Petroleum and Coal

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A Study on the Properties and Applications of Acrylate Terpolymers as Viscosity and Rheology Modifiers for Lube Oil

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Received May 4, 2023; Accepted July 19, 2023

Abstract

In this study, we prepared eighteen terpolymers by free radical chain polymerization of different combinations of alkyl acrylate, styrene, and vinyl pyrrolidone monomers. We used F.T.I.R, 1H-NMR and GPC methods to confirm the structures and determine the Mn values of the terpolymers. We found that the terpolymers were soluble in lube oil (SAE-30) and could improve its viscosity index. We investigated the effects of terpolymer concentration (up to $30.00*10^3$ppm), ester side chain length, and alkyl acrylate content in the terpolymer on the viscosity index improvement. We also calculated the sensitivity of the terpolymer additives and found that additive C1 had the highest value. We measured the rheological properties of the lube oil mixed with the terpolymer additives and found that they followed a simple Bingham fluid model.

Keywords: *Lubricating oil additives; Viscosity index improvers; Rheology; Flow curve; Consistency.*

1. Introduction

The principle of supporting a sliding load on a friction reducing film is known as lubrication. The substance of which the film is composed is a lubricant, and to apply it is to lubricate. Though the basic principle still prevails the prevention of metal-to-metal contact by means of an intervening layer of fluid or fluid-like material, modern lubrication has become a complex study. Modern equipment must be lubricated in order to prolong its lifetime. A lubricant performs a number of critical functions. These include lubrication, cooling, cleaning and suspending, and protecting metal surfaces against corrosive damage. Lubricant comprises a base fluid and an additive package [1-2]. Additives are chemical compounds added to lubricating oils to impart specific properties to the finished oils. Some additives impart new and useful properties to the lubricant; some enhance properties already present, while some act to reduce the rate at which undesirable changes take place in the product during its service life.

Probably the most important single property of a lubricating oil is its viscosity. A factor in the formation of lubricating films under both thick and thin film conditions, viscosity affects heat generation in bearings, cylinders, and gears; it governs the sealing effect of the oil and the rate of consumption or loss; and it determines the ease with which machines may be started under cold conditions. For any piece of equipment, the first essential for satisfactory results is to use an oil of proper viscosity to meet the operating conditions. VI improvers, [3], are long chain, high molecular weight polymers that function by causing the relative viscosity of an oil to increase more at high temperatures than at low temperatures. Generally this result is due to a change in the polymer's physical configuration with increasing temperature of the mixture. It is postulated that 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 and the oil produces a proportionally greater thickening effect [4].

All commercial viscosity modifiers, [5], consist of the polymethylene backbone. Thus, side groups differentiate the structures of various polymers. The side groups are alkyls, carbonyl oxyalkyls and phenyls. Common polymers that are used in this capacity include polymethacrylates (PMAs), olefin copolymers (OCPs), styrene-diene copolymers, and styrene-ester copolymers.

Consistency, flow properties, or viscosity in the case of oils, are key parameters to create lubrication efficiency and the application of lubricants. These are terms which appear in nearly all lubricant specifications. Viscosity is also the only lubricant value which is adopted into the design process for hydrodynamic and elasto-hydrodynamic lubrication [6-12]. The shearing forces lead to a mechanical change or reduction in the size of the polymer molecules so that their desired effects are minimized. These effects have been observed, in particular, with multigrade engine oils and high-VI hydraulic oils. The shear stability of these polymers is therefore an important quality parameter [13-16].

In the present work eighteen terpolymers were synthesized via free radical chain addition polymerization. The prepared terpolymers were evaluated as viscosity index improvers and rheology modifiers for lubricating oil.

2. Experimental

2.1. Esterification of acrylic acid with octyl, decyl and dodecyl alcohol.

One mole of acrylic acid was esterified with 1 mole of octyl alcohol, decyl alcohol, or dodecyl alcohol using 0.50% of p- Toluene sulfonic acid as a catalyst, 0.25% hydroquinone as inhibitor, and xylene as a solvent [17]. The reactants were placed in 4-neck flask connected to a Dean-Stark trap containing xylene (azeo-tropic) solvent, condenser, mechanical stirrer and a thermometer. All the reactants were refluxed at 130±5°C, until all the calculated amount of water was trapped. The obtained esters octyl acrylate (A), decyl acrylate (B), and dodecyl acrylate (C) then ready to be used.

2.2. Terpolymerization

Alkyl [octyl (OA), decyl (DA) & dodecyl (DDA)] acrylate, styrene (S) and vinyl pyrrolidone (VP) were polymerized by free radical chain polymerization, using 1% by weight of benzoyl peroxide as initiator, acetone as a solvent. At 70°C, for about 8 hours, using an inert medium of N_2 gas to prevent oxidation [18].

2.3. Characterization

2.3.1. Infra-Red spectroscopic analysis

IR spectra of the synthesized ester and different terpolymers were measured by using FTIR spectrometer model type Mattson – Infinity Series Bench top 961 for the purified esters, as a spectroscopic technique for elucidating the structure.

2.3.2. ^{1}H-NMR spectroscopic analysis

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

2.3.3. Determination of molecular weight of prepared esters and terpolymers

The molecular weights of the prepared esters were determined by using Vapour Pressure Osmometer. The number average molecular weight (Mn) of the polymers was determined by GPC Waters model 510 using polystyrene standard, Ultra-styragel column, and tetrahydrofuran as an eluent.

2.4. Evaluation of the prepared terpolymers as lubricating oil additives

2.4.1. 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, [19]. Different concentrations ranging between (2.5, 5.00, 10.00, 20.00 and 30.00) x 10^3 ppm were used to study the effect of the prepared additives concentration on VI.

2.5. Studying the rheological properties of the prepared terpolymers doped with lubricating oil (SAE-30)

Rheological studies were performed on an oil samples containing (2.50-30.00*10^3ppm) additives, using Brookfield rheometer (Model DV-III+). shear rate (sec^{-1}), shear stress (N/m^2), and dynamic viscosity (mPa.s) were measured at different temperatures (40°C, 60°C, and 100°C), using controlled oil path unit attached to the Brookfield apparatus.

3. Results and discussions

For many years, engine oil formulators have been including polymers to make their oils perform all year round. This allows them to combine good low temperature cranking and pumpability with satisfactory high temperature wear protection. However, it has also been recognized that the polymers added, when exposed to chemical and physical stresses in the engine, can break down or deform, causing partial or total loss of their functions. The relative resistance of VI improvers to breakdown depends on internal structural parameters (chemical type, ratio of the monomers, degree of branching), as well as on external factors (test type, duration, severity).

3.1. Elucidation of the chemical composition using FTIR and ^{1}H-NMR

The compositions of the prepared esters, [octyl (OA), decyl (DA) & dodecyl (DDA)] acrylate were confirmed by FTIR spectra, and molecular weight. 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	Theoretical MW	Experimental MW
Octyl acrylate (A)	185	184.28
Decyl acrylate (B)	213	212.40
Dodecyl acrylate (C)	240	243

From IR spectrum of octyl acrylate 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. These bands are broad peak extending from 3200 to 2500cm^{-1} due to hydrogen bonded (-OH) and the (-C –H) stretching vibrations. Appearance of the ester group band at 1720±10cm^{-1} and 1250 ± 100 cm^{-1} due to (C=O) and (C-O-C) stretching respectively. Disappearance of the strong band at 3200Cm^{-1} and the characteristic bands of (-COOH) group indicate that all hydroxyl and carboxyl groups of alcohols and acids, respectively, were consumed in the esterification reaction. The number average molecular weight of the prepared terpolymers and their designation were given in Table 2. The prepared terpolymers were elucidated by using F.T.I.R. spectroscopy, Fig. 2, it was found, disappearance of (CH_2=CH-) beak of acrylate esters, which appears at 1465cm^{-1}. The presence of aromatic – CH group of styrene at 763cm^{-1}. The presence of (–C-N) group of Vinyl Pyrrolidone at 1254cm^{-1}. The presence of (C=O) group of vinyl pyrrolidone at 1785cm^{-1}. From these data, one can dedicate that, the three monomers were reacted to form the final terpolymers, Fig. 2.

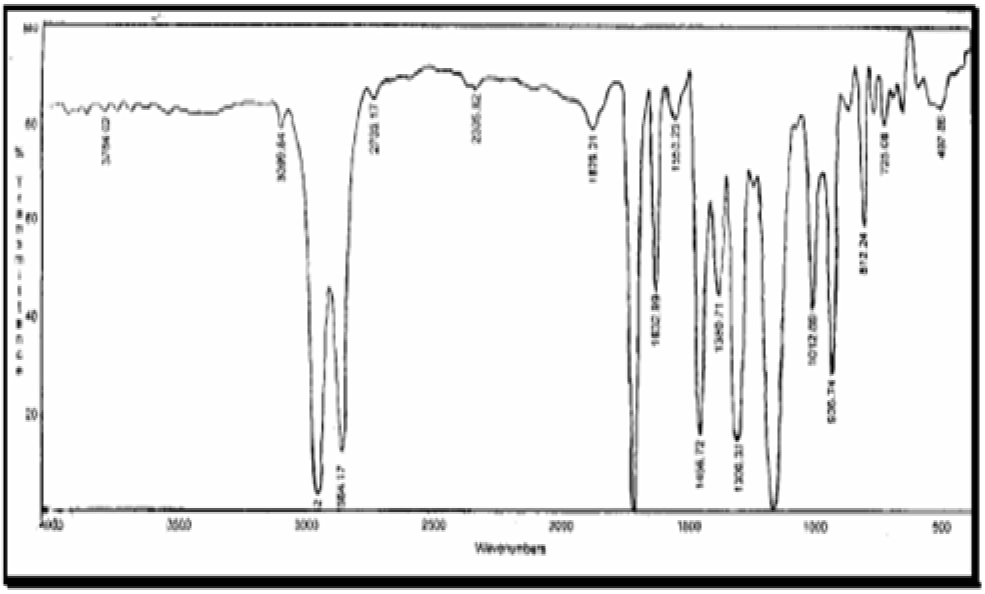

Figure 1. FTIR spectrum of octyl acrylate

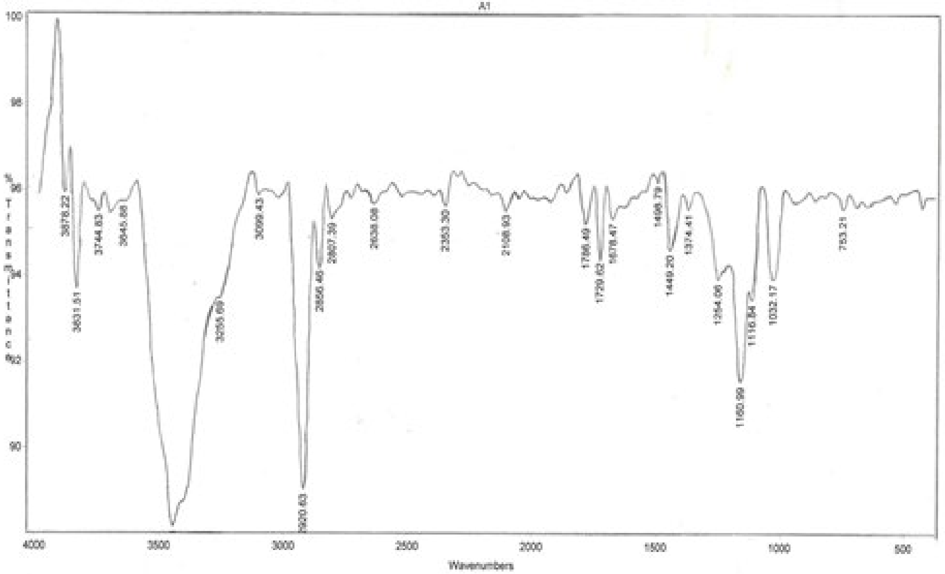

Figure 2. FTIR spectrum of A1 terpolymer

Table 2. The number average molecular weight of the prepared

Terpolymer designation	Mn	Terpolymer designation	Mn
A1	82393	B4	82110
A2	80862	B5	81968
A3	80338	B6	81678
A4	78684	C1	90632
A5	78560	C2	88589
A6	78000	C3	86820
B1	85484	C4	85430
B2	82432	C5	84320
B3	82284	C6	83868

The structure of the prepared terpolymers were confirmed by using ^{1}H-NMR, Fig. 3, and from ^{1}H-NMR spectra, there was found characteristics peak signals corresponding to δ-0.9 for

(– CH_3) of alkyl acrylate, δ-3.5 for (- O – CH_2) of alkyl acrylate, δ-4.00 for (N – CH) of vinyl pyrrolidone and δ-7.00 for (C – H) of benzene ring of styrene were obtained, data were calculated. The composition of the prepared terpolymer obtained by ^{1}H-NMR, were given at Table 3.

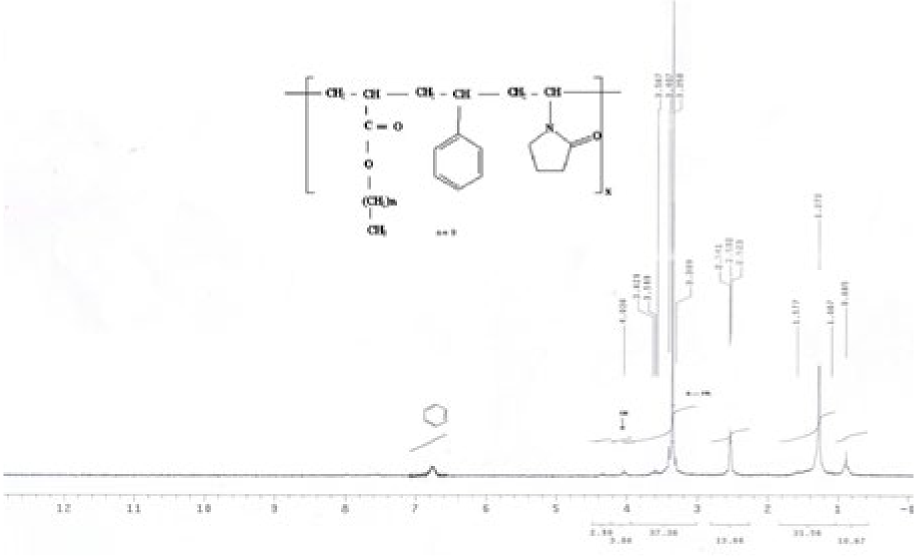

Figure 3 ^{1}H-NMR spectrum of B1 terpolymer

Table 3. Analysis of the data for the determination of (alkyl acrylate – styrene– vinyl pyrrolidone) terpolymer composition of (A1-A6) to (C1-C6)

Designation	Terpolymer composition (mol %)			Designation	Terpolymer composition (mol %)			Designation	Terpolymer composition (mol %)		
	[C8- acrylate]	[St]	[VP]		[C10-acrylate]	[St]	[VP]		[C12-acrylate]	[St]	[VP]
A1	80.00	8.30	11.66	B1	63.15	26.31	10.52	C1	58.82	22.98	17.24
A2	79.68	7.81	12.50	B2	60.00	13.33	26.67	C2	27.27	36.36	36.36
A3	80.85	10.63	8.50	B3	60.00	20.00	20.00	C3	78.94	10.52	10.52
A4	81.25	10.41	8.33	B4	68.73	18.75	12.50	C4	33.33	44.44	22.22
A5	78.94	10.52	10.52	B5	72.23	16.68	11.10	C5	38.46	46.15	15.38
A6	58.82	17.64	23.52	B6	66.68	20.00	13.33	C6	55.55	22.22	22.22

3.2. Evaluation of the prepared compounds as lube oil additives

3.2.1. 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) [18]. The prepared compounds (A_1-A_6), (B_1-B_6) and (C_1-C_6) 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 octyl acrylate (A), decyl acrylate (B) and dodecyl acrylate (C) ranging between (2.5 - 30.00) x 10^3 ppm were used to study the effect of the additive concentration on V.I., 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 [20]. 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 [21].

Table 4. Dependence of VI on the concentration of (A1-C1) to (A6-C6) additives

	A1	B1	C1	A2	B2	C2	A3	B3	C3
30	110	112	116	108	110	114	106	108	110
20	106	108	112	104	106	110	104	106	108
10	102	104	107	102	102	104	102	102	104
5	100	100	102	100	100	100	100	100	100
2.5	98	98	98	98	98	98	98	98	98
0.0	96	96	96	96	96	96	96	96	96

	A4	B4	C4	A5	B5	C5	A6	B6	C6
30	104	106	110	104	106	108	103	104	106
20	102	104	106	102	104	106	102	104	106
10	102	102	104	102	102	102	100	102	102
5	100	100	100	100	100	100	100	100	100
2.5	98	98	98	98	98	98	98	98	98
0.0	96	96	96	96	96	96	96	96	96

The effect of alkyl chain length on the efficiency of the prepared additives as viscosity index improvers is given in Fig. 4, which indicates that the efficiency increases with increasing the alkyl chain length of the acrylate used. This may be due to the influence of the molecular weight on the effective coil radius and hence the VI [22].

The effect of monomer ratios is shown at Fig. 5**,** as an example of group (A); it was found that, the viscosity index increases with increasing the ratio of the acrylate monomer at the final terpolymers composition, Table 3.

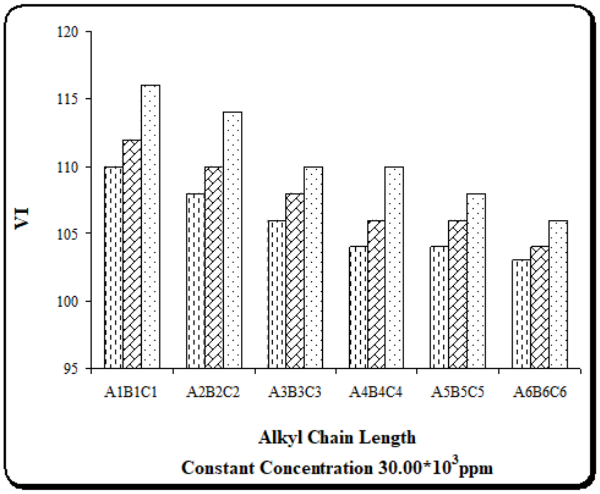

Figure 4. Effect of alkyl chain length of the prepared terpolymers on VI of lube oil

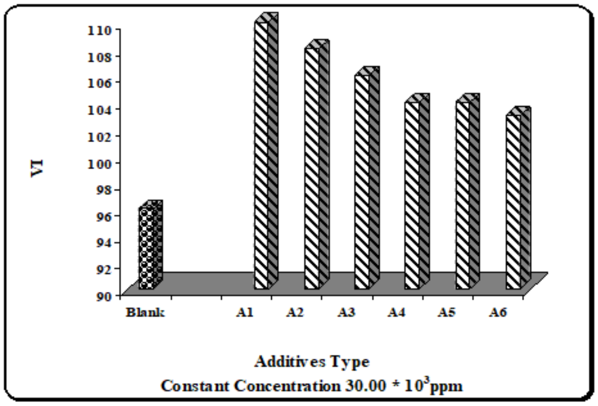

Figure 5. Effect of monomers ratios of (A1-A6) on viscosity index of lube oil

3.3. Sensitivity of the prepared additives to mechanical stresses

The sensitivity of prepared viscosity index improvers to mechanical stresses increases with increasing the molecular weight of the prepared additives. To clarify this point the sensitivity of VI to addition was calculated in each case from the following equation:

$$S=\frac{C_d[VI]}{VI_d[C]}=\frac{dln[VI]}{dln[C]};$$

where C.is the concentration of the polymer, (ppm).

Plots of *ln[VI]* against *ln[C]*, the slopes of the fitted straight lines represent the sensitivity of VI to addition in each case. Then a relation between the sensitivity and VI, Fig. 6, was made, represents that among all additives, the additive **C_1** display the highest sensitivity. This occurs as a result of the highest molecular weight.

3.3.1. Studying of the flow curve of the oil samples

A list of experiments was done using the Brookfield rheometer to examine the flow characteristics of the used oil samples. These oil samples prepared by adding different concentration (2.5 -30.00 *10^3ppm) of each type of polymer additives to the blank oil (SAE 30) at temperatures (40°C, 60°C and 100°C), Fig. 7, was taken as an example for compound (A_1) at 100°C. By studying the flow curve of the oil doped with different prepared additives, it obvious that the oil samples behave like simple-Bingham fluids.

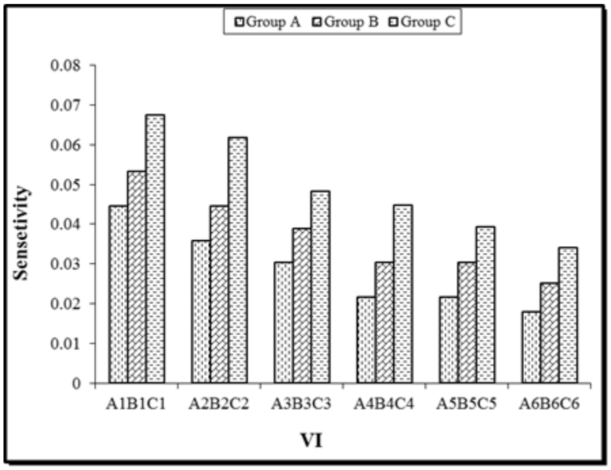

Figure 6. Sensitivity of the prepared additives against VI

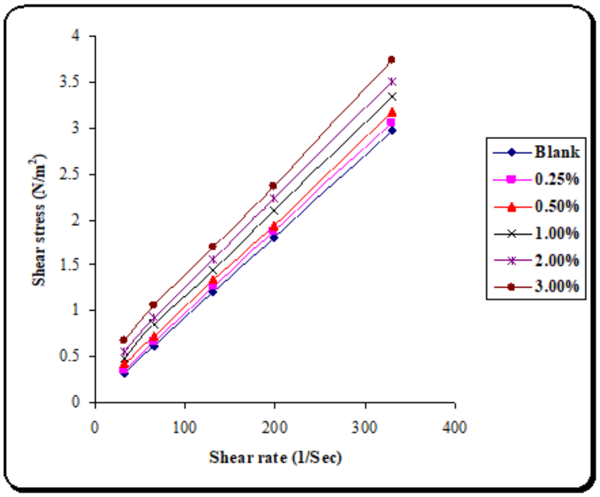

Figure 7. Flow curve of additive A1at 100°C

3.3.2. Viscosity-shear rate dependence

The apparent viscosity of each oil sample was measured by the same rheometer Brookfield at different temperatures. The data were plotted on Fig. 8, crossponding to compound B_1 at 40°C as an example. The curve shows that the viscosity slightly decreases with the increase of shear rate. This means that the prepared terpolymers tolerate the decrease of oil viscosity which has been caused as a result of the presence of the shear.

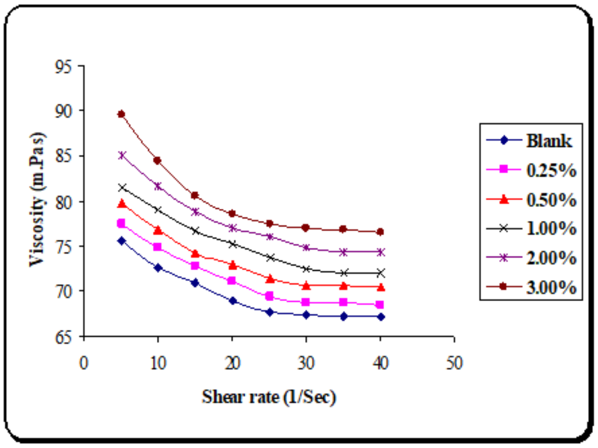

Figure 8. Viscosity – shear rate curve of B_1

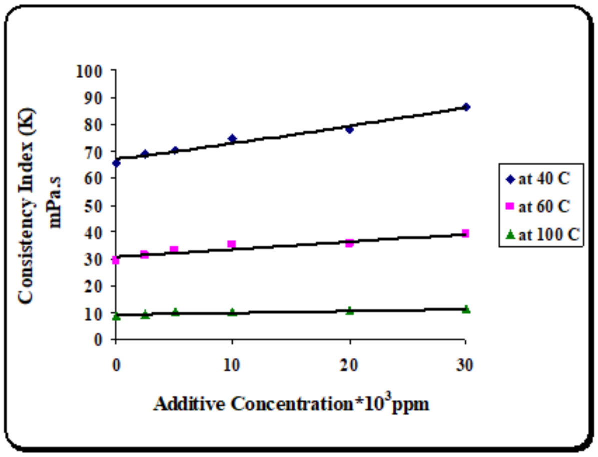

Figure 9. Effect of additive concentration on K value of B1 as function of temperature

3.3.3. Effect of polymer concentration on the consistency index of oil samples

The consistency index *K* of a liquid is meanly represented to apparent viscosity from the physical point of view. The consistency index '*K*' of each oil sample was plotted against the additive concentration '*C*'' at each temperatures (40, 60 and 100°C), Fig. 9, corresponding to B_1 terpolymer, represents that the consistency index "apparent viscosity", increase with increasing the polymer concentration. This may be due to the increase of the hydrodynamic volume of the polymer.

4. Conclusion

Eighteen terpolymers were prepared via free radical chain polymerization of different alkyl acrylate, styrene, and vinyl pyrrolidone using different molar ratios. The structures of the prepared terpolymers were confirmed by using FTIR, ^{1}H-NMR and GPC, for determination of number average molecular weight (Mn). All the prepared terpolymers were found to be soluble in lube oil (SAE-30).

The prepared terpolymers were evaluated as viscosity index improvers for lube oil. It was found that the efficiency of the prepared additives as viscosity index improvers for lube oil increases with increasing the concentration of terpolymer up to $30.00*10^3$ppm. Viscosity index increase with increasing the alkyl side chain length of ester and with increasing alkyl acrylate percent at the final terpolymer composition.

The sensitivity of the prepared viscosity modifiers was calculated and it was found that among all additives, additive C_1 display the highest sensitivity. The rheological properties of the prepared additives doped with lube oil SAE-30, were studied and it was found that the oil treated with the prepared additives may behave as simple Bingham fluid.

Conflict-of-interest statement

The authors have no conflict of interest.

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