

CHAPTER 2

THEORETICAL CONSIDERATION

Engine oil is used primarily to reduce frictions and to prevent wears between engine components by forming thin oil film between engine surfaces. The most important property of engine oil is the viscosity. The viscosity directly influences the thickness of the film in engine. The engine oil must have the right viscosity in order to produce the appropriate film layers. If the viscosity in engine oil is low, the film produced will be too thin thus, unable to prevent any wears that might occur. On the other hand, if the viscosity is too high, the viscous engine oil will produce thick film layers, and therefore, add an additional exertion to the engine.

The viscosity of engine oil depends on several factors, such as temperature and shear rate.

2.1 Influence of temperature on viscosity (V-T behavior) [1]

Engine oil viscosity reduces when temperature decreases. The relationship is in a hyperbolic form. The following equation describes this relationship:

$$m = \log \log(\nu + C) = K - m \cdot \log T \quad (1)$$

where

ν is viscosity of liquid, C , K are the constant values, T are the temperature and m are the slope of ν versus T curve

Note C for mineral oil is approximately 0.6-0.9.

From Eq.1, C has only a minor effect on viscosity, however, the effect is greater if the temperature gets too low.

“ m ” can be used to analyze the relationship of the viscosity and oil temperature. From the graph of m versus T , and from the graph, the lower m is, the minimal the affect of T on viscosity. Slope (m) is known to have a value between 1.1 to 4.5 and can be calculated by using the following equation:

$$m = \frac{\log \log(\nu_1 + 0.8) - \log \log(\nu_2 + 0.8)}{\log T_2 - \log T_1} \quad (2)$$

2.2 The Effect of shear rate on viscosity [1]

Viscosity in Newtonian fluid is constant even when shear force applies. This means, applying shear force in an environment where temperature and pressure are constant does not influence the fluid’s viscosity. Pure mineral base oil is a Newtonian fluid at normal room temperature. Lubricant with polymer and thickener added and mineral base oil at very low temperature are on the other hands non-Newtonian, thus, its viscosity is influenced by shear force. Shear force dependent is an undesirable behavior in lubricant. Polymer (VI improver) in multi-grade lubricant is known to be one of the causes of its shear force dependent.

Briefly, multi-grade engine oil’s viscosity decreases when shearing occurs and increases back when the shearing stops (structural-viscosity effect). However, if the applied load exceeded the polymer’s shear stability point, the polymer chains will be broken and thus causing a permanent viscosity loss in the engine oil. Shear stability property in engine oil is therefore, crucial in lubricant production.

2.3 Physical description of viscosity index [1,2,3]

Engine oil viscosity can be forecasted using viscosity index. Viscosity index is an empirical number that indicates the degree of change in viscosity of an oil within a given temperature range. The accepted temperatures for calculating VI are at 40°C and 100°C using the ASTM D 2270 equation as the following:

$$VI = [(L - U)/(L - H)] \times 100 \quad (3)$$

where

L is the kinematic viscosity @ 40°C of the zero VI standard, H is the kinematic viscosity @ 40°C of the 100 VI standard, and U is the kinematic viscosity @ 40°C of test sample.

The result of the calculation can be interpreted as; the higher VI, the more temperature tolerance for the engine oil. In the other words, when there is a temperature change, the viscosity of a high VI engine oil remains constant or has minimal changes comparing to lubricants with lower VI. Normally, lubricant in domestic market is known to have the VI value in a range of 80 to 120.

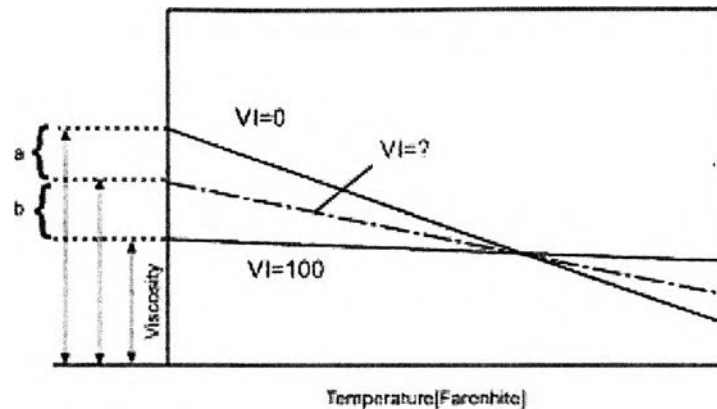


Figure 2.1 Graphical illustration of VI

2.4 VI Improvement mechanism [1]

Polymer as viscosity index improver helps in widening the usable temperature range in multi-grade engine oil. The viscosity of polymer added mineral oil at 40°C is in general, not significantly different from single grade engine oil because, at this temperature, the polymer shape is compact and plays minimal roles when dissolved in mineral base oil, however, the situation is different at 100°C. At 100°C, polymer in multi-grade engine oil functions by stretching its original curly shape thus causing additional contact surface area with mineral base oil. Consequently, the surface area interrupted the normal flow of base oil and hence, increases the viscosity of the lubricant.

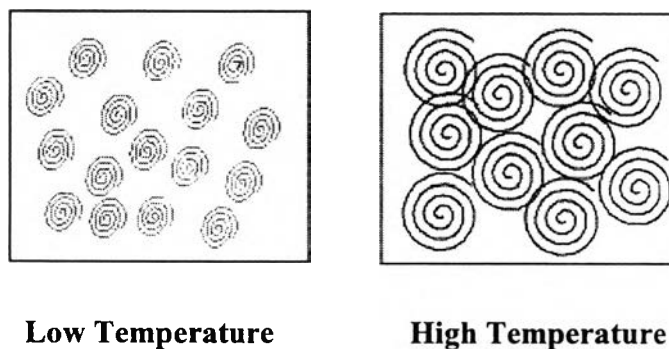


Figure 2.2 Polymer shape in lubricant

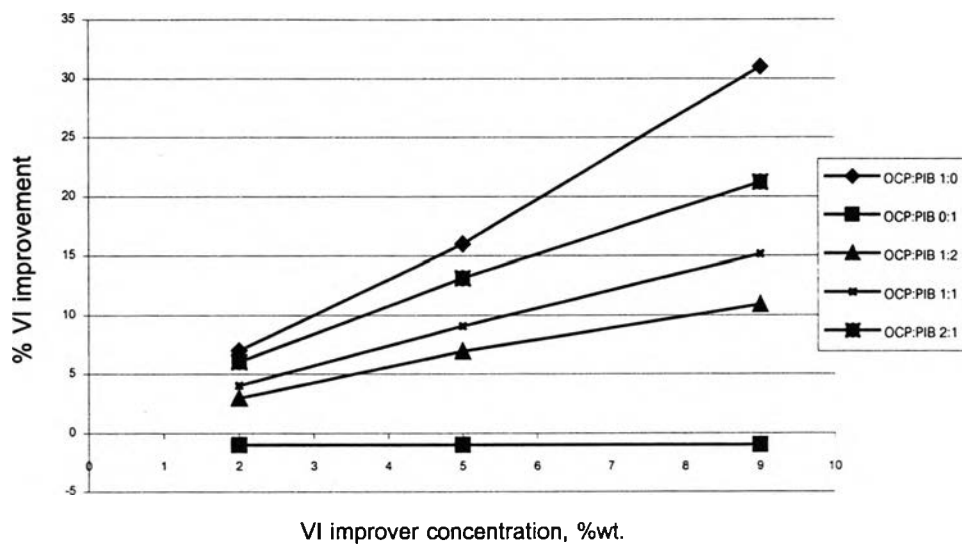


Figure 4.4c VI improvement of mineral base oil containing OCP, PIB and OCP-PIB systems

Figure 4.4c shows VI improvement of the dual OCP-PIB viscosity index improvers in blended base oil. The viscosity indexes of the blended oil containing OCP increase when its ratios in blended oil increase. PIB represented with a square line stays parallel with the concentration axis. This means PIB does not improve the viscosity index of the blended oil.

The ability of polymer to increase viscosity in engine oil (also known as the thickening effect) depends on its molecular weight and concentration (neglecting the chemical branching of the polymer). In the domestic industry, VIIs with molecular weight between 10000 to 250000 $\text{g}\cdot\text{mol}^{-1}$ are used at the concentration of approximately 3 to 25 %wt.

One undesired behavior of polymer with good thickening effect in engine oil is its poor shear stability index. Polymer containing base oil is a non-Newtonian fluid and therefore subject to shear force. The polymer chain can be broken and shorten, causing permanent viscosity loss in the oil. As a rule, the longer the polymer chains, the more chance of permanent viscosity loss in engine oil. Multi-grade engine oil potential loss due to shear stress can be measured using Permanent Shear Stability Index (PSSI, Fig. 2.3).

Besides permanent viscosity loss, there is a temporary viscosity loss, which occurs when there is a short relaxation of polymer chain causing temporarily abnormal alignment of chain [1]. The temporary loss of viscosity is measured using temporary shear stability index (TSSI). The thickening effect and shear stability of engine oil are illustrated in Figure 2.4.

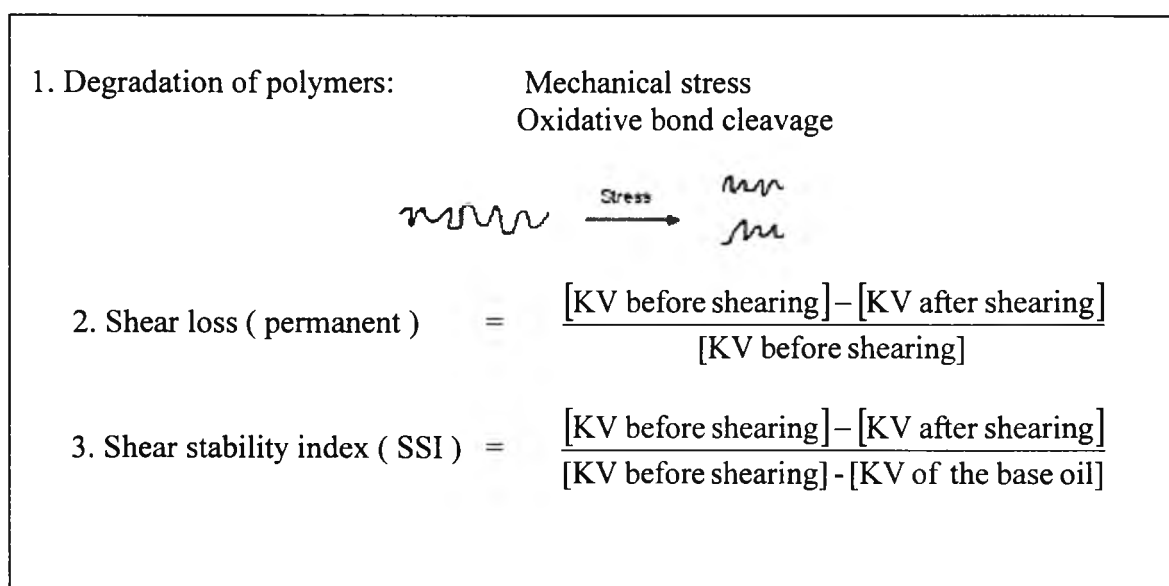


Figure 2.3 Calculation of degradation, shear loss and SSI

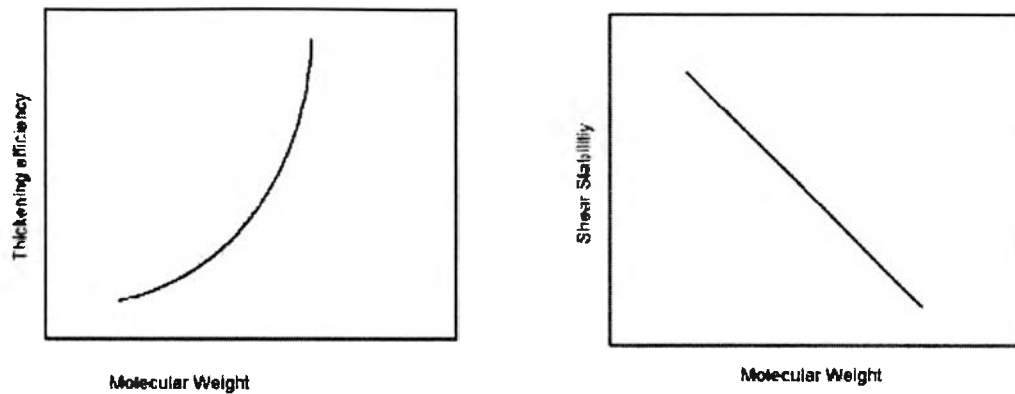


Figure 2.4 Relationship of lubricating oil properties

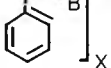
2.5 Thermal-oxidative stability [4]

Since viscosity index improver is used at high temperature, there are high possibilities that hydrocarbon polymer will be oxidized cause polymer chains to break apart. The chemical reaction occurs randomly, and leading to the breaking of the polymer chain at different location within the chains [4]. If the breaking happens at the tip of the chains, the broken tips will be left in small bits and pieces (can be seen as residual in lubricant) and will cause damages to the engine.

2.6 Types of VI Improvers

Table 2.1 shows lists of the chemical structures of viscosity index improver.

Table 2.1 Chemical structure of VI improver used in the experiment [1]

VI improver Types	Repeating unit
Olefin copolymer	$\left[\left(\text{CH}_2 - \text{CH}_2 \right)_A \left(\text{CH}_2 - \overset{\text{CH}_3}{\underset{ }{\text{C}}} \text{H} \right)_B \right]_X$
Poly(meth)acrylate	$\left[\text{CH}_2 - \overset{\text{CH}_3}{\underset{ }{\text{C}}} \begin{array}{l} \\ \text{C}=\text{O} \\ \\ \text{O} \\ \\ \text{C}_n \text{H}_{2n+1} \end{array} \right]_X$
Hydrogenated styrene-isoprene copolymer	$\left[\left(\text{CH}_2 - \text{CH}_2 - \overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}} - \text{CH}_2 \right)_A \left(\text{CH} - \overset{\text{H}}{\underset{ }{\text{C}}} \right)_B \right]_X$ 
Polyisobutylene	$\left[\text{CH}_2 - \overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}} \right]_X$

2.6.1 Olefin copolymer (OCP)

2.6.1.1 Chemistry

OCP is ethylene propylene copolymer (EP Copolymer) derives from polymerization of ethylene and propylene with the ethylene content 40-60 %wt (or 50-70 %mol). It should be noticed that OCP contains less ethylene content than other ethylene propylene copolymer in non-lubricant application. The ethylene-propylene ratio in OCP affects its thickening efficiency. OCP with high ethylene content has a good thickening effect, but at the same time, possesses undesired properties such polymer crystallinity and insolubility at low temperature. In addition, at low temperature, the exceeded ethylene interacts with wax in mineral base oil, resulting in an increase in the viscosity of the engine oil.

The polymerization technique of ethylene and propylene plays an important role in determining the property of OCP. Traditional fusing monomers technique knows as “random distribution” is replacing by a better technique “tapered composition”. OCP produces by tapered composition technique is superior in terms of its thickening effect and low temperature properties. Typically, OCP produced in domestic industry has molecular weight between 50,000 to 200,000. [4]

2.6.1.2 Advantages and Disadvantages

Advantages: good thickening effect

Disadvantages: poor low temperature properties (for OCP with low molecular weight)

2.6.1.3 Application

Uses in diesel and gasoline engine oil.

2.6.2 Hydrogenated styrene-diene copolymer

2.6.2.1 Chemistry

The diene part of this polymer can be either butadiene or isoprene. The structure of the copolymer is in random, block or star-shape. Hydrogenated styrene-diene copolymer have the following characteristics:

- Random shaped copolymer is styrene and butadiene copolymer in which composes of 50-60%wt styrene and 40-50%wt butadiene. The styrene when polymerize with 1,2-butadiene will yield VI improver with optimum thickening effect. The result of the polymerization is further synthesized known as “hydrogenation” by promotion conversion at butadiene. The molecular weight of random polymer is approximately 75000 to 200000 and the molecular distribution (M_w / M_n) is less than 1.5. [4]

- Block shaped copolymer of styrene and isoprene is either in diblock (A-B) or triblock (A-B-A), where A and B are polyisoprene and polystyrene respectively. The hydrogenation occurs only at polyisoprene molecules. The thickening effect of block copolymer yields from the insolubility of polystyrene in mineral base oil, thus acts as a thickener. The molecular weight of polystyrene should not be too heigh (30000 to 50000) while the isoprene block molecular weight is around 50000 to 70000. [4]

- Star shaped copolymer composes of two parts: the arms and the core. The arms are hydrogenated isoprene and the core is divinylbenzene. The quantity of

divinylbenzene depends on the molecular weight of the polymer but in general, less than 1% of the molecular weight of the polymer. Polymer molecular weight is around 300000 to 700000. [4]

2.6.2.2 Advantages and Disadvantages

Advantages: good shear stability index and low temperature properties.

Disadvantages: does not optimize VI by much

2.6.3 Polymethacrylate

2.6.3.1 Chemistry

Polymethacrylate VI improver is a copolymer of three methacrylic acid esters: short, intermediate and long-chain alkyl methacrylate. The short-chain alkyl methacrylate is methyl or butyl (either *n*-butyl or isobutyl). The intermediate-chain alkyl methacrylate is either 2-ethylhexyl alcohol, isodecyl alcohol or any alcohol mixture with C between 8-10, 12-14 or 12-15 atoms. The carbon atom of average ratio of each of the three monomers is however always at 9 atoms[4], as this will set a standard viscosity for polymethacrylate regardless the type of monomer used in the production.

2.6.3.2 Advantages and Disadvantages

Advantages: good thickening effect

Disadvantages: poor shear stability

2.6.4 Polyisobutylene (PIB)

2.6.4.1 Chemistry

PIB is a highly saturated hydrocarbon polymer (isobutylene), composed of long straight chain molecules containing only chain-end unsaturated bond (isobutylene). The molecular structure leads to chemical inertness and resistance to chemical and oxidation attack but can be dissolved in hydrocarbon solvents. Polyisobutylene is classified into three groups according to molecular weight: low, medium and high molecular weight. In petrol-chemical industry, only low molecular weight PIB is used as VI improver. The appearance of low molecular PIB is clear, odorless, tasteless, and non-toxic.

2.6.4.2 Advantages and Disadvantages

Advantages: good shear stability, cheap.

Disadvantages: poor thickening effect, does not improve VI by much, poor low temperature properties.

2.7 Literature Survey

Messina [5] studied the differences of each viscosity index improver by comparing its properties in applications. Polymethacrylate and olefin copolymer, each was added to API grade SE SAE 10W50 lubricant. It was found that polymethacrylate yielded a better result at both high and low temperatures. This was believed to cause by the dominating shear loss over the permanent shear loss.

In 2001, Gao and Jason [6] used polymethacrylate, olefin copolymer and hydrogenated diene copolymer to mix with SAE 0w40 lubricant. The experiment was

conducted by using each polymer as a single viscosity index improver and using two mixtures of polymers (polymer system) together. Results showed that, polymethacrylate 954C alone produced a superior shear stability values, in comparison with the others VI improvers. Further results showed that all polymers used in this experiment either single or mixture qualified for the industry required standards though polymethacrylate had a better result comparing to olefin copolymer.

Rhodes and Barnett [7] conducted the experiment using star polymer with hydrogenated polyisoprene external arms and hydrogenated polybutadiene internal arms VI improver, mixed with SAE 10W40 lubricant. The star polymer VI improver provided excellent VI improver characteristics at low temperature.

Kapuscinski [8] and co-worker conducted an experiment using olefin copolymer ethylene-propylene, ethylene-propylene-third monomer polymer and ethyl vinyl acetate copolymer combined together with polymethacrylate to formulate engine oil. Results showed a significant improvement on the lubricant's VI and distribution and also minimize the cost of the multi-grade lubricant production.