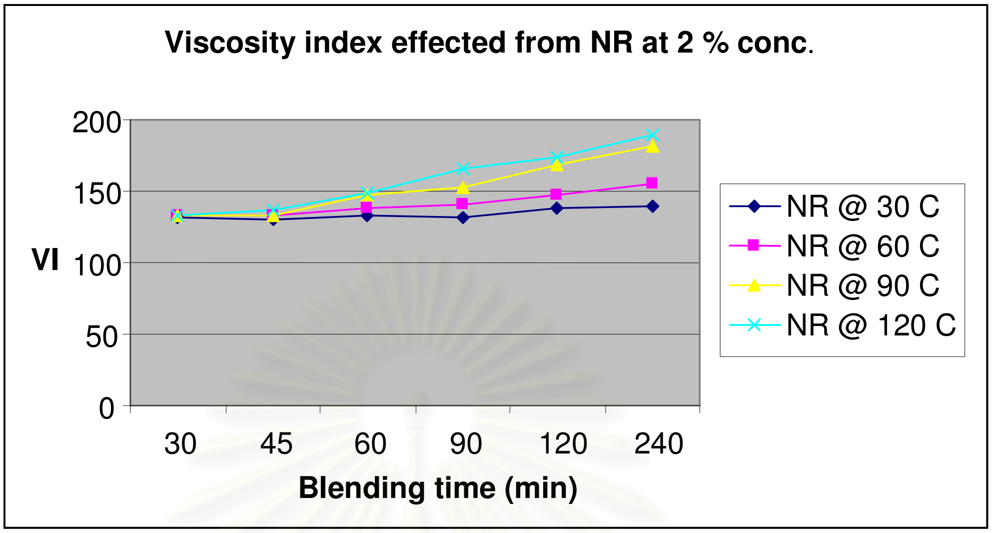


Figure 4.6 VI of natural rubber blended with oil blended for 2 % NR varying on blending time.

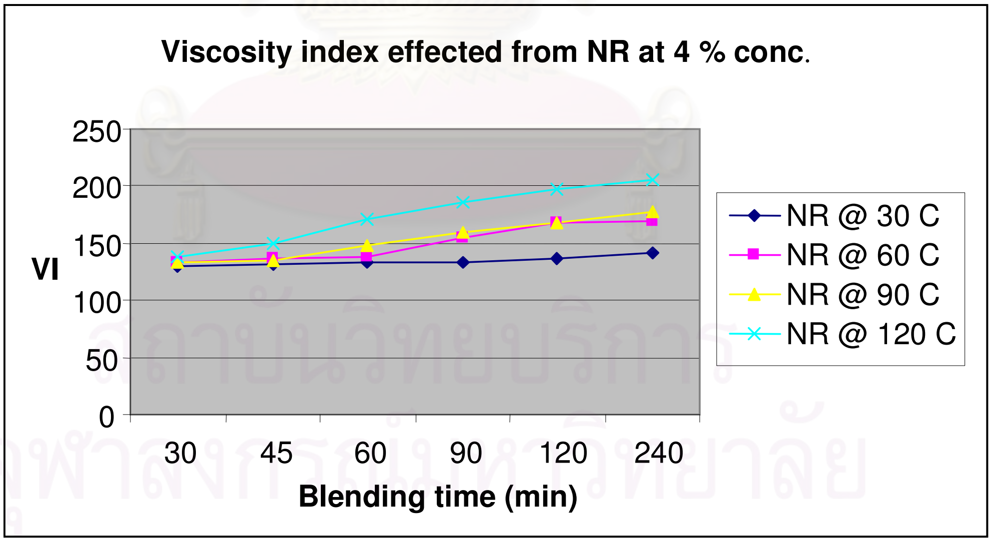


Figure 4.7 VI of natural rubber blended with oil blended for 4 % NR varying on blending time.

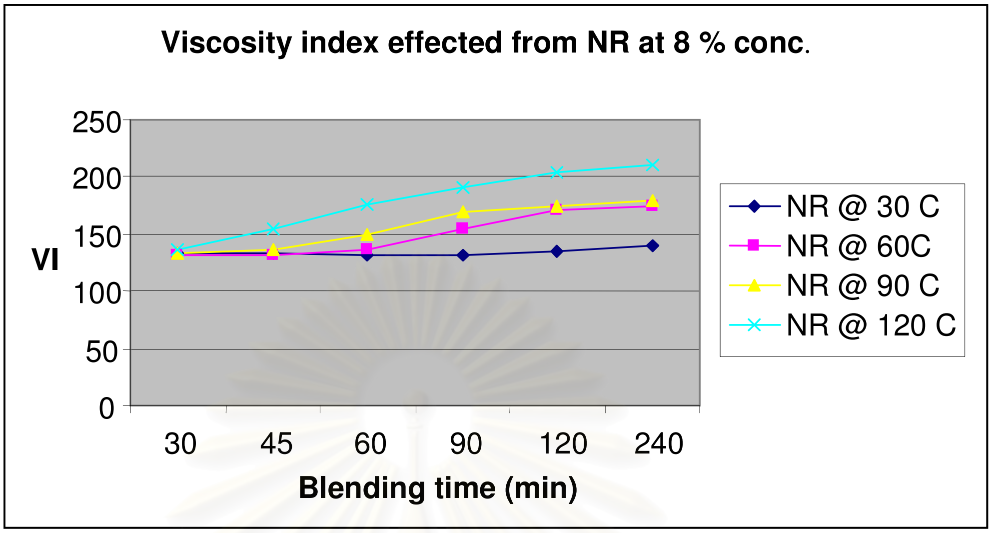


Figure 4.8 VI of natural rubber blended with oil blended for 8 % NR varying on blending time.

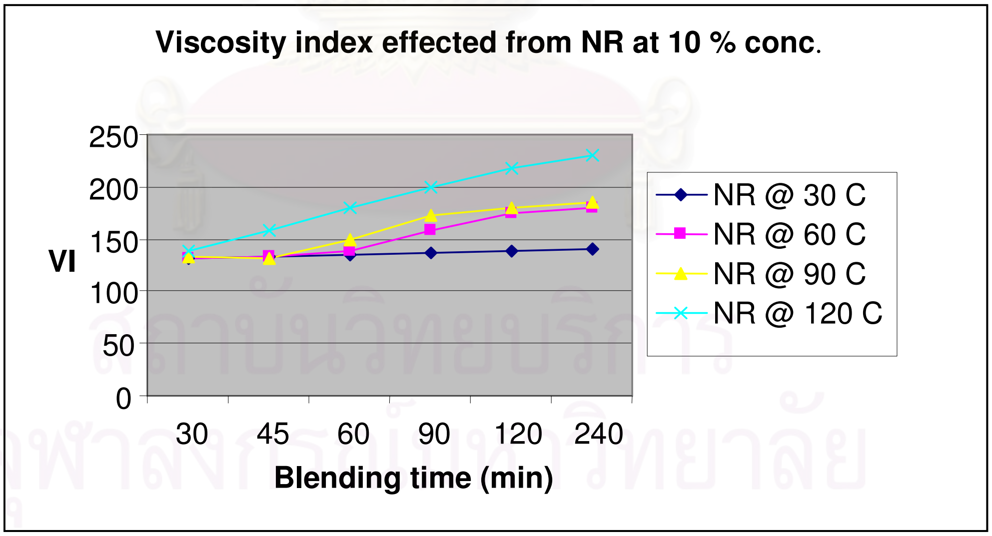


Figure 4.9 VI of natural rubber blended with oil blended for 10% NR varying on blending time.

Result of base oil mixed with natural rubber at various concentration ratios of natural rubber are shown in Figures 4.6, 4.7, 4.8 and 4.9. At ambient temperature, it was indicated that no significant changing on viscosity index was found even though concentration of natural rubber was increased, viscosity index increasing has begun at 60˚C and can be observed for significant change at 8 % and 10 % concentration. The highest viscosity index was obtained at 220 in this experiment when mixing temperature was 120˚C and 10 % (by weight) of natural rubber blended concentration.

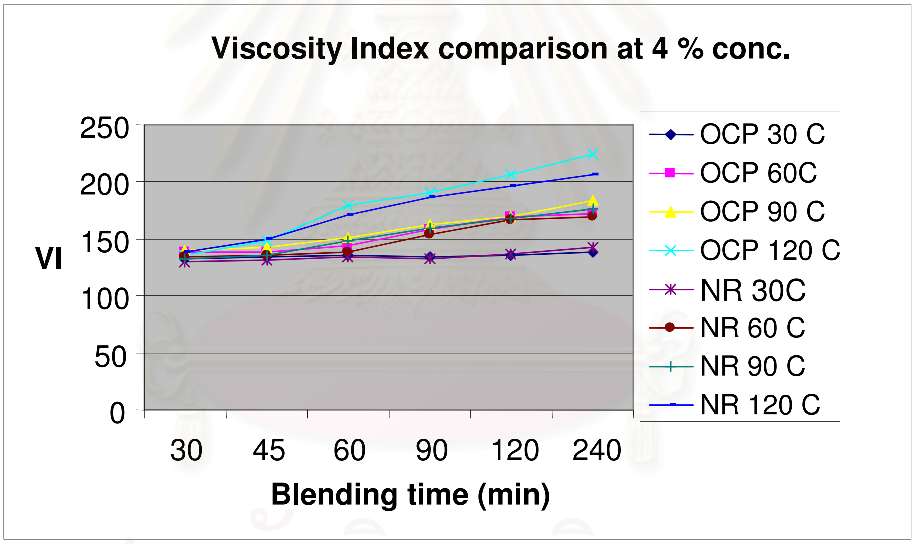


Figure 4.10 VI comparison of base oil blend with 4% NR and 4% OCP in different blending temperature.

Viscosity index improving by natural rubber blend compare to OCP is shown in Figure 4.10 the tendency of viscosity index increasing was obviously related to blending time and temperature. OCP gave higher VI at the same blending condition and both polymers gave similar increasing tendency of VI at 120˚C blending. At low temperature 30˚C and 60 ˚C, there was no significant changing on viscosity index of both NR and OCP.

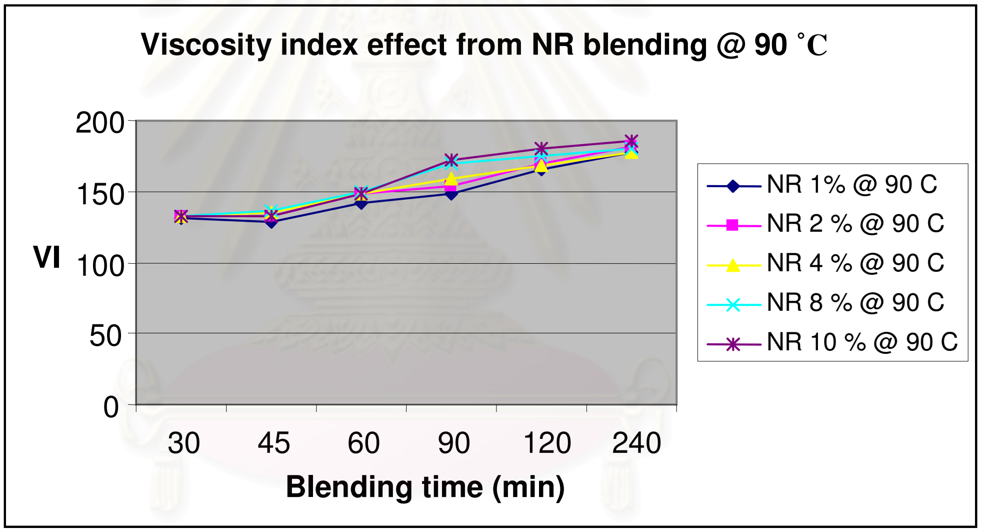


Figure 4.11 VI of blended base oil at 90˚C with different concentration of NR.

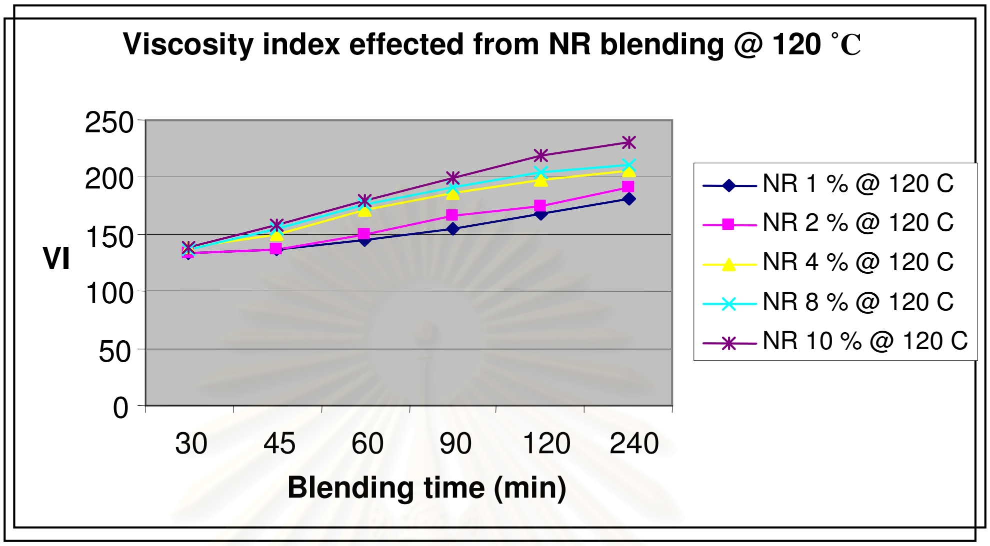


Figure 4.12 VI of blended base oil at 120°C with different concentration of NR.

Figure 4.11 and 4.12 present relationship between viscosity index and blending time with various concentrations of NR at 90°C and 120°C. The result implied that viscosity index would be increased when concentration of NR increased as shown by slope rising in Figures 4.11 and 4.12. At 120°C blending VI was increased much more than that at 90°C blended this could be explained from the solubility of NR, which was higher at 120°C than that at 90°C.

4.2.2.2 Density effect

The assumption of density of mixing material would not been changed even when temperature, concentration and time changed as shown by below graphical illustrations.

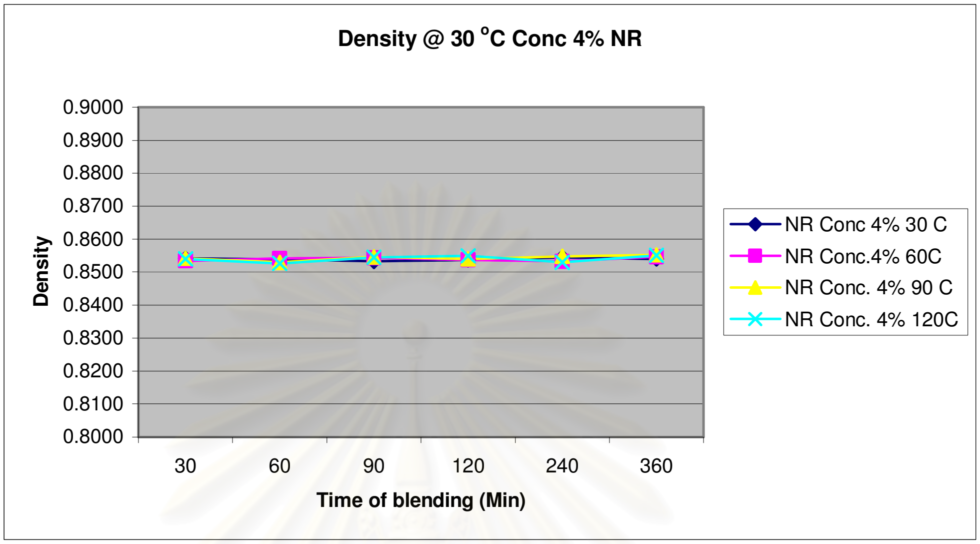


Figure 4.13 Relationship between density at 30˚C and blending times (with 4% of NR).

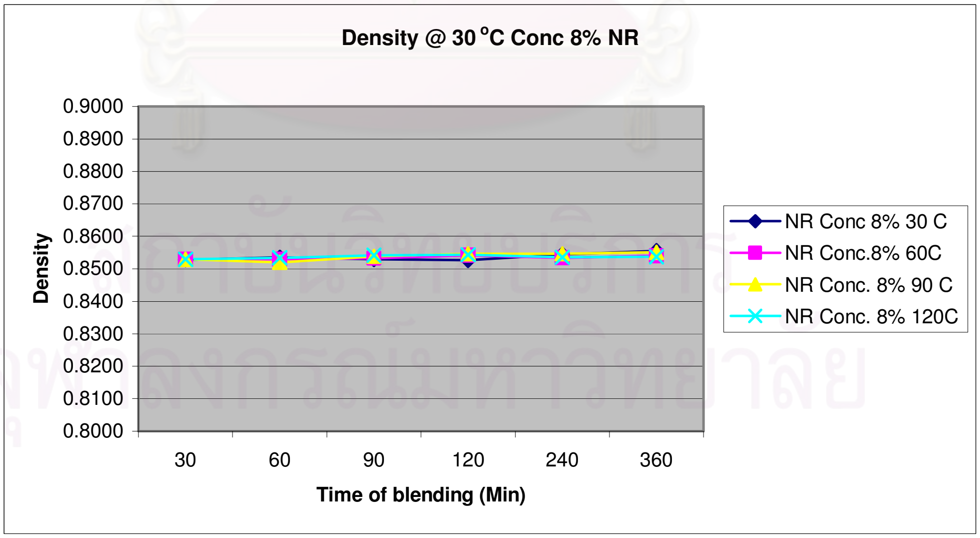


Figure 4.14 Relationship between density at 30˚C and blending times (with 8% of NR).

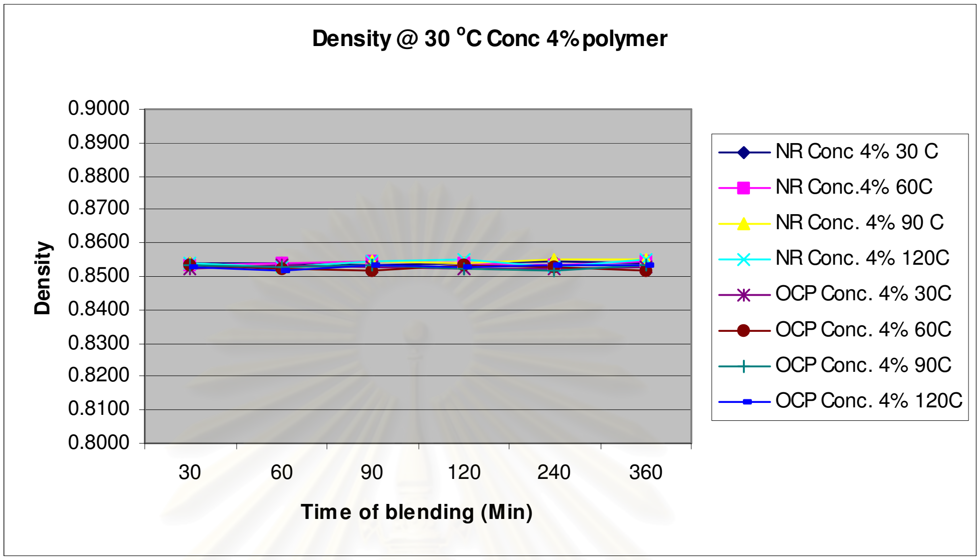


Figure 4.15 Relationship between density at 30˚C and blending times (with 4% of NR compare to OCP).

Figures 4.13 – 4.15 show the effect of NR and OCP to base oil density. There was no clear difference with this physical property by using both polymers. The densities that were obtained from all experiments have compliance with the range of base oil quality control. The conclusion from this testing was to provide assumption that NR has no effect on density of this blending product.

4.3 Lubricant oil effect from viscosity index improver

Multi-grade engine oil SEA 15W-40 was applied by using actual components referring to current production blending formula to this experiment in order to indicate the effect of natural rubber blend oils to physical properties compared to OCP blending oils.

Viscosity index is the intentional property to study the effect from blended oil when the polymer was changed. The standard lubricating oil had blended according to commercial oil formulation and all quality control subjects was measured and VI of 152 was obtained and set as target VII efficiency comparison to NR blended oils.

Analysis of effect from different type polymer and condition would have to compare with standard blending oil to understand tendency or deviation of those properties that can be indicated applicable of natural rubber in lubrication oil.

4.3.1 Viscosity index effect

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The viscosity index that was influenced by using OCP and NR at various concentrations, mixing time and temperature has been studied and measured. The viscosity index effect can be shown following to figures 4.16 - 4.19.

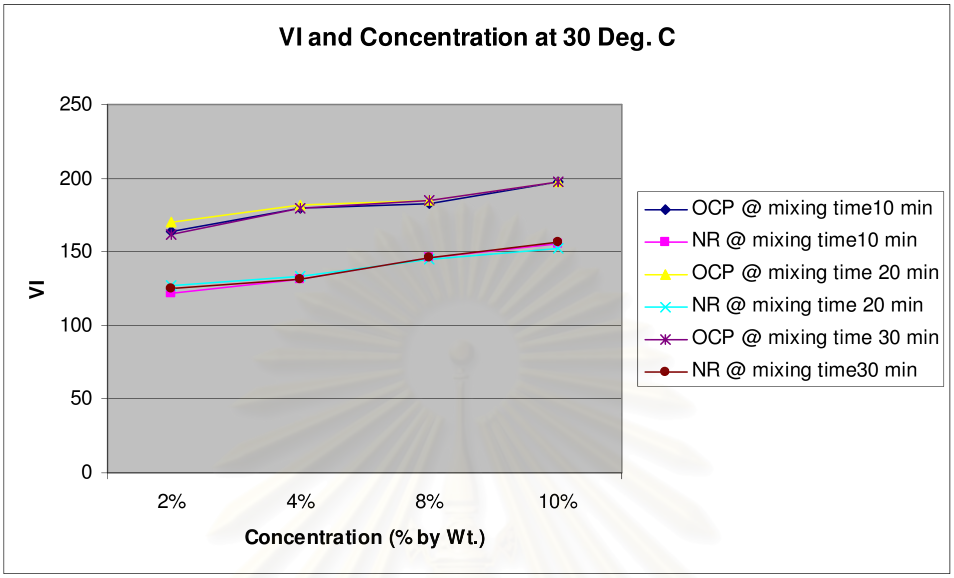

Figure 4.16 Relationship between VI and % concentration of polymer at 30 °C

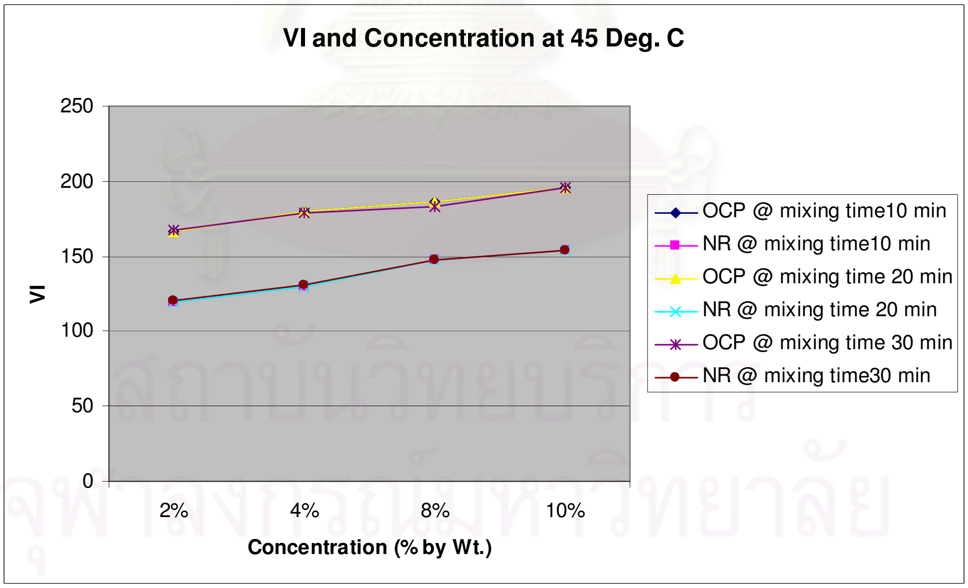

Figure 4.17 Relationship between VI and % concentration of polymer at 45 °C

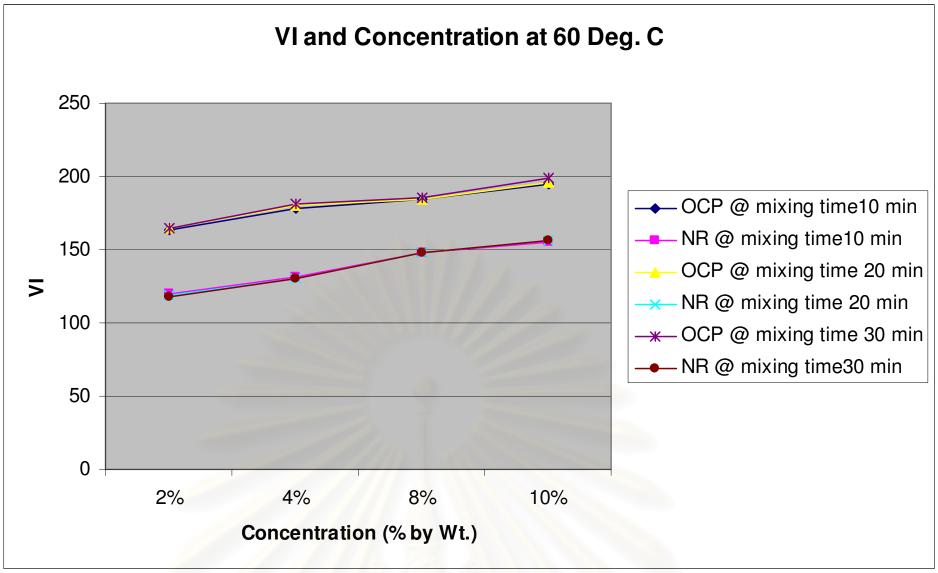

Figure 4.18 Relationship between VI and % concentration of polymer at 60 °C

The most effective factors that influence to viscosity index of lubricating oil were concentration and type of polymer while temperature and mixing time had no effect on viscosity index developing.

Figure 4.16, 4.17 and 4.18 indicated viscosity index of lubricating oil that was obtained from OCP blending oil is significant higher than natural rubber with approximately 30 %. Both polymers had a similar trend on the viscosity index increasing that was related to polymer concentrations.

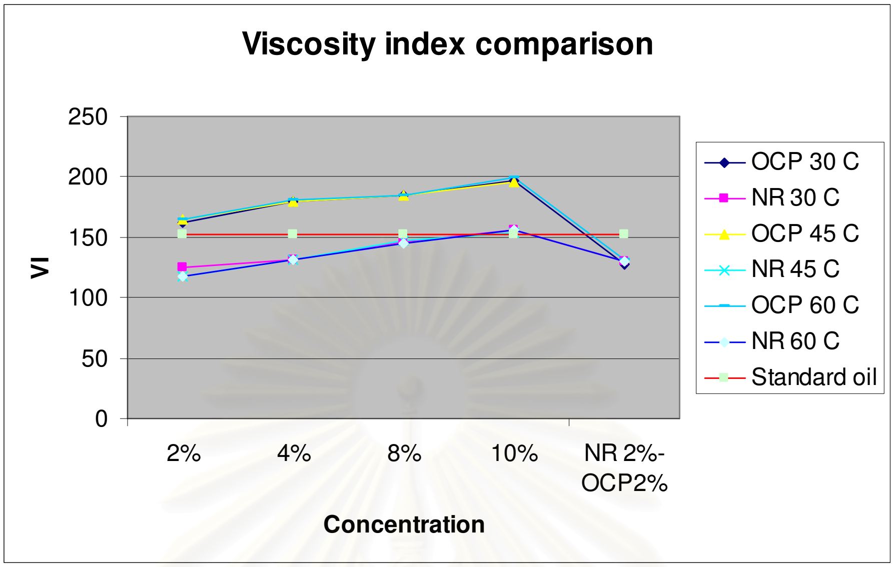

Figure 4.19 Relationship between VI and % concentration of polymer at 30 min blending

Figure 4.19 shows viscosity index improvement from both polymers at actual manufacturing time on lubricant blending and with comparison to the standard finishing oil at VI 152.

The maximum VI that NR could be improved is 156 at 10 % concentration of polymer and just a little bit higher than 152 of standard oil. For mixing both OCP and NR at 50:50, the performance on VI improving was lower and even lower when compare to 4 % NR. Thus they did not show any synergistic effect.

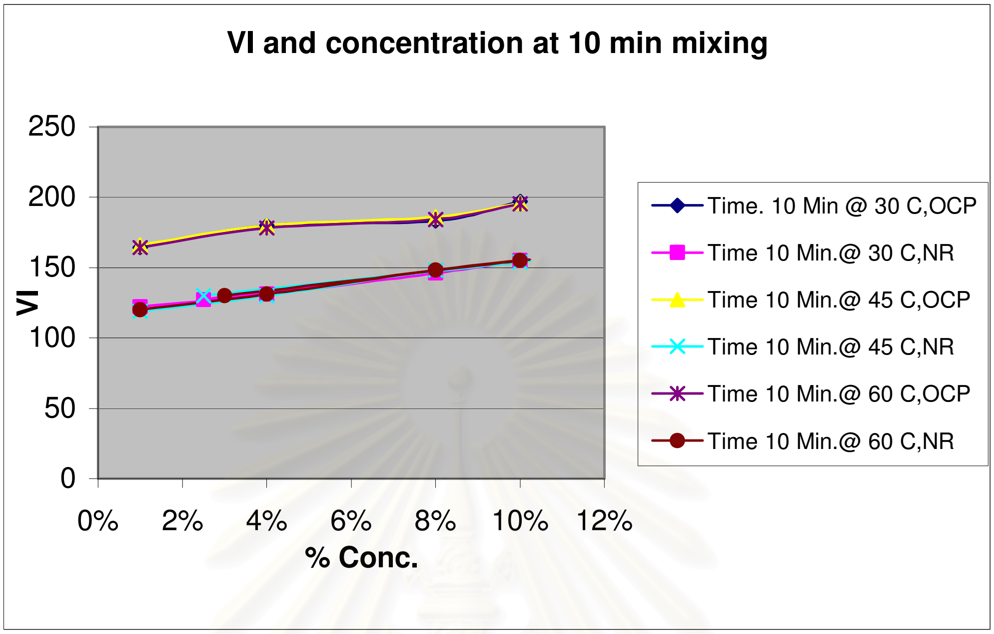

Figure 4.20 Relationship between VI and % concentration of polymer at 10 min blending

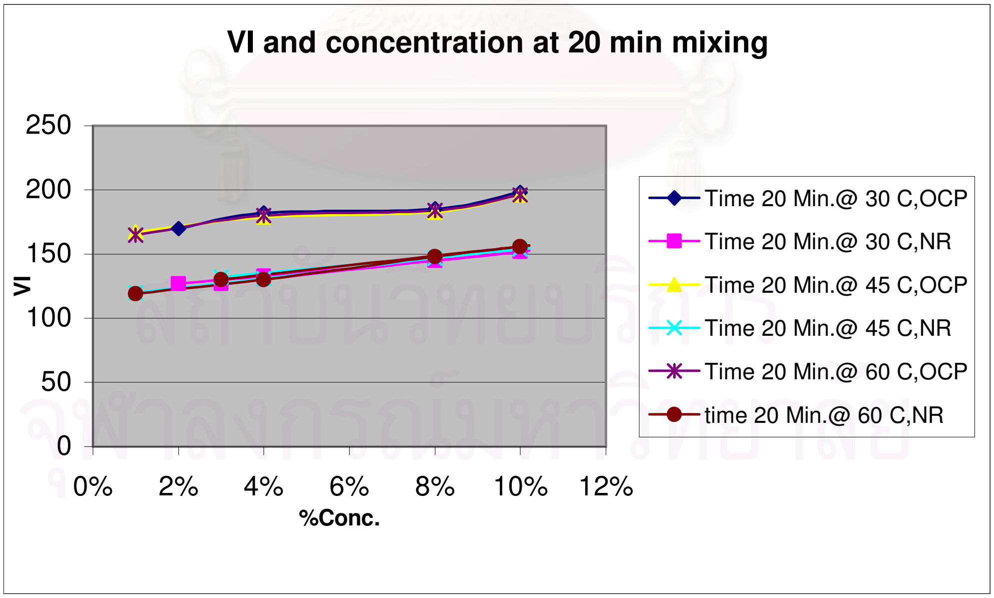

Figure 4.21 Relationship between VI and % concentration of polymer at 20 min blending

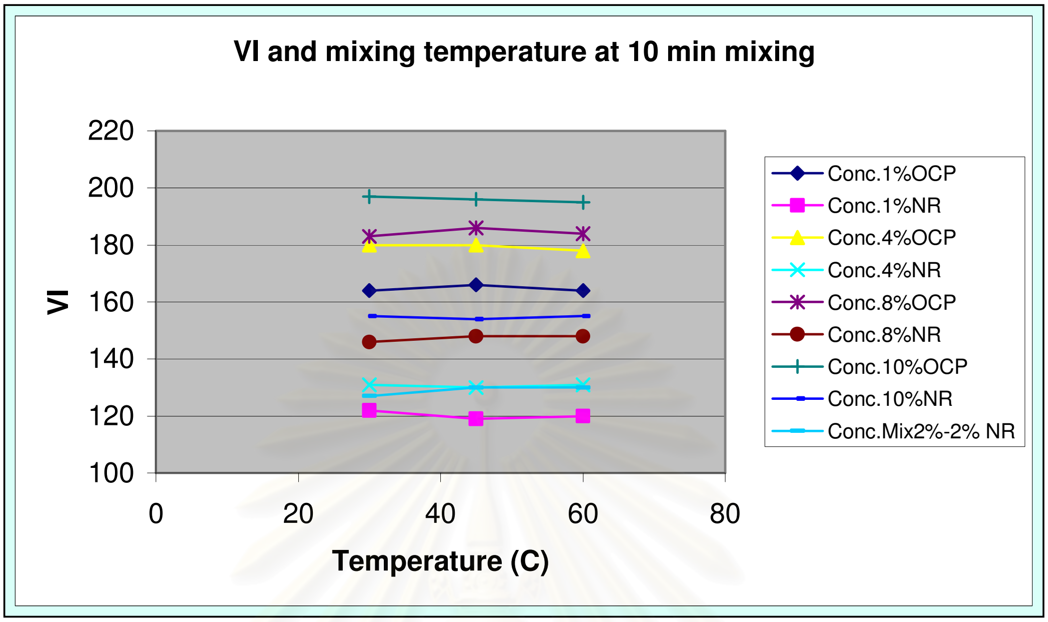

Figure 4.22 Relationship between VI and temperature at 10 min blending

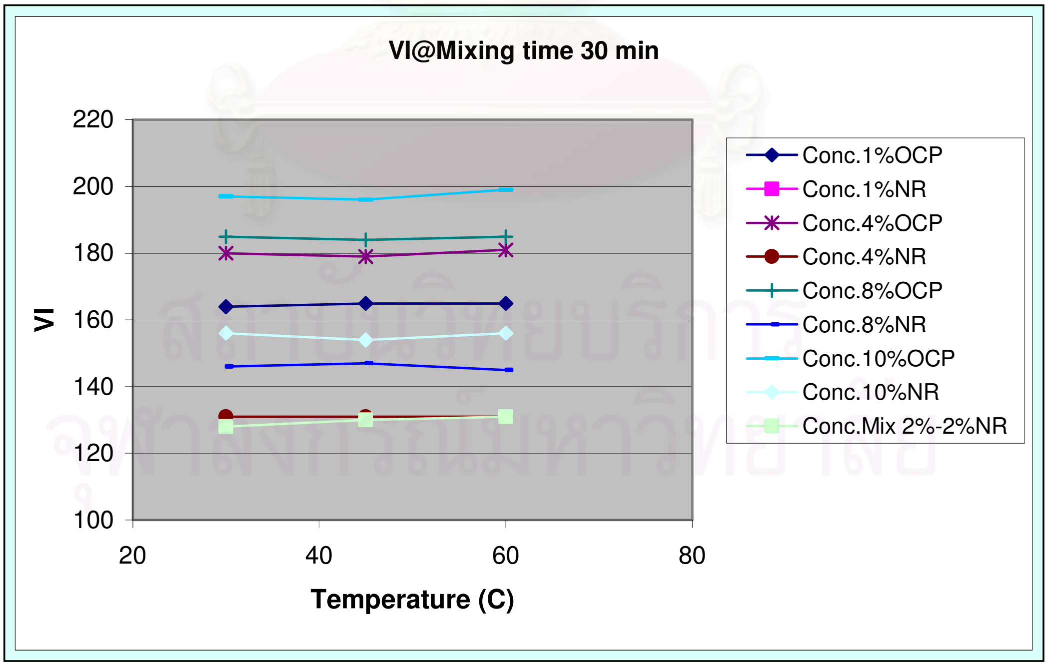

Figure 4.23 Relationship between VI and temperature at 30 min blending

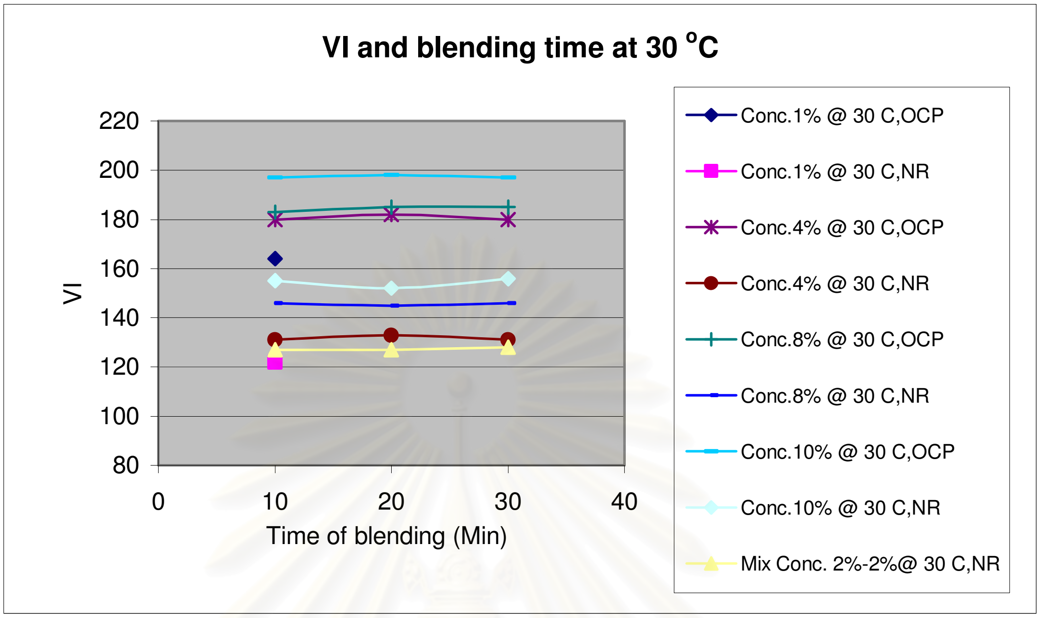

Figure 4.24 Relationship between VI and time of blending at 30 °C

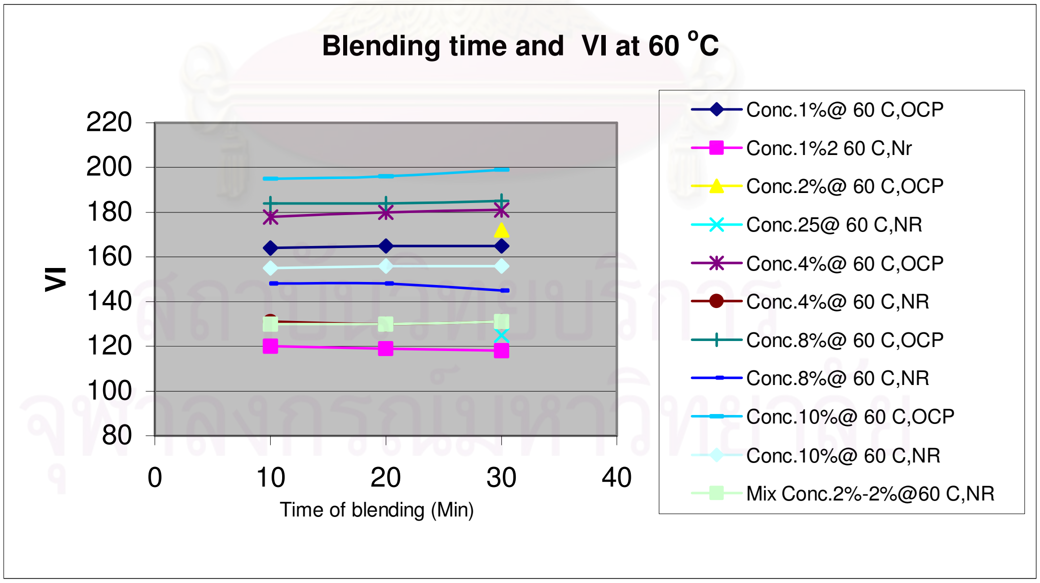

Figure 4.25 Relationship between VI and time of blending at 60 °C

Figure 4.22 – 4.25 indicated that there were no effect on viscosity index of lubricating oil from mixing time and temperature changing.

4.3.2 Physical properties of blended lubricant oil

4.3.2.1 Appearance

From figure 4.27, there was no effect on appearance on blending natural rubber in lubricating oil with standard components.

Figure 4.26 Appearance of lubricating oil 15W-40 (left) and NR blended (right)

4.3.2.2 Density effect

The effect on density of lubricating oil from all parameters can be presented in the following figures below. Comparison with density at 30 ˚C of standard lubricating oil in range 0.7780 – 0.9520 Kg/Lt and target 0.8560 Kg/L according to all parameters of blending are shown.

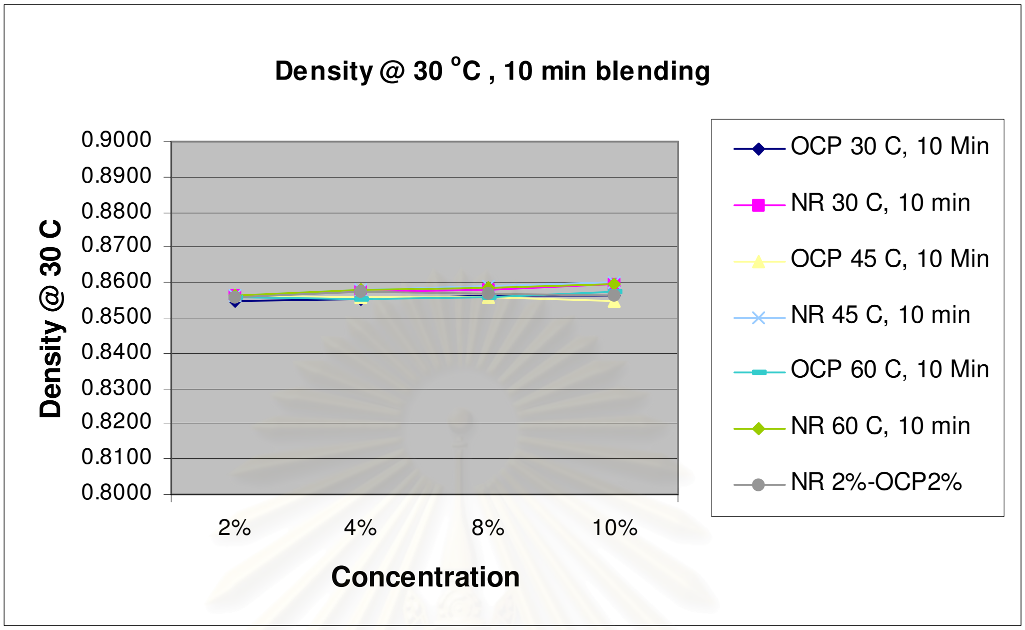

Figure 4.27 Relationship between density at 30 °C and polymer concentration at 10 min blending

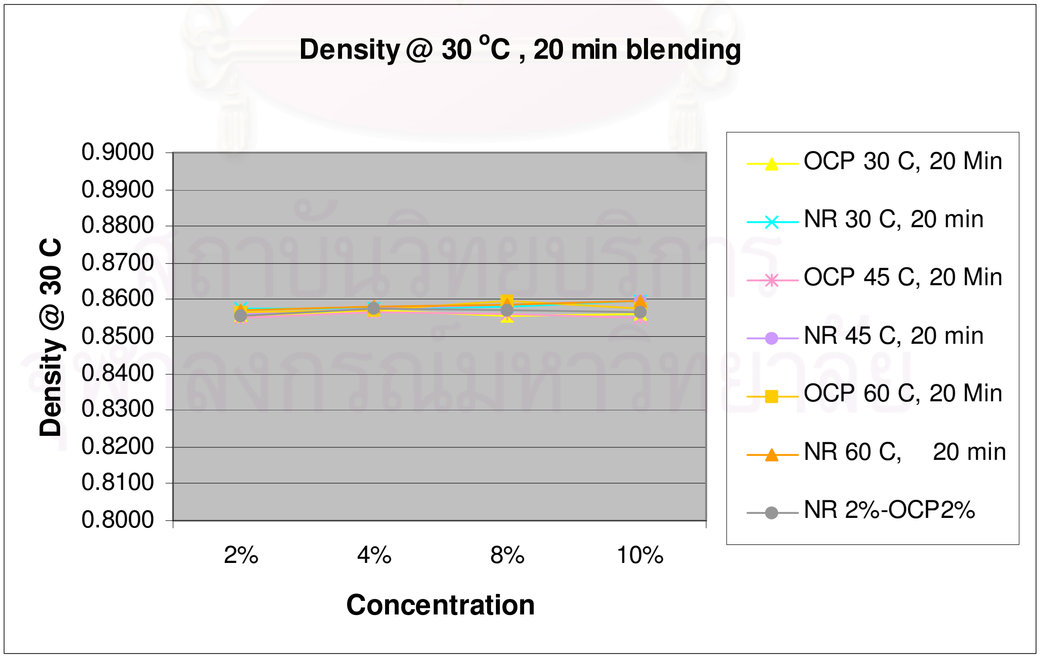

Figure 4.28 Relationship between density at 30 °C and polymer concentration at 20 min blending

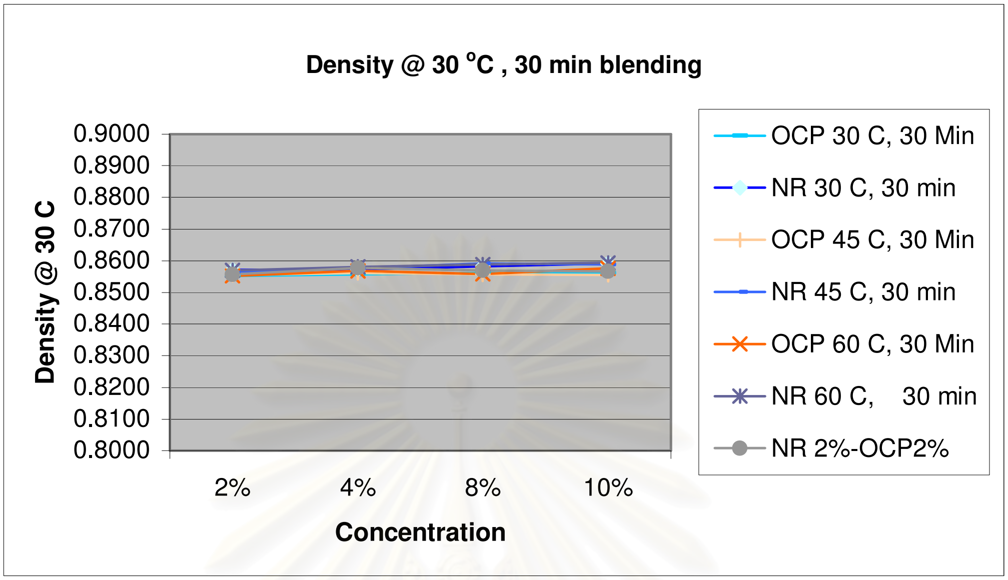

Figure 4.29 Relationship between density at 30 °C and polymer concentration at 30 min blending

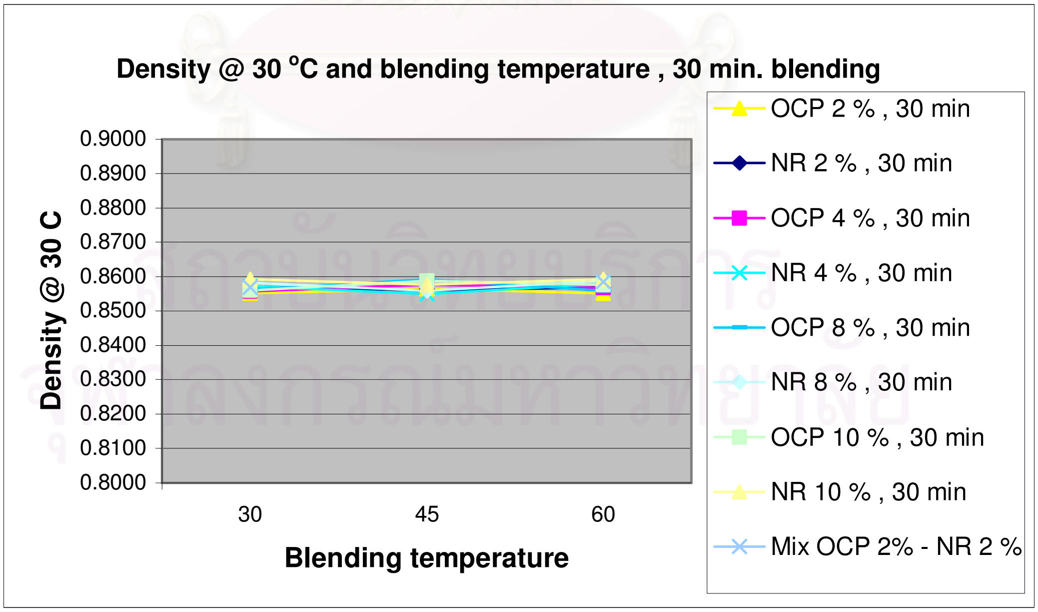

Figure 4.30 Relationship between density at 30 °C and polymer blending temperature at 30 min mixing.

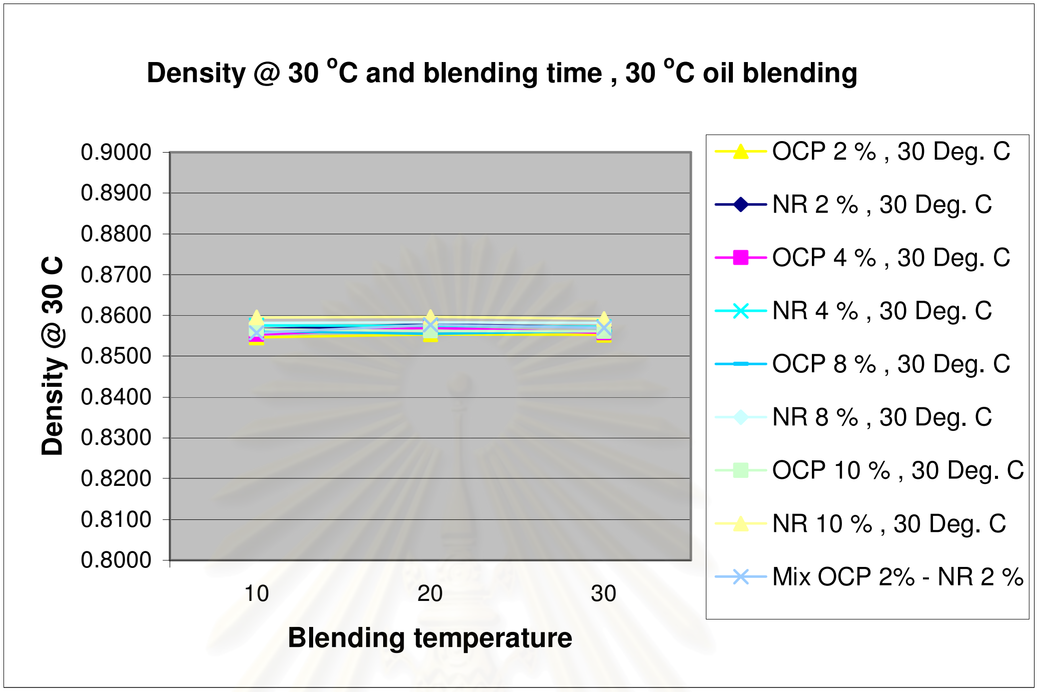

Figure 4.31 Relationship between density at 30 °C and polymer blending time at 30 °C mixing.

Results from all experiments indicated that the density densities at 30 ˚C of all samples were in the controlled range of standard lubricating oil and there was O.K. significant different.

4.4.2.3 Calcium content

The calcium content in lubricating oil was controlled by the requirement range of 0.2260 –0.3100 % and preferable at 0.2880 % as basic property requirement of lubricating oil

Table 4.3 Calcium content effect in lubricating oil from polymer

Conc.	Temp (°C)	Time (Min)	Calcium content (% mass)	
			NR	OCP
2%	30	10	0.2650	0.2710
2%	30	20	0.2680	0.2690
2%	30	30	0.2680	0.2640
2%	45	10	0.2660	0.2700
2%	45	20	0.2700	0.2710
2%	45	30	0.2680	0.2690
2%	60	10	0.2690	0.2650
2%	60	20	0.2640	0.2700
2%	60	30	0.2700	0.2640
4%	30	10	0.2680	0.2710
4%	30	20	0.2660	0.2680
4%	30	30	0.2640	0.2680
4%	45	10	0.2680	0.2690
4%	45	20	0.2660	0.2640
4%	45	30	0.2700	0.2700
4%	60	10	0.2680	0.2660
4%	60	20	0.2690	0.2700
4%	60	30	0.2670	0.2680
8%	30	10	0.2690	0.2690
8%	30	20	0.2650	0.2710
8%	30	30	0.2660	0.2690
8%	45	10	0.2650	0.2650
8%	45	20	0.2710	0.2700
8%	45	30	0.2690	0.2680
8%	60	10	0.2710	0.2660
8%	60	20	0.2640	0.2640
8%	60	30	0.2690	0.2670
10%	30	10	0.2670	0.2690
10%	30	20	0.2680	0.2700
10%	30	30	0.2710	0.2690
10%	45	10	0.2690	0.2710
10%	45	20	0.2710	0.2640
10%	45	30	0.2690	0.2690
10%	60	10	0.2650	0.2670
10%	60	20	0.2700	0.2680
10%	60	30	0.2680	0.2670

Conc.	Temp (°C)	Time (Min)	Calcium content (% mass) Mix NR and OCP
Mix 2%-2%	30	10	0.2710
Mix 2%-2%	30	20	0.2640
Mix 2%-2%	30	30	0.2690
Mix 2%-2%	45	10	0.2670
Mix 2%-2%	45	20	0.2680
Mix 2%-2%	45	30	0.2710
Mix 2%-2%	60	10	0.2690
Mix 2%-2%	60	20	0.2700
Mix 2%-2%	60	30	0.2710

Results from the experiments in Table 4.3 show that calcium content of both OCP and NR was not affected by type of polymers whether condition or ratio has been varied. Thus NR had no impact on calcium content of lubricating oil.

4.4.2.4 Zinc content

Similarly the percentage of calcium contamination zinc content in lubricating oil has been measured and controlled by the requirement range of 0.098 – 0.114 % and expected target at 0.106 % as basic property required of lubricating oil.

Table 4.4 Zinc content effect in lubricating oil from polymer

Conc.	Temp (°C)	Time (Min)	Zinc content (% mass) NR	OCP
2%	30	10	0.104	0.101
2%	30	20	0.104	0.103
2%	30	30	0.101	0.103
2%	45	10	0.101	0.102
2%	45	20	0.101	0.101
2%	45	30	0.103	0.104
2%	60	10	0.103	0.101
2%	60	20	0.103	0.101
2%	60	30	0.103	0.103
4%	30	10	0.103	0.103
4%	30	20	0.102	0.103
4%	30	30	0.101	0.101
4%	45	10	0.102	0.101
4%	45	20	0.101	0.103
4%	45	30	0.104	0.103
4%	60	10	0.101	0.102
4%	60	20	0.101	0.101
4%	60	30	0.101	0.102
8%	30	10	0.103	0.101
8%	30	20	0.102	0.104
8%	30	30	0.102	0.104
8%	45	10	0.102	0.104
8%	45	20	0.103	0.104
8%	45	30	0.103	0.101
8%	60	10	0.102	0.101
8%	60	20	0.101	0.103
8%	60	30	0.102	0.102
10%	30	10	0.101	0.102
10%	30	20	0.104	0.102
10%	30	30	0.101	0.101
10%	45	10	0.102	0.104
10%	45	20	0.101	0.104
10%	45	30	0.104	0.101
10%	60	10	0.104	0.101
10%	60	20	0.101	0.102
10%	60	30	0.104	0.101

Conc.	**Temp (°C)**	**Time (Min)**	**Zinc content (% mass) Mix NR and OCP**
Mix 2%-2%	30	10	0.104
Mix 2%-2%	30	20	0.101
Mix 2%-2%	30	30	0.102
Mix 2%-2%	45	10	0.104
Mix 2%-2%	45	20	0.104
Mix 2%-2%	45	30	0.101
Mix 2%-2%	60	10	0.101
Mix 2%-2%	60	20	0.105
Mix 2%-2%	60	30	0.104

Results from the experiments in Table 4.4 show that zinc content was not affected by both OCP and NR whether condition and ratio have been varied. Thus NR had no impact on zinc content of lubricating oil.

4.4.2.5 Pour point

Pour point property was measure as a key quality control property of comical lubricating oils. The control range is - 90 ˚C to - 30 ˚C and expected target at - 60 ˚C. Measuring had been made and result can be found following to Table. 4.5.

Table 4.5 Pour point effect in lubricating oil from polymer

Conc.	Temp (°C)	Time (Min)	Pour point (°C) NR	OCP
2%	30	10	-30	-30
2%	30	20	-28	-29
2%	30	30	-27	-30
2%	45	10	-28	-28
2%	45	20	-30	-28
2%	45	30	-30	-30
2%	60	10	-30	-30
2%	60	20	-29	-27
2%	60	30	-29	-30
4%	30	10	-27	-30
4%	30	20	-28	-29
4%	30	30	-30	-30
4%	45	10	-30	-28
4%	45	20	-29	-28
4%	45	30	-29	-30
4%	60	10	-27	-30
4%	60	20	-28	-30
4%	60	30	-30	-29
8%	30	10	-30	-30
8%	30	20	-30	-29
8%	30	30	-29	-29
8%	45	10	-29	-27
8%	45	20	-29	-28
8%	45	30	-27	-29
8%	60	10	-28	-29
8%	60	20	-30	-27
8%	60	30	-28	-28
10%	30	10	-30	-30
10%	30	20	-29	-30
10%	30	30	-29	-29
10%	45	10	-27	-27
10%	45	20	-28	-29
10%	45	30	-30	-29
10%	60	10	-30	-27
10%	60	20	-29	-28
10%	60	30	-27	-30

Conc.	**Temp (°C)**	**Time (Min)**	**Pour point (°C) Mix NR and OCP**
Mix 2%-2%	30	10	-28
Mix 2%-2%	30	20	-30
Mix 2%-2%	30	30	-30
Mix 2%-2%	45	10	-28
Mix 2%-2%	45	20	-30
Mix 2%-2%	45	30	-29
Mix 2%-2%	60	10	-29
Mix 2%-2%	60	20	-27
Mix 2%-2%	60	30	-28

The physical properties of lubricating oil which are controlled in lubricating oil product grade 15W-40 in this research experiment show that there was no effect by both polymers and all blending parameters. Figure 4.26 – 4.31 and Table 4.1 – 4.6 supported the assumption that polymer change will not effect other physical properties except viscosity index. Therefore, low molecular weight natural rubber is applicable for lubricating oil on viscosity index improvement.

4.4 Lubricating oil stability effected by viscosity index improver

Low-grade engine oil that formulated with natural rubber was used in operating engine test on routine working pump, with the objective to find out effect from natural rubber blending oil that might impact real working machine and to support assumption that natural rubber usable for lubricant. Physical properties were measured particularly on oxidation stability to understand lubricating oil steadiness when it would be used in machine operating.

4.4.1 Oxidation stability

Table 4.6 Oxidation stability results

Product	Density @ 30	VK @ 40 °C	VK @ 100 °C	VI	%Ca	%Zn	Pour point	Oxidation Stability	Remark
	Kg/L	Cst.	Cst.		%wt	%wt	Deg.C	Minute	
Marine (OCP)	0.8861	127.2	14.14	110	0.338	0.077	-18	223	For low speed diesoline engine
Marine (NR)	0.8883	130.6	14.95	107	0.286	0.076	-15	189	
X-100 (OCP)	0.8814	130.6	14.38	109	N/A	0.100	-12	178	For general diesoline engine
X-100 (NR)	0.8836	135.2	15.38	107	N/A	0.061	-9	154	

Most of the physical properties from this testing were found not to be effected by natural rubber, but slightly lower oxidation stability to both grades of lubricants has been found that could be caused from amount of double bonds of non hydrogenated natural rubber and protein structures which may be not extracted from natural rubber.

4.4.2 Real engine operation testing

The test has been set up by using diesoline engine pump to operate with NR blended lubricating oil filled and running daily for 4 hours in real condition of water pumping during 6 weeks.

Figure 4.32 Diesoline engine pump.

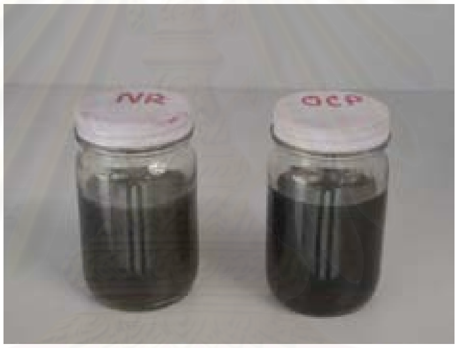

Figure 4.33 Use oil after 6 weeks operation.

The operation of the engine after it was filled with NR blended lubricating oil instead was found to give smooth running of machine without significant effect in term of operation. The used oil was found to be similar to normal used oil when the operation was finished. Therefore low molecular weight natural rubber can be formulated in commercial lubricating oil and is able to be used in real operation without negative impact to the engine according to this experimental condition. In term of cost comparison it can be reflected as by using NR has gotten cheaper than OCP in about 16 Baht / 100 liters that is equivalent to 66.67 %.

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

In this research, the effect of low molecular weight natural rubber or polyisoprene that performed as viscosity index improver was investigated. Comparison result of viscosity index increasing with hydrogenated styrene-isoprene copolymer (OCP) that is currently used in real production was carried out.

The solubility of both polymers have similar behavior which at initial blending they started with swollen temperature point at 90 ^{o}C and reached completion at 120 ^{o}C. The difference in solubility characteristic that can be observed are that natural rubber has a little bit faster miscible at the same condition. The viscosity index of OCP was significantly higher with an average of 10.84 %. The maximum viscosity index of NR solution is 220, which can be met by condition of 10 % NR concentration with 120 ^{o}C blending temperature and 240 minutes mixing time. Comparison of the mixing time and temperature in this research refers to commercial production. Natural rubber could be developed to production scale with regard to result of blending time being minimized of which could lead to cost and energy saving. The density at 30 ^{o}C of mineral base oil had not been significantly changed whether used NR or OCP, however the appearance of solution indicated that OCP gave a bit clearer solution than that of natural rubber.

Quality of base oil and polymer mixing consist of 3 key performance factors, mixing technique, temperature and mixing time. Time and temperature are simpler to control than agitation method thus development of heating and time control are the key success in lubricant blending and cost reduction in manufacturing.

Lubricating oil blended with commercial components and formulations that are used in plant production line was carried out with different viscosity index improvers and various working environments, it was demonstrated that low molecular weight natural rubber was able to perform as a viscosity index improver. Result of lubricating oil formulated with natural rubber in the same formulation of OCP and compared to the standard oil SEA15W-40 indicated that the viscosity index developed by rubber has a significant effect on the blending oil's viscosity index, but was lower value, an average of 12 .29 % less than VI obtained by OCP making. The maximum viscosity index of NR blended oil is 156 by using 10 % concentration and it was met minimum specification required at 152. In the cost evaluation natural rubber was cheaper than OCP, around 37 %, and it is reasonable to be extended into the commercial production line. Moreover, energy saving could be seen from 2 hours mixing on polymer dilution compared to OCP needs more than 4 hours of preparation.

This experiment has been extended to the scope of testing of applying low molecular weight natural rubber in actual commercial formula blend for low-grade diesoline lubricant oils and tested with real engine operation. The result of oxidation stability that has been measured result in little reduction compared to OCP blended and there was no affect on another physical properties compared to actual product. Using finish-blended oil containing NR resulted in no effect on engine performance during 6 weeks, 4 hours daily operation whether smoothly run machine. Used oil appearance that was not different from actual oil. In summary view the result of this research can be concluded and presented in table 5.1 regarding to 3 parts of testing.

Table 5.1 Summary of research and experiments

Description	LMNR	OCP	Target
1. Polymers blending in base oil			
Soluble temperature	120 C	120 C	-
Completely blend time usage	120 Min	240 Min	-
Maximum viscosity index	220	268	-
	(Conc. 10 %)	(Conc. 10 %)	
Appearance	Brown	Clear	-
Mixing base oil density changing	No	No	No
2. Polymers were use as VI improver in lubricating oil 15 W-40			
Maximum viscosity index	156	181	Minimum 152
	(Conc. 10 %)	(Conc. 4 %)	
Cost comparison	350 Baht	462 Baht	Saving 24%
Controlling physical properties change	No	No	-
Appearance	Brown	Brown	Brown
3. Polymers were use as VI improver in low grade lubricating oil			
Oxidation stability			
- Marine engine oil	189	223	-
- Diesoline engine oil	154	178	-
Cost comparison /100 liters oil	8 Baht	24 Baht	Saving 67 %
Engine test affect	No	No	No

The suggestions that could be made to develop or extend benefit of this research are firstly variability of low molecular weight natural rubber either structure adaptation from other source should be selected to the experiment to study, or find a more efficient viscosity index improving property. Hydrogenated forming and extracted protein natural rubber would be expected to be able to increase oxidation stability and VI developing property since it has less double bonds in the structure and protein would not effect the oil’s property. Other local natural polymers can be an option to be widely studied to keep continuity developing from this initiative.

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APPENDIX

Table A 1 Polymer solubility and viscosity index effect at 1 % concentration

Conc.	Temp	Time	VI		Solubility		Density @ 30
(% Wt.)	(°C)	(min)	NR	OCP	NR	OCP	kg / l
1%	30	30	132	132	No	No	0.8528
1%	30	45	133	135	No	No	0.8535
1%	30	60	138	140	No	No	0.8529
1%	30	90	140	144	No	No	0.8527
1%	30	120	144	144	No	No	0.8545
1%	30	240	144	148	No	No	0.8555
1%	60	30	132	132	No	No	0.8530
1%	60	45	133	134	No	No	0.8529
1%	60	60	135	133	No	No	0.8532
1%	60	90	140	144	Slightly	Slightly	0.8541
1%	60	120	145	152	Slightly	Slightly	0.8534
1%	60	240	151	160	Slightly	Slightly	0.8540
1%	90	30	131	133	No	No	0.8530
1%	90	45	129	132	No	No	0.8520
1%	90	60	142	153	Slightly	Slightly	0.8538
1%	90	90	148	162	Slightly	Slightly	0.8546
1%	90	120	165	171	Significant	Partially	0.8546
1%	90	240	178	185	Significant	Significant	0.8551
1%	120	30	133	139	No	No	0.8529
1%	120	45	136	148	Slightly	Slightly	0.8534
1%	120	60	145	156	Partially	Partially	0.8541
1%	120	90	154	169	Significant	Significant	0.8543
1%	120	120	168	180	Completely	Most	0.8535
1%	120	240	181	208	Completely	Completely	0.8537

Table A 2 Polymer solubility and viscosity index effect at 2 % concentration

Conc.	**Temp**	**Time**	**VI**		**Solubility**		**Density @ 30**
(% Wt.)	**(^{o}C)**	**(min)**	**NR**	**OCP**	**NR**	**OCP**	**kg / l**
2%	30	30	132	133	No	No	0.8537
2%	30	45	130	133	No	No	0.8521
2%	30	60	133	136	No	No	0.8520
2%	30	90	131	142	No	No	0.8541
2%	30	120	138	147	No	No	0.8539
2%	30	240	140	149	No	No	0.8527
2%	60	30	133	131	No	No	0.8520
2%	60	45	133	131	No	No	0.8529
2%	60	60	138	138	No	No	0.8543
2%	60	90	141	146	Slightly	Slightly	0.8535
2%	60	120	147	157	Slightly	Slightly	0.8540
2%	60	240	155	165	Slightly	Slightly	0.8535
2%	90	30	133	131	No	No	0.8534
2%	90	45	133	138	No	No	0.8540
2%	90	60	148	158	Slightly	Slightly	0.8528
2%	90	90	153	166	Slightly	Slightly	0.8532
2%	90	120	169	180	Significant	Partially	0.8536
2%	90	240	181	191	Significant	Significant	0.8546
2%	120	30	133	133	No	No	0.8527
2%	120	45	137	148	Slightly	Slightly	0.8530
2%	120	60	149	161	Partially	Partially	0.8534
2%	120	90	166	177	Significant	Significant	0.8540
2%	120	120	174	189	Completely	Most	0.8536
2%	120	240	190	211	Completely	Completely	0.8565

Table A 3 Polymer solubility and viscosity index effect at 4 % concentration

Conc.	**Temp**	**Time**	**VI**		**Solubility**		**Density @ 30**
(% Wt.)	**(°C)**	**(min)**	**NR**	**OCP**	**NR**	**OCP**	**kg / l**
4%	30	30	130	133	No	No	0.8562
4%	30	45	132	134	No	No	0.8539
4%	30	60	134	136	No	No	0.8533
4%	30	90	133	134	No	No	0.8537
4%	30	120	137	135	No	No	0.8545
4%	30	240	142	138	No	No	0.8540
4%	60	30	134	138	No	No	0.8535
4%	60	45	136	138	No	No	0.8542
4%	60	60	138	144	No	No	0.8544
4%	60	90	154	158	Slightly	Slightly	0.8537
4%	60	120	167	169	Slightly	Slightly	0.8532
4%	60	240	170	172	Slightly	Slightly	0.8546
4%	90	30	133	140	No	No	0.8542
4%	90	45	135	142	No	No	0.8530
4%	90	60	148	151	Slightly	Slightly	0.8546
4%	90	90	159	162	Slightly	Slightly	0.8540
4%	90	120	168	170	Significant	Partially	0.8548
4%	90	240	177	183	Significant	Significant	0.8552
4%	120	30	138	136	No	No	0.8540
4%	120	45	150	148	Slightly	Slightly	0.8526
4%	120	60	171	180	Partially	Partially	0.8545
4%	120	90	186	191	Significant	Significant	0.8549
4%	120	120	197	206	Completely	Most	0.8529
4%	120	240	206	224	Completely	Completely	0.8551

Table A 4 Polymer solubility and viscosity index effect at 8 % concentration

Conc.	**Temp**	**Time**	**VI**		**Solubility**		**Density @ 30**
(% Wt.)	**(^{o}C)**	**(min)**	**NR**	**OCP**	**NR**	**OCP**	**kg / l**
8%	30	30	133	131	No	No	0.8562
8%	30	45	133	133	No	No	0.8539
8%	30	60	132	133	No	No	0.8533
8%	30	90	131	136	No	No	0.8537
8%	30	120	135	138	No	No	0.8545
8%	30	240	139	141	No	No	0.8540
8%	60	30	132	133	No	No	0.8535
8%	60	45	131	135	No	No	0.8542
8%	60	60	137	145	No	No	0.8544
8%	60	90	155	159	Slightly	Slightly	0.8537
8%	60	120	171	174	Slightly	Slightly	0.8532
8%	60	240	175	179	Slightly	Slightly	0.8546
8%	90	30	133	136	No	No	0.8542
8%	90	45	137	144	No	No	0.8530
8%	90	60	150	155	Slightly	Slightly	0.8546
8%	90	90	170	175	Slightly	Slightly	0.8540
8%	90	120	175	178	Significant	Partially	0.8548
8%	90	240	180	190	Significant	Significant	0.8552
8%	120	30	137	138	No	No	0.8540
8%	120	45	155	158	Slightly	Slightly	0.8526
8%	120	60	176	185	Partially	Partially	0.8545
8%	120	90	191	196	Significant	Significant	0.8549
8%	120	120	204	209	Completely	Most	0.8529
8%	120	240	211	232	Completely	Completely	0.8551

Table A 5 Polymer solubility and viscosity index effect at 10 % concentration

Conc.	Temp	Time	VI		Solubility		Density @ 30
(% Wt.)	(°C)	(min)	NR	OCP	NR	OCP	kg / l
10%	30	30	131	133	No	No	0.8540
10%	30	45	133	131	No	No	0.8542
10%	30	60	135	133	No	No	0.8549
10%	30	90	136	134	No	No	0.8540
10%	30	120	138	139	No	No	0.8529
10%	30	240	140	145	No	No	0.8535
10%	60	30	132	133	No	No	0.8540
10%	60	45	133	133	No	No	0.8538
10%	60	60	139	146	No	No	0.8525
10%	60	90	158	161	Slightly	Slightly	0.8545
10%	60	120	175	178	Slightly	Slightly	0.8551
10%	60	240	180	188	Slightly	Slightly	0.8544
10%	90	30	133	140	No	No	0.8530
10%	90	45	132	150	No	No	0.8530
10%	90	60	149	158	Slightly	Slightly	0.8555
10%	90	90	172	181	Slightly	Slightly	0.8562
10%	90	120	180	188	Significant	Partially	0.8555
10%	90	240	185	195	Significant	Significant	0.8560
10%	120	30	138	140	No	No	0.8565
10%	120	45	158	165	Slightly	Slightly	0.8565
10%	120	60	179	199	Partially	Partially	0.8545
10%	120	90	199	210	Significant	Significant	0.8551
10%	120	120	218	235	Completely	Most	0.8544
10%	120	240	220	268	Completely	Completely	0.8530

Table A 6 Finished blending oil test result of controlled properties on VI and Density

Conc. (% Wt.)	Temp (°C)	Time (min)	VI		Density @ 30	
			OCP	NR	OCP	NR
1%	30	10	164	122	0.8546	0.8566
2%	30	20	170	127	0.8554	0.8578
2%	60	30	172	125	0.8552	0.8571
1%	45	10	166	119	0.8562	0.8566
1%	45	20	167	120	0.8549	0.8562
1%	45	30	165	118	0.8556	0.8565
1%	60	10	164	120	0.8561	0.8564
1%	60	20	165	119	0.8566	0.8570
1%	60	30	165	118	0.8552	0.8569
4%	30	10	180	131	0.8554	0.8576
4%	30	20	182	133	0.8569	0.8575
4%	30	30	180	131	0.8557	0.8572
4%	45	10	180	130	0.8559	0.8579
4%	45	20	179	131	0.8566	0.8576
4%	45	30	179	131	0.8562	0.8576
4%	60	10	178	131	0.8551	0.8578
4%	60	20	180	130	0.8569	0.8584
4%	60	30	181	131	0.8568	0.8580
8%	30	10	183	146	0.8562	0.8582
8%	30	20	185	145	0.8555	0.8583
8%	30	30	185	146	0.8562	0.8582
8%	45	10	186	148	0.8556	0.8589
8%	45	20	183	147	0.8561	0.8586
8%	45	30	184	147	0.8557	0.8592

Conc.	Temp	Time	VI		Density @ 30	
(% Wt.)	(°C)	(min)	OCP	NR	OCP	NR
8%	60	10	184	148	0.8559	0.8585
8%	60	20	184	148	0.8596	0.8589
8%	60	30	185	145	0.8559	0.8588
10%	30	10	197	155	0.8566	0.8595
10%	30	20	198	152	0.8562	0.8596
10%	30	30	197	156	0.8561	0.8592
10%	45	10	196	154	0.8550	0.8599
10%	45	20	196	154	0.8552	0.8597
10%	45	30	196	154	0.8556	0.8589
10%	60	10	195	155	0.8577	0.8595
10%	60	20	196	156	0.8574	0.8596
10%	60	30	199	156	0.8576	0.8593
Mix 2%-2%	30	10		127	0.8557	
Mix 2%-2%	30	20		127	0.8577	
Mix 2%-2%	30	30		128	0.8569	
Mix 2%-2%	45	10		130	0.8566	
Mix 2%-2%	45	20		132	0.8574	
Mix 2%-2%	45	30		130	0.8556	
Mix 2%-2%	60	10		130	0.8588	
Mix 2%-2%	60	20		130	0.8579	
Mix 2%-2%	60	30		131	0.8585	

Table A 7 Finished blending oil test result of controlled physical properties on Calcium, Zinc content and pour point

Conc.	**Temp**	**Time**	**Calcium content**		**Zinc content**		**Pour point**	
(% Wt.)	**(^{o}C)**	**(min)**	**OCP**	**NR**	**OCP**	**NR**	**OCP**	**NR**
1%	30	10	0.1040	0.1010	0.2650	0.2710	-30	-30
2%	30	20	0.1040	0.1030	0.2680	0.2690	-28	-29
2%	60	30	0.1010	0.1030	0.2680	0.2640	-27	-30
1%	45	10	0.1010	0.1020	0.2660	0.2700	-28	-28
1%	45	20	0.1010	0.1010	0.2700	0.2710	-30	-28
1%	45	30	0.1030	0.1040	0.2680	0.2690	-30	-30
1%	60	10	0.1030	0.1010	0.2690	0.2650	-30	-30
1%	60	20	0.1030	0.1010	0.2640	0.2700	-29	-27
1%	60	30	0.1030	0.1030	0.2700	0.2640	-29	-30
4%	30	10	0.1030	0.1030	0.2680	0.2710	-27	-30
4%	30	20	0.1020	0.1030	0.2660	0.2680	-28	-29
4%	30	30	0.1010	0.1010	0.2640	0.2680	-30	-30
4%	45	10	0.1020	0.1010	0.2680	0.2690	-30	-28
4%	45	20	0.1010	0.1030	0.2660	0.2640	-29	-28
4%	45	30	0.1040	0.1030	0.2700	0.2700	-29	-30
4%	60	10	0.1010	0.1020	0.2680	0.2660	-27	-30
4%	60	20	0.1010	0.1010	0.2690	0.2700	-28	-30
4%	60	30	0.1010	0.1020	0.2670	0.2680	-30	-29
8%	30	10	0.1030	0.1010	0.2690	0.2690	-30	-30
8%	30	20	0.1020	0.1040	0.2650	0.2710	-30	-29
8%	30	30	0.1020	0.1040	0.2660	0.2690	-29	-29
8%	45	10	0.1020	0.1040	0.2650	0.2650	-29	-27
8%	45	20	0.1030	0.1040	0.2710	0.2700	-29	-28
8%	45	30	0.1030	0.1010	0.2690	0.2680	-27	-29

Conc. (% Wt.)	Temp (^oC)	Time (min)	Calcium content		Zinc content		Pour point	
			OCP	NR	OCP	NR	OCP	NR
8%	60	10	0.1020	0.1010	0.2710	0.2660	-28	-29
8%	60	20	0.1010	0.1030	0.2640	0.2640	-30	-27
8%	60	30	0.1020	0.1020	0.2690	0.2670	-28	-28
10%	30	10	0.1010	0.1020	0.2670	0.2690	-30	-30
10%	30	20	0.1040	0.1020	0.2680	0.2700	-29	-30
10%	30	30	0.1010	0.1010	0.2710	0.2690	-29	-29
10%	45	10	0.1020	0.1040	0.2690	0.2710	-27	-27
10%	45	20	0.1010	0.1040	0.2710	0.2640	-28	-29
10%	45	30	0.1040	0.1010	0.2690	0.2690	-30	-29
10%	60	10	0.1040	0.1010	0.2650	0.2670	-30	-27
10%	60	20	0.1010	0.1020	0.2700	0.2680	-29	-28
10%	60	30	0.1040	0.1010	0.2680	0.2670	-27	-30
Mix 2%-2%	30	10	0.1040		0.2710		-28	
Mix 2%-2%	30	20	0.1010		0.2640		-30	
Mix 2%-2%	30	30	0.1020		0.2690		-30	
Mix 2%-2%	45	10	0.1040		0.2670		-28	
Mix 2%-2%	45	20	0.1040		0.2680		-30	
Mix 2%-2%	45	30	0.1010		0.2710		-29	
Mix 2%-2%	60	10	0.1010		0.2690		-29	
Mix 2%-2%	60	20	0.1050		0.2700		-27	
Mix 2%-2%	60	30	0.1040		0.2710		-28	

VITAE

Mr. Rakpao Ponerattana was born on February 7, 1973 in Nakhornpanom, Thailand. He received his Bachelor Degree of Engineering from Khonkaen University in 1996. He has studied for the Master Degree of Science in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University since 2004 and graduated in 2007.

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