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STUDIES ON THE EFFICIENCY OF SOME TERPOLYMERS BASED ON ALKYLACRYLATES AS LUBE OIL ADDITIVES

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Abstract

Seven terpolymers were synthesized and evaluated as lubricating oil additives. The synthesis process occurs via esterification reaction of acrylic acid with (octanol, decanol, dodecanol, tetradecanol, hexadecanol, octadecanol and docosanol) separately. Then polymerization of each ester with vinyl acetate and 1-tetradecene were carried out. The prepared compounds were elucidated by using FTIR (Fourier Transform Infrared Spectroscopy), ^{1}H-NMR (Proton Nuclear Magnetic Resonance), 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 increases with increasing the concentration of the prepared compounds, and with increasing the alkyl chain length of the alkylacrylate used from octylacrylate till tetradecylacrylate, then decreases with increasing the chain length. The prepared additives were evaluated as pour point depressants and it was found that the pour point 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 own 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. There are three major types of lubricants: gaseous lubricants (air, helium), liquid lubricants (oils, water) and solid lubricants (graphite, grease, teflon, molybdenum disulphide etc). Liquid lubricant is the most commonly used lubricant because of its wide range of possible applications while gaseous and solid lubricants are recommended in special applications [4- 5].

Additives for lubricating oils were used first during the 1920s and their use has since increased tremendously today practically all types of lubricating oil contain at least one additive and some oil contains additives of several different types . Additives may be classified according to their functions into: surface protectors additives (extreme pressure additives, friction modifiers, anti-wear agents, rust inhibitors and corrosion inhibitors), oil protectors additives (antioxidant, detergent, dispersant), and performance modifiers additives (antifoam additive, viscosity index improver and pour point depressant) [1-5].

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].

The pour point of lubricating oil is the lowest temperature at which the oil will pour or flow without disturbance under prescribed conditions. 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 seven terpolymers were prepared via free radical chain polymerization. The prepared terpolymers were elucidated using FIIR, GPC, ^{1}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 kittle 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°C ± 5°C. The extent of reaction was followed by monitoring the amount of librated 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 tetradecene 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.

2.3. Identification of the prepared compounds

Infra-Red spectroscopic analysis

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

^{1}H-NMR spectroscopic analysis

The structure of the synthesized polymeric additives were followed up by ^{1}H-NMR spectra using a 300 MHz Varion NMR 300 spectrometer using DMSO as a solvent.

Molecular weight determination

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) model waters model 510 using polystyrene standard, Ultra-styragel column, and tetrahydrofuran as an eluent.

Thermal analysis for the prepared terpolymers.

TGA and DSC experiments were carried out using Simultaneous Q- 600 DSC/TGA (USA). The experiments use 0.01 g polymer sample, at a heating rate of 10°C min^{-1} from 25 to 600°C, under a flowing (25 ml min^{-1}) nitrogen atmosphere.

3. Evaluation of the prepared terpolymers as lube oil additives

3.1. 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), was 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].

Photomicrographic analysis

The photomicrographs showing wax crystallization behavior of the untreated and treated lube oil sample with C_1 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.

3.2. 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).

4. 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 IR of tetradecylacrylate (D) which in Fig. (1), one can arrive to the following: no sign for the presence of strong absorption band at 3200cm^{-1} of aliphatic (-OH) group or the characteristic absorption bands of the carboxylic acid. Appearance of the ester group band at 1720±10 cm^{-1} and 1250 ± 100 cm^{-1} due to (C=O) and (C-O-C) stretching respectively. The band for methylene group (- CH=CH -) appear near 1465 cm^{-1}. The band for methyl group that appears near 1370-1465 cm^{-1}.The band for (-C-H) aliphatic appears near 2840 cm^{-1} and 2950 cm^{-1}. Disappearance of the strong band at 3200Cm^{-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 mole-cular weight are determined and it is obvious from data given in Table (1) that the expe-rimental 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.

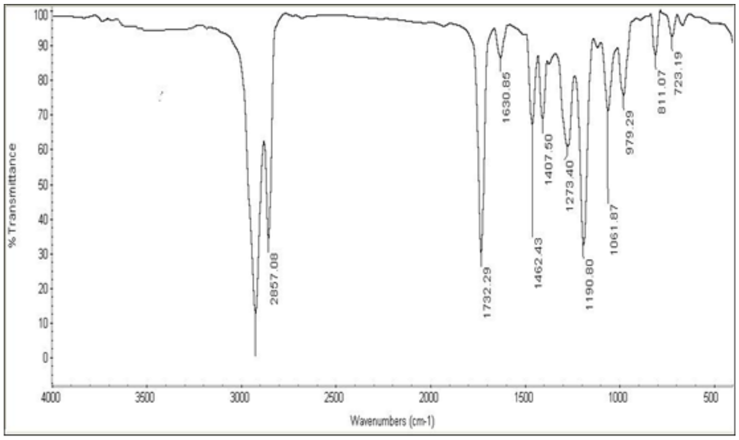

Figure 1. FTIR spectrum of tetradecylacrylate

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

Ester type	Theoretical M.wt.	Experimental M.wt.
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), it was found, disappearance of (CH_2=CH-) beak of acrylate esters, which appears at 1465cm^{-1}. From these data, one can dedicate that, the three monomers were reacted to form the final terpolymers.

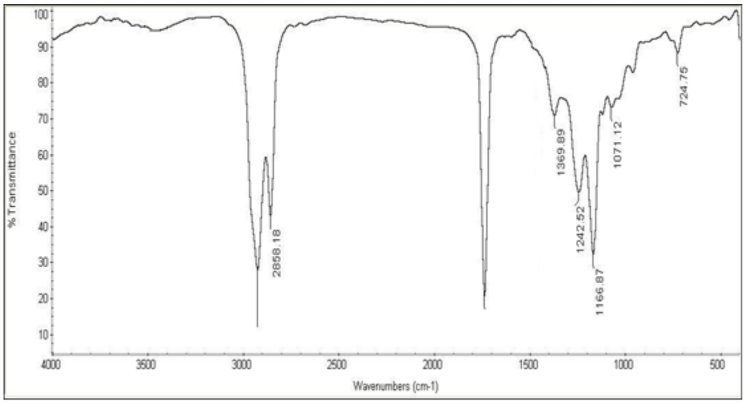

Figure 2. FTIR spectrum of A_1 terpolymer

The structure of the prepared terpolymers were confirmed by using ^{1}H-NMR, as in Fig. (3), ^{1}H-NMR spectrum of (C_1), it was found characteristics peak signals corresponding to δ-0.865 for ($–CH_3$) of alkylacrylate, δ-3.5 for ($-O–CH_2$) of alkylacrylate, and δ-4.015 for ($-O–CH_3$) of vinyl acetate.

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

Table 2. Terpolymers compositions, designations and their number average molecular weight (Mn), weight average molecular weight (Mw), and the polydispersity index (PI).

Terpolymer composition	Designation	Mn	Mw	PI
Octylacrylate : Vinyl acetate : Tetradecene	A_1	20018	35076	1.843
Decylacrylate : Vinyl acetate : Tetradecene	B_1	22543	39495	1.752
Dodecylacrylate : Vinyl acetate : Tetradecene	C_1	25620	47371	1.849
Tetradecylacrylate : Vinyl acetate : Tetradecene	D_1	30027	53597	1.785
Hexadecyacrylate : Vinyl acetate : Tetradecene	E_1	23706	39242	1.655
Octadecylacrylate : Vinyl acetate : Tetradecene	F_1	19214	33593	1.748
Docosylacrylate : Vinyl acetate : Tetradecene	G_1	16565	23721	1.432

4.1. Thermal stability of the prepared terpolymers

The thermal stability of the prepared terpolymers was investigated, Figs. (3, 4), both integral and differential, are shown for all the investigated terpolymers. All the terpolymers degrade in the temperature range between 315°C and 436°C, showing no solid residue. The primary degradation product occurs at 315°C, with weight loss of 14.94%. The major degradation occurs at 436°C, with weight loss of 95.855%. 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].

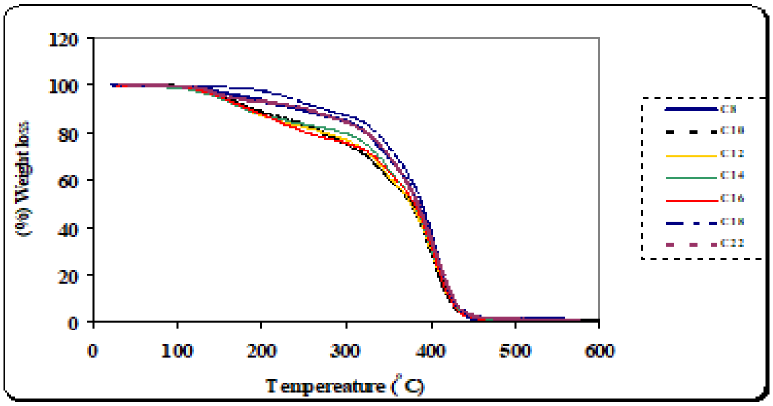

Figure 3. TGA analysis of (A_1- G_1) terpolymers

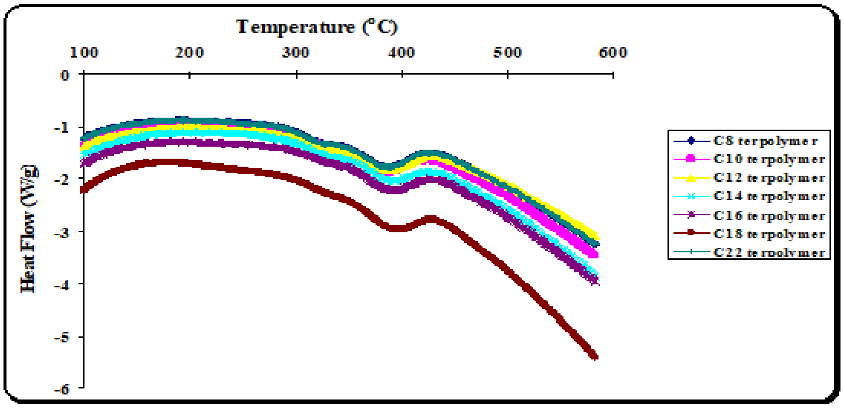

Figure 4. DSC analysis of (A_1- G_1) terpolymers

4.2. Evaluation of the prepared compounds as lube oil additives

A- As pour point depressants

Different concentrations of prepared compounds (A_1-G_1) 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 (3) which indicates that the prepared compounds are efficient as pour point depressants and the efficiency increases by decreasing concentration of the prepared additive. This is explained by the solvation power of any solvent decreases with decreesing temperature and vise 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.(5) 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 3. Dependence of pour point on the concentration of (A_1-E_1) additives

Conc. of 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	-9	-15	-9	-6	-6	0
0.50%	-9	-9	-15	-9	-6	-6	0
1.00%	-9	-6	-12	-6	-3	-3	0
2.00%	-6	-3	-12	-6	-3	-3	0
3.00%	-6	-3	-12	-3	-3	-3	0

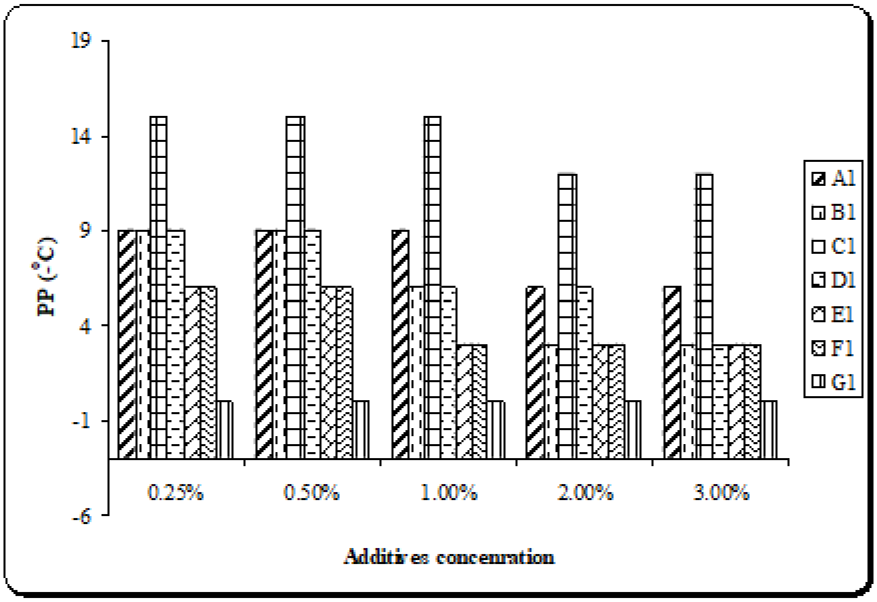

Figure 5. Effects of additive concentration of (A_1-G_1) additives on their pour point

- **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. (6) showed variant wax morphology for untreated lube oil showed large cyclic like crystals which on treatment with terpolymer C_1 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.

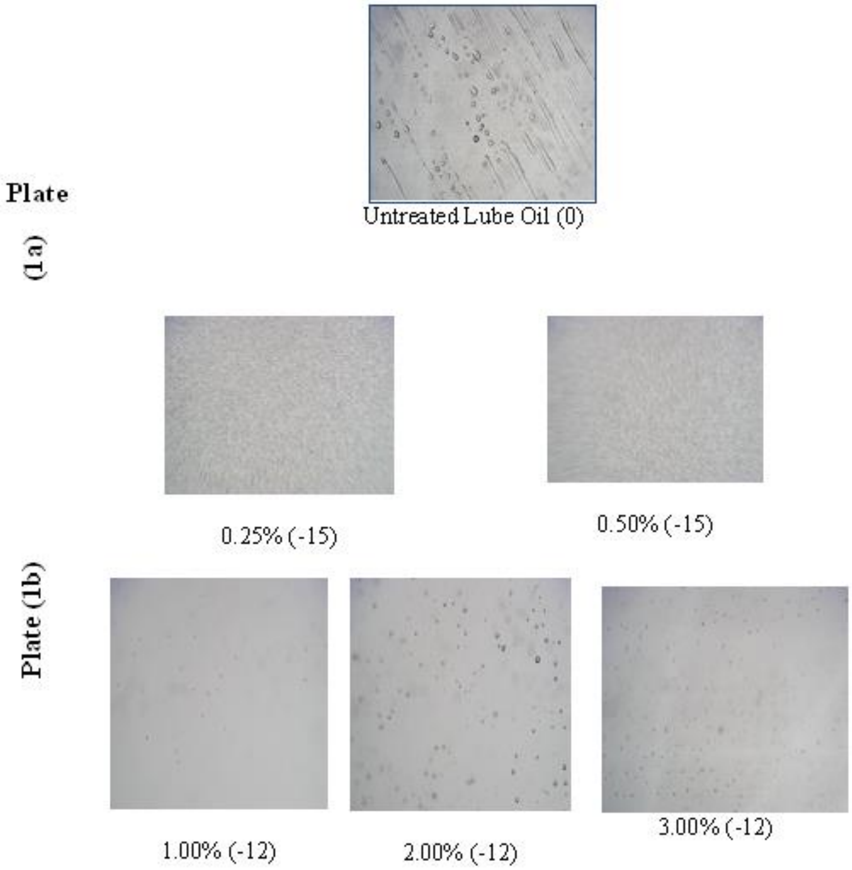

Fig. 6. Photomicrographs of (1a) untreated lube oil (0) and (1b) treated lube oil (-15) for 0.25% and 0.5%: (-12) for 1.0%, 2.00% and 3.00% concentrations

B. 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 (A_1-G_1) 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 (4).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 interaction 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 4. Dependence of viscosity index on the concentration of (A_1-G_1) additives.

Conc of 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%	104	106	108	112	102	100	98
0.50%	106	108	112	116	104	102	98
1.00%	108	110	116	118	106	104	96
2.00%	110	112	120	122	108	106	96
3.00%	112	116	124	128	110	108	94

The effect of alkyl chain length on the efficiency of the prepared additives as viscosity index improvers is given in Fig. (7) 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.

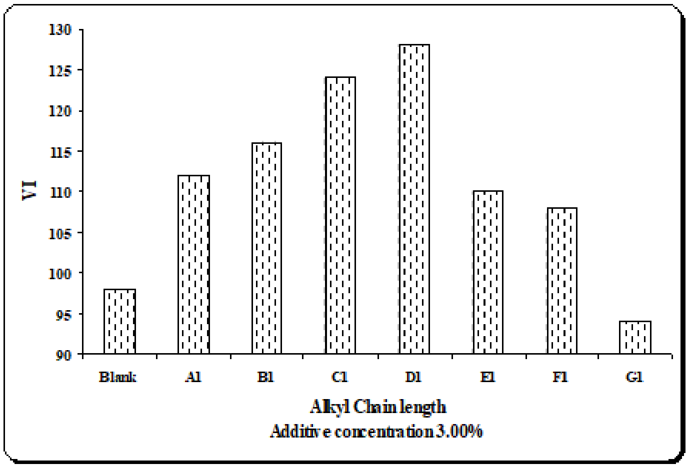

Figure 7. Effect of alkyl chain length of (A_1-G_1) additives on their viscosity index

5. Conclusion

All findings and discussions outlined to arrive the following conclusions:

- Seven terpolymers were synthesized and elucidated by using FTIR, ^{1}H-NMR, GPC.
- Thermal analysis (TGA, and DSC) 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.

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