

JOJOBA POLYMERS AS LUBRICATING OIL ADDITIVES

Amal M. Nassar², Nehal S. Ahmed², Rabab M. Nasser^{1*}

¹ Chemistry Department, University College of Samtah, Jazan University, Saudi Arabia

² Department of Petroleum Applications, Egyptian Petroleum Research Institute.

Correspondence to: Rabab M. Nasser (E-mail: rabab_nasser@yahoo.com)

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Abstract

Jojoba homopolymer was prepared, elucidated, and evaluated as lube oil additive, then novel six copolymers were prepared via reaction of jojoba oil as a monomer with different alkylacrylate, (dodecylacrylate, tetradecylacrylate, and hexadecylacrylate), and with different α - olefins (1-dodecene, 1-tetradecene, and 1-hexadecene), separately with (1:2) molar ratio. The prepared polymers were elucidated using Proton Nuclear Magnetic Resonance (¹H-NMR) and Gel Permeation Chromatography (GPC), for determination of weight average molecular weight (Mw), and the thermal stability of the prepared polymers was determined. The prepared polymers were evaluated as viscosity index improvers and pour point depressants for lubricating oil. It was found that the viscosity index increases with increasing the alkyl chain length of both α - olefins, and acrylate monomers, while the pour point improved for additives based on alkyl acrylate.

Keywords: Lubricating oil additives; viscosity modifiers; pour point depressants; jojoba - acrylate copolymers; jojoba- α olefins copolymers; TGA and DSC analysis.

1. Introduction

Lubricants and lubrication were inherent in a machine ever since man invented machines. It was water and natural esters like vegetable oils and animal fats that were used during the early era of machines. During the late 1800s, the development of the petrochemical industry put aside the application of natural lubricants for reasons including its stability and economics [1].

Jojoba oil is a liquid ester mixture extracted from seeds of a desert shrub native to Arizona, California, North-Western Mexico and Baja California [2]. Jojoba nut oil differs from most other animal and vegetable oils in that it is not a fat but a liquid wax. Jojoba oil is unique among vegetable oils, as sperm oil is unique among animal oils. Such a vegetable oil has never before been available to industry in commercially usable quantities. The following characteristics make jojoba oil valuable: its natural purity and molecular simplicity and its stability; it is a non-drying oil, having high resistance to oxidation; it can be stored for years without becoming rancid; its lubricity; its unsaturation (double bonds) [3]. The growing awareness of the lower biodegradability and higher toxicity of petrochemical - based lubricants created the requirements of the best possible protection of nature. The recent research on the adverse effect of mineral oil-based lubricants on the environment has reconfirmed its role in polluting groundwater for up to 100 years and its effects on reducing the growth of trees and the life span of aquatic life [1]. This awareness, of the use of ecofriendly processes and materials, increases interest in tribology for the use of natural esters in lubrication processes [4]. The use of vegetable oils is encouraged in applications where recycling is not easy or the usage is total loss lubrication. The current major areas of applications where biodegradable lubricants have been put to real use are boating two- stroke lubricants, forestry and chain saw lubricants, concrete mould release fluids, hydraulic system oils and manufacturing industries [5-6].

Bisht *et al.* [7]. studied the utilization of jojoba oil as a compound and as an additive in lubricating oil base stocks; properties such as viscosity index (VI), rust protection, foaming, friction, and wear characteristics were evaluated. Their results showed that jojoba oil can enhance or impart certain desirable characteristics, such as VI improvement, antirust, antifoam, antiwear, and friction reduction properties to the blend [8].

Jojoba oil is like whale sperm oil which is a liquid wax. It consists primarily of wax esters of eicosenoic acid (C_{20}), eicosenol (C_{20}) and docosenol (C_{22}). It contains a very small amount of saturated material and the main constituents are mostly mono unsaturated [9-10]. The use of jojoba oil, with its high polarity straight and longer chain length of 40-42 carbon atoms, as a component of lubricant reduces wear because of strong adsorption of the polar molecules on the metal surfaces [11]. The viscosity of jojoba oils falls within SAE 20 range and the oil can be used as a base stock without any dilution. The viscosity index is quite high compared with (High Viscosity Index) HVI paraffinic base stocks which can improve lubrication especially at higher temperature [11].

In selecting the proper oil for a given application, viscosity is a primary consideration. It must be high enough to provide proper lubricating films but not so high that friction losses in the oil will be excessive. Since viscosity varies with temperature, it is necessary to consider the actual operating temperature of the oil in the machine. Other considerations, such as whether a machine must be started at low ambient temperatures, must also be taken into account.

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. In the absence of long interlocking crystals or swollen particles, oil can move freely through any solid wax particles that are present [12].

By studying the literature survey about using jojoba as a lubricant additive, one can find that; jojoba was taken as it is with different percentage as viscosity index improvers [9-10], or by adding a pour point depressant to improve the flow properties of jojoba imparted with lubricating oil. In the present work, jojoba was polymerized as a homopolymer and copolymer and novel six copolymers built basically on jojoba were prepared and compared in its properties with jojoba homopolymer. The prepared polymers were evaluated as lubricating oil additives, viscosity index improvers, and pour point depressants.

2. Experimental

2.1 Esterification of Acrylic acid with different fatty alcohols

Three esters were prepared via the esterification reaction of one mole of acrylic acid with one mole of (dodecanol, tetradecanol, and hexadecanol) separately. The reactions were carried out in a resin kettle in the 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 a solvent. The esterification reactions were carried out under a slow stream of deoxygenated nitrogen. The reactions were agitated using a mechanical stirrer at 500 rpm. The reactants, which were mixed with an equal weight of xylene, were heated gradually from room temperature to $130^{\circ}\text{C} \pm 5^{\circ}\text{C}$ using a well-controlled thermostat. The extent of reaction was followed by monitoring the amount of liberated water to give products dodecylacrylate, tetradecylacrylate, and hexadecylacrylate [13-14].

2.2 Polymerization of jojoba

Jojoba was polymerized individually and with other monomers to yield jojoba homopolymer and different jojoba copolymers [15].

2.2.1 Homopolymerization of jojoba

Jojoba was allowed to free radical polymerization, The polymerization was carried out using magnetic stirrer in a 3-neck, round-bottom flask equipped with an efficient condenser, thermometer, and an inlet for the introduction of nitrogen, an efficient weight of benzoyl peroxide

(1% by weight) was used at the desired temperature $80 \pm 10^\circ\text{C}$. When the reaction was completed, the temperature was allowed to reduce to room temperature. Then the reaction mixture was poured drop by drop in cooled methanol with continuous stirring, filtered off, and dried.

2.2.2 Copolymerization of different monomers with jojoba

Six copolymers were prepared via free radical chain addition polymerization of one mole of jojoba with two moles of (dodecylacrylate, tetradecylacrylate, hexadecylacrylate, 1-dodecene, 1-tetradecene, and 1-hexadecene) separately. The polymerization was carried out using magnetic stirrer in a 3-neck, round-bottom flask equipped with an efficient condenser, thermometer, and an inlet for the introduction of nitrogen, an efficient weight of benzoyl peroxide (1% by weight) was used at the desired temperature $80 \pm 10^\circ\text{C}$. When the reaction was completed, the temperature was allowed to reduce to room temperature. Then the reaction mixture was poured drop by drop in cooled methanol with continuous stirring, filtered off, and dried.

2.3. Elucidation of the prepared copolymers

Infrared Spectroscopic Analysis. Infrared spectra of the synthesized esters, jojoba homopolymer and different jojoba copolymers were measured by using FTIR—Spectrometer Model Type Mattson Infinity Series Bench Top 961 for the purified esters.

^1H -NMR spectroscopic Analysis. The structure of the synthesized polymeric additives were elucidated by Proton Nuclear Magnetic Resonance (^1H -NMR) spectra using a 300 MHz Varion NMR 300 spectrometer using DMSO as a solvent.

Determination the Molecular Weight of Prepared Esters and Copolymers. The molecular weights of the prepared esters were determined by using a Vapor Pressure Osmometer, while the molecular weights of the prepared homopolymer and copolymers were determined by using Agilent GPC, Germany Poly Strogel (Germany), particle size 100, 104, 105A°.

Thermal Analysis for the prepared copolymers. 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 $10^\circ\text{C min}^{-1}$ from 25 to 600°C , under a flowing (25 ml min^{-1}) nitrogen atmosphere.

2.4 Evaluation of the Prepared Polymers as Lubricating Oil Additives

As Viscosity Index Improvers for Lube Oil. The prepared homopolymer and copolymers were evaluated as viscosity index improvers using free additive base oil (SAE 30) through the viscosity index (VI) test, according to the ASTM D-2270-93. The Kinematic viscosity of the oil containing the tested compound was determined at 40°C and 100°C . Different concentrations ranging between 0.0 and 3.0 wt% were used to study the effect of additive concentration on VI.

As Pour Point Depressants for Lube Oil. The evaluation was carried out by using the ASTM-D 97-93 for measuring the pour point (PP).

3. Results and discussion

The compositions of the prepared esters were confirmed by IR spectra and by determination of molecular weight. It is obvious from the data given in Table 1 that the experimental and theoretical values of the molecular weight are in good accord. This indicates that the reactions were completely successful and confirms the formation of the desired compounds.

From IR spectrum of dodecylacrylate, which is shown in Fig. 1, one can arrive at 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 bands 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 -CH scissoring of the -CH=CH- group appear at 1462cm^{-1} . The band for methyl group appears near $1370\text{--}1465\text{cm}^{-1}$. The band for (C-H) aliphatic appears near 2840cm^{-1} and 2950cm^{-1} . 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 spectrum of jojoba oil, Fig. 2, indicates that it contains the following functional groups [16]: ester (C=O with frequency 1820-1660 cm^{-1} and C-O with frequency 1465-1375 cm^{-1}).

Table 1 Theoretical and experimental molecular weights of Jojoba oil and the prepared esters

Ester	Theoretical M.wt.	Experimental M.wt.
Jojoba oil	324	324.66
Dodecylacrylate	240	243
Tetradecylacrylate	268.45	268
Hexadecylacrylate	297.02	298

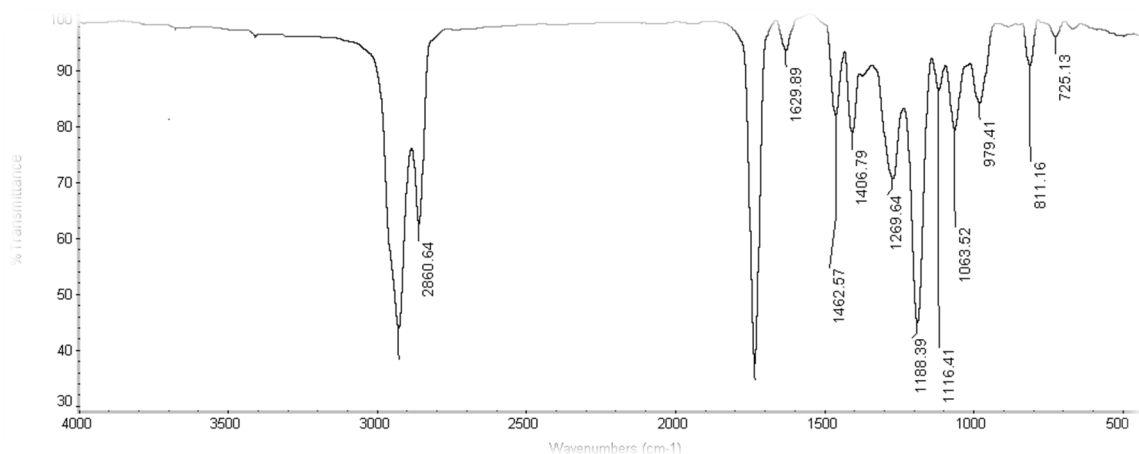


Figure1 IR spectrum of dodecylacrylate.

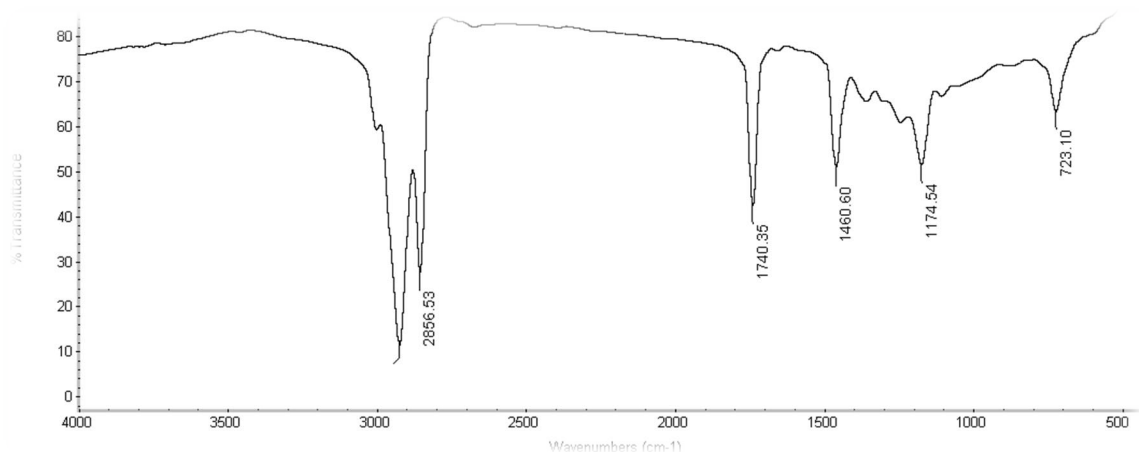


Figure 2 IR spectrum of Jojoba oil

The structure of the prepared copolymers, Schemes (1-3), were confirmed by using ^1H -NMR, as in Fig. 3, ^1H -NMR spectrum of (G), 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, δ -2.254 for ($-\text{CO}-\text{CH}$) of alkyl acrylate, and peak signal at δ 3.8 corresponding to ($-\text{COO}-\text{CH}_2$) - of jojoba oil.

The weight average molecular weight (M_w), number average molecular weight (M_n), and the polydispersity index of the prepared polymers, their designation and their composition

were given in Table 2, which indicates that the molecular weight of copolymers increases with increasing the molecular weight of acrylate and the molecular weight of the olefin used.

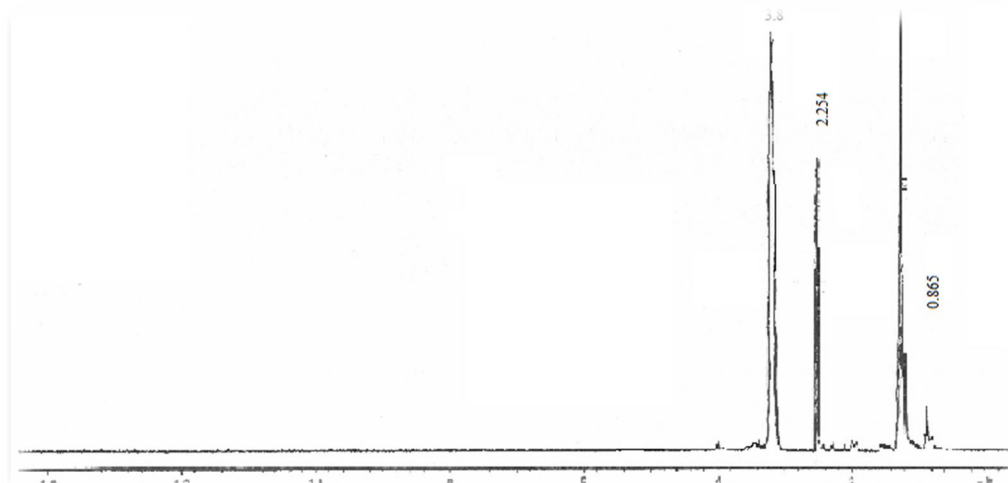
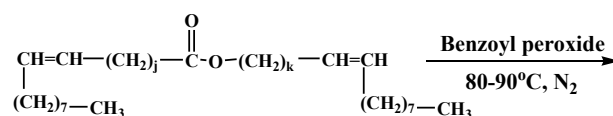


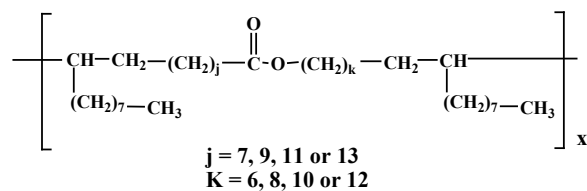
Figure 3 ^1H -NMR spectrum of (G) copolymer

Table 2 Polymers designation, Monomers feed, polymers composition, mean molecular weight (M_n), average molecular weight (M_w) and poly dispersity index (PI)

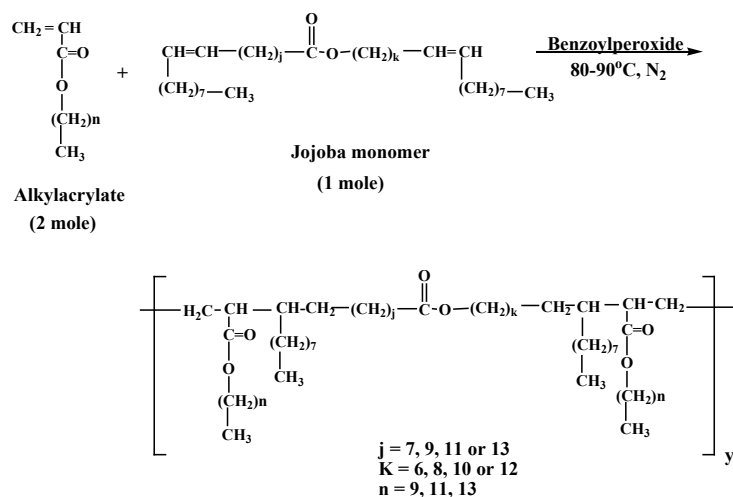
symbol	Polymer designation	Monomer feed		Polymer composition		M_n	M_w	PI
		Jojoba	-----	Jojoba	-----			
A	Jojoba homopolymer	100	zero	100	-----	1045	1470	1.407
Jojoba : α -olefins		Jojoba	α -olefins	Jojoba	α -olefins			
B	Jojoba : 1-Dodecene	33.33	66.66	35	65	1083	1623	1.420
C	Jojoba : 1-Tetradecene	33.33	66.66	33	67	1298	1541	1.187
D	Jojoba : 1-hexadecene	33.33	66.66	32	68	1455	1612	1.108
Jojoba : Alkylacrylate		Jojoba	alkylacrylate	Jojoba	alkylacrylate			
E	Jojoba : Dodecylacrylate	33.33	66.66	30	70	18785	29857	1.589
F	Jojoba : Tetradecylacrylate	33.33	66.66	25	75	22835	32426	1.420
G	Jojoba : Hexadecylacrylate	33.33	66.66	22	78	25690	40821	1.589



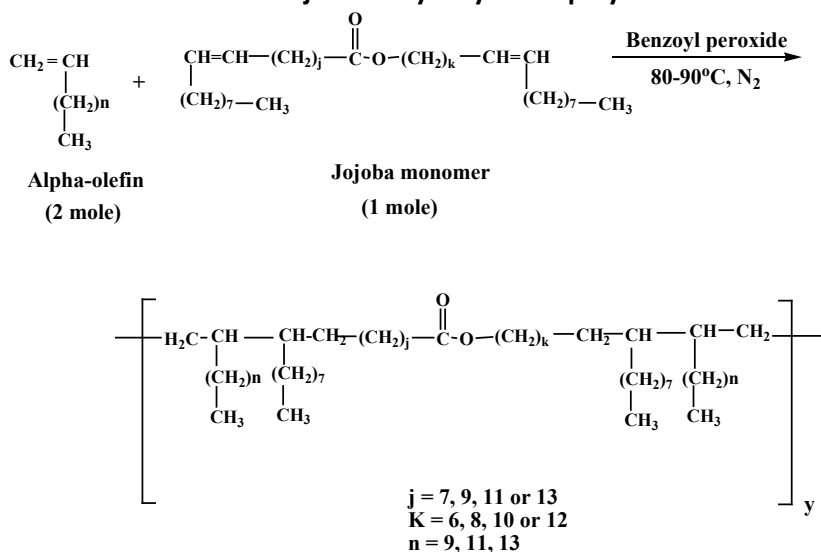
Jojoba monomer



Scheme 1 Jojoba homopolymer



Scheme 2 Jojoba –alkylacrylate copolymers.



Scheme 3 Jojoba –olefin copolymers

3.1 Thermal stability of polymers

The thermal stability of the prepared polymers was investigated, Figs. 4 and 5, both integral (TGA) and differential (DSC) analysis were done for all the investigated polymers. It was found that the primary degradation of polymers, Fig. 4, based on jojoba –alkyl acrylate (E, F and G) occur at 311°C, with 9.46% weight loss, while the complete degradation occur at 434°C with 92.393% weight loss.

Copolymers consist of (dodecene – jojoba) shows the primary degradation at 312°C, with 11.65% weight loss, while the complete degradation occur at 436°C with 92.992% weight loss.

Copolymers consist of (Jojoba -tetradecene) and (Jojoba - hexadecene) degraded on three steps. The primary degradation occurs at 194°C with 24.56% weight loss. The secondary degradation occurs at 351°C with 40.73% weight loss, while the complete degradation occurs at 406°C with 91.018% weight loss. Therefore, the thermo-gravimetric study has shown a much greater thermal stability for copolymers prepared from (alkylacrylate – jojoba) and (dodecene – jojoba), than that prepared from (Jojoba -tetradecene) and (Jojoba - hexadecene) and this confirms the suitability of the prepared polymers as lubricating oil additives.

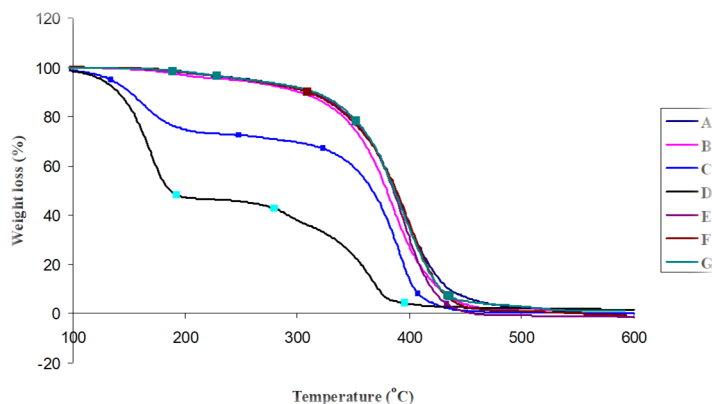


Figure 4 TGA of (A-G) polymers

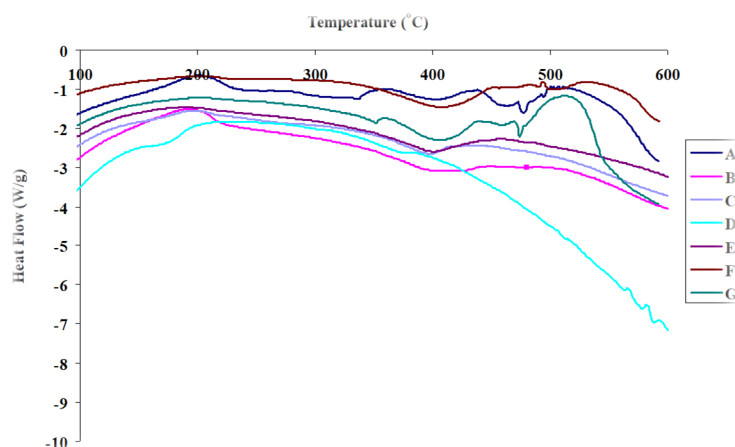


Figure 5 DSC of (A-G) polymers

From Fig. 5, there were small endothermic peaks around 470°C -480°C, this is the temperature which were required to break the polymer backbone, and this prove the stability of the prepared polymers to be used at elevated temperatures and there suitability as lubricating oil additives.

3.2. Evaluation of the prepared compounds as lube oil additives

3.2.1 As viscosity index improves for lube oil

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-G) were tested for their effectiveness as viscosity index improvers for the lube oil. In this respect, the kinematic viscosity of the undoped oil, and oil contains different concentrations of the tested additives was determined at 40°C and 100°C. The viscosity index and pour point of the lube oil (SAE-30) and jojoba oil were given on Table 3.

3.2.1.1 Effect of additive concentration on viscosity index of lube oil

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 additive concentration on VI, the data are tabulated in Table 3, 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 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 [17-20]. 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 [20].

Tab. 3 Viscosity Index and pour point of lube oil (SAE-30), Jojoba oil and lube oil treated with the Prepared Polymers

Physical Property	Viscosity index (VI)					Pour point, (°C)				
Conc, (g/100mL)	0.25%	0.50%	1.00%	2.00%	3.00%	0.25%	0.50%	1.00%	2.00%	3.00%
Lube oil SAE-30	98					0				
Jojoba oil	140					9				
Lube oil (SAE30)+ Jojoba oil	104	106	106	106	106	9	9	9	9	9
A	104	106	107	108	109	-3	-3	-3	0	0
B	106	108	110	112	115	-6	-6	-3	-3	0
C	106	108	112	114	118	-6	-6	-3	-3	0
D	108	110	112	116	120	-6	-6	-3	-3	0
E	108	112	114	116	122	-21	-21	-21	-18	-15
F	110	114	115	118	124	-9	-6	-6	-3	-3

3.2.1.2 Effect of alkyl chain length of the prepared additives on viscosity index of lube oil

The effect of alkyl chain length on the efficiency of the prepared additives as viscosity index improvers for lube oil, Table 3, indicates that the efficiency increases with increasing the alkyl chain length of both alkylacrylate and α -olefin used. This may be due to the influence of the molecular weight on the effective coil radius and hence the viscosity index.

3.2.1.3 Effect of monomer type on viscosity index of lube oil

The copolymers depend on jojoba – alkylacrylate has a greater effect as viscosity index improvers than that depend on jojoba α -olefin copolymers of the same alkyl chain length, Table 3. This may be due to greater molecular weight of the acrylate copolymers than α -olefin copolymers.

3.2.2 As pour point depressants

3.2.2.1 Effect of additive concentration on the pour point of lube oil

Different concentrations of prepared compounds (A-G) 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 additives. This is explained by that 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 [21]. As the molecular weight and the structure of the polymeric pour point depressants enable them to be effective over a wider range than their low molecular weight counterparts. As the temperature decreases, different polymer segments become successively co-crystallizable [21].

3.2.2.2 Effect of alkyl chain length on pour point of lube oil

The effect of alkyl chain length on the efficiency of the prepared additives as pour point depressants was studied. It was found that copolymers which prepared from (Jojoba – dodecylacrylate) are more efficient as pour point depressants, Table 3. This may be due to lower molecular weight.

3.2.2.3 Effect of monomer type on pour point of lube oil

The effect of monomer type on the efficiency of the prepared additives as pour point depressants was studied, as in Fig. 6, it was found that polymers prepared from (Jojoba – alkylacrylate) copolymers are more efficient than that prepared from (jojoba – α -olefins) copolymers.

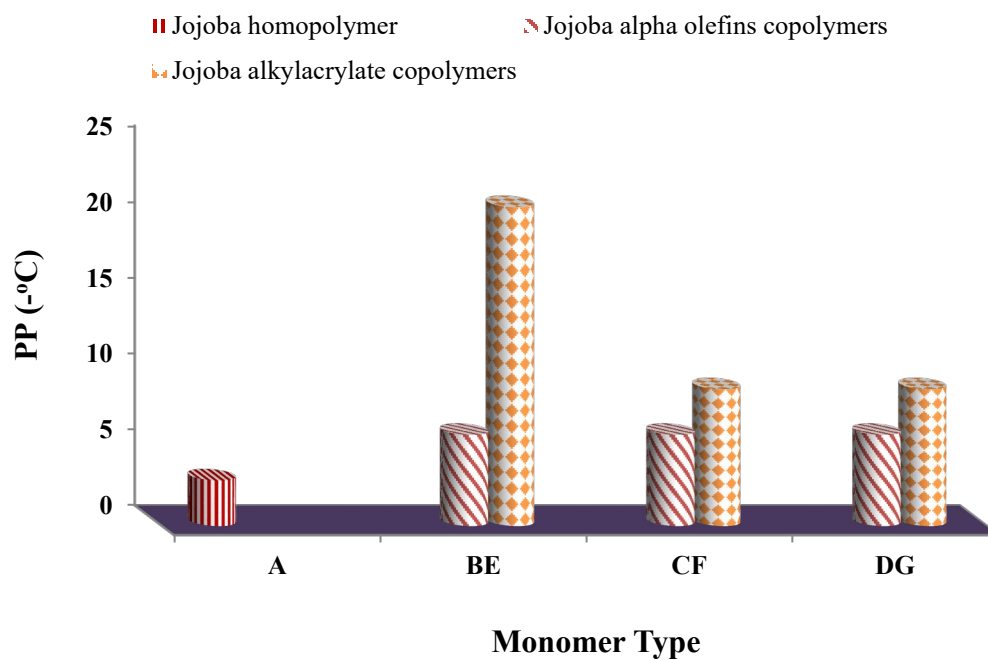


Figure 6 Effect of monomer type of (A-G) copolymers on pour point of lube oil (SAE-30)

4. Conclusions

All findings and discussion outlined to arrive the following conclusions:

1. Polymers were synthesized and elucidated by using FTIR, $^1\text{H-NMR}$ and GPC.
2. Thermal analysis (TGA) for the prepared polymers was measured and it was found they are stable to degradation at high temperature.
3. The prepared polymers were evaluated as lubricating oil additives (pour point depressants and viscosity index improvers).
4. It was found that the viscosity index of lube oil increase by increasing the concentration of polymer and by increasing the alkyl chain length of α -olefins and alkylacrylate.
5. It was found that the prepared polymers modify pour point of lube oil (SAE 30) and the jojoba – decylacrylate give the most efficient as pour point depressant.

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