

## Influence of Some Terpolymers on Flow Characteristics of Mineral Base Oil: Experimental and Quantum Calculations

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### Abstract

Mineral oil undergoes several chemical and physical changes with temperature change and time of storage. The lubricating additives are widely applied to the engine lubrication to suppress undesirable base oil properties like pour point depressants and viscosity index (VI) improvers. The current study aimed to prepare lube oil additives by preparing terpolymers as follows: reacting acrylic acid with various linear alcohols (decanol, dodecanol, and hexadecanol), several alkyl acrylates can be produced. Different imides were produced as a result of the reaction of maleic anhydride with different amines (aniline, triethylenetetramine, and tetraethylenepentamine). Fourier transforms infrared spectroscopy (FTIR) was utilized for investigating the structures of prepared compounds. Various terpolymers were synthesized during the polymerization reaction of different imides, different alkyl acrylates, and octene. The molecular weights of all polymers were detected through the use of gel permeation chromatography (GPC). Thermal gravimetric analysis (TGA) was used to determine the thermal stability of the prepared terpolymers, and the results demonstrated that the prepared terpolymers had high heat resistance. Above 300°C, the polymers deteriorated. Shear-thinning is observed in the rheological behavior, which approaches perfect Newtonian behavior at a high shear rate. The terpolymers created lowered the pour point of oil to -24 in the case of polymer C<sub>2</sub> and viscosity index is increased to 140 in the case of polymer C<sub>3</sub>. Quantum calculations prove that compound C<sub>3</sub> has more atom capacity to receive electrons compared to A<sub>3</sub>, which allows the formation of hydrogen bonds with other monomers making the resultant polymer bulkier and hence giving oil higher viscosity index.

**Keywords:** *Terpolymers; Lube oil additives; Viscosity index improvers; Pour point depressants; Quantum calculations.*

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## 1. Introduction

Application of substance with an appropriate viscosity to form a protective layer between mechanical parts to avoid wear, excessive heat, and noise due to friction is referred to as lubrication. Any material used for this purpose is lubricant [1-2]. Lubricants are divided according to their sources into two major categories: mineral and synthetic oils. Mineral oils are more common because they are available and are cheaper in production than oils. Mineral oils are produced during crude oil distillation [3] and cannot be utilized as they are without additives because their chemical and physical properties change as temperature and pressure change [4-5]. Chemicals known as lubricating oil additives are created to enhance the chemical and physical properties of basic oils (mineral, synthetic, vegetable, or animal), resulting in improved lubricant performance and equipment longevity [6-7]. The viscosity index is the most widely used measure of relative viscosity change of oil with changing temperature. The higher the viscosity index, the lower the change in viscosity with temperature [8]. Additives called viscosity index improvers are used to raise the viscosity index of lubricants. They are high molecular weight polymers [9] that create random coil shapes. When linear polymers are dissolved in a solvent

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such as oil, each polymer strand is split from its neighbors and resides in isolation in the solution. The polymer is dissolved in oil but keeps a coiled structure, filling the empty spaces inside the coil. The polymer then takes on a spherical form and expands with rising temperature to compensate for the drop in viscosity [10-11]. Waxy hydrocarbons are present in all mineral-derived base oils used for lubrication. They may construct a three-dimensional wax crystal network by lowering the temperature, leading to stopping oil flow and hence damage to machine elements. Polymers that can lower the pour point of base oil are known as pour point depressants. The mechanism of a pour point depressant is the modification of wax crystals formation to minimise wax crystal interlocking at low temperatures and promote wax crystal mobility near flexible pour point depressants by adsorbing these types of chemicals on the wax crystal and blocking the formation of a lattice interlocking network, the oil can continue to flow [12]. All pour point depressants are structures in which portion is like the crystals of paraffin wax. This portion provides nucleation sites and co-crystallizes with the paraffin waxes, but the other portion of the structure, unlike the wax crystals, prevents the wax matrices from becoming too large. As a result, the bulk stream can continue to be pumped and poured [13-14]. The current study seeks to manufacture various terpolymers by reacting various alkyl acrylates with various imides and octene, as well as to evaluate the generated terpolymers in lubricating oils to act as viscosity index improvers and pour point depressants.

## 2. Experimental

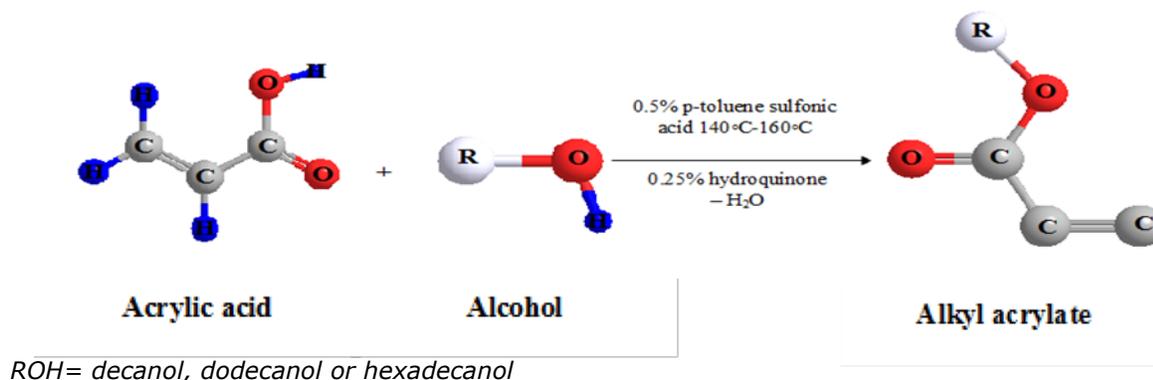
### 2.1. Materials

Lube oil is an additive-free mineral base oil (SAE 30) obtained from the Petroleum Cooperative Society. Acrylic acid, alcohols (decyl alcohol, dodecyl alcohol, and hexadecyl alcohol), amines (aniline, triethylenetetramine, and tetraethylenepentamine), and maleic anhydride used in the present study were obtained from Merck company. p-toluene sulfonic acid used was provided by Alfa Aesar Co. with CAS no. 6192-52-5. Octene and solvents (tetrahydrofuran (THF), xylene, toluene, and methanol) used were obtained from Aldrich Chemical Co. Ltd. (UK).

### 2.2. Procedure

#### 2.2.1. Acrylic ACID ESTERIFYING

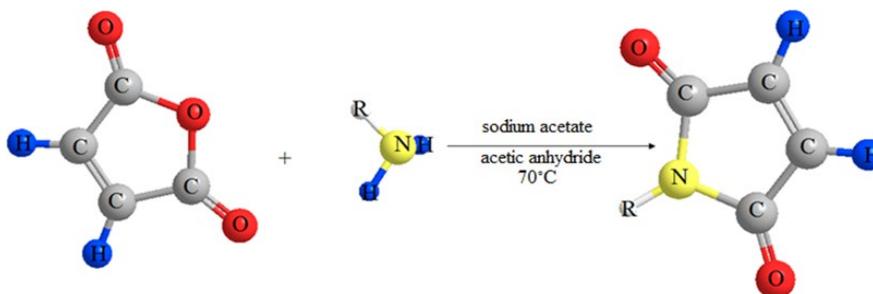
Ester of alkyl acrylate is produced through reacting equimolar quantities of acrylic acid with alcohols, namely, decanol, dodecanol, and hexadecanol. The reactions took place in xylene as a solvent, and decyl acrylate (Ac<sub>1</sub>), dodecyl acrylate (Ac<sub>2</sub>), and hexadecyl acrylate (Ac<sub>3</sub>) were obtained and well purified [15-16]. The acrylate formation reaction is shown in Scheme 1.



Scheme 1. Preparation of alkyl acrylate ester.

### 2.2.2. Imide preparation

To form three types of imides, dropwise additions of one mole of various amines (aniline, triethylenetetramine, and tetraethylenepentamine) dissolved in 50 mL of tetrahydrofuran (THF) to maleic anhydride were done as in Scheme 2. Im<sub>1</sub>, Im<sub>2</sub>, and Im<sub>3</sub> [17-19] were obtained.



where  $RNH_2 =$  aniline, triethylenetetramine or tetraethylenepentamine.

Scheme 2. preparation of imide.

### 2.2.3. Preparation of terpolymers with changing imides and esters

Free radical polymerization of prepared imides (Im<sub>1</sub>, Im<sub>2</sub>, and Im<sub>3</sub>), esters (Ac<sub>1</sub>, Ac<sub>2</sub>, and Ac<sub>3</sub>), and octene produced three distinct sets of polymers. The polymerization took place in a flask with four necks, a thermometer, a stirrer, an effective condenser, and nitrogen input. Toluene was employed as a solvent, while benzoyl peroxide was utilized as a catalyst. The reactants (imide, ester, and octene) were mixed for 8 hours at temperatures ranging from 60 to 80°C. Following the entire reaction, to separate the polymer, the result was agitated in cold methanol, then filtered, and dried [20-21]. Table 1 shows the codes of the prepared terpolymers.

Table 1. Monomer designation of groups (A, B, and C) of prepared terpolymers.

Polymer code	Monomer ratio	Polymer code	Monomer ratio	Polymer code	Monomer ratio
A <sub>1</sub>	Im <sub>1</sub> + Ac <sub>1</sub> + octene 5 : 70 : 25	B <sub>1</sub>	Im <sub>2</sub> + Ac <sub>1</sub> + octene 5 : 70 : 25	C <sub>1</sub>	Im <sub>3</sub> + Ac <sub>1</sub> + octene 5 : 70 : 25
A <sub>2</sub>	Im <sub>1</sub> + Ac <sub>2</sub> + octene 5 : 70 : 25	B <sub>2</sub>	Im <sub>2</sub> + Ac <sub>2</sub> + octene 5 : 70 : 25	C <sub>2</sub>	Im <sub>3</sub> + Ac <sub>2</sub> + octene 5 : 70 : 25
A <sub>3</sub>	Im <sub>1</sub> + Ac <sub>3</sub> + octene 5 : 70 : 25	B <sub>3</sub>	Im <sub>2</sub> + Ac <sub>3</sub> + octene 5 : 70 : 25	C <sub>3</sub>	Im <sub>3</sub> + Ac <sub>3</sub> + octene 5 : 70 : 25

## 2.3. Characterization of prepared compounds

### 2.3.1. Infrared spectroscopic examination

The IR spectra of the generated esters and imides were detected using an FTIR Spectrometer Model Type Mattson Infinity series Benchtop 961.

### 2.3.2. Molecular weight of the synthesized terpolymers determination

Waters model 510 Gel Permeation Chromatography (GPC) with polystyrene standard, T.H.F as an eluent, and Ultra-styragel column were used to determine the molecular weights of the produced compounds.

### 2.3.3. <sup>1</sup>H-NMR spectroscopic analysis

Bruker's 300 MHz spectrometer W.P. 300 was utilized for measuring the <sup>1</sup>HNMR spectra of synthetic polymers.

## 2.4. Evaluating prepared compounds as lube oil additives

### 2.4.1. Prepared compounds as viscosity index improver

The ASTM D2270-87 technique for measuring the viscosity index was used to conduct the study viscosity index (VI).

### 2.4.2. Prepared compounds as pour point depressants

The synthesised compounds were evaluated as pour point depressants utilising base oil (SAE 30) and the ASTM-97-87 pour point test. Various concentrations were utilized for exploring additive concentration's impact. The pour point was determined through the use of a cryostat apparatus.

## 3. Results and discussion

In the present study, improvers of the viscosity index and depressors of the pour point were synthesized as follows:

- 1- Acrylic acid esterification with various alcohols.
- 2- The reaction of maleic anhydride with various amines.
- 3- Terpolymerization reaction of octene with prepared esters and imides.

The addition of prepared additives to the base fluid may result in the formulation of a more cost-effective and higher-performing lubricant [22].

### 3.1. Physicochemical characterization of prepared alkyl acrylate and imides

IR spectrum and molecular weight confirmed the chemical structures of the generated esters (AC<sub>1</sub>-AC<sub>3</sub>) and imides (Im<sub>1</sub>-Im<sub>3</sub>). The infrared spectra of compounds (AC<sub>1</sub>, AC<sub>2</sub>, and AC<sub>3</sub>) are displayed in Figure 1, which corresponds to the data provided in Table 2.

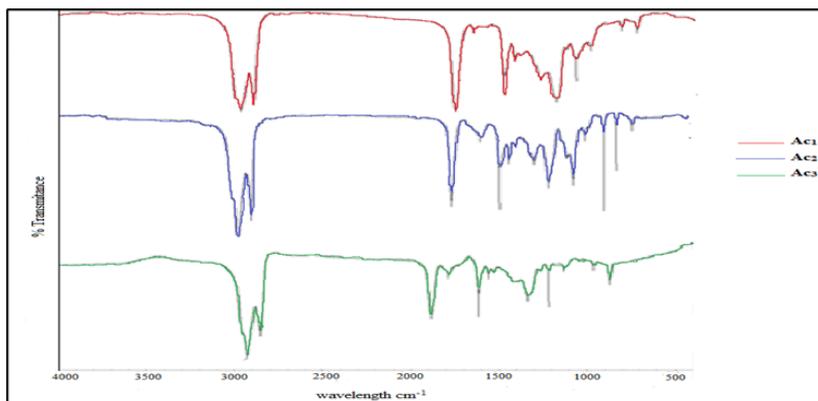


Figure 1. IR spectra of compounds AC<sub>1</sub>, AC<sub>2</sub>, and AC<sub>3</sub>.

Table 2. Analysis of chart results of IR spectra for compounds (AC<sub>1</sub>-AC<sub>3</sub>).

Polymer code	Peak position	Indication
AC <sub>1</sub> -AC <sub>3</sub>	The peak appeared at the range between 1170 cm <sup>-1</sup> and 1188 cm <sup>-1</sup> and at the range between 1260 cm <sup>-1</sup> -1270 cm <sup>-1</sup>	Presence of C-O stretch
	The peak appeared at the range between 1560 cm <sup>-1</sup> -1630 cm <sup>-1</sup>	Presence of C=C
	The peak appeared at 1730 cm <sup>-1</sup>	Presence of ester C=O group
	Peaks appeared at 2923 cm <sup>-1</sup> , 2854 cm <sup>-1</sup>	SP <sup>3</sup> -CH stretching vibration of asymmetrical & symmetrical hydrocarbon

Strong bands representing acid and alcohol that are supposed to appear at  $3500\text{ cm}^{-1}$  have been eliminated as a result of ester well purifying, indicating that acids and alcohols are consumed for ester synthesis. Products  $\text{Im}_2$  and  $\text{Im}_3$  [23] have the same functional groups. Thus,  $\text{Im}_3$  was taken as an example for both products. The prepared compounds' chemical structures ( $\text{Im}_1$  and  $\text{Im}_3$ ) are investigated through the use of IR as shown in Figure 2, which illustrates the results presented in Table 3.

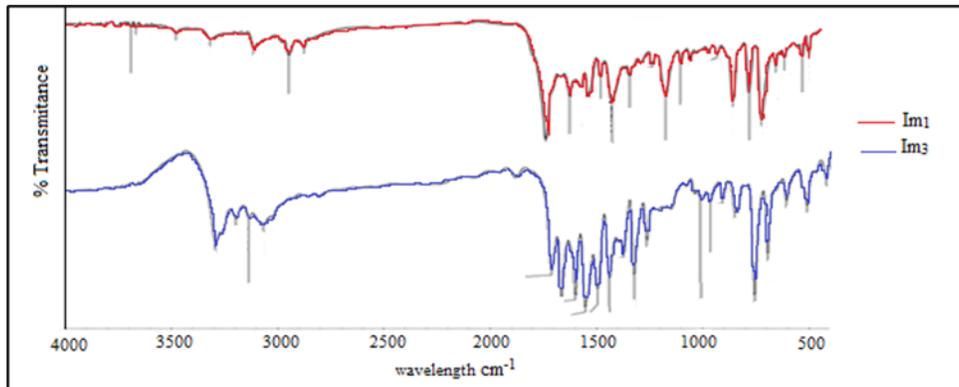


Figure 2. IR spectra of compound ( $\text{Im}_1$ ,  $\text{Im}_3$ ).

Table 3. Analysis of chart results of IR spectra for compounds ( $\text{Im}_1$ ,  $\text{Im}_3$ ).

Polymer code	Peak position	Indication
$\text{Im}_1$	The appearance of a peak at $695\text{ cm}^{-1}$	-CH bending benzene derivative
	The appearance of a medium peak at $1594\text{ cm}^{-1}$	cyclic alkene
	The appearance of a peak at $1311\text{ cm}^{-1}$	Presence of C-N imide group
	The appearance of a peak at $1710\text{ cm}^{-1}$	-C=O imide
	The disappearance of two peaks at $1870\text{ cm}^{-1}$ & $1790\text{ cm}^{-1}$	Absence of C=O anhydride group
$\text{Im}_3$	The appearance of a peak at $3293\text{ cm}^{-1}$	-NH primary amine
	The appearance of a peak at $1709\text{ cm}^{-1}$	-C=O imide
	The appearance of a peak at $1320\text{ cm}^{-1}$	Presence of C-N imide group
	The disappearance of two peaks at $1870\text{ cm}^{-1}$ & $1790\text{ cm}^{-1}$	Absence of C=O anhydride group

The absence of two peaks which are supposed to locate at  $1818\text{ cm}^{-1}$  and  $1750\text{ cm}^{-1}$  indicates that carbonyl of the anhydride group is not present, and a  $\text{-C=O}$  imide peak at  $1710\text{ cm}^{-1}$  as a replacement reveals that every anhydride has been converted into an imide.

## 3.2. Characterization of the prepared terpolymers

### 3.2.1. Using IR spectroscopy

The structure of terpolymer  $\text{A}_3$  was elucidated by using IR spectroscopy as an example for terpolymers as shown in Figure 3. The results were illustrated in Table 4.

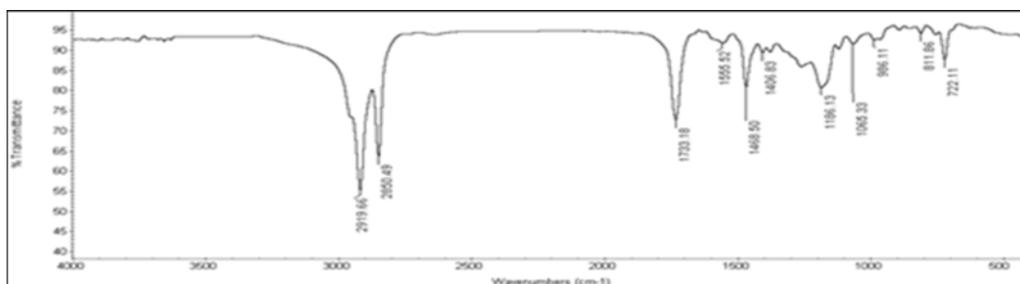


Figure 3. IR spectrum of product  $\text{A}_3$ .

Table 4. Analysis of chart results of I.R spectrum for compound A<sub>3</sub>.

Compound	Peak position	Indication
A <sub>3</sub>	Peak appearance at 1733 cm <sup>-1</sup>	Presence of carbonyl group of the ester
	The appearance of a peak at 1360 cm <sup>-1</sup>	Presence of C-N imide group
	Peaks appearance at 2919 cm <sup>-1</sup> , 2850cm <sup>-1</sup>	SP <sup>3</sup> -CH stretching vibration of assymetrical& symmetrical hydrocarbon
	Absence of peak at 1630 cm <sup>-1</sup>	Absence of -C=C- aliphatic

From the above data, we can deduce that the three monomers react with each other to form a terpolymer.

### 3.2.2. Using <sup>1</sup>H-NMR spectroscopy

The structure of the synthesized terpolymer (A<sub>2</sub>), used as an example for terpolymers, was studied using <sup>1</sup>H-NMR spectroscopy, as shown in Figure 4. The results were illustrated in Table 5.

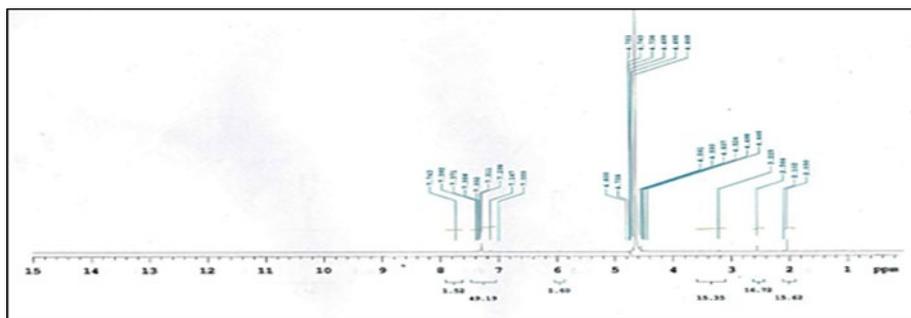

 Figure 4. <sup>1</sup>H-NMR Spectrum of product A<sub>2</sub>.

 Table 5. Analysis of <sup>1</sup>H-NMR spectrum results for compounds (A<sub>2</sub>).

Peak position	Indication
Peak appearance at 1.3 ppm	Indicates the presence of CH attached to the alkyl group
Peak appearance at 2.1 ppm	Indicates the presence of proton CH attached to - CONR <sub>2</sub> group
Peak appearance at 2.4 ppm-3.3 ppm	Indicates the presence of proton CH attached to - COR
Peak appearance at 4.6 ppm	Indicates the presence of proton CH <sub>2</sub> attached to the (O-C=O) group
Peak appearance at 7.1 ppm-7.3 ppm	Indicate the presence of proton in a benzene ring

### 3.2.3. Using gel permeation chromatography (GPC)

Table 6 shows the mean molecular weights of the produced terpolymers. The molecular weight of terpolymers (A<sub>1</sub>-A<sub>3</sub>) grows as the acrylate chain length increases, reaching 41000 when dodecyl acrylate is utilized and 42001 in case of using hexadecyl acrylate. A<sub>3</sub>, B<sub>3</sub>, and C<sub>3</sub> terpolymers' molecular weights rise in proportion to the number of nitrogen atoms involved in the imide used, reaching 70168 in the case of terpolymer (C<sub>3</sub>), when product Im<sub>3</sub> is used in polymerization.

Table 6. Mean molecular weight of groups (A, B, and C) of prepared terpolymers.

Terpolymer designation	Mean molecular weight	Terpolymer designation	Mean molecular weight	Terpolymer designation	Mean molecular weight
A <sub>1</sub>	29000	B <sub>1</sub>	20061	C <sub>1</sub>	26409
A <sub>2</sub>	41000	B <sub>2</sub>	40473	C <sub>2</sub>	53528
A <sub>3</sub>	42001	B <sub>3</sub>	43993	C <sub>3</sub>	70168

### 3.2.4. Thermal analysis

The produced polymers' thermal stability was investigated. Through the use of thermogravimetric analysis (TGA). TGA is a method for determining the thermal characteristics of materials as a function of temperature. The weight and enthalpy of the sample vary when it is

heated in the thermal testing. The thermal resistance of the prepared terpolymers ( $A_1$ - $A_3$ ), ( $B_2$ ,  $B_3$ ), and ( $C_1$ - $C_3$ ) was investigated and given in Figures 5–7.

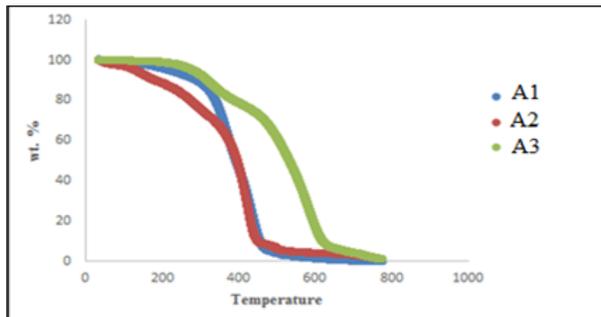


Figure 5. TGA analysis of ( $A_1$ - $A_3$ ).

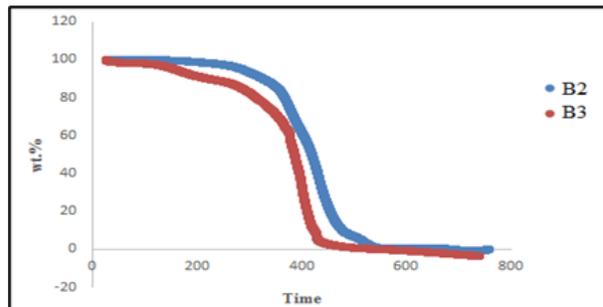


Figure 6. TGA analysis of ( $B_2$ ,  $B_3$ ).

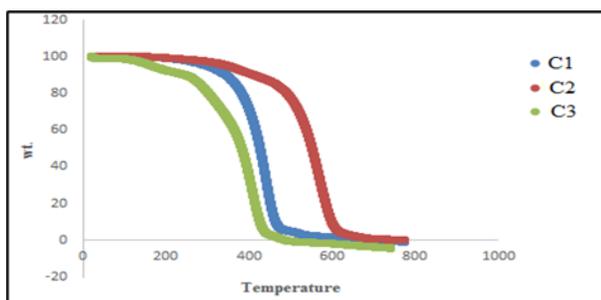


Figure 7. TGA analysis of ( $C_1$ - $C_3$ ).

The thermogravimetric curve of the terpolymers  $A_1$  generated exhibits two periods of weight decrease, as presented in Figure 5. The primary decline begins around 100°C, resulting in a weight loss of 37.3%. This is due to moisture in the intramolecular and intermolecular space's evaporation. At 390°C, the major deterioration commences, resulting in a weight loss of 62.9%, correlating to polymer breakdown.

The principal deterioration occurs at about backbone 75°C, with a 9.35 percent weight decrease, according to the  $A_2$  curve. At 410°C, the most dramatic degradation occurs, with a weight loss of 90.65%. According to the  $A_3$  curve, with a weight loss of 18.7%, the first deterioration commences at about 125°C. At 300°C, the second and most serious decline occurs, with a weight loss of 66.8%. At 450°C, the third deterioration occurs, resulting in a weight loss of 14%. As shown in Figure 6, the thermogravimetric curves of the generated terpolymer  $B_2$  demonstrate two periods of weight loss. At 110°C, the main decline starts, resulting in a weight loss of 10.5%. This is due to moisture in the intramolecular and intermolecular space's evaporation. At 325°C, the most significant deterioration occurs, with a weight loss of 82.6%, corresponding to polymer backbone disintegration. According to terpolymer  $B_3$ , the initial degradation begins at 75°C, with a weight loss of 2.6%.

The most substantial decline occurs at 300°C, with a weight loss of 87.2%. As shown in Figure 7, the thermogravimetric curve of the produced terpolymer  $C_1$  demonstrates that the primary deterioration occurs at 350°C with a weight loss of 90%, corresponding to polymer backbone degradation. The initial deterioration occurs at 110°C, with a weight loss of 10.6%, according to terpolymer  $C_2$ . The most significant deterioration occurs at 375°C, with a weight loss of 89.5%. The initial deterioration occurs at 110°C, with a weight loss of 3.1%, according to terpolymer  $C_3$ . The main deterioration occurs at 330°C, with a weight loss of 71.5%, indicating that the produced terpolymers have good thermal stability, confirming their eligibility for application as lubricating oil additives.

### 3.3. Evaluating the synthesized compounds as lubricating oil additives

#### 3.3.1. As viscosity index improvers

The effectiveness as viscosity index improvers of terpolymer soluble groups ( $A_1$ - $A_3$ ,  $B_1$ - $B_3$ , and  $C_1$ - $C_3$ ) was assessed. To investigate the influence of additive concentration on lube oil viscosity index, prepared additives with concentrations of 0.25%, 0.50%, 1.00%, 2.00%, and

3.00% were utilized. Table 7 presents the results, and it was revealed that the viscosity index of the lubricating oil rises as the additive concentrations rise.

Table 7. Dependence of VI on the concentration of groups (A, B and C) of prepared additives.

Conc. of additives	The viscosity index of lube oil in presence of different additives								
	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>
0.00%	91	91	91	91	91	91	91	91	91
0.25%	84	92	93	98	99	100	99	98	101
0.50%	99	96	100	99	102	105	100	100	106
1.00%	102	98	103	101	107	109	102	110	114
2.00%	103	105	105	101	108	114	104	113	129
3.00%	105	113	118	105	111	119	106	117	140

The aforementioned findings demonstrate that the viscosity index (VI) of lubricating oil is increased by increasing the concentration of manufactured additives in solution. The viscosity of lubrication oil falls as temperature rises. However, at higher temperature owing to additive molecule expansion, when temperature rises, the size of solvated additives increases, which offsets the drop in lubricant viscosity. Increased polymer concentration leads to a rise in the entire volume of polymer molecules that have been solvated, which has a greater thickening effect and enhances the VI property [24].

The effect of alkyl acrylate chain length and polarity of imide used in polymer composition (number of nitrogen atoms) on the efficacy of the produced additives, doped in SAE 30 oil in concentration=3%, as viscosity index improves as shown in Figure 8, indicates that the efficiency rises as the alkyl chain length grows.

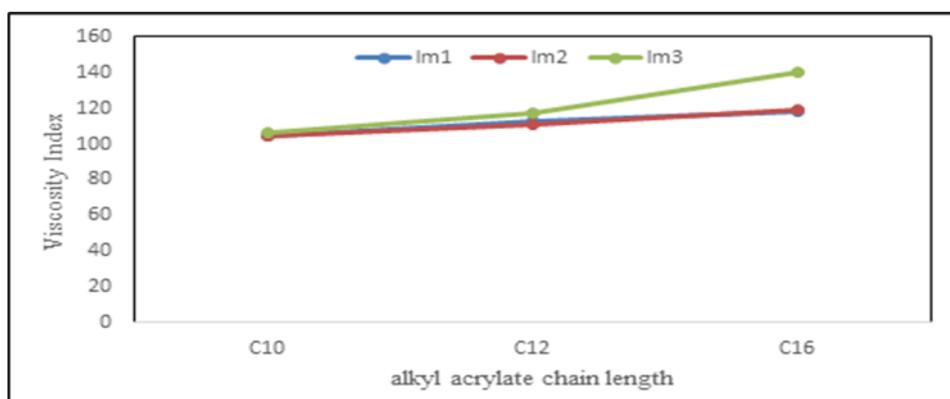


Figure 8. The effect of alkyl acrylate chain length and polarity of imide used in polymer composition (number of nitrogen atoms) on the efficiency of the prepared additives, doped in SAE 30 oil in concentration = 3%, as viscosity index improves.

This might be because molecular weight has an effect on the effective coil radius, and, as a result, the VI. The efficiency improves as the amount of nitrogen atoms in the terpolymer increases. This may be due to the concept that increasing heteroatoms (polarity) allows graft polymerization by forming covalent bond with monomers and hence increases the molecular weight of polymer in comparison with linear polymer [25]. Because of the higher degree of polymerization, the polymer units of higher molecular weight polymers will be bigger, implying that their hydrodynamic volumes will be greater, which may explain their higher VI value.

### 3.3.2. Investigation of rheological properties of lube oil

The behaviour of the blank oil and the mixtures oils/viscosity index improver additives, when subjected to rheometric tests, was studied using a rheometer (Anton Paar Rheo Compass). The parameters of the rheometer include shear rate ( $\text{sec}^{-1}$ ), shear stress ( $\text{N/m}^2$ ), and viscosity ( $\text{mPa}\cdot\text{s}$ ). A series of tests were carried out to investigate the flow properties of oil samples. The oil samples were made by adding 3.00% by weight of additive A<sub>3</sub> to the blank

oil (SAE 30) at 40°C, 60°C, and 100°C compared to blank oil samples. Figures 9 and 10 depict the rheological results.

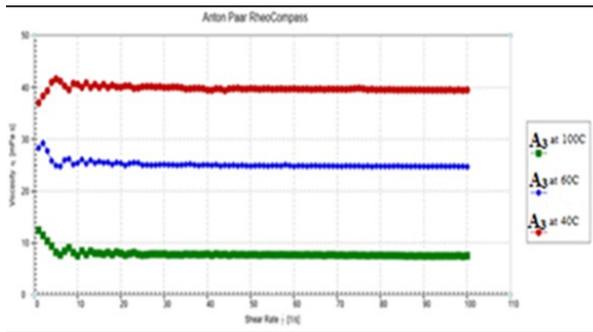


Figure 9. Viscosity – shear rate curve of (A<sub>3</sub>) additive with constant concentration 30.00\*10<sup>3</sup> ppm at 40°C, 60°C, and 100°C.

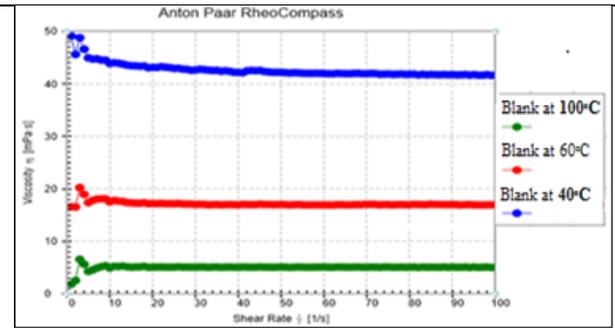


Figure 10. Viscosity – shear rate curve of blank oil at 40°C, 60°C, and 100°C.

With the increase in the shear rate, the viscosity of lubricant oil without additives remains nearly constant. This means that, at any shear rate, pure lubricating oil behaves as a Newtonian fluid. It was discovered that when lubricating oil with additives is exposed to a mild rate of shear, the viscosity of the lubricant progressively declines and acts as a non-Newtonian fluid. The viscosity of the lubricant, on the other hand, remains almost constant at high shear rates and behaves like a Newtonian fluid. In the absence of shear, viscosity modifiers in lubricating oil exist as spherical coils with random orientation at low temperatures, exerting high viscosity, when shear is applied, they begin to rearrange themselves in the flow direction, and lubricant viscosity is reduced [26]. At greater shear rates, all of the polymers are oriented flow-wise, and the viscosity changes just a little. Polymers are readily ordered flow-wise under shear because viscosity modifiers exist in expanded form at higher temperatures, and viscosity stays virtually constant at high shear rates for all polymer mixed lubricating oil. As temperature increases, the rate of viscosity loss accelerates, and the shear rate decreases with the addition of a viscosity index improver. The viscosity of Newtonian fluids remains constant regardless of how quickly they are compelled to travel via a conduit or channel (i.e., the rate of shear does not affect viscosity). Because of these circumstances, the lubricating oil has a long life and does not need to be replaced.

### 3.3.3. Investigation of tribological behavior of lube oil

Tribological experiments were conducted under pure sliding circumstances in an Anton-Paar modular compact rheometer MCR 302 equipped with a tribology cell T-PTD 200 and a Peltier hood H-PTD 200 for precise temperature control. The influence of sliding distance and sliding velocity on friction using oil containing (C<sub>3</sub>) additive with a constant concentration of 30.00\*10<sup>3</sup> ppm is shown in Figures 11 and 12. The comparison between values of friction coefficient for C<sub>3</sub> and blank refers to lower values of friction coefficient obtained by using C<sub>3</sub>.

### 3.3.4. As pour point depressants

Pour point depressants (PPDs) operate by adsorbing to the surface of the wax crystals. The resulting pour point depressant surface layer inhibits wax crystal formation as well as their capacity to absorb oil and form gels [13]. As pour point depressants, several concentrations of produced compounds (A<sub>1</sub>-A<sub>3</sub>), (B<sub>1</sub>-B<sub>3</sub>), and (C<sub>1</sub>-C<sub>3</sub>) (with a range of 0.25 percent, 0.50 percent, 1.00 percent, 2.00 percent, and 3.00 percent by weight) were investigated. Figures 13–15 show a summary of the experimental findings.

According to the results of the pour point of the group (A, B, and C) shown in Figures 13–15, the pour point decreases with the increase in the concentration of the additive until reaching 1% additive ratio, and then the pour point increases. The pour point drops as the alkyl

acrylate chain length grows till it reaches -18, -21, and -24 according to A<sub>2</sub>, B<sub>2</sub>, and C<sub>2</sub>. However, it increases when C<sub>16</sub> acrylate is used.

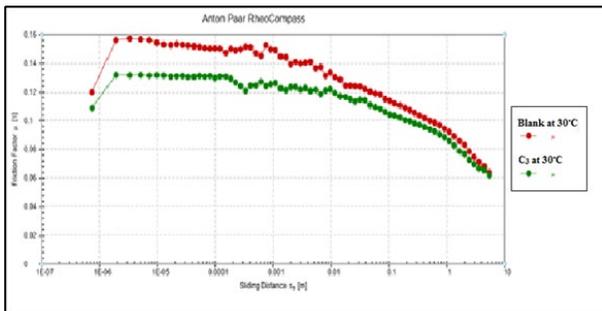


Figure 11. Relation between friction factor and sliding distance of blank oil and oil-containing (C<sub>3</sub>) additive with constant concentration 30.00\*10<sup>3</sup> ppm at 30°C.

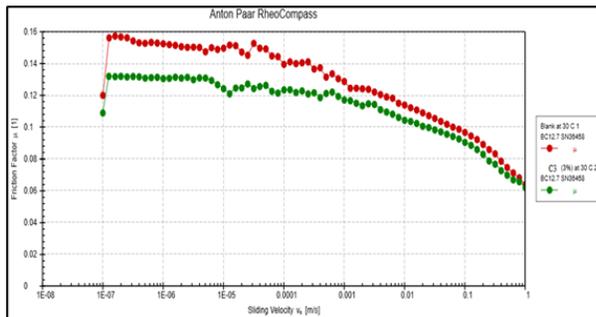


Figure 12. Relation between friction factor and sliding velocity of blank oil and oil-containing (C<sub>3</sub>) additive with constant concentration 30.00\*10<sup>3</sup> ppm at 30°C.

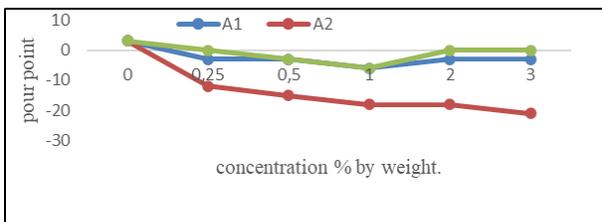


Figure 13. Pour point results of different concentrations of prepared compounds (A<sub>1</sub>-A<sub>3</sub>), ranging from (0.25%, 0.50%, 1.00%, 2.00% and 3.00% by weight).

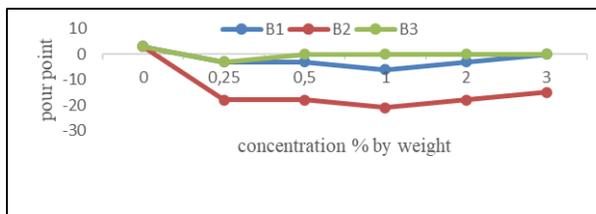


Figure 14. Pour point results of different concentrations of prepared compounds (B<sub>1</sub>-B<sub>3</sub>), ranging from (0.25%, 0.50%, 1.00%, 2.00% and 3.00% by weight).

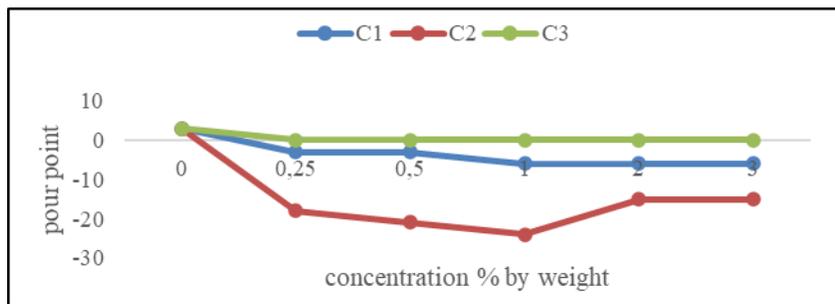


Figure 15. Pour point results of different concentrations of prepared compounds (C<sub>1</sub>-C<sub>3</sub>), ranging from (0.25%, 0.50%, 1.00%, 2.00% and 3.00% by weight).

The results in Figures 13–15 reveal that increasing the number of nitrogen atoms in the polymer improves the efficacy of pour point depressants because the polymers may interact with the lubricating oil's paraffinic wax and modify their crystal size. When compared to other polymers, polymer C<sub>2</sub> has higher efficiency as a PPD. It might be owing to its stronger polarity, which allows it to be absorbed by the wax crystals found in lubricating oil.

### 3.4. Quantum chemical calculations

ISIS Draw 2.1.4 was utilized for creating the 2D sketch and geometric structure of A<sub>3</sub> and C<sub>3</sub> terpolymers in their ground state, as well as the topology of electron densities in the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) shown in Figure 16 (a, b). electronegativity ( $\chi$ ), global hardness ( $\eta$ ), softness ( $\sigma$ ), electron affinity (A),

and ionization potential (I) are all included in the Unrestricted Hartee Fock (UHF) level, which is implemented in Hyperchem 8.0 [26].

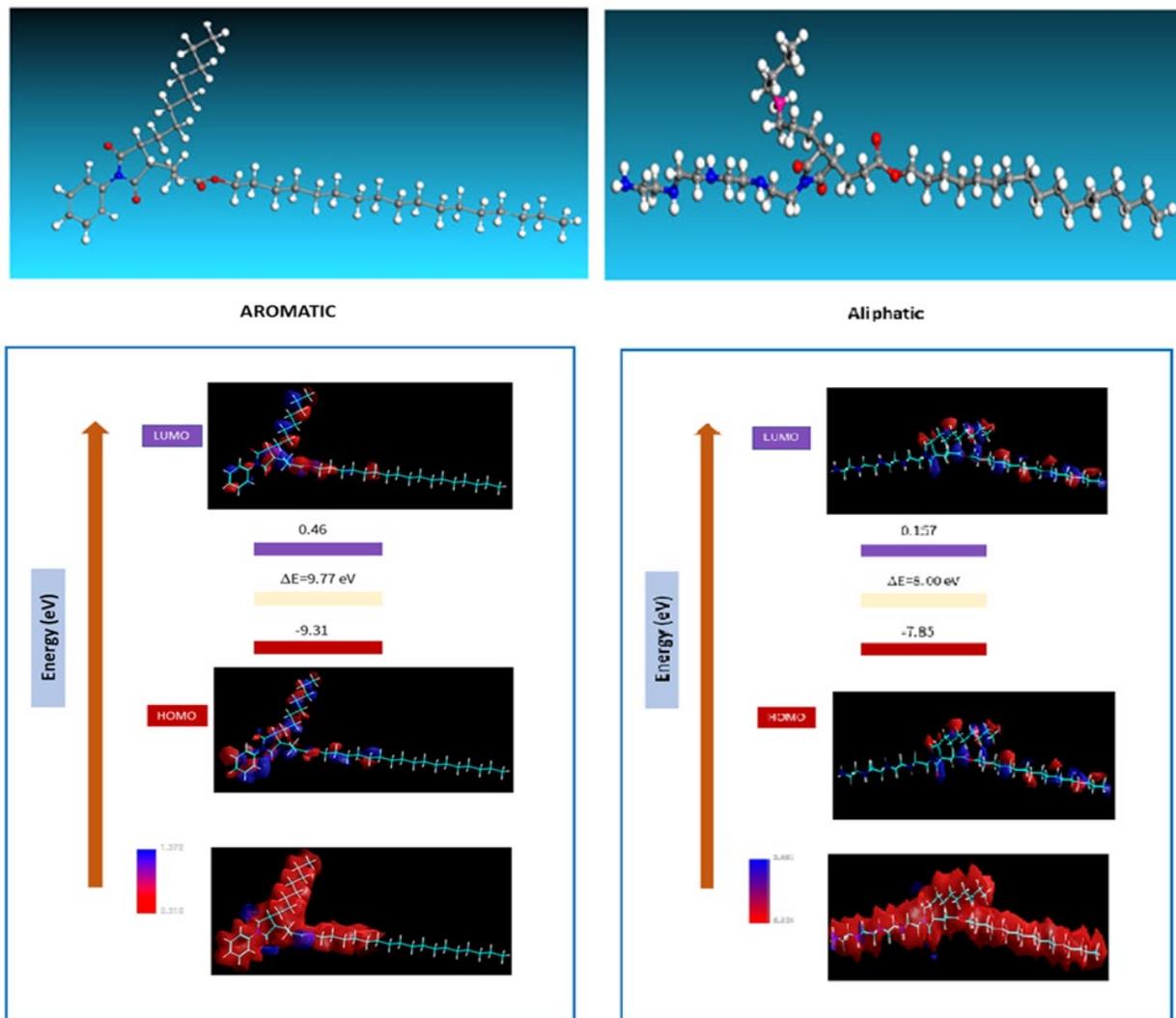


Figure 16. Geometry structure of  $A_3$  and  $C_3$  terpolymers in their ground state and the electron density distribution topology in the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).

Table 8. Quantum chemical calculated parameters of the investigated terpolymers  $A_3$  and  $C_3$ .

Quantum parameters	Aromatic ( $A_3$ )	Aliphatic ( $C_3$ )
EHOMO(eV)	-9.31	-7.85
ELUMO(eV)	0.46	0.157
$\Delta E$ (eV)=ELUMO-EHOMO	9.77	8.00
$\mu$ (Debye)	7.41	4.32
I(eV)=-EHOMO	9.31	7.85
A(eV)=-ELUMO	-0.46	-0.157
$X$ (eV)=-1/2(EHOMO+ELUMO)	4.42	3.84
$\eta$ (eV)=-1/2(EHOMO-ELUMO)	4.88	4.00
$\sigma=1/\eta \cong -2/(E_{HOMO} - E_{LUMO})$	0.20	0.24
$\Delta N = \chi_{Fe} - \chi_{inh} / 2(\eta_{Fe} - \eta_{inh})$	0.86	0.76

The outcomes are shown in Table 8. In general, the energy of the HOMO (EHOMO) indicates a molecule's tendency to transfer electrons to a species that lacks them. With the rise in the tendency of molecule to give electrons to a species that lacks them. The value of EHOMO decreases as the tendency of the polymer to donate its electron to other monomers increases.

When the EHOMO for A<sub>3</sub> and C<sub>3</sub> are compared, it can be seen which molecules have the strongest inclination to give electrons.

It's worth mentioning that the collected data, as shown in Table 8, show that compound C<sub>3</sub> has more atom capacity to receive electrons than A<sub>3</sub>, allowing the formation of hydrogen bonds to form as a result of a dipole-dipole interaction between a hydrogen atom bound to a highly electronegative atom and another highly electronegative atom lying in other imide monomers that make the resulting polymer bulkier and hence give oil higher viscosity index.

#### 4. Conclusion

Lube oil dissolves all of the produced terpolymers. All the prepared terpolymers are effective as viscosity index improvers and pour point depressants for lube oil. As the concentration of prepared additive increases, the lubricant's viscosity index rises. As the alkyl chain length of the acrylate in the polymer grows till hexadecyl acrylate, the viscosity index of the lubricant increases. Pour point decreases with the increase in the concentration of additives until reaching a 1% additive ratio. The pour point reduces as the alkyl acrylate chain length grows until C<sub>12</sub> acrylate is used, but it increases when C<sub>16</sub> acrylate is used. The efficiency of pour point depressants improves as the number of nitrogen atoms in the terpolymer increases.

At every shear rate, pure lubricant oil behaves as a Newtonian fluid. Lube oil including additives acts as a non-Newtonian fluid. However, at large shear rates, the lubricant's viscosity remains almost constant and behaves like a Newtonian fluid. Quantum calculations prove that compound C<sub>3</sub> has more atom capacity to receive electrons compared to A<sub>3</sub>, which allows the formation of hydrogen bonds with other monomers making the resultant polymer bulkier and hence giving oil higher viscosity index.

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#### Conflicts of interest

*The authors of the present article would like to declare that they have no known conflict financial interests or personal relationships that could have appeared to influence the work reported in this paper.*

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