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Lube Oil Performance Enhancement Using Nano-Polymers Additives during Copolymerization Reaction

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Abstract

Under the parameters of normal engine operation, lubricating oil typically experience periodic shifts in its viscosity. Because of this, engine oils often include polymeric additives that are referred to as viscosity modifiers. The oil is able to give acceptable fluid lubrication at extreme temps due to these additives, which are oil-soluble polymers. The aim of present work to use polymers in form of nano-composites such as Styrene, Octadecyl-methacrylate (ODMC) and Dodecyle-methcrylate (DDMC) for lube oil viscosity index and pour point enhancement during copolymerization reaction. The benzoyl peroxide was used as an initiator. Solubilizes were made using SN-150 mineral base oil from the Al-Dorha refineries in Baghdad, which had a viscosity index of 128, and a viscosity range of 0 to 100°C. Styrene and methacrylate monomer combinations were copolymerized in an SN-150 mineral base oil solution in a nitrogen atmosphere at 60-80°C. A 200 mm3 oil glass reactor fitted with a magnetic stirrer and a reflux condenser was used to conduct the reactions. Five percent by weight of the total monomer was the concentration used. With respect to the monomers, the initiator concentration was 1.0% wt. Seven hours are needed for the whole reaction cycle. The copolymer composition was modified from 5 to 25% wt.% styrene by changing the monomer combination ratio. The advanced statistical analysis is performed to find the optimum conditions by mean of surface response and multiple regression using MINITAB. The optimization finding is obtained at Styrene of 5%, DDMC of 18% and ODMC of 18%, which promotes viscosity index of 197 leading to 51% enhancement in Al-Dora lube oil.

1. Introduction

Emulsified polymerization is significant as a polymerization process since it is the most popular technique for producing polymers for several uses, such as concrete additives and drug delivery systems [1-3]. Emulsion polymerization is economically significant since it accounts for 10–15% of whole polymer types [4]. Rapid polymerization at high solid concentrations with very little change in viscosity makes the emulsion polymerization method applicable technology. This allows for the possibility of achieving high molecular weights and the efficient removal of reaction heat. In addition, using water as a dispersant means that organic solvents are not required, which is helpful for applications like coatings and adhesives where volatile organic compounds emissions may be minimized. Polymers with tailored properties may be mass-produced cheaply by copolymerization. However, as the reaction advances during batch copolymerization, the composition of the generated polymer may change due to differences in reactivity and the partitioning of the monomers during the distinct stages. Composition drift may be prevented by regulating the monomer concentration at the polymerization free roots [5, 6]. This could be easier with the aid of semi-continuous methods.

Thus, monomer addition techniques where the monomer feed rate is modified according to the process kinetics [7-10] seem to be more advantageous in terms of product quality and economics. There are a few of ways to do this, the most common being open- or closed-loop control. In the open loop method, a process model is used to produce a fixed monomer addition rate profile. Either a purely mechanical [11-13] or an iterative [14-16] method of producing the model is possible.

The problem with these methods is that they don't allow for the mitigation of process disturbances, which may lead to the loss of compositional control. Since an on-line sensor controls the monomer feed rate directly, this has led to a preference for the closed loop approach [17]. Given the high conversion rates and non-linear behavior of emulsion polymerization, it is clear that the sensor must be robust, accurate, and rapid. Unfortunately, few sensors now available are suitable for use in emulsion polymerization due to not meeting these requirements.

The emulsion (co)polymerization process involves the integration of thermodynamic component compositional distribution and mass transfer processes among multiple phases with free radical (co)polymerization kinetics. The present discourse will commence with an overview of the fundamental tenets of emulsion polymerization, followed by a brief analysis of the kinetics of free radical (co)polymerization. The comprehension of the kinetics of emulsion copolymerization is of utmost importance as it governs the prompt copolymer microstructure. The polymer properties are significantly influenced by the copolymer microstructure's chain length distribution and copolymer composition distribution (CCD), as stated in previous studies [9, 18-21].

The concentration of monomer in monomer droplets, monomer-swollen polymer particles, and the aqueous phase are all controlled by the thermodynamics of the system. Utilizing the Flory-Huggins lattice theory and taking into account the effect of the interfacial energy, Morton et al. [22] developed a model that describes the monomer's partitioning between droplets and polymer particles. To account for partial swelling, Vanzo et al. [23] and Ugelstad [24] extended the equations for multi-monomer systems, respectively, using this equation. To sum up, in these models, the molar volumes, monomer/polymer interaction(s), and -usually to a small extent- interfacial tension and particle size dictate the distribution of the monomer across the monomer, polymer, and aqueous phases. The monomer content of latex particles may vary from 85% for vinyl acetate and ethyl acrylate to 70% for methyl methacrylate, 60% for styrene, 50% for butadiene, and 20% for ethylene [25]. The monomer partitioning models were simplified by Maxwell et al. [26]. Numerous studies have shown that entropic factors, rather than enthalpic contributions, govern the partitioning behavior of many (co)monomer systems including monomers with low to moderate water solubility. It was also shown that in multi-monomer systems, the monomer ratios in droplets and particles are equivalent [27, 28].

Lubricating oils typically use polymers based on alkyl methacrylates as additives to alter their rheology by increasing their viscosity, boosting their viscosity index, or lowering their pour point. They are long-chained, linear terpolymers made up of monomers that include a varying number of lateral alkyl groups, generally from carbon atoms 1 to 18. It was found that the pour point of solutions may be lowered by using methacrylate with medium-sized lateral alkyl groups (C10-C14), that long-chained groups (C16-18) contributed mostly to this effect, and that the methyl group contributed to the rigidity of the polymer chain [7,8].

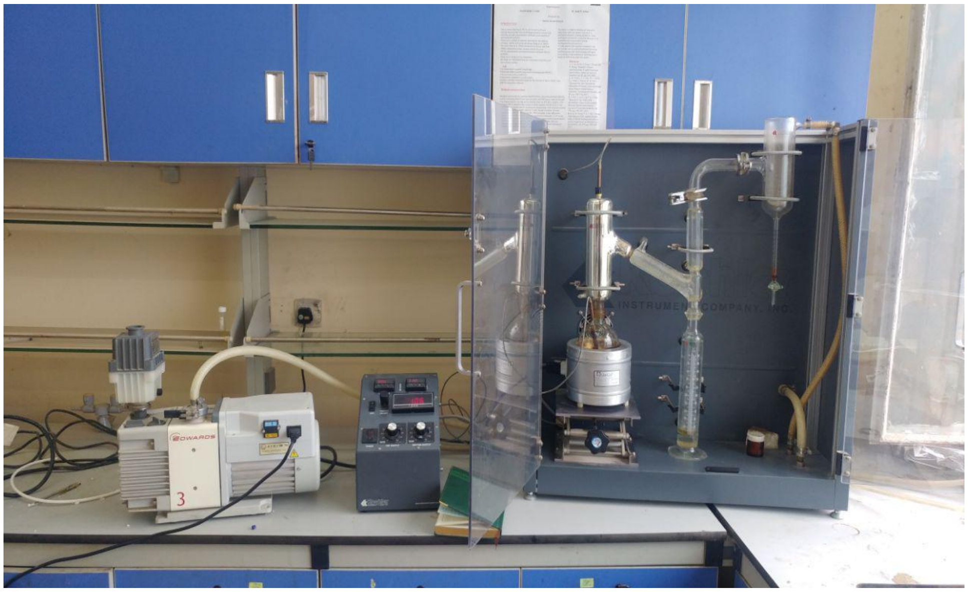
The matching monomer unit ratio is adjusted to offer the best possible attributes for a given use. The properties of an additive are determined not only by its composition but also by structural aspects of the copolymer, such as its molar mass and molar mass distribution. These polymers need to have high solution viscosities and viscosity index values, but they also need to be resistant to the high shear stress that occurs under lubricating conditions, across a broad temperature range, and under substantial mechanical pressures. Recent studies of methacrylic additions have concentrated on improving the material's resilience to mechanical breakdown, heat, and oxidation.

As part of the current inquiry, an experimental research was conducted to determine how Nano monomers additives affect the viscosity index of motor oil. In addition, cutting-edge statistical methods for determining optimal mixture proportions are included. This research details the rheological characteristics of terpolymers of styrene, dodecyl methacrylate, and octadecyl methacrylate, which are used to modify the viscosity index and pour point of lubricating mineral oils. This additive was made by polymerizing a solution of mineral base oil and peroxide. Viscosity index changes in solutions are investigated as a function of polymer content. In order to determine surface response, correlative analysis, ANOVA table, Interaction plot, and optimization from the resulting data, and the MINITAB statistics program were used.

2. Experimental Procedure

Rotating viscometers, a pour point tester, an oxygen detector, an ASTM distillation apparatus, make up the rest of the testing apparatus. The sample of raw lube oil was evaporated and condensed under controlled conditions, and the temperatures at which different percentages are recovered and/or the percentages recovered at specified temperatures are recorded and analyzed to determine whether the sample meets the criteria for Koehler K45000 / K45090 Petroleum. Stainless steel condenser and heater units with excellent insulation. The heater unit has a rack and pinion heater elevation mechanism with a push-turn control knob, a viewing glass, a 1000W heater with step-less variable control, and a platform to hold a flask as shown in Figure (1). System for Manual Vacuum Distillation VDS3000 finds the range of liquid temperatures at which petroleum products may be totally or partly vaporized at pressures below atmospheric. Distillation occurs at a low pressure under well calibrated circumstances to provide around one theoretical Figure fractionation from the material. The system's aluminum frame and cold rolled steel walls make up its primary body, or cabinet. The basic distilling equipment includes a 500 mL quartz flask with a thermowell, a vacuum jacketed distilling column and condenser assembly, a water jacketed receiving cylinder, a 90 degree elbow adapter tube, a Dewar-type cold trap with a 10 mL graduated receiver and a stopcock drain, a PT100 probe adapter, a PT100 vapor temperature probe, and a PT100 flask temperature probe. In addition to the heating mantle, retention springs, ball joint clamps, connecting tubing, hose clamps, fast connect adapters and fittings, vacuum grease, and jacketed glassware, the system comes with a set of adjustable scissor jacks as shown in Figure (2). Styrene, dodecyl methacrylate, and octyl methacrylate (manufactured by Covalent/ South west/ USA) were employed as bought polymerization grade monomers which mentioned in table (1). Benzoyl peroxide was utilized as the catalyst. Terpolymerizations of styrene and methacrylate monomer mixtures were carried out at 60-80 °C in SN-150 mineral base oil solution, under nitrogen atmosphere. The solvents used were mineral base oil (al-dorha refinery, Iraq), specifically SN-150, which has a kinematic viscosity of v = 22.4 and 4.38 $mm^2\ s^{-1}$ at 40°C and 100°C, respectively; a viscosity A 200 mm^3 oil glass reactor fitted with a magnetic stirrer and reflux condenser was used for the reactions. This monomer mixture included 5% monomer by weight.

Figure (1). Heater Unit Components contains: (1) Rack and Pinion Heater Elevation Mechanism, (2) Push-Turn Control Knob, (3) Viewing Glass, (4) 1000W Heater with Stepless Variable Control and (4) Flask Platform.



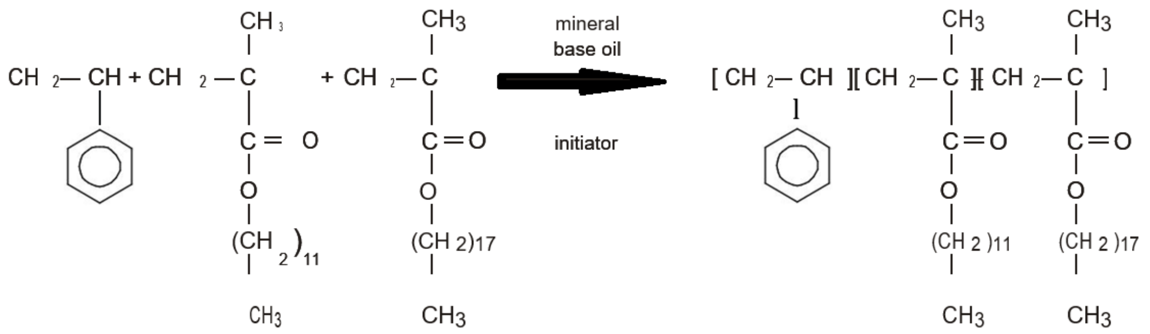
(a)

(b)

Figure (2). (a) Vacuum distillation**, (b)** ASTM Distillation units.

Table (1). Nano-polymers specifications and origin.

Material	Origin	General Specifications
Poly Styrene nanomaterial	Covalent, USA	Molecular Weight: 100,000 - 300,000 g/mol
		Melting Point: 240-260 °C
		Glass Transition Temperature: 100-105 °C
		Density: 1.04 - 1.06 g/cm³
Poly Octadecyl-methacrylate (ODMC) nanomaterial	Southwest, USA	Molecular Weight: 150,000 - 200,000 g/mol
		Melting Point: 55-60 °C
		Glass Transition Temperature: -25 to -15 °C
		Density: 0.88 - 0.92 g/cm³
Poly Dodecyl-methacrylate (DDMC) nanomaterial	Southwest, USA	Molecular Weight: 80,000 - 120,000 g/mol
		Melting Point: 40-45 °C
		Glass Transition Temperature: -40 to -30 °C
		Density: 0.90 - 0.94 g/cm³



With respect to the monomers, the initiator concentration was 1.0 wt%. Seven hours is the average period of a reaction cycle. By altering the monomer mixture's proportions, the styrene content of the terpolymer was made to range from 5 to 25 weight percent. The kinematic viscosity was estimated using a Rotational Viscometer (fungi lab), which measures the torque exerted by a rotating spindle inside a sample while the spindle is moving at a predetermined speed. Viscosity is measured by dipping a spindle into a sample at a predetermined temperature and volume, and the result is shown digitally.

Kinematic viscosity measurements at 40 °C and 100 °C were crossed in tables to determine the viscosity index. Equation is used to verify the obtained values (1).

$$\mathrm{VI} = \frac{L-U}{L-H} \times 100 \qquad (1)$$

Where, **L** is the kinematic viscosity at 40 $^{\circ}$C of an oil of 0 VI, mm^2/s (Cst), **H** is the kinematic viscosity at 40 $^{\circ}$C of an oil of 100 VI, mm^2/s (CSt), **U** is the kinematic viscosity of the oil of interest at 40°C, mm^2/s (CSt).

The resultant data are analyzed by using MINITAB statistics package to find surface response, correlative analysis, ANOVA table, Interaction plot and optimization.

3. Results and Discussion

In direct method, the addition of monomers has influenced the lubricating oil characteristics gently but not superior. Figures (3) and (4) illustrate the effect of styrene weight percentage (St%) n the viscosity index and viscosity index enhancement percentage for various DDMC to ODMC ratio. In general, the increasing of St% reduces the viscosity index enhancement values for DDMC/ODMC equals to 1 and 3 where the different behavior is achieved for ODMC/DDM equals to 3. The viscosity increases by increasing St% below 15% and begins to drop for higher St% for ODMC/DDMC=3. The maximum enhancement was 65.68%, was achieved at St% equals to 5% and DDMC/ODMC=3. This behavior is observed due to the action of copolymerization reaction and dispersive action of monomers in which the based oil is considered suitable solvent. The hydrodynamic characteristics of the lubricating oil are modified through copolymerization with monomers that involve free radicals. The observed phenomenon can be elucidated by the findings of prior research conducted by [29] and [30]. These studies have demonstrated that the copolymerization process experiences a significant reduction in efficacy as the concentration of styrene (St%) increases, as evidenced by the experimental data presented in Table (2).

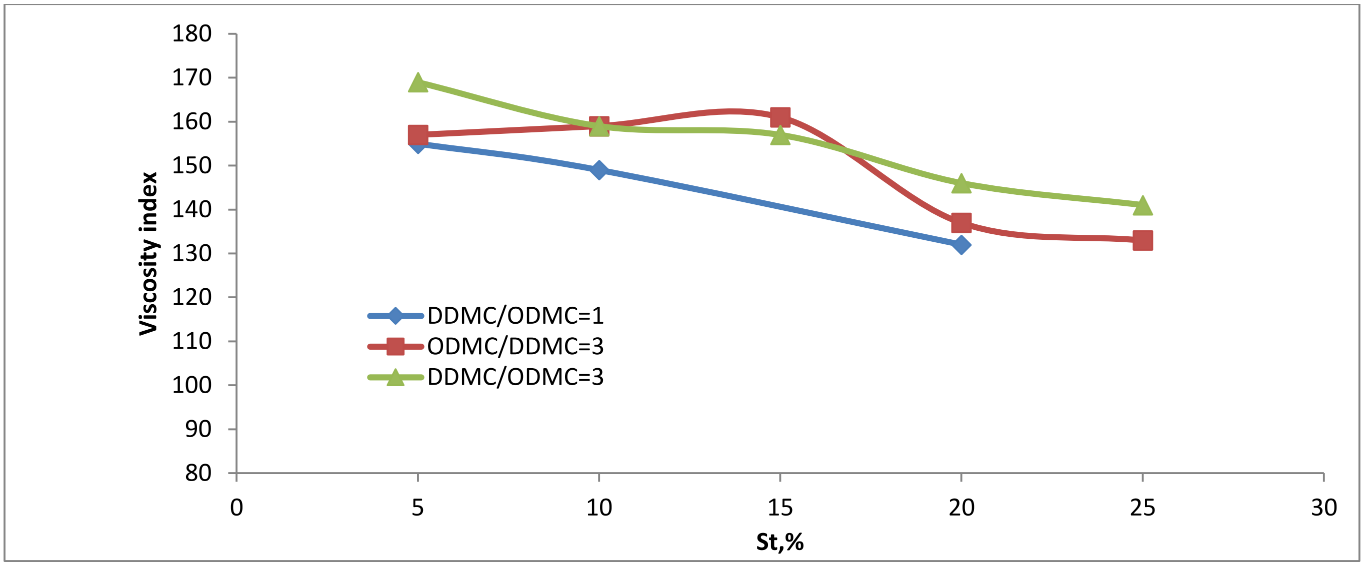


Figure (3). Viscosity index vs. St% for various DDMC/ODMC by using direct addition method.

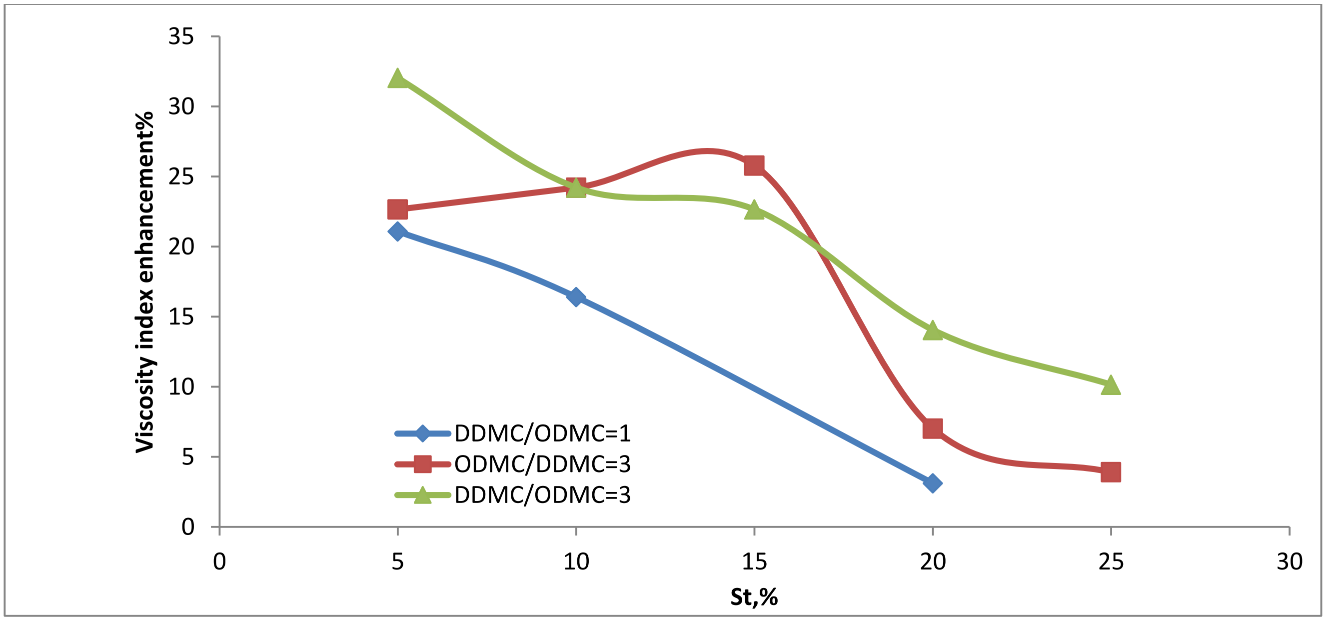
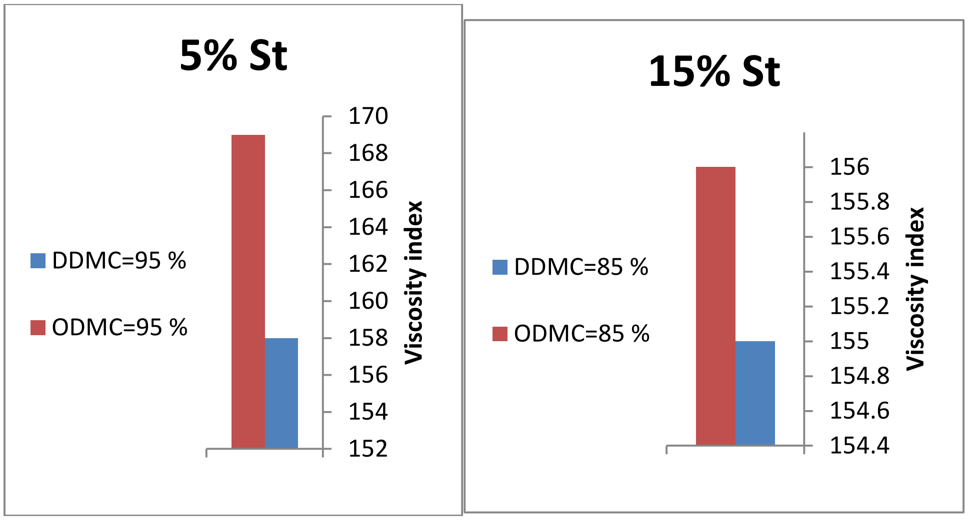


Figure (4). Viscosity index enhancement% vs. St% for various DDMC/ODMC by using direct addition method.

Table (2). Viscosity index values for various St% and Various DDMC/ODMC ratios by using direct addition method and SN150 lubricating oil.

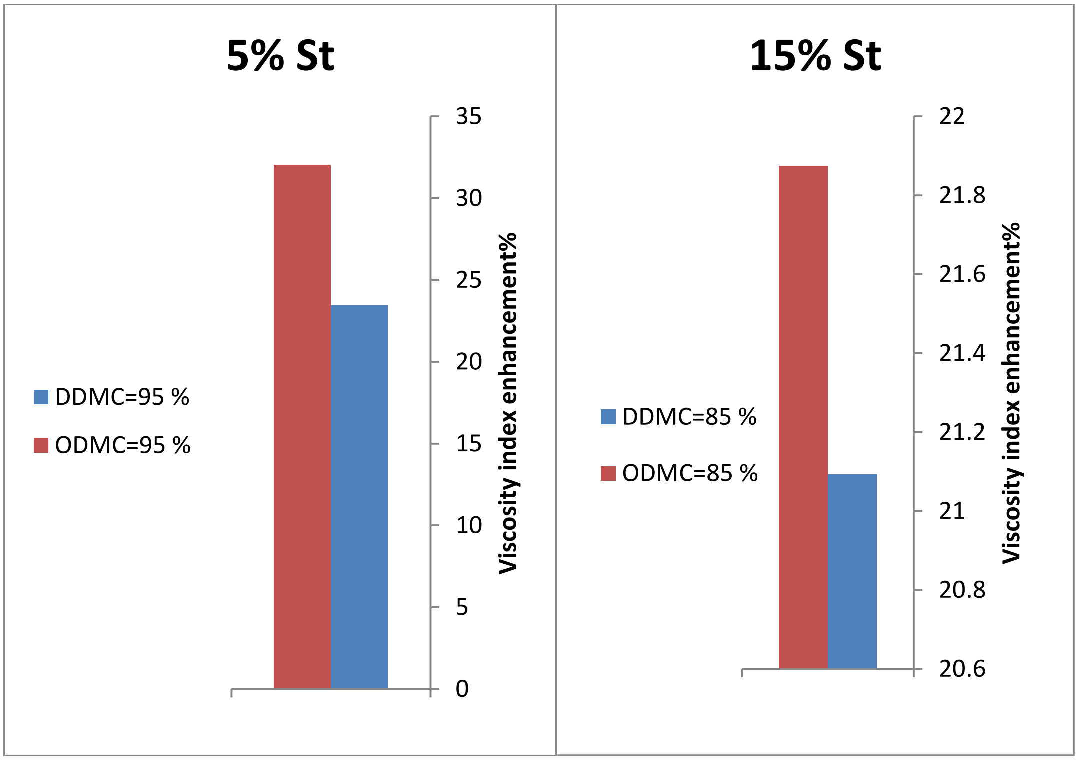
St%	**5**	**10**	**15**	**20**	**25**
DDMC/ODMC=3	169	159	157	146	141
ODMC/DDMC=3	157	159	161	137	133
DDMC/ODMC=1	155	149		132	

The effect of addition of monomers of different molecular weight is also proved by applying two (DDMC/St or ODMC/St) additives in lubricating oil instead of three (DDMC, ODMC and St together) to ensure the behavior of the three additives. The using of 85% of ODMC with 15% of St gives the similar value by applying 95% of DDMC and 5% of St which gives us an idea of the copolymerization free radical molecular weight effect on the hydrodynamic properties of lubricating oil as shown in Figures (5 & 6).



a. 5% St b. 15% St

Figure (5). The Significance of two additives system (DDMC/St or ODDMC/St) on Viscosity index for various St percentages by using direct addition method.



a. 5% St b. 15% St

Figure (6). The Significance of two additives system (DDMC/St or ODDMC/St) on Viscosity index enhancement percentage for various St percentages by using direct addition method.

The experimental set up utilized the two step addition method for copolymerization reactions. Figure (7) shows viscosity index enhancement% vs. St% for various DDMC/ODMC ratio by using SN500 based oil. The viscosity index enhancement behavior is the same to SN150 under the same conditions for DDMC/ODMC=3 while the different trend is observed for ODMC/DDMC=3 for St concentration equals to 15%. The viscosity index improvement in SN500 case is superior to the case of SN150 under similar operation conditions. Figures (8 & 9) discuss effect of DDMC% and ODMC% on the viscosity index and viscosity index enhancement in two additives system by using two steps method. The maximum viscosity index is achieved at 95% DDMC, the 95% ODMC gives the same effect to 85% DDMC. This behavior differs from the three additive system, where the higher molecular weight rule has no function on the stability of lubricating oil viscosity. In other words, the present work produced the optimum viscosity index, which is achieved by using 95% DDMC and 5% St to form two additive system. This mixture is used in two steps addition method.

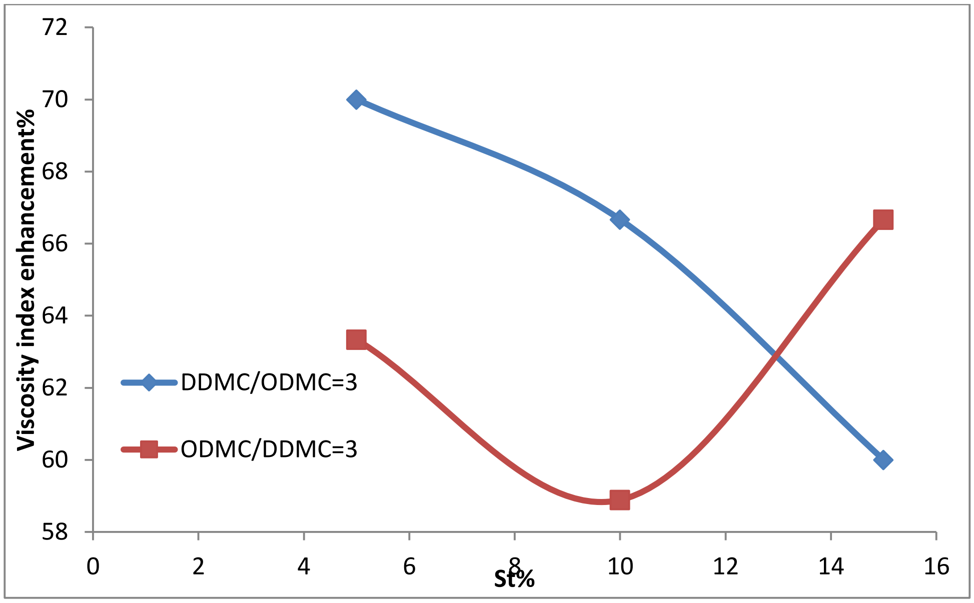


Figure (7). Viscosity index enhancement% vs. St% for various DDMC/ODMC by using two step addition method using SN500 lube oil.

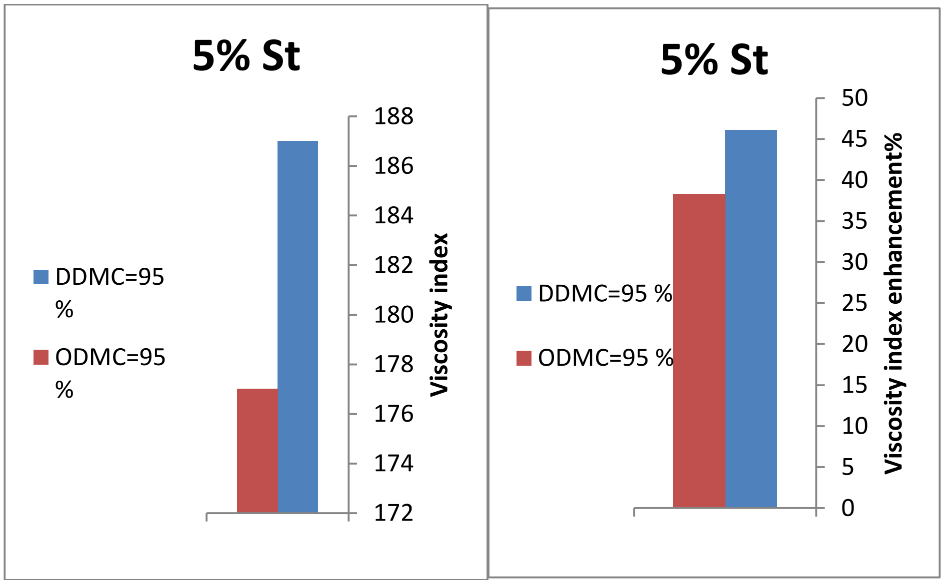


Figure (8). The Significance of two additives system (DDMC/St or ODDMC/St) on viscosity index and Viscosity index enhancement percentage for 5% St by using two steps addition method.

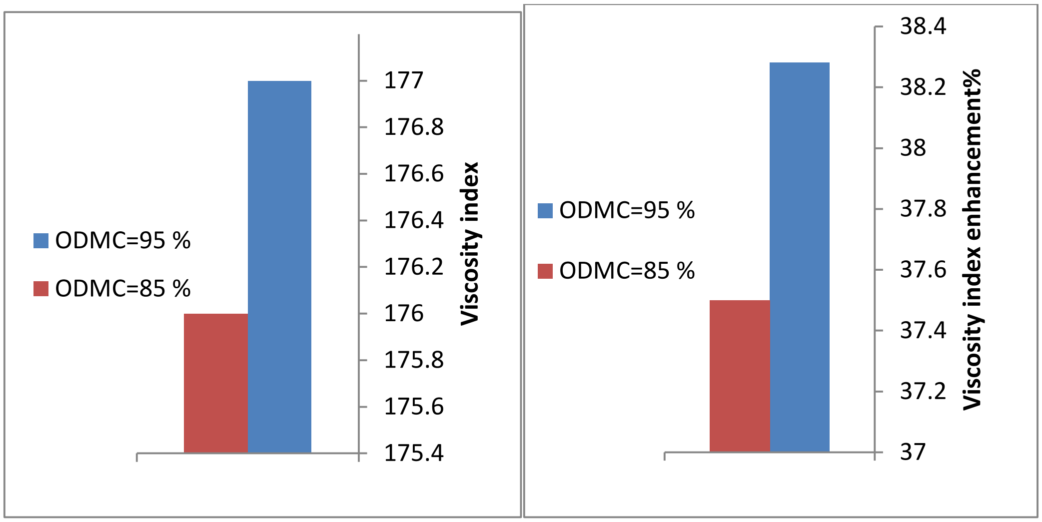


Figure (9). The Significance of two additives system ODDMC/St on viscosity index and Viscosity index enhancement percentage for various St% by using two steps addition method.

Figures (10 -12) shows the surface response of composition effect on VI. The effect of DDMC% is not sharp like ODMC% at fixed value of St%. The effect of St% is the highest sharp among other compositions. The correlative analysis is also included bellow, the Table (3) shows the F value higher than P Value which means the correlation is validated according to ANOVA table analysis. The optimum viscosity according to MINITAB statistics package is obtained at 5% St%, 18 ODMC% and 18 DDMC% where the maximum value is 196.

$$VI = 232.6 - 5.61\,St - 0.300\,DDMC - 0.166\,ODMC + 0.0449\,St \times DDM + 0.0432\,St \times ODMC - 0.02275\,DDMC^2 \qquad (2)$$

Figure (13) shows the interaction parameters chart. The St% is critical parameter as compared with other. The ODMC% and DDMC% interaction has the major effect higher than St%. The interaction with St% - ODMC% and St%- DDMC% has the same portion, less than the individual effect.

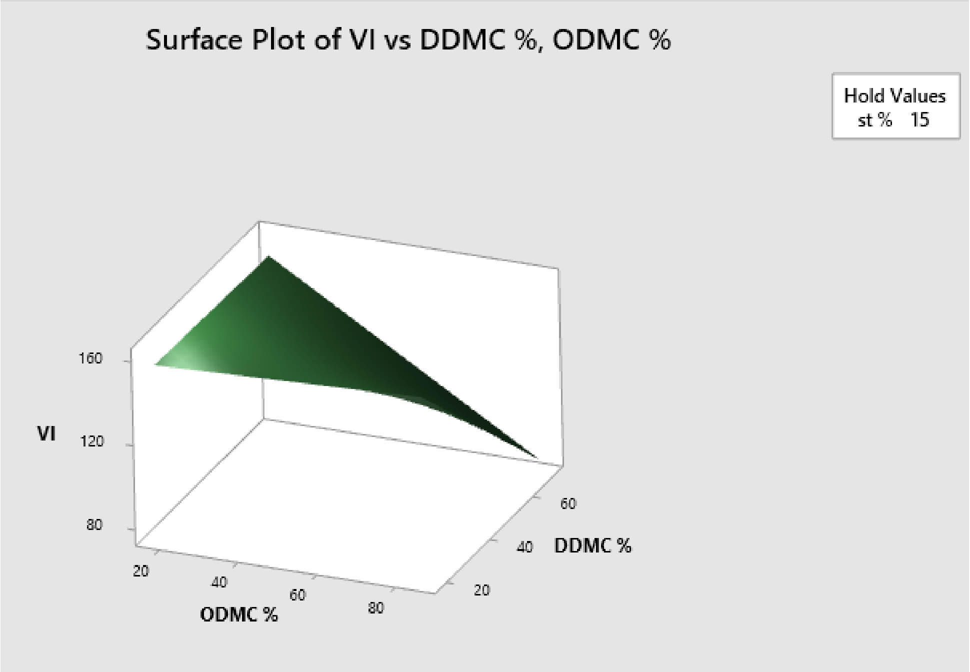


Figure (10). Surface response of ODMC% and DDMC% effect.

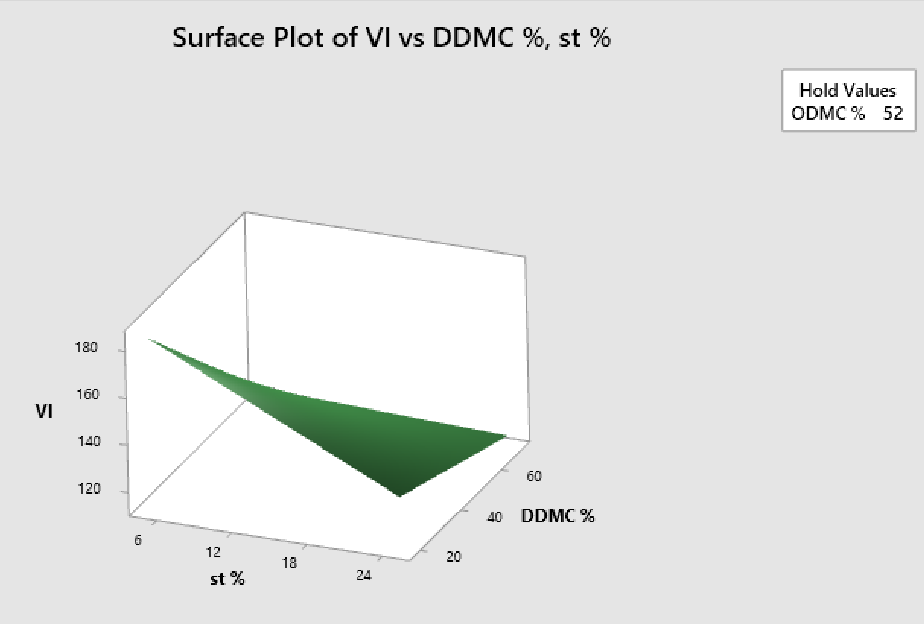


Figure (11). Surface response of St% and DDMC% effect.

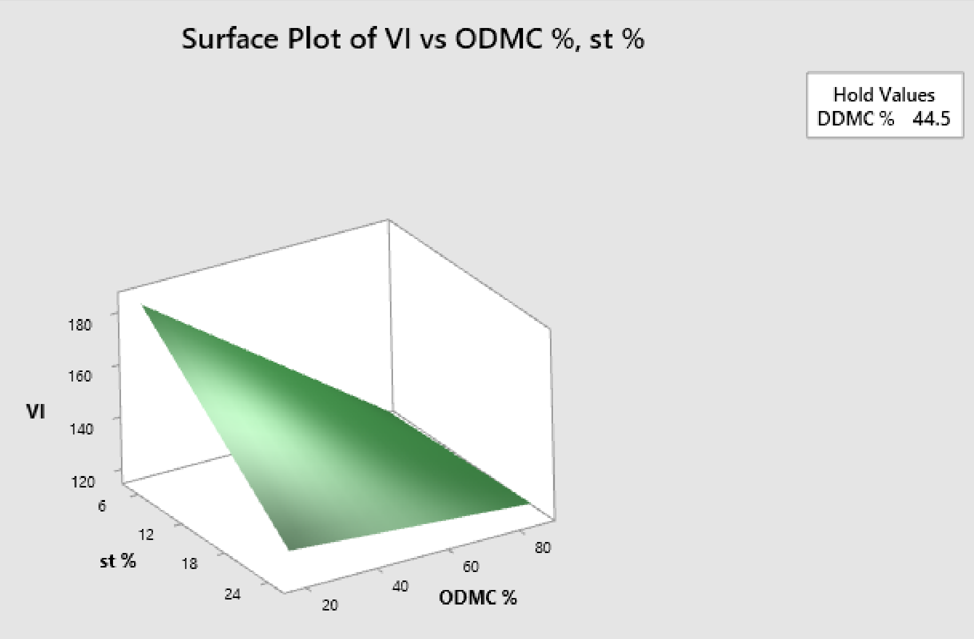


Figure (12). Surface response of ODMC% and St% effect.

Table (3). ANOVA analysis of present investigation.

Source	**DF**	**Adj SS**	**Adj MS**	**F-Value**	**P-Value**
Model	6	1445.67	240.95	7.25	0.015
Linear	3	293.46	97.82	2.94	0.121
St%	1	203.88	203.88	6.13	0.048
DDMC%	1	68.15	68.15	2.05	0.202
ODMC%	1	43.09	43.09	1.30	0.298
2-Way Interaction	3	270.10	90.03	2.71	0.138
St%*DDMC%	1	29.33	29.33	0.88	0.384
St%*ODMC%	1	29.34	29.34	0.88	0.384
DDMC%*ODMC%	1	255.24	255.24	7.68	0.032
Error	6	199.41	33.23		
Total	12	1645.08			

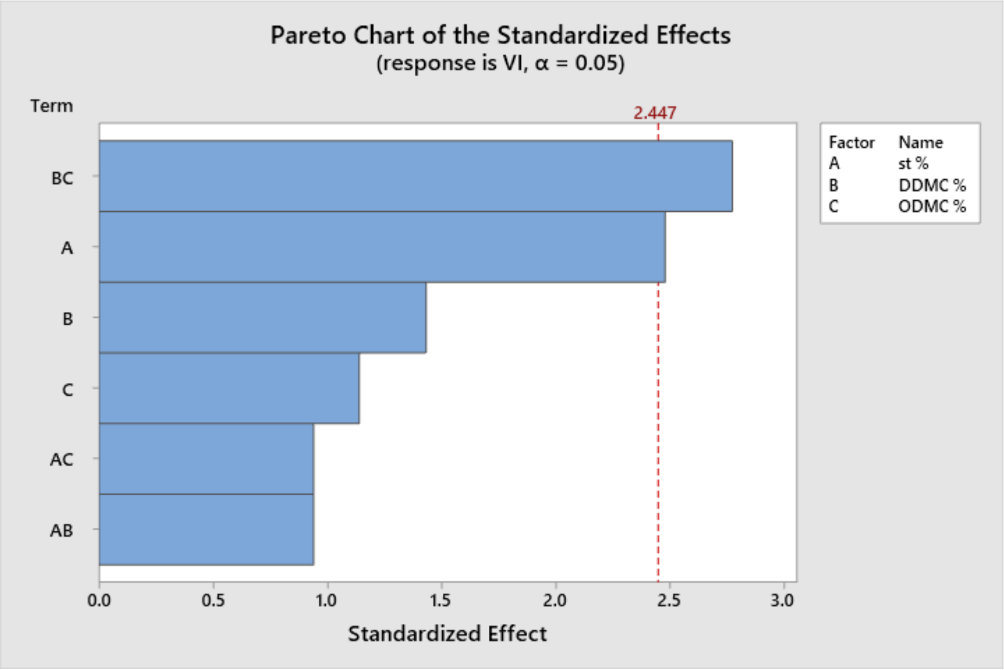


Figure (13). The parameters interaction chart.

4. Conclusions

The experimental examination of lube oil co-polymerization employing Nano-polymers was effective, and the viscosity index was greatly increased. The largest boost of 65.68% was obtained when St% equaled 5% and DDMC/ODMC=3. This characteristic is seen as a result of the copolymerization process and the dispersive action of monomers, for which the based oil provides a suitable solvent. The hydrodynamic properties of the lubricating oil are altered by copolymerization with monomers free radicals. The impact of adding monomers of varying molecular weight is also shown by using two additives (DDMC/St or ODMC/St) in lubricating oil instead of three (DDMC, ODMC, and St combined) to assure the behavior of the three additives. Using 85% ODMC and 15% St Yields a comparable result to using 95% DDMC and 5% St, giving us an understanding of the copolymerization free radical molecular weight influence on the hydrodynamic characteristics of lubricating oil. Under the same circumstances, the viscosity index enhancement behavior is similar to that of SN150 for DDMC/ODMC=3, however a distinct trend is found for ODMC/DDMC=3 for St Concentrations greater than 15%. Under identical operating circumstances, the viscosity index improvement in the SN500 case is better than the SN150 case. The greatest viscosity index is obtained at 95% DDMC; 95% ODMC has the same impact as 85% DDMC. This behavior varies from the three additive systems, where the larger molecular weight rule has no effect on lubricating oil viscosity stability. In other words, the current study established the optimal viscosity index by combining 95% DDMC and 5% St to build a two additive system. This combination is employed in the two-step addition procedure. According to the MINITAB statistics software, the best viscosity is attained at 5% St%, 18 ODMC%, and 18 DDMC%, with a maximum value of 196. When compared to other parameters, the St% is crucial. The interaction between ODMC% and DDMC% has a greater impact than St%. The interaction between St% - ODMC% and St% - DDMC% has the same proportion as the individual impact, which is smaller.

Conflict of Interest: The authors declare that there are no conflicts of interest associated with this research project. We have no financial or personal relationships that could potentially bias our work or influence the interpretation of the results.

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