# **CHAPTER 4**

## **RESULTS AND DISCUSSION**

There are several different classes of polymer today offered for use as viscosity modifier in multigrade gasoline and diesel engine oils. Four different commercially available viscosity modifiers were used in this study including olefin ethylene-propylene copolymers (OCP1), hydrogenated isoprene and hydrogenated styrene isoprene star type polymers (STAR1, STAR2 and STAR3). The selection of which viscosity modifier to use is based on a compromise between maximising performance and cost. Each type offers a unique combination of properties which need to be assessed in accordance with a particular application.

### Viscosity lift to base oil  $4.1$

In order to obtain the viscosity target, viscometric data for both light (150 SN) and heavy (500 SN) base oil fractions were collected (Table 4.1). These were based on the same amount of additive package and treat rate for each of viscosity modifier type.

Base oil	Type	Kinematic viscosity $@$ 100 °C (cSt) for 1 to 10 % weight treat rate								
	OCP1	6.85	7.75	8.29	8.78	9.46	10.11	10.74	11.45	12.54
150 SN	STAR1	7.33	8.01	8.9	9.84	10.8	12.13	12.94	14.23	15.57
	STAR2	7.27	8.17	8.94	9.97	10.78	11.82	12.82	14.24	15.45
	STAR3	7.29	8.03	8.7	9.67	10.33	11.41	12.42	13.37	14.38
	OCP1	13.66	14.74	15.58	16.51	17.63	18.55	19.75	20.84	21.79
500 SN	STAR1	13.84	15.26	16.58	18.04	19.03	21.22	20.65	24.06	26.91
	STAR <sub>2</sub>	13.67	15.05	16.42	17.67	17.98	20.72	22.09	22.48	25.33
	STAR3	14.1	15.35	16.78	18.31	19.86	21.7	23.31	24.34	28.01

Table 4.1 Thickening efficiency of different viscosity modifiers.

It can be seen from Table 4.1 that all star type viscosity modifiers give higher viscosity lift than the olefin type. STAR3 gave the highest viscosity for all treat rates, then STAR2 and STAR1 respectively. This trend also was observed in both base oils (150 SN and 500 SN). The viscosity results comparing the relative thickening efficiencies of each viscosity modifier are represented graphically in Figure 4.1.





It was found that linearity is better for the light base oil data sets than for the heavier base stock data sets. This suggests a relatively greater chemical interaction between the viscosity modifier and the heavy viscosity grade base oil than for the lighter grade base oil.

Viscosity lift As thickening efficiency of a viscosity modifier is a measure of viscosity thickening relative to their polymer treat rate. However, the thickening efficiency of any polymeric additive will also vary with polymer composition and structure. Data of actual polymer content (Table 4.2) shows that the highest polymer content gives the better thickening efficiency. The actual polymer content used in this study was varied in the range between 10 and 15 %. Commercially available viscosity modifiers are usually sold in a concentrate form for ease of handling. These consist of the polymer dissolved in a base oil and polymer concentration depends mainly on its solubility in the base oil. Therefore, the thickening efficiency is strongly dependent on the molecular weight of the polymer rather than the actual polymer content. This statement is also supported by comparing the thickening efficiencies between viscosity data produced from STAR1 and STAR2 viscosity modifiers. The polymer content however, is also related to the solubility of the polymer in solvent oil, with the higher molecular weight polymers being less soluble than the lower molecular weight polymers.

<b>Viscosity modifiers</b>	Molecular weight	<b>Polymer</b> content % wt/wt
Ethylene propylene copolymer (OCP1)	180,000	12
Hydrogenated polyisoprene polymer (STAR1)	309,000	15
Hydrogenated polyisoprene polymer (STAR2)	420,000	13.5
Hydrogenated isoprene styrene coplymer (STAR3)	478,000	10.5

Table 4.2 Commercial Viscosity Modifiers used in this study.

### $4.2$ Formulating multigrade oil

### 4.2.1 Determination of light and heavy base oils fraction

Viscosity data collected from light and heavy base oils with different viscosity modifier treat rates was then used for calculating the light and heavy weight fractions needed to obtain an expected viscosity grade. A fully formulated oil was used in this study to gain the actual data of a commercial type oil. Oil blend formulations including calculated percentage base oil fractions to obtain targeted viscosity at 100 ° C are shown in Appendix VI.

Viscometric results show that all viscosity modifiers with minimum treat rate of 1 % are possible to obtain viscosity SAE 30 and 40 grades. These grades could not be produced with STAR1 and STAR2 types at treat rate greater than 6%. This is due to the original high viscosity of these viscosity modifiers.

High viscosity grades; SAE 50 and SAE 60 could be obtained with minimum treat rate of 5%. Star type polymers show an extended viscosity range as expected than OCP1 again due to viscosity of viscosity modifier concentrate. These results also show that viscosity at high temperature of oil is strongly dependent on the molecular weight and polymer content in viscosity modifier. Higher molecular weight polymer is expected to give better thickening efficiency than the lower molecular weight polymer. This gives an additional benefit in term of using lower viscosity modifier treat rate. Therefore required viscosity grade is a very important factor in selecting the viscosity modifier to give the maximum benefits in term of performance and economic.

Multigrade oils must pass viscosity specifications, as given in SAE J300 (Appendix I), which are measured at both high and low temperature ranges. This study included only two viscosity test criteria, kinematic viscosity at 100 °C and cold cranking simulator viscosity, in order to focus on the permanent shear stability characteristics of each

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viscosity modifier. Generally, low levels of pour point depressant (ca. < 0.3 weight %) are normally used in order to satisfy the low temperature mini rotary viscometric properties stipulated in SAE J 300.

#### $4.2.2$ Cold cranking simulator viscosity test results

Low temperature viscometric is another criteria that taken into account to claiming multigrade lubricant as classified in SAE J300 specification. Temperature of which cold cranking simulator performed will depend on the required "W" grade. In this study there were only two temperatures -10 °C for 20W and -20°C for 10W grade. This cold cranking simulator test is specified as low shear and low temperature test which can be used to determine the pumpability of the oil. Cold cranking simulator results of oil blends with different viscosity modifier types and treat rates observed are shown in Appendix VII.

Same trend on cold cranking simulator viscosity was obtained as thickening efficiency of each viscosity modifier, STAR1 and STAR2 allowed blending oil of higher viscosity grades. Thus STAR1 and STAR2 polymers gave small contribution to viscosity at low temperatures. This gives an additional benefit in term of lower volatility oil loss by allowing the heavier base oil to be used in formulation. STAR3 showed poor performance on cold cranking simulator results and therefore a lower viscosity grade could only be obtained i.e. using a larger portion of lighter base oil. To reach similar viscosity target, viscosity modifier treat level of OCP1 was expected to be higher by 1-2% than the STAR types. At treat rate greater than 5% showed clearly that highest viscosity obtained amongst the star type polymers for the same cold cranking simulator viscosity.

Cold cranking simulator viscosity results showed that STAR1 and STAR2 viscosity modifiers give overall better low temperature property i.e. less contribution to low temperature viscosity than STAR3 and OCP1. Higher molecular weight of both viscosity modifiers would then require less amount of viscosity modifier and thus minimise the content of heavy base oil. However, STAR3 which has largest molecular weight gave low temperature contribution similar to the OCP1. Low temperature performance of STAR3 is found to deviate from other star polymers at treat rate greater than 5%. This suggests that molecular structure and treat rate again play an important part in low temperature performance. Lower targeted viscosity oils (e.g. SAE 30) were found to be easily to pass the cold cranking simulator test as they contained larger amount of light base oil which would give a less contribution on viscosity at lower temperatures. Minimum treat rates of 1-2 % of viscosity modifier are required for 20W/30 and 20W/40 grades.

In order to satisfy the cold cranking simulator test for higher targeted viscosity grades, they require a higher amount of viscosity modifier to replace the heavy base oil content in formulations. For lower temperature test condition of 10W grade at -20 °C, a larger amount of viscosity modifier is then expected as observed in this study. Sample of 20W/30 viscosity grade requires at least 4% treat rate for star type polymer and more than 5% for olefin copolymer. In addition, ideal viscosity modifier would minimise the cold cranking simulator viscosity for a given degree of thickening at high temperature. This would then permits maximum flexibility in the blending and also the use of high viscosity with low volatility base oils for fuel economy purpose.

As previously mentioned, low contribution to cold cranking simulator viscosity facilitating the use of higher viscosity base oils which then reduces the oil consumption and prevents evaporative oil loss. It can be found for all type of viscosity modifiers from this study that cold cranking simulator test results strongly depend on the base oil composition. The higher the light base oil content would give less effect on viscosity of oil at low temperature. The superior cold cranking simulator performance (i.e. lower viscosity at low temperature test) of oils would allow the engines to start easily in cold weather. Varying the portions of two light and heavy base oils would therefore need to minimise the oil volatility by using the larger portion of higher viscosity low volatility base oil. Some amount of lighter viscosity base oil is also required to assist in achieving low temperature viscosity property. Exact relationship on composition of light and heavy base oils in order to pass both low and high temperature criteria could not be drawn. Viscosity modifier treat rate also gives affect on the composition between light and heavy base oils.

Mini rotary viscometer and Scanning Brookfield tests are also other two industry standards used as an indication on the pumpability of oils at low temperatures. This study did not include these two tests because the unavailability of equipment. However, the cold cranking simulator performance can be used as an indication for low temperature performance. The ability of an oil to pump at low temperature is primarily influenced by the microscopic structures formed by the waxy components in the base oil. The more highly regular branched structure would not have any wax-like segments that interact with the wax structures naturally occurring in the base oils. This also gives benefit in base oil and pour point depressant choice flexibility.

Formulations that satisfied the multigrade oil criteria of SAE multigrade 10W/30, 10W/40, 10W/50, 20W/30, 20W/40 and 20W/50 were based on results of kinematic viscosities at 100 °C and cold cranking simulator viscosity results at -10 °C and -20 °C. Results obtained reveal information on viscosity modifier ability to formulate multigrade oil in term of treat rate and base oil compositions. Completed formulation detail of these formulations may be found in Appendix VIII and their viscometric properties are shown in Appendix X.

For SAE 20W/30 grade, it was observed that only STAR3 type at only minimum treat rate of 2% was possible to make this grade. This may due to the fact that STAR 3 contains a lowest amount of polymer content. SAE 30 grade oil is being considered

as a thin oil with low viscosity and only a limited amount of viscosity modifier can be added. From previous section, STAR3 was expected to give better thickening efficiency than OCP1. Other type of viscosity modifiers have higher polymer content would give a greater thickening of oil at low temperature.

All polymers can be used to formulate most viscosity grades. Viscosity modifier performance can be distinguished when formulate high viscosity grade with more severe temperature conditions eg. none of viscosity modifiers included in this study is possible to produce 10W/50 and 10W/60 grades and only high molecular weight polymer STAR1 and STAR3 were possible to make up the 20W/50 grade. STAR2 which has a slightly higher molecular weight than STAR1 but lower than STAR 3 could not produce the 20W/50 viscosity grade. It is suggested that not only molecular weight contributes the thickening efficiency but also molecular structure is also significant in viscosity modifier selection.

STAR3 was found to give the most efficient thickening to formulate various viscosity grades with the lowest polymer content. Polymer content is an important parameter in determining the actual treat cost of the viscosity modifier and also the engine cleanliness caused by degradation of polymer during service.

### $4.2.3$ Effect of base oil fraction on evaporation loss

Stricter limits on engine oil volatility (ACEA and ILSAC specifications) to meet clean air legislation are pressuring oil companies to offer base oils with improve on volatility properties. Due to the use of small oil sumps and high engine speeds of four-stroke motorcycles, the control of oil consumption is also an important consideration. Noack volatility test (ASTM D5800<sup>30</sup>) then used in this study to measure evaporative loss of oil by measuring the weight change during the test. This test is also known to correlate with motorcycle oil consumption service. The use of heavier base stock hence lower percentage

evaporative loss while meeting cold cranking simulator viscosity requirement offers an attractive alternative which can be far less costly than solving the volatility problem of base oil at refinery.

Evaluating the evaporation loss of the oil blends was done for oils formulated with STAR1 and STAR2 viscosity modifiers in order to minimise the effect of base oil composition differences. No systematic influence of different molecular weight and actual polymer contents within same polymer type between STAR1 and STAR2 becomes obvious. These results indicate that the evaporation loss is greatly influenced by the evaporation losses of the base oil composition between 150 SN and 500 SN. JASO T 903 standard has given that the maximum evaporation loss of 20% test. Percentage evaporation test results of all blend samples were all well pass this evaporative loss limit. High viscosity base oil, 500 SN used in this study has limit of 7% maximum evaporative loss and 18% for 150 SN which have far less evaporative loss than given limit. For 20 W-viscosity-grade oil can contains 150 SN with maximum of 30-40% but for 10W can contain up to 60-80%. Therefore, viscosity grades that are expected to contain largest amount of 150 SN would be SAE 10W/30 and 10W/40 viscosity grades. Table 4.3 demonstrates comparison of 150 SN base oil content and the viscosity modifier treat rates for both oil grades. It was observed that treat rate of polymer did not give a big impact on the percentage evaporation loss of total formulation.



Table 4.3 Light base oil contents for SAE 10W/30 and 10W/40 viscosity grades

### $4.2.4$ Effect of viscosity modifier on viscosity index

All blends of different viscosity modifier types in this study did not show any great differences on viscosity index property. It is obvious that a greater treat rate to produce different oil viscosity grade would give a higher magnitude of viscosity index. This statement is in good agreement with results obtained in this study (Appendix X). Oils produced in this study can achieve viscosity indices up to 150 with the lowest value of 100.

## 4.2.5 Effect of viscosity modifier on pour point

Similar to the cold cranking simulator test, base oils composition plays an important role to the low temperature characteristics of oils. In this study therefore characterisation of low temperature characteristics based on base pour point test was included for the same type of viscosity modifier chemistry but of different molecular weight ie STAR1 and STAR 2 viscosity modifiers. Table 4.4 shows pour point results of tested oils. It was observed that there was little effect of molecular weight and polymer concentration on the pour point results. Base oil ratio was suggested to be the major factor that influenced on pour point property of oils in this study. Thus type of base oil used for study performance of viscosity modifier was also an important factor.

<b>Viscosity Grade</b>	STAR1	STAR <sub>2</sub>
10W/30	$-27$	$-27$
10W/40	$-24$	$-21$
20W/30	$-21$	$-24$
20W/40	$-21$	$-21$
20W/50	$-24$	$-24$

Table 4.4 Effect of molecular weight on pour point.

#### $4.3$ Permanent shear stability: Viscosity losses by mechanical shearing

### $4.3.1$ Shear stability specification

The lubricant industry commonly uses the 30 cycles Kurt Orbahn shear test (Appendix IX) to define the level of permanent viscosity loss to be encountered in the field performance. JASO T 903 standard (Appendix II) was also included this test for shear stability performance evaluation to compare the stay-in-grade performance of each viscosity modifier. A uniform method for expressing shear stability of lubricant is described in ASTM D 6022 as permanent shear stability index, SSI which is a measure of oil viscosity changes after mechanical shear.

### 4.3.2 Shear stability test results

Full shear test results can be found in Appendix XI. Shear stability indices obtained were greatly varied from less than 10 % up to 70 % in association of viscosity polymer types and concentrations. It is obvious that formulations contain larger viscosity modifier independent of chemistry structure type would give a larger percentage viscosity loss (SSI). However, these formulated oils of various SAE viscosity grades were all passed the shear stability limit given in JASO specification. Thus all viscosity modifier types used in this study can be used in formulating four-stroke motorcycle oil based on the shear stability test criteria. Overall, STAR1 and STAR2 viscosity modifiers were found to give most shear stable to mechanical shear test. OCP1 and STAR3 viscosity modifiers showed similar shear stability levels.

### 4.3.3 Relative permanent viscosity loss

Another convenient way to compare the permanent viscosity loss of oils containing different viscosity modifiers is to plot relative kinetic viscosity against the number of cycles in the Orbahn injector rig, where

> Relative viscosity loss = viscosity of sheared oil viscosity of new oil

This technique was used to compensate slight differences of initial viscosities among various oil blends.







Figure 4.1 Relative permanent viscosity loss of various oil grades.



Relative permanent viscosity of oil grade 20W/30



Figure 4.6 Relative permanent viscosity loss of various oil grades (ctd.).



Relative permanent viscosity loss of oil grade 10W/30



Figure 4.1 Relative permanent viscosity loss of various oil grades (ctd.).

Figure 4.1 shows the effects of different viscosity modifiers on permanent viscosity loss after 30 ,60, 90 and 250 cycles. It was found that olefin ethylene propylene copolymer (OCP1) and hydrogenated isoprene styrene (STAR3) lost most of their viscosities after first 30 cycles. Hydrogenated polyisoprene stars (STAR1 and STAR2) showed the most shear stable to mechanical shear for all viscosity grades. Differences of base oil ratio to formulate various grades did not give a major effect to the viscosity losses as shear resistant trend applied for all viscosity grades.

Sample blends that passed the shear stability criteria from JASO 4T then were used in further 60,90 and 250 cycles in order to compare the result with previous works and to identify if there are any relationships between number of shearing cycles and viscosity loss. The styrene star polymer, STAR1 and STAR2 demonstated a continuous permanent viscosity loss profile and levelled out after 90 cycles. Linearity relationship could not be obtained between viscosity loss and number of cycles of rig shear test. This observed trend is consistent with early study conducted on SAE 5W-30 oils, even in different oil viscosity grades.<sup>31</sup> Figure 4.1 also shows that the degress of relative viscosity loss for each viscosity modifier type is dependent of starting oil viscosity for all ranges of viscosity from SAE 30 to SAE 60.

### Effect of mechanical shear on viscosity index  $4.3.4$

Viscometric results in Appendix X show viscosity index comparisons between before and after mechanical shear tests. It can be seen that there are slightly increase of viscosity indices after sheared observed for all oil blends with different viscosity modifier types and viscosity grades. This is also in agreement with early studied of Bart and co worker<sup>35</sup> suggested that viscosity indices omit the important effect of shear rate on multigrade engine

oil performance This study was done using olefin, styrenebutadiene, styreneisoprene copolymers and also polyalkylmethacrylate.

#### $4.3.5$ Effect of mechanical shear on the cold cranking simulator viscosity

Cold cranking simulator viscosity results observed in this study showed that was not affected by mechanical shearing. It is suggested that within the same viscosity modifier class, cold cranking simulator viscosity depends primarily on base oil composition and viscosity modifier concentration, both of which remain constant throughout the Kurt Orbahn test.

Similar study on Low temperature of engine oil by Bart<sup>34</sup> showed that mini rotary viscosities of SAE 5W/30 grade varied as the number of shear cycles increased. It was found that there is no relationship between mini rotary viscosity and shear stability index within the same viscosity modifier chemistry. However, there was some deviation observed for higher shear stress conditions after 100 cycles. This study also found that scanning brookfield results did not correlate with the mini rotary test results and no significant effect on with increase number of shearing cycles for olefin copolymer and hydrogenated star polymer.

Low temperature characteristic of different viscosity modifier chemistry cannot be compared based results of 30 cycles Kurt Orbahn shear test only. Some viscosity modifier types are suggested to behave differently after some critical point of number of shearing cycles. However, for isoprene star polymers, the sheared fragments are no longer attach to the core. Since Mini rotary viscometric performance is minimally affected by mechanical shearing, the core appears to have little effect on the interaction of oil components.

### Molecular basis for properties of multigrade oil  $4.4$

In dilute solution, most polymer chains exist as isolated coils, average coil size can be measured by light scattering techniques, weight average molecular weight is proportional to coil size. The total volume fraction of polymer coils and associated solvated oils, in turn is proportional to solution viscosity. Therefore, for dilute solutionis, the thickening contributions of various viscosity modifiers should be related to their relative molecular sizes as measured by GPC only when polymer concentration rises to a point where the polymer coils begin to entangle which can also be influenced to the solution viscosity. Bezot and coworkers estimated the limiting concentration for the dilute regime for various viscoity modifier from intrinsic viscosity data (see Table 4.5)<sup>31</sup>.

Table 4.5 Maximum polymers concentration for dilute solution behaviour.

<b>Polymer Type</b>	Molecular weight	<b>Maximum Polymer</b> concentration $g/cm^3, \%$
Polymethacrylate	140,000	
Hydrogenated polyisoprene	495,000	$2.8^{\circ}$
Ethylene-propylene copolymer	160,000	2.8

Polymer concentrations used in formulating multigrade oils of this study are well below the limiting concentrations found in the above table thus dilute solution theory can still be applied.

Early discussion has shown that polymer structure also plays an important part in the thickening characteristics caused by the interaction between polymer and base oil molecules. Olefin copolymer (OCP) is a straight chain, ethylene propylene copolymer with a minimum

number of side chains. It is expected that this polymer would give the highest contribution to the total viscosity because there is no conferring between polymer side chain and the base oil. The STAR type polymeric viscosity modifier is made up of relatively short multiple styrene side chains which may give a larger contribution with base oil than normal ethylene propylene copolymer. However, similar molecular weight levels does not necessarily result in the same thickening performance when comparing viscosity modifiers of different polymer types. Therefore, within the viscosity modifier polymer type, thickening efficiency tends to increase with an increase in molecular weight.

Moreover, oil thickening efficiency and molecular treat level is very important with regards to the level of engine oil deposits. The high thickening efficiencies of STAR type polymers coupled with the relatively high polymer content in their concentrates, result in using lower treat rates. This offers savings in transport costs and greater base oil flexibility.

Shear stresses led to break down of polymer molecules into smaller fragments caused an decrease in the average molecular mass and narrowing the molecular-mass distribution. This resulted reduction of viscosity and also viscosity index. The mechanical shearing starts at a given critical molecular mass and increases with increasing molecular mass. Results on the viscosity losses of this experiments also demonstrate that the higher molecular mass would expected to give greatest viscosity losses (STAR 3).

For most oil, relative molecular weight which is a ratio between molecular weight of sheared oil and new oil, is linearly proportional to relative viscosity. Bart found an exception on this statement for styrene isoprene block copolymer. He found that relative kinematic viscosity loss of this type polymer was much larger than for other polymers of the same

relative molecular weight<sup>34</sup>. Earlier study done by George and Hendrick that copolymer existed in the oil solution in micelle form with the less soluble polystyrene segments making up the core and the more soluble hydrogenated polyisoprene chain segments radiating out into the oil phase<sup>35</sup>. When this polymer was subjected to shear in diesel injector rig, the bond between isoprene and styrene were no longer connected, and the thickening mechanism changed from that of micelle association to that of linear chain behaviour. This suggested that the chain scission of styrene isoprene polymer occurred near the end of the polystyrene block and the micelle did not disassociate as they pass through the diesel injector. Similar behaviour also observed for styrene isoprene star polymer in this study and molecular scission occurred could be explained by above statement. Molecular scission of more shear stable isoprene star polymer with lower molecular weight can be expected. Because it has a slightly lower molecular weight with stronger bonding and thus the isoprene star polymer has more resistant to chain rupture. Viscosity loss shows gradually decrease over range of shearing cycles thus lower rate of molecular degradation. Degraded isoprene segments are also more soluble in oil solution and therefore adding the thickening effect to the oil solution.

Covitch also stated that linear polymers with molecular weight less than about 80,000 appear to be resistant to viscosity loss in diesel injector rig test<sup>36</sup>. The critical molecular weight of star polymers of 400,000 is about three times that of linear polymers. Styrene isoprene star polymer did not shear down to simulate the behaviour of the shear stable polyisoprene star. They degraded to simulate the behaviour of linear chains instead.

Bart also proposed the shearing mechanism of styrene isoprene star polymer from molecular level analysis by GPC that the high molecular weight peak appeared in GPC corresponds to the assembled star polymers and the low molecular weight peaks represents

unattached "orphan" arms of hydrogenated polyisoprene<sup>34,37</sup>. The molecular weight of low molecular weight peak remained constant after the shearing, while for polyisoprene star. It was found small increase in arm fraction molecules. This suggested the mechanical sheared the entire arms and chemical breaking occurred near the core and as the shearing proceeds, the star peak rapidly decreased in size but the concentration of arm rapidly increased and caused this type of star approach the linear chain polymer behaviour.

Molecular weight distribution is another important property that must be taken into account in selecting viscosity modifier for specific type application. STAR type polymer would offer greater advantage over olefin type polymer. This is because polymerisation process of this polymer allowed the production of very consistent polymer with very narrow molecular weight distribution. The molecular weight of each arm of STAR polymer can also be varied to achieved different shear stability levels to meet requirements for different applications.