

SYNTHESIS AND EVALUATION OF TERPOLYMERS AS VISCOSITY INDEX IMPROVERS AND POUR POINT DEPRESSANTS

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Abstract

The present work aims to synthesize and evaluate fourteen terpolymers which used as improving performance additive for lubricating oil especially viscosity index improvers and pour point depressants. The synthesis process occurs via esterification reaction of acrylic acid with different alcohols (octanol, decanol, dodecanol, tetradecanol, hexadecanol, octadecanol and docosanol) separately. Then polymerization of the prepared esters with vinyl acetate and different α -olefins (1-dodecene, 1-hexadecene) were carried out. The prepared compounds were elucidated by using FTIR (Fourier Transform Infrared Spectroscopy), ¹H-NMR (Proton Nuclear Magnetic Resonance), TGA (Thermogravimetric analysis) and the molecular weight was determined by using GPC (Gel Permeation Chromatography). The efficiency of the prepared terpolymers as viscosity index improvers and pour point depressants for lubricating oil was investigated and compared with that of the mineral base oils, it was found that the viscosity index of lube oil with the prepared additives increases with increasing its concentration and with increasing the alkyl chain length of the acrylate used from octylacrylate till tetradecylacrylate, then decreases with increasing the chain length. The prepared additives were evaluated as pour point depressants for lube oil and it was found that the efficiency of the prepared compound as pour point depressants decreases with decreasing the concentration of the terpolymers used, while increases with increasing the molecular weight of the prepared terpolymers. The additives depend on dodecylacrylate have the best efficiency as pour point depressants.

Keywords: Lubricating oil additives; oil performance additives; acrylate terpolymers; thermal analysis; viscosity index improvers; pour point depressants.

1. Introduction

Lubrication is simply the use of a material to improve the smoothness of movement of one surface over another and the materials which are used in this way are called lubricants [1-3]. A lubricant prevents the direct contact of rubbing surfaces and thus reduces wear. It keeps the surface of metals clean. Lubricants can also act as coolants by removing heat effects and also prevent rusting and deposition of solids on close fitting parts [4-5].

Viscosity is the most important physical property of lubricating oil; it is a measure of its internal friction or resistance to flow. In simple terms, it provides a measure of the thickness of lubricating oil at a given temperature; the higher the viscosity, the thicker the oil. Viscosity index improvers are normally high molecular linear polymers, and oil soluble polymers [6]. The viscosity index is an indicator of the change in viscosity as the temperature is changed. The higher the viscosity index (VI), the less the viscosity of an oil changes for a given temperature change [7]. Viscosity index improvers function by increasing the relative viscosity of oil more at high temperatures than at low temperatures. Generally this results from the polymer changing its physical configuration with increasing temperature of the mixture. It is believed that the polymer molecule in solution exists as a random coil, which is swollen by the lube oil solvent. The volume of this molecule determines the viscosity increase. In cold oil the molecules

of the polymer adopt a coiled form so that their effect on viscosity is minimized. In hot oil, the molecules tend to straighten out, and the interaction between these long molecules, having greater volume and the oil produces a proportionally greater thickening effect which in turn raises the VI of the oil [8-9].

Most oils contain some dissolved wax which begins to separate as crystals that interlock to form a rigid structure. It has been suggested that it is more logical to add a pour point depressant. Pour point depressants are high molecular weight polymers that function by inhibiting the formation of a wax crystal structure that would prevent oil flow at low temperature. The additives do not entirely prevent wax crystal growth, but rather lower the temperature at which a rigid structure is formed. Pour point depressants act through surface adsorption on the wax crystals. The resulting surface layer of pour point depressant inhibits the growth of the wax crystals and their capacity to adsorb oil and form gels. In the absence of long interlocking crystals or swollen particles, oil can move freely through any solid wax particles that are present [10-11].

In the present work fourteen terpolymers were prepared via free radical chain polymerization. The prepared terpolymers were elucidated using FTIR, GPC, $^1\text{H-NMR}$. The thermal characteristics (TGA and DSC) for the prepared terpolymers were measured and they were evaluated as lube oil additives (viscosity index improvers and pour point depressants).

2. Experimental

2.1. Esterification of acrylic acid with different types of alcohol

Esterification has been carried out by reacting one mole of acrylic acid with one mole of the selected alcohol (octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl and docosanol) separately. The reactions were carried out in a resin kettle in presence of 0.5 % *p*-toluene sulphonic acid as a catalyst, 0.25 % hydroquinone as inhibitor for the polymerization of acrylic acid, and xylene as an azeotropic solvent. Esterification reactions were carried out under a slow stream of deoxygenated nitrogen. The reaction heated gradually from the room temperature up to $130^\circ\text{C} \pm 5^\circ\text{C}$. The extent of reaction was followed by monitoring the amount of liberated water. The prepared esters were purified {octylacrylate(A), decylacrylate(B), dodecylacrylate(C), tetradecylacrylate(D), hexadecylacrylate(E), octadecylacrylate(F) and docosylacrylate(G)} [6-7].

2.2. Synthesis of polymeric additives based on alkylacrylate

Polymeric additives were prepared by free radical polymerization of the prepared esters separately, with vinyl acetate, and (dodecene or hexadecane) using the ratio of (1 mole: 0.5 mole: 0.5 mole). The reaction was carried out in a three necked round bottom flask equipped with a stirrer, efficient condenser, thermometer, and an inlet for introduction of dry nitrogen, the desired weight of initiator (benzoyl peroxide), was heated for 8 hours at 80°C in the presence of toluene as a solvent. When the reaction was completed, the temperature was reduced to room temperature, and then they were purified by precipitation in excess volume of cold methanol and filtration.

3. Identification of the prepared compounds

The infrared spectra obtained using an FTIR spectrometer model type Mattson-Infinity Series Benchtop 961 have been employed for identification of the purified esters and the prepared terpolymers.

The structure of the synthesized polymeric additives were followed up by $^1\text{H-NMR}$ spectra using a 300 MHz Varian NMR 300 spectrometer using DMSO (dimethylsulfoxide) as a solvent.

The molecular weight of the prepared esters was measured using vapor pressure osmometer, while the weight average molecular weight (Mw), number average molecular weight (Mn), and polydispersity index (PI) of the prepared terpolymers were determined by using gel permeation chromatography (GPC) Waters model 510 using polystyrene standard, Ultra-styrigel column, and tetrahydrofuran as an eluent.

TGA was carried out using Simultaneous Q-600 TGA (USA). The experiments use 0.01 g polymer sample, at a heating rate of $10^{\circ}\text{C min}^{-1}$ from 25 to 600°C , under a flowing (25 mL min^{-1}) nitrogen atmosphere.

4. Evaluation of the prepared terpolymers as lube oil additives

4.1. Evaluation of the prepared terpolymers as pour point depressants for lube oil

Different concentrations of the prepared terpolymers (0.25%, 0.5%, 1%, 2% and 3% by weight), were used to evaluate the effectiveness of the prepared compounds as pour point depressants for lubricating oil using free additive lube oil (SAE-30). The evaluation was carried out by using the ASTM – D98 – 87 for measuring the pour point (PP) on Cold Filter Plugging and Pour Point Automatic Tester Model 1 SL CPP 97 -2 [8-10].

The photomicrographs showing wax crystallization behavior of the untreated and treated lube oil sample with C_1 and C_2 terpolymer at different concentrations (0.25%, 0.5%, 1%, 2% and 3% by weight), have been recorded. An Olympus Polarizing Microscope Model BHSP fitted with an automatic camera with a 35 mm format was used for photomicrographic analysis. The light source was a helium lamp. The temperature of the tested lube oil sample was controlled on the microscope slide by an attached cooling thermostat. All photos were taken at -3°C , -12°C and -15°C . The adopted magnification was 100X.

4.2. Evaluation of the prepared terpolymers as viscosity index improvers for lube oil

The prepared terpolymers were evaluated as viscosity index improvers using free additive base oil (SAE 30) through the viscosity index test (VI) according to the ASTM D- 2270 -87. The kinematic viscosity of the oil contains the synthesized compounds was determined at 40°C and 100°C . Different concentrations ranging between (0.25%, 0.5%, 1%, 2% and 3% by weight) were used to study the effect of the prepared additives concentration on (VI).

5. Results and discussion

The compositions of the prepared esters [octylacrylate (**A**), decylacrylate (**B**), dodecylacrylate (**C**), tetradecylacrylate (**D**), hexadecylacrylate (**E**), octadecylacrylate (**F**), and docosylacrylate (**G**)] were confirmed by FTIR spectra, and it was found that all the prepared esters are identical in IR spectrum, so we select the I.R. of tetradecylacrylate (D) which in Fig. 1, one can arrive to the following: no sign for the presence of strong absorption band at 3200 cm^{-1} of aliphatic (-OH) group or the characteristic absorption bands of the carboxylic acid.

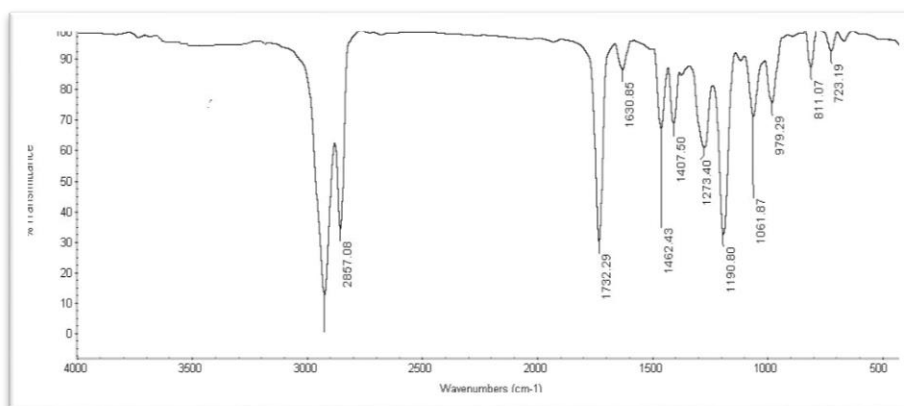


Figure 1. FTIR spectrum of tetradecylacrylate

Appearance of the ester group band at $1720 \pm 10 \text{ cm}^{-1}$ and $1250 \pm 100 \text{ cm}^{-1}$ due to (C=O) and (C-O-C) stretching respectively. The band for methylene group (-CH₂-CH₂-) appear near 1630 cm^{-1} . The band for methyl group that appears near $1370\text{-}1465 \text{ cm}^{-1}$. The band for (-C-H) aliphatic appears near 2840 cm^{-1} and 2950 cm^{-1} . Disappearance of the strong band at 3200 cm^{-1}

and the characteristic bands of (-COOH) group indicate that all hydroxyl group of alcohols and carboxyl groups of acids were consumed in the esterification reaction.

The molecular weight are determined and it is obvious from data given in Table 1 that the experimental and theoretical values of the molecular weight are in a good accord, this indicates that the esterification reactions were completed successfully and confirm the formation of the desired compounds.

Table 1. Theoretical and experimental molecular weights of the prepared esters

Ester type	Theoretical MW	Experimental MW
Octylacrylate (A)	184.28	186
Decylacrylate (B)	212.65	213
Dodecylacrylate (C)	240	243
Tetradecylacrylate (D)	268.45	268
Hexadecylacrylate (E)	297.02	298
Octadecylacrylate (F)	324	324.55
Docosylacrylate (G)	380.64	380

The prepared terpolymers were elucidated by using FTIR spectroscopy, Fig. (2,3), it was found, disappearance of (CH₂=CH-) beak of acrylate esters, which appears at 1630 cm⁻¹. From these data, one can dedicate that, the three monomers were reacted to form the final terpolymers.

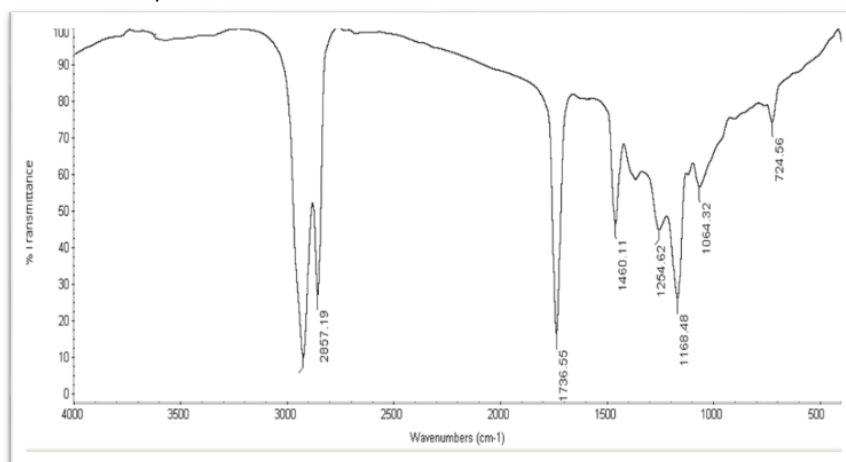


Figure 2. FTIR spectrum of C₁ terpolymer

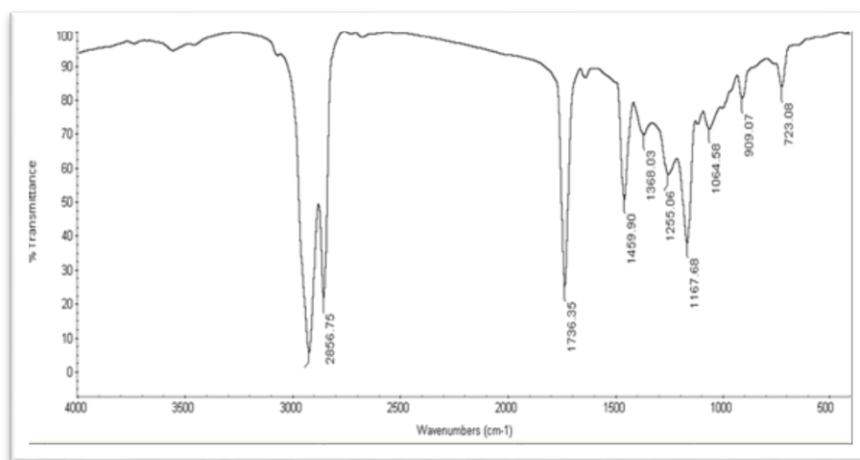


Figure 3. FTIR spectrum of C₂ terpolymer

The structure of the prepared terpolymers were confirmed by using $^1\text{H-NMR}$, as in Fig. (4, 5), $^1\text{H-NMR}$ spectrum of the prepared terpolymers (C_1, C_2), it was found characteristics peak signals corresponding to δ -0.865 for ($-\text{CH}_3$) of alkylacrylate, δ -3.5 for ($-\text{O}-\text{CH}_2$) of alkylacrylate, and δ -4.015 for ($-\text{O}-\text{CH}_3$) of vinyl acetate.

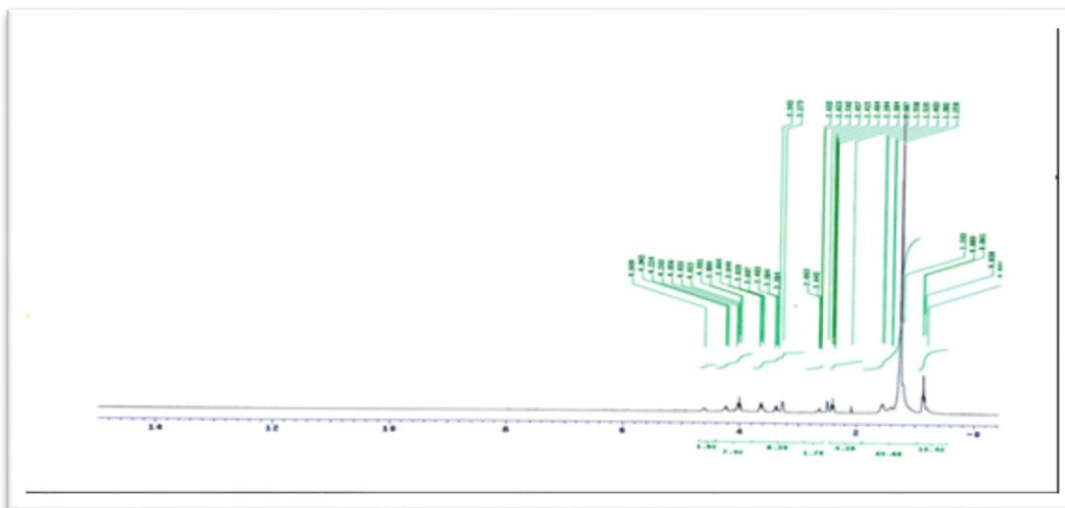


Figure 4. $^1\text{H-NMR}$ spectrum of C_1 terpolymer.

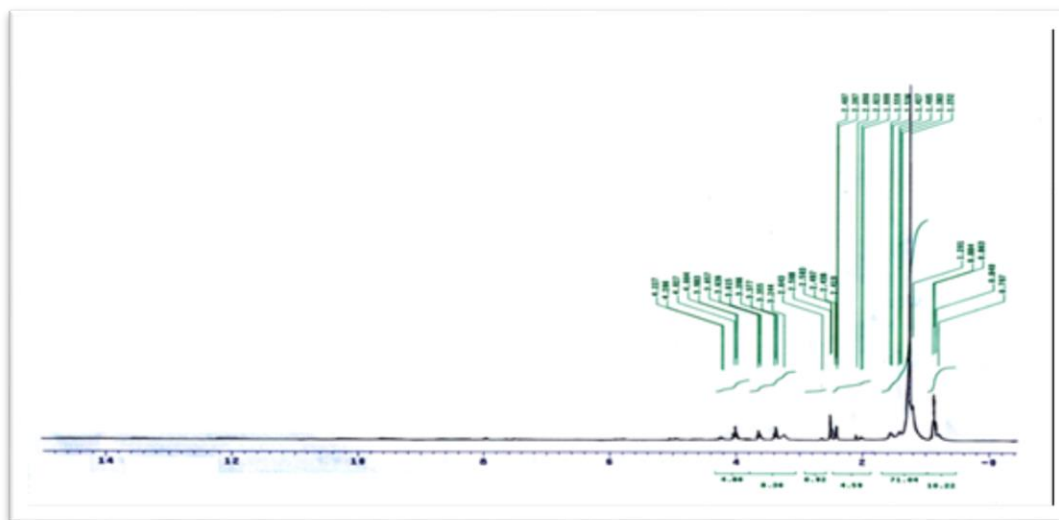


Figure 5. $^1\text{H-NMR}$ spectrum of C_2 terpolymer

The number average molecular weight (M_n), weight average molecular weight (M_w), and the polydispersity index (PI) of the prepared terpolymers, their designation and their composition were given in Table (2, 3)

Table 2. The mean molecular weight of the prepared (A_1 - G_1) terpolymers)

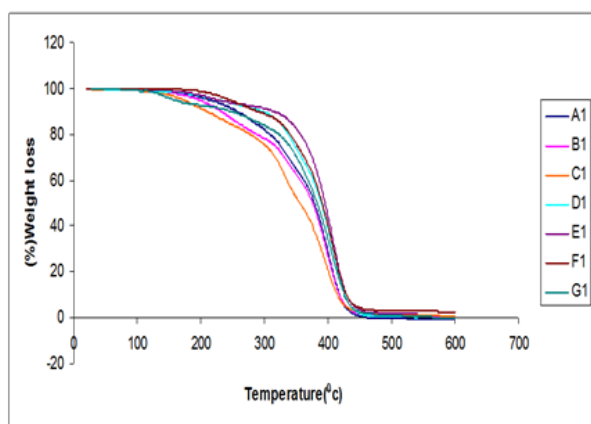
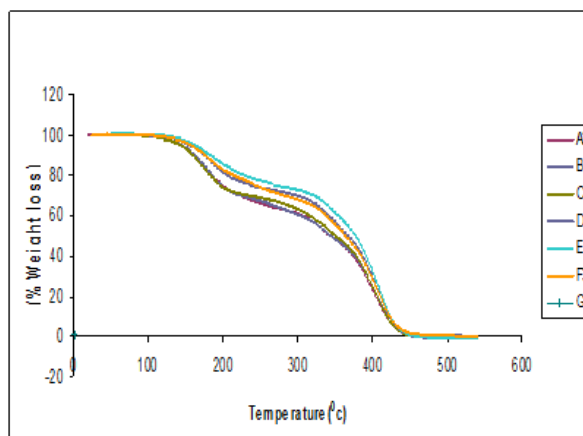
Terpolymer composition	Designation	M_n	MW	D.P
Octylacrylate : Vinyl acetate : dodecene	A_1	19120	33904	1.77
Decylacrylate : Vinyl acetate : dodecene	B_1	21500	35775	1.66
Dodecylacrylate : Vinyl acetate : dodecene	C_1	24640	42842	1.74
Tetradecylacrylate : Vinyl acetate : dodecene	D_1	29450	50538	1.71
Hexadecylacrylate : Vinyl acetate : dodecene	E_1	22500	37975	1.68
Octadecylacrylate : Vinyl acetate : dodecene	F_1	18200	31920	1.75
Docosylacrylate : Vinyl acetate : dodecene	G_1	15400	22600	1.43

Table 3. The mean molecular weight of the prepared (A₂-G₂) terpolymers

Terpolymer composition	Designation	Mn	MW	D.P
Octylacrylate : Vinyl acetate : hexadecene	A ₂	18430	29488	1.60
Decylacrylate : Vinyl acetate : hexadecene	B ₂	20120	30784	1.53
Dodecylacrylate : Vinyl acetate : hexadecene	C ₂	22100	37570	1.70
Tetradecylacrylate : Vinyl acetate : hexadecene	D ₂	24200	39930	1.65
Hexadecylacrylate : Vinyl acetate : hexadecene	E ₂	20200	30300	1.50
Octadecylacrylate : Vinyl acetate : hexadecene	F ₂	17400	28362	1.63
Docosylacrylate : Vinyl acetate : hexadecene	G ₂	14850	22720	1.53

5.1. Thermal stability of the prepared terpolymers

The thermal stability of the prepared terpolymers (A₁-G₁) was investigated, and given in Fig. (5). All the terpolymers degrade in the temperature range between 192°C and 435°C while the thermal stability of the prepared terpolymers (A₂-G₂) was investigated, and given in Fig. (6). All the terpolymers degrade in the temperature range between 148°C and 434°C. The first degradation can be attributed to the cleavage of ester group and corresponding to the evaporation the intra and intermolecular moisture whereas the second degradation is corresponding to polymer backbone. Therefore, the thermogravimetric study has shown a much greater thermal stability for the prepared terpolymers, and this confirms the suitability of using the prepared terpolymers as lubricating oil additives [11-12].

Figure 5. TGA analysis of (A₁- G₁) terpolymersFigure 6. TGA analysis of (A₂- G₂) terpolymers

5.2. Evaluation of the prepared compounds as lube oil additives

5.2.1. Additive as pour point depressants

Different concentrations of prepared compounds (A₁-G₁), (A₂-G₂) ranging from (0.25%, 0.5%, 1.00%, 2.00% and 3.00% by weight) were tested as pour point depressants and experimental data are tabulated in Table (4,5) which indicates that the prepared compounds are efficient as pour point depressants for lube oil and the efficiency increases by decreasing concentration of the prepared additive. This is explained by the solvation power of any solvent decreases with decreasing temperature and vice versa. This reduction in solvation power becomes more obvious when the molecular weight of the solute and its concentration increases [13].

The effect of alkyl chain length on the efficiency of the prepared additives as pour point depressants was studied, and as in Fig.(7), it was found that terpolymers which prepared from dodecylacrylate are more efficient as pour point depressants. This may be due to the lower molecular weight.

Table 4. Dependence of pour point on the concentration of (A₁-G₁) additives

Conc. of additives	Pour point (°C) in presence of different additives						
	A ₁	B ₁	C ₁	D ₁	E ₁	F ₁	G ₁
0.00%	0	0	0	0	0	0	0
0.25%	-9	-12	-18	-15	-9	-9	0
0.50%	-9	-12	-18	-15	-9	-9	0
1.00%	-6	-9	-15	-12	-6	-6	0
2.00%	-6	-6	-12	-9	-6	-6	0
3.00%	-3	-3	-9	-6	-3	-3	0

Table 5. Dependence of pour point on the concentration of (A₂-G₂) additives

Conc. of additives	Pour point (°C) in presence of different additives						
	A ₂	B ₂	C ₂	D ₂	E ₂	F ₂	G ₂
0.00%	0	0	0	0	0	0	0
0.25%	-6	-9	-12	-12	-6	-6	0
0.50%	-6	-9	-12	-9	-6	-6	0
1.00%	-3	-6	-9	-9	-3	-3	0
2.00%	-3	-3	-6	-6	-3	-3	0
3.00%	-3	-3	-3	-3	-3	-3	0

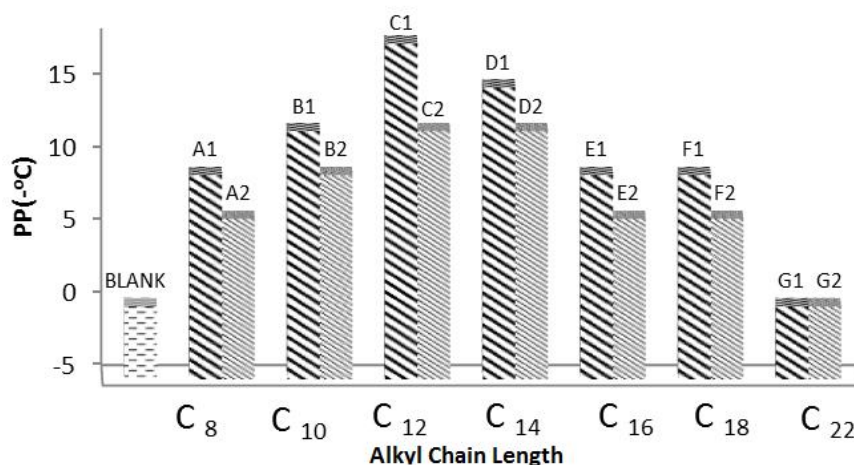


Figure 7. Effect of alkyl chain length of (A₁-G₁) & (A₂-G₂) additives on their pour point

5.2.2. Effect of pour point depressant type on wax crystal modification

Pour point depressants act through surface adsorption onto the wax crystals. The resulting surface layer of pour point depressant inhibits the growth of the wax crystals and their capacity to adsorb oil and form gels. Photoanalysis confirms other standard flow tests that evaluate the cold flow properties of untreated/treated lube oil through wax crystallization behavior. It is applied herein for assessing the action of the previously prepared terpolymers flow additives as wax inhibitor/pour point depressant through wax modification according to their type, and concentration [14].

Photomicrographs illustrated in Fig.(8, 9), showed variant wax morphology for untreated lube oil showed large cyclic like crystals which on treatment with terpolymer C₁,C₂ using different concentration (0.25%, 0.5%, 1.00%, 2.00% and 3.00% by weight), show a significant reduction of wax crystal size and formation of abundant number of fine dispersed crystals.

Photomicrographic analysis: C1

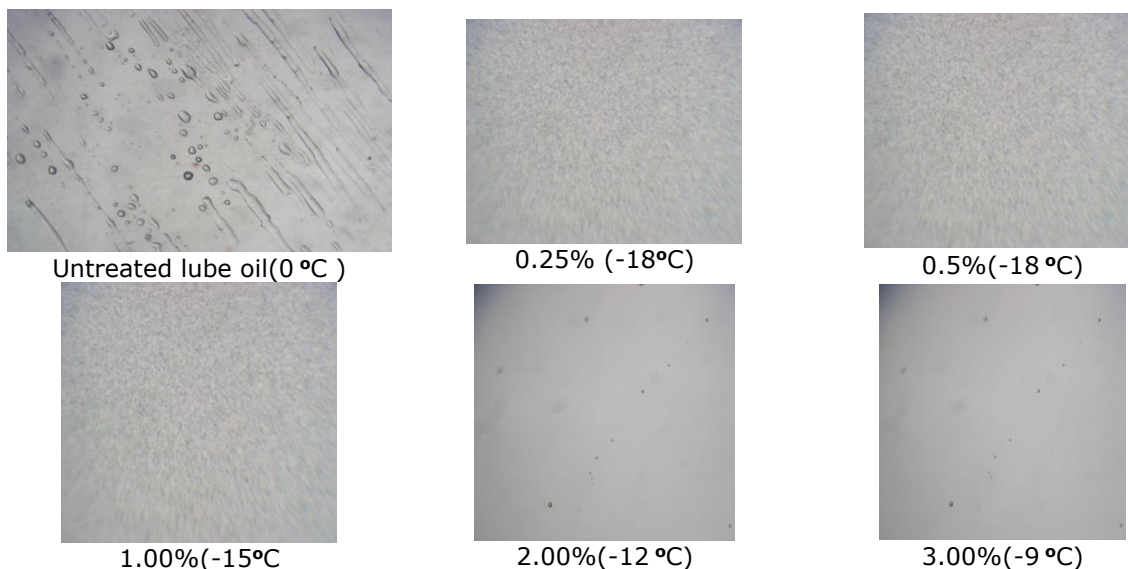


Figure 8. Photomicrographs of untreated lube oil (0 °C) and treated lube oil (-18 °C) for 0.25% and 0.5%: (-15 °C) for 1.0%, (-12 °C) for 2.00% and (-9 °C) for 3.00% concentrations

Photomicrographic analysis: C2

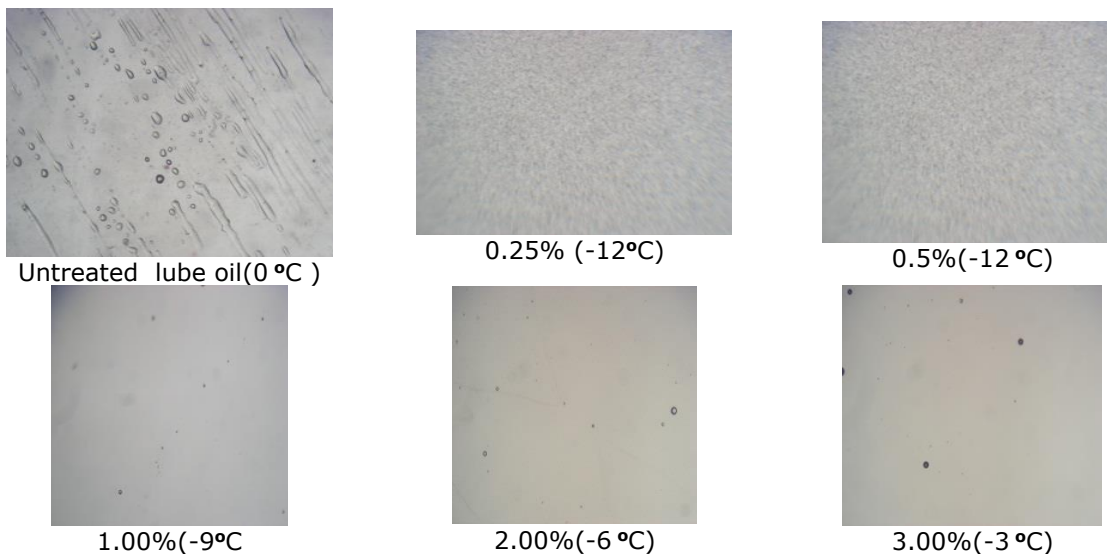


Figure 9. Photomicrographs of untreated lube oil (0°C) and treated lube oil (-12°C) for 0.25% and 0.5%: (-9 °C) for 1.0%,(-6 °C) for 2.00% and (-3 °C) for 3.00% concentration

5.2.3. Additive as viscosity index improvers

The effect of the polymeric compounds as viscosity index improvers depends mainly on the behavior of polymer molecules in the dispersed phase (base oil). The prepared compounds (A₁-G₁), (A₂-G₂) were tested for their effectiveness as viscosity index improvers for the base oil. In this respect, the kinematic viscosity of the undoped oil contains different concentration of the tested additives was determined at 40°C and 100°C. Different concentrations of the prepared additives ranging from 0.25%, 0.50%, 1.00%, 2.00%, and 3.00% were used to study the effect of the additives concentration on VI the data are tabulated in Table (6, 7), which indicates that the VI increases with increasing the concentration of the prepared additives in solution. The viscosity of a particular fluid is not constant, however, but varies with temperature. As oil is heated, its viscosity decreases, and it becomes thinner. The polymer – oil inter-

action at low temperature is minimal but increases as the temperature rises. This interaction of the polymer with the base oil at elevated temperatures increases the effective hydrodynamic volume of the polymer, thereby increasing the effective volume fraction of the viscosity modifier. This, in turn, leads to an increase in lubricant viscosity. The increase of the concentration of the polymer leads to an increase in the total volume of polymer micelles in the oil solution. Consequently, a high concentration of polymer will impart a higher viscosity index than a low concentration of the same polymer [8].

Table 6. Dependence of viscosity index on the concentration of (A₁-G₁) additives

Conc. of additives	Viscosity index of lube oil in presence of different additives						
	A ₁	B ₁	C ₁	D ₁	E ₁	F ₁	G ₁
0.00%	96	96	96	96	96	96	96
0.25%	105	103	105	109	101	104	98
0.50%	105	107	110	112	103	106	98
1.00%	106	108	112	115	107	108	98
2.00%	106	110	115	120	110	109	98
3.00%	112	113	122	124	114	110	98

Table 7. Dependence of viscosity index on the concentration of (A₂-G₂) additives

Conc. of additives	Viscosity index of lube oil in presence of different additives						
	A ₂	B ₂	C ₂	D ₂	E ₂	F ₂	G ₂
0.00%	96	96	96	96	96	96	96
0.25%	100	102	103	106	101	104	98
0.50%	102	104	109	108	103	106	98
1.00%	104	106	110	114	107	108	98
2.00%	106	108	116	118	110	108	98
3.00%	108	110	120	122	113	108	98

The effect of alkyl chain length on the efficiency of the prepared additives as viscosity index improvers is given in Fig. (10, 11), which indicates that the efficiency increases with increasing the alkyl chain length of the acrylate used from octylacrylate to tetradecylacrylate, then a noticeable decrease occur in the viscosity index with increasing the alkyl chain length for hexadecylacrylate and octadecylacrylate, on contrary docosylacrylate had a bad effect on viscosity index. This may be due to the influence of the molecular weight on the effective coil radius and hence the VI.

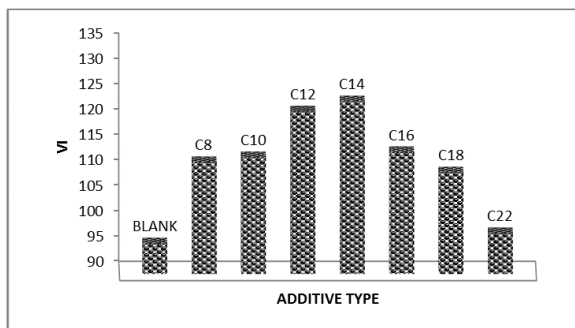


Figure 10. Effect of alkyl chain length of (A₁-G₁) additives on their viscosity index

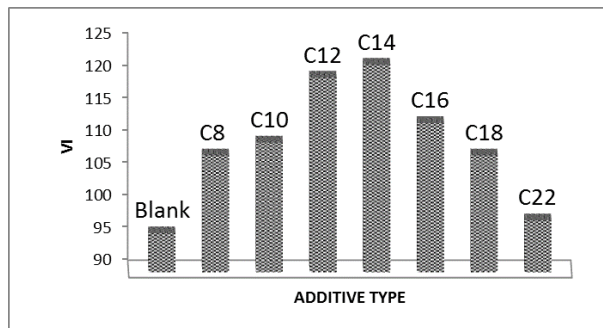


Figure 11. Effect of alkyl chain length of (A₂-G₂) additives on their viscosity index

6. Conclusion

All findings and discussions outlined to arrive the following conclusions:

- Fourteen terpolymers were synthesized and elucidated by using FTIR, ¹H-NMR, GPC.
- Thermal analysis (TGA) for the prepared terpolymers were measured and it was found that they are stable to degradation at high temperature.
- The prepared terpolymers were evaluated as lubricating oil additives (pour point depressants and viscosity index improvers).
- It was found that the viscosity index increases with increasing the alkyl chain length from octylacrylate to tetradecyl acrylate, then decreases with increasing the alkyl chain.
- All the prepared terpolymers act as good pour point depressants, the most efficient terpolymer as pour point depressants composed from dodecylacrylate.

References

- [1] Boffa A. Lubricating oil compositions for internal combustion engines, US 8703677 B2 (2014).
- [2] Nassar AM, Ahmed NS, Nasser RM. Jojoba polymers as lubricating oil additives, *Pet. Coal.*, 2015; 57(2): 120-129.
- [3] Mang T. and Dresel W. *Lubricants and Lubrication*, 2nd Ed. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 105 -120 (2007).
- [4] Leslie R. *Lubricant additives chemistry and applications* 2nd Ed. CRC Press, (2009).
- [5] Rizvi SQA. *A Comprehensive Review of Lubricant Chemistry, Technology, Selection and Design*, ASTM International, West Conshohocken, PA., 2009;100-211.
- [6] Ahmed NS, Nassar AM, Nasser RM, Khattab AF and Abdel-Azim AA. Synthesis and Evaluation of Some Polymers as Lubricating Oil Additives; *Journal of Dispersion Science and Technology*, 2012; 33:668-675.
- [7] Nehal SA, Amal MN and Rabab MN. Jojoba modified polymers as performance modifiers additives for engine oil, *Ind. Lubr. Tribol. Journal*, 2015; 425-433.
- [8] Abdel-Azim AA and Abdel-Azim RM. Polymeric Additives for Improving the Flow Properties and Viscosity Index of Lubricating Oils, *Journal of Polymer Research*,2001; 8(2): 111-118).
- [9] Rasha SK, Nehal SA, Amal MN. Study the efficiency of some compounds as lubricating oil additives, *Applied Petrochemical Research*, 2013;3: 1-8.
- [10] Zhang J, Wu Ch, Li W, Wangand Y and Cao H. The Performance Mechanism of Pour Point Depressants Study, *Journal of Fuel*, 2004; 83(3): 315-326.
- [11] Janović Z, Jukić A, and Vidović E. Viscosity behavior of maleic anhydride and long chain alkyl methacrylate copolymers in mineral oil solutions, *Journal of Chemistry and Technology of Fuels and Oils*, 2009; 45(4): 267-275.
- [12] Boztuğ A, and Basan S. Thermal characterization of n-alkyl maleate -styrene- allyl propionate terpolymers, *Journal of Applied Polymer Science*, 2007; 103: 600-604.
- [13] Chen W, Zhao Z, Yin C. The interaction of waxes with pour point depressants, *Journal of Fuel*, 2010; 89(5): 1127-1132.
- [14] Al-Sabagh AM, Sabaa MW, Saad GR, Khidr TT and Khalil TM. Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties, *Egyptian Journal of Petroleum*2012; 21: 19-30.

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