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THE INFLUENCE OF VISCOSITY INDEX IMPROVER TYPE ON SHEAR STABILITY OF LUBRICATING ENGINE OILS

Abstract

During use of engine oils many reasons cause change in viscosity. Decrease in viscosity can be caused by shear stress or dilution of oil with fuel. Oxidation products and presence of soot lead to viscosity increase. In this paper, shear stability of different viscosity index improvers is tested using test method DIN 51382 and testing procedure FIAT 128A-064 in motor laboratory, where liquified petroleum gas was used as a fuel. Use of gaseous fuel excludes the possibility of oil dilution and soot generation. Length of test (25 hours) also excludes the possibility of oxidation product forming. Only change in viscosity comes as a consequence of shear stress. Based on the results, quality of used viscosity index improvers is evaluated and correlation is determined between the results of method DIN 51382 and the results of bench engine test. Olefin-copolymer improvers are less shear resistant comparing to hydrogenated star polyisoprene and hydrogenated styrene-butadiene copolymer improvers. It is also showed that DIN 51382 test method represents tougher shear stability test than the procedure FIAT 128A-064, which makes it especially suitable for assessment of improver quality.

Key words: *lubricating engine oils, polymer viscosity index improvers, shear stability, test method DIN 51382, procedure FIAT 128A-064*

1. Introduction

In order to achieve primary function of engine oil – lubrication, oil has to possess good viscosity-temperature properties. At low temperatures, oil has to be fluent enough to reach all parts of the engine easily when engine is just started. At high temperatures, it has to form thick enough layer on metal surfaces of the engine. These required engine oil properties are provided by using suitable base oils and viscosity index improvers – VIIs [1]. VIIs are certain polymers - high molecular mass compounds. During the use of engine oils, high shear stresses are present, which leads to accelerated mechanical degradation of polymer chains. VII's ability to resist shear stress is called shear stability [2].

Different types of VIIs have different thickening effects and different shear stabilities. Mostly used are VIIs of polyester type (poly(alkyl-methacrylates)) (PAMA), or hydrocarbon type (polyisobutylene, olefin copolymer, hydrogenated styrene-butadiene copolymer...). Figure 1 shows some of the polymer VII's structures.

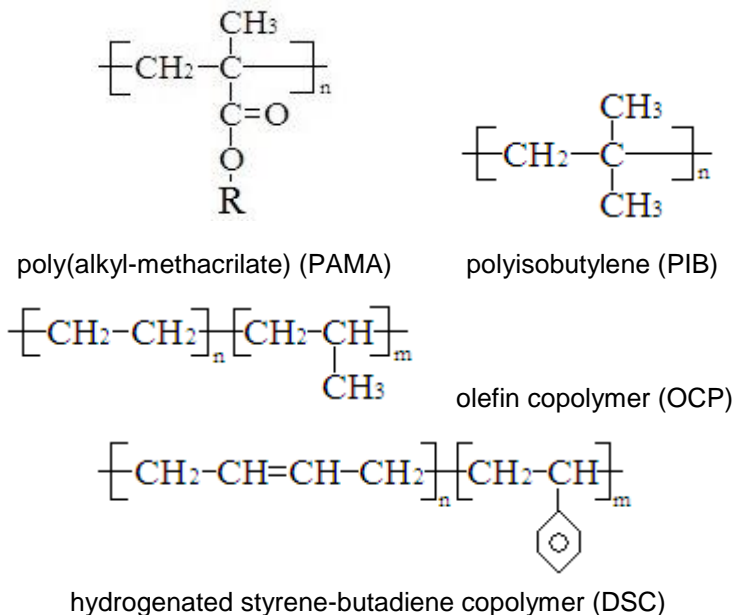


Figure 1: Different structures of VI improvers

Degradation of improver chains decreases VII's thickening function. However, series of other factors have an effect on oil viscosity change during use. Processes of oxidation and polymerization increase oil viscosity. Diesel engines produce large amount of soot, that also leads to viscosity increase. There is always a certain level of oil dilution with liquid fuel present in engine, that leads to decrease in oil viscosity [3-5].

This study focuses on testing and determining effects of different VIIs on shear stability of engine oils. Four VIIs were tested. To determine the effect of VII's shear stability on oil viscosity change, all the other factors have to be eliminated. Gaseous fuel does not produce significant amount of soot in the engine, so there is no oil thickening caused by soot. Also, gaseous fuel does not lead to oil dilution, so there is no consequent oil thinning. Based on the earlier bench engine tests that used gaseous fuel, it is determined that no significant amount of oxidation products are present in first 25 working hours. With this working conditions, viscosity change depends mostly on VII's shear stability. Shear stability of selected VIIs has been tested in bench engine test and using laboratory test method DIN 51382. Bench engine test has been performed following procedure FIAT 128.A.064.

2. Test procedure

2.1 Materials

VII I: Olefin copolymer, 10 % m/m solution (manufacturer's recommendation) in hydrocracked base oil ($\nu_{100^\circ\text{C}} = 4.5 \text{ mm}^2/\text{s}$). VII II: Hydrogenated star polyisoprene, 5 % m/m solution (manufacturer's recommendation) in hydrocracked base oil ($\nu_{100^\circ\text{C}} = 4.5 \text{ mm}^2/\text{s}$). VII III: Olefin copolymer, 10 % m/m solution (manufacturer's recommendation) in hydrocracked base oil ($\nu_{100^\circ\text{C}} = 4.5 \text{ mm}^2/\text{s}$). VII IV: Hydrogenated styrene-butadiene copolymer, 8.25 % m/m solution (manufacturer's recommendation) in hydrocracked base oil ($\nu_{100^\circ\text{C}} = 4.5 \text{ mm}^2/\text{s}$). Hydrocracked base oil ($\nu_{100^\circ\text{C}} = 6.0 \text{ mm}^2/\text{s}$) (HC-6). Additive package for engine oils for passenger vehicles, quality level ACEA A3, API SL; 7.4 % mas. in final formulation (manufacturer's recommendation). Pour Point Depesant (PPD) – acrylic polymer; 0.5 % mas. in final (manufacturer's recommendation).

Solutions of VIIs in base oil are prepared – shredded improver is diluted in base oil at the temperature $110^\circ\text{C} - 120^\circ\text{C}$, with constant mixing. After 6 h and 10 h samples are taken and 10 % dilutions in hydrocracked oil of viscosity $6 \text{ mm}^2/\text{s}$ are made. If viscosities of dilutions are equal after 6 h and 10 h, it is concluded that solid VII is completely dissolved.

Table 1: Formulations of engine oil SAE 10W-40 with different VIIs

Formulation	MO1	MO2	MO3	MO4
VII	Olefin copolymer	Hydrogenated star polyisoprene	Olefin copolymer	Hydrogenated styrene-butadiene copolymer
VII content (solution in HC-4), %	11.7	27.5	11.5	18.2
Base oil content (HC-6), %	80.4	64.6	80.6	73.9
Additive package content, %	7.4			
PPD content, %	0.5			
Active substance content (solid VII), %	1.2	1.4	1.2	1.5
Viscosity at 100°C , mm^2/s	14.5	14.6	14.4	14.6

Four samples of engine oil SAE 10W-40 have been made, following formulations for commercial engine oil for passenger vehicles of ACEA A3, API SL quality level. VII content was adjusted so that initial viscosity values of all four formulation at 100°C are between $14.4 \text{ mm}^2/\text{s}$ and $14.6 \text{ mm}^2/\text{s}$. Formulations are shown in Table 1. Viscosities at 100°C and content of solid VII are also shown. Viscosity is determined using laboratory test method ISO 3104, with glass capillary viscometer.

2.1 Methods

High-temperature engine test on FIAT 128.A.064 engine, following procedure FIAT 128A-064 was conducted. Gaseous mixture propane-butane was used as motor fuel. Test was conducted in four cycles, each cycle lasted 25 working hours. As shown in Table 2, different formulation was used for each cycle. Samples were taken every five hours and most important physical and chemical characteristics of oil were analyzed. Content of wear metals was also tested. At the end of each 25-hours cycle, FT-IR method (Fourier Transform Infrared Spectrometry) was used to determine chemical changes in oil.

Table 2: Bench engine test cycles

Formulation	MO1	MO2	MO3	MO4
Cycle	1	2	3	4
Duration, h	25	25	25	25

Test method DIN 51382 was used for laboratory testing of shear stability. Apparatus is shown in Figure 2. Method DIN 51382 gives conditions for engine oil shearing during defined number of cycles. Shearing leads to mechanical degradation of polymer chains, resulting in viscosity decrease comparing to initial viscosity.

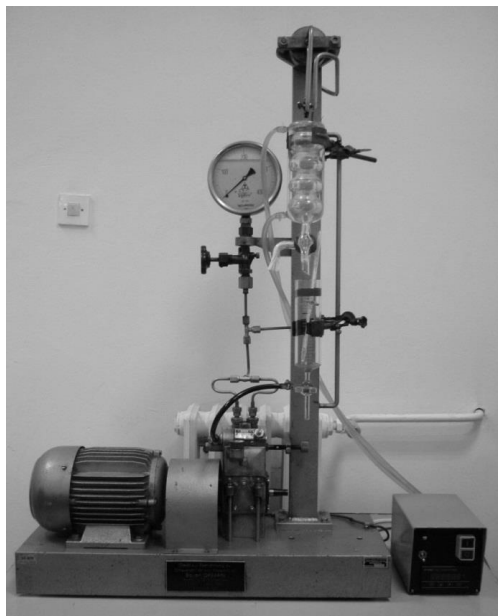


Figure 2: Apparatus for shear stability testing using method DIN 51382

Shear stability testing was conducted at 30, 60 and 90 cycles. Viscosity decrease is expressed in percentages, calculated using equation (1):

$$\text{Viscosity decrease, \%} = [(v_0 - v) / v_0] \times 100 \quad (1)$$

v_0 i v – viscosity values before and after shear stability analyses.

3. Test results and discussion

3.1 Bench engine test

Conducting engine tests with gaseous fuel it was determined that biggest changes in oil viscosity occurred within first 25 hours of test. Table 3 and Figure 3 show results of 100 working hours engine test with gaseous fuel.

Table 3: Oil viscosity (commercial sample of SAE 10W-40 grade) at 100 working hours engine test, with gaseous fuel

Working hours	0	25	50	75	100
Viscosity at 100 °C, mm ² /s	14.5	13.3	13.1	13.1	12.8
Viscosity decrease, %	0	8.3	9.7	9.7	11.7

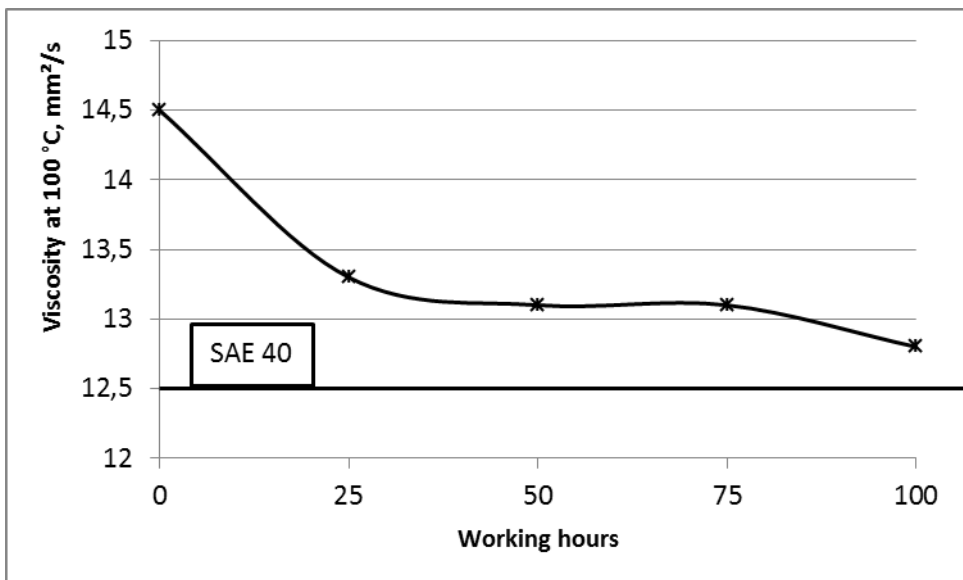


Figure 3. Viscosity decrease of commercial SAE 10W-40 oil at 100 working-hours engine test

Biggest viscosity decrease, 70 %, occurs within first 25 working hours. For that reason, 25 working hours engine test was conducted for VII's shear stability testing. During test, changes in oil properties were tested every five hours. Table 4 shows viscosity values at 100 °C during test. To be sure that no other factors that could influence viscosity change are present, change in flash point, oxidation products and soot content are monitored (decrease in flash point could indicate potential oil dilution with fluid). Table 5 shows the results of these analyses. Figures 4-7 show the results of FT-IR analyses at the end of each 25-hour cycle.

Table 4: Results of viscosity analyses at the engine test

Working hours		0	5	10	15	20	25
Viscosity, mm ² /s	MO1	14.5	13.9	13.8	13.9	13.7	13.6
	MO2	14.6	14.3	14.2	14.4	14.2	14.1
	MO3	14.4	14.1	13.9	13.9	13.7	13.7
	MO4	14.6	15.1	15.2	15.2	15.0	14.7

Table 5: Soot content and oxidation level at the end of each 25-hour cycle

Characteristics	Unit	MO1	MO2	MO3	MO4
Soot (1970 cm ⁻¹)	%	0.001	0.000	0.000	0.001
Oxidation (1710 cm ⁻¹)	Abs/cm	0.0	0.0	0.0	0.5
Δ Flash point	°C	4	3	1	3

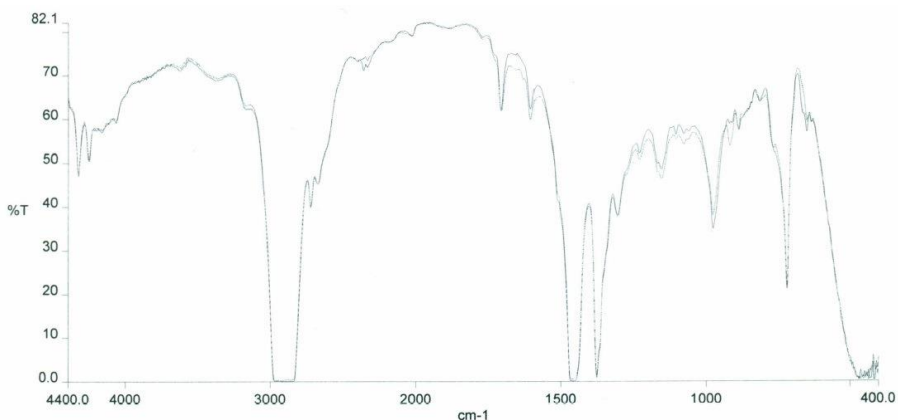


Figure 4. FT-IR characteristic spectrum for MO1 formulation

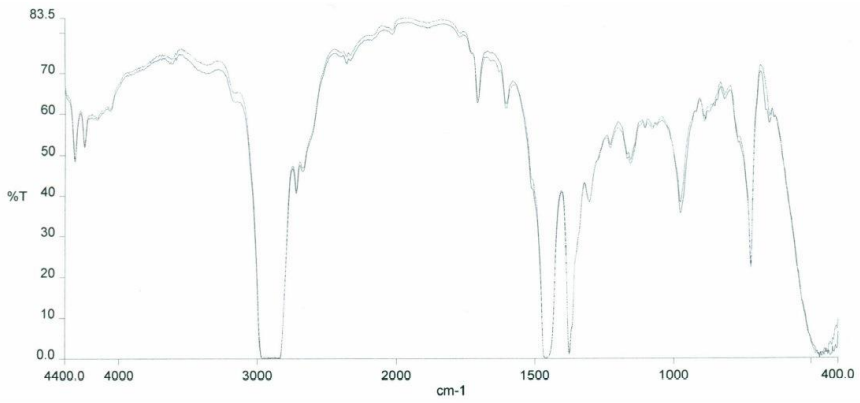


Figure 5. FT-IR characteristic spectrum for MO2 formulation

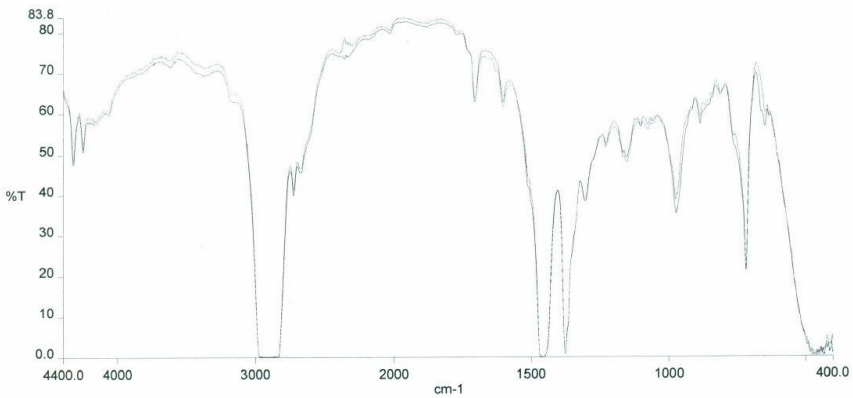


Figure 6. FT-IR characteristic spectrum for MO3 formulation

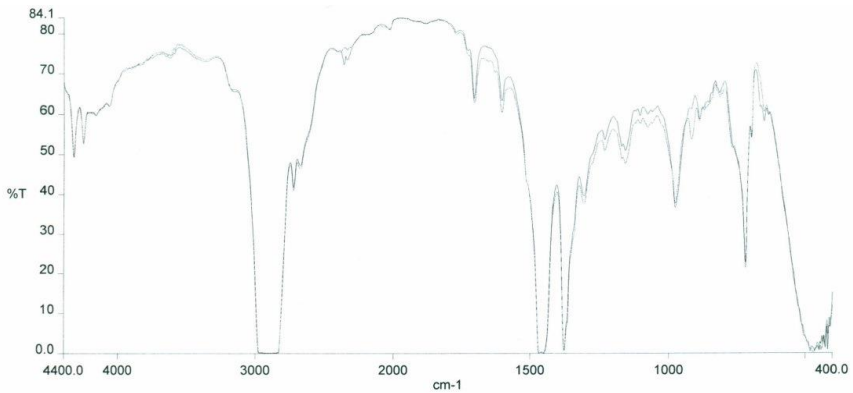


Figure 7: FT-IR characteristic spectrum for MO4 formulation

Based on the data shown in Table 5, it is confirmed that there is no soot in the oil and that oxidation is very low, so two of those factors have no influence on viscosity change. Very small change in flash point shows that there was no dilution of oil. Only effect on viscosity change is due to VII's shear stability. Figure 8. shows viscosity change during engine test.

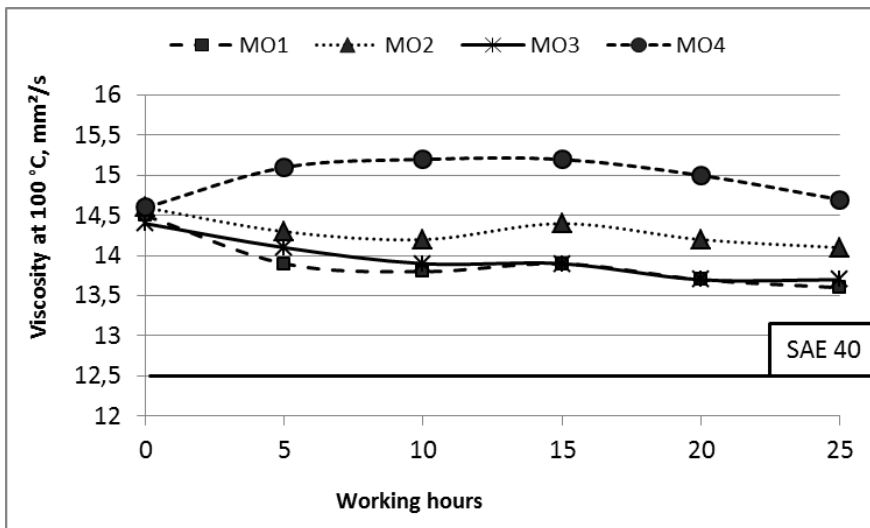


Figure 8: Viscosity decrease during engine test

During 25 h of engine test, formulations MO1, MO2 and MO3 demonstrate viscosity decrease, while formulation MO4 does not. More significant viscosity decrease takes place in formulations with olefin copolymer VII (MO1 i MO3). Formulation MO4 does not show viscosity decrease; at first, it even shows slight viscosity increase. Only after 10 working hours viscosity starts to decrease. This phenomenon is not present when testing oil using method DIN 51382 and will be subject of further testing. Since the only influence on viscosity comes from VII's shear stability, it is concluded that formulations MO1 i MO3, that use olefin copolymer VII, are the least shear stable, i.e. show the biggest viscosity decrease.

3.2 Laboratory shear stability test

Table 6 shows results of shear stability testing for all four samples, after 30, 60 and 90 cycles. Fig. 9 shows viscosities of fresh oils and after 30 and 90 cycles of analyses. Fig. 10 shows percentual viscosity decrease after 90 cycles. As shown in Fig. 9, initial viscosities are approximately equal for all formulations. It's important to emphasize that all formulations, even after 90 cycles, retain viscosities within the limits of SAE 40 grade. Based on above described tests, all four VIIs can be used when formulating engine oil of this grade. However, Fig. 10 shows much bigger viscosity decrease of formulations MO1 i MO3 then of formulations MO2 i MO4.

Based on this investigation, formulations MO1 and MO3, that use olefin copolymer VII, demonstrate the poorest results. It is also shown that the largest viscosity decrease occurs within first 30 cycles. After that, viscosity still decreases but significantly slower.

Table 6: Results of shear stability test using DIN 51382 test method

Formulation	MO1	MO2	MO3	MO4
Viscosity at 100 °C, mm ² /s	14.5	14.6	14.4	14.6
Viscosity at 100 °C, mm ² /s after 30 cycles	13.2	14.4	13.1	14.2
Viscosity decrease, %	9.0	1.4	9.0	2.7
Viscosity at 100 °C, mm ² /s after 60 cycles	13.1	14.3	12.7	14.2
Viscosity decrease, %	9.7	2.1	11.8	2.7
Viscosity at 100 °C, mm ² /s after 90 cycles	12.8	14.3	12.9	14.2
Viscosity decrease, %	11.7	2.1	10.4	2.7

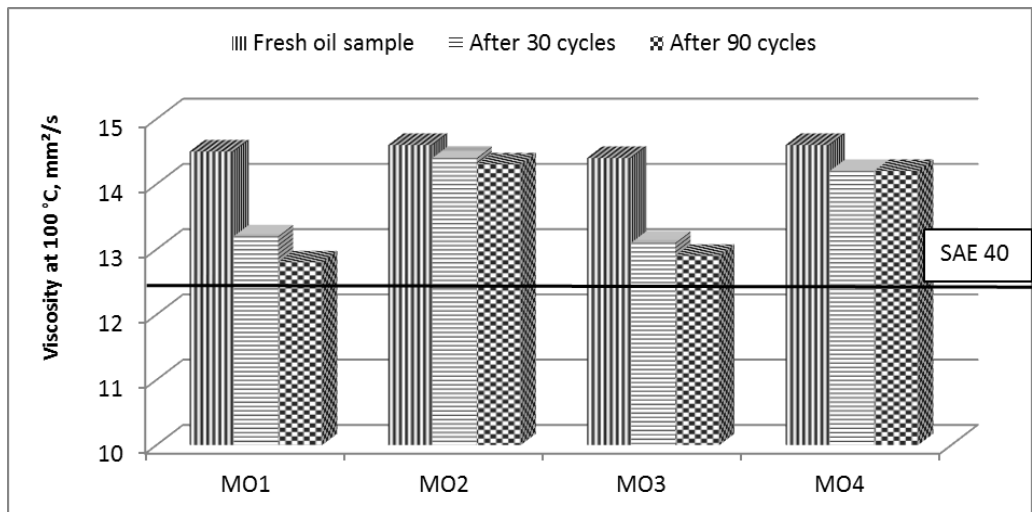


Figure 9. Viscosity after 30 and 90 cycles

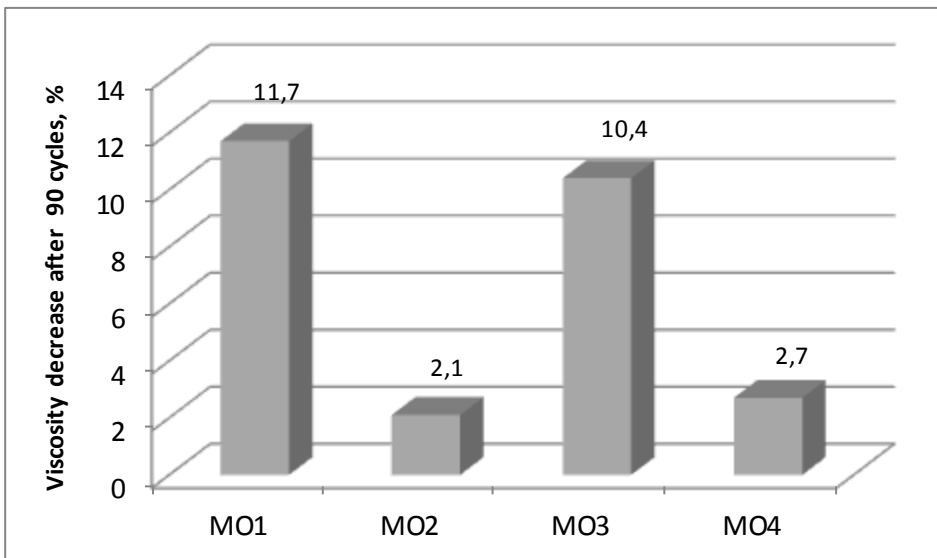


Figure 10: Procentual viscosity decrease after 90 cycles

3.3 Correlation between bench engine test and laboratory test

Results of shear stability analyses in laboratory are compared with results in engine test. Changes in viscosity for both tests are shown in Table 7, and Figures 11 (for engine test) and 12 (for laboratory test). Formulations MO2 and MO4 do not display big changes in viscosity; those changes are practically within 1 mm²/s. Results of laboratory test are in accordance with the results of engine test, i.e. changes in viscosity are very small even after 90 cycles. Formulations MO1 and MO3 display more significant viscosity decrease, both in engine test and laboratory test. During laboratory testing, viscosity decrease is slightly bigger, so it can be conducted that method DIN 51382 represents tougher shear stability test than FIAT procedure 128A-064.

Table 7: Change in viscosity during engine test and laboratory test

Viscosity change		Working hours						Number of cycles		
		0	5	10	15	20	25	30	60	90
Viscosity mm ² /s	MO1	14.5	13.9	13.8	13.9	13.7	13.6	13.2	13.1	12.8
	MO2	14.6	14.3	14.2	14.4	14.2	14.1	14.4	14.3	14.3
	MO3	14.4	14.1	13.9	13.9	13.7	13.7	13.1	12.7	12.9
	MO4	14.6	15.1	15.2	15.2	15.0	14.7	14.2	14.2	14.2

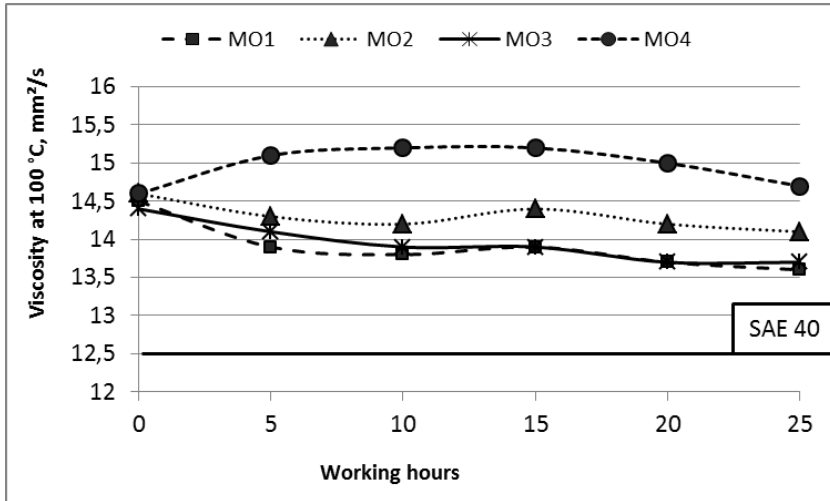


Figure 11: Change in oil viscosity during engine test

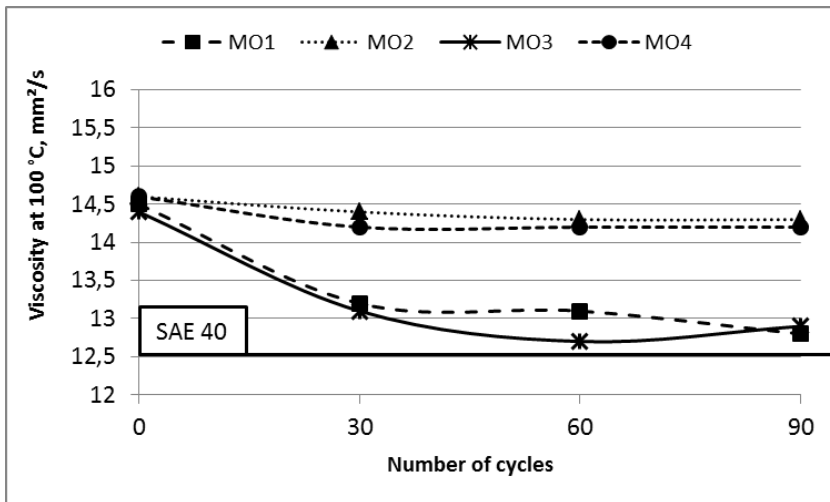


Figure 12: Change in oil viscosity using DIN 51382 test method

VIIIs with better shear stability show smaller viscosity decrease than less shear stable VIIIs – both on engine test and in laboratory test; correlation between engine and laboratory test is relatively good for VIIIs with better shear stability (hydrogenated star polyisoprene (VII II) and hydrogenated styrene-butadiene copolymer (VII IV)). Less shear stable VIIIs show bigger viscosity decrease in laboratory test than in engine test – after only 30 cycles of laboratory testing, olefine copolymer (VII I and VII III) displays significantly bigger viscosity decrease than on engine test.

4. Conclusion

- All tested formulations retain viscosities within the limits of SAE 40 grade after both laboratory and engine test.
- There is a correlation between results of laboratory and engine tests.
- Significant viscosity decrease on engine test is present in oils formulated with olefin copolymer VIIs. On laboratory testing, significant viscosity decrease is also shown for oil formulated with olefin copolymer VIIs.
- Correlation between laboratory and engine tests is relatively good for hydrogenated star polyisoprene (VII II) and hydrogenated styrene-butadiene copolymer (VII IV), that display excellent shear stability.
- Olefine copolymer (VII I and VII III) displays significantly bigger viscosity decrease after only 30 cycles of laboratory testing than on engine test.
- Generally speaking, bigger changes in viscosity occur on laboratory test than during engine test.
- By comparing results of the both tests, it can be concluded that shear stability test method DIN 51382 is highly reliable for VII's quality assessment. Based on the this method results, evaluation of VII's shear stability can be made.

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