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Green lubricating oil additives

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ABSTRACT

By increasing the world awareness for the importance of green lubricants and green lubricating oil additives, six terpolymers based on (alkylacrylate: Jojoba: alkylacrylate) were prepared via free radical chain polymerization, using (1: 1: 1) molar ratios. The prepared terpolymers were elucidated using Fourier Transform Infrared Spectroscopy (FTIR), Proton Nuclear Magnetic Resonance (^{1}H-NMR), Gel Permeation Chromatography (GPC) for determining the weight average molecular weight (Mw) and the thermal stability of the prepared polymers was determined. The prepared terpolymers were evaluated as viscosity index improvers and pour point depressants for lubricating oil. It was found that the viscosity index (VI) increase with increasing concentration of the prepared terpolymers till 3.00% by weight, by studying the effect of the prepared terpolymers composition on VI it was found that VI increase with increasing the molecular weight and alkyl chain length from ***A-D*** *terpolymers, while VI decrease for* ***E*** *and* ***F*** *terpolymers.The efficiency of the prepared terpolymers as pour point depressants (PPDs) was studied and it was found that they are efficient as PPDs for lube oil (SAE-30) free of additives, and their efficiency increase by decreasing concentration of the prepared terpolymers. By studying the effect of alkyl chain length on the efficiency of the prepared terpolymers as PPDs it was found that the effect of* ***(A-C)*** *terpolymers was excellent,* ***(D and E)*** *terpolymers have moderate effect, while* ***(F)*** *terpolymer have weak effect.*

Keywords: Green chemistry, green lubricating oil additives, viscosity index improvers, pour point depressants, terpolymers and thermal gravimetric analysis.

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. A lubricant is a substance introduced between two moving surfaces to primarily reduce friction, improve efficiency, and reduce wear. A lubricant may also serve the function of dissolving or transporting foreign particles, carrying away contamination and debris, preventing corrosion or rust, sealing clearance, and dissipating heat. Typically lubricants contain 90% base oil and less than 10% additives. In general, there are three categories of lubricants, liquid, solid and gas. Liquid lubricants may be characterized in a variety of methods. One of the most common method is by the type of base oil used. The most common types of base oils are lanolin (wool grease, natural water repellant), water, mineral oils (derived from crude oil), vegetable oils (derived from plants and animals), and synthetic oils (consisting of chemical compounds which are synthesized from compounds other than crude oil). The growing awareness of the lower biodegradability and higher toxicity of petrochemical – based lubricants created the requirements of the best possible protection of nature [1-4].

Additives can be defined as substances which improve the performance of lubricants, either by imparting new properties to a base oil or grease, or by enhancing the properties already present. Additives offer very important improvement possibilities and are indispensable in the production of modern lubricants. The use of additives, in the modern sense, began in the 1930's and enormous growth has been seen since in both their production rates and the scope of their applications. The type of additive determines the importance and extent of its application. Hence, additives may be classified as primary and special. Primary additives are commonly employed in the most frequently used groups of lubricating oils, e.g. automotive oils. Special additives impart specific properties to certain types of lubricants. The large quantity and number of additives are used for the improvement of petroleum-based oils in the manufacture of finished engine oils. Many lubricant additive exhibit multifunctional properties, such as viscosity index (*VI*) improvers which also act as pour point (*PP*) depressants. Manufacture of additive components themselves is an important area of chemical technology, but selection of the best balance of component spies and relative dosages for each application is an equally demanding and expansive field of study [5].

The practice of chemistry in a manner that maximizes its benefits while eliminating or at least greatly reducing its adverse impacts has come to be known as green chemistry [6]. The environmental and toxicity issues of conventional lubricants as well as their rising cost related to a global shortage and their poor biodegradability led to renewed interest in the development of environmentally friendly lubricants. The increasing of the awareness for vegetable oils, as they are viable and good alternative resources because of their environmental friendly, non-toxic and readily biodegradable nature [7]. Jojoba, *Simmondsia Chinensis L*, is native to the desert southwestern, United States and northern Mexico, it is also grown in Australia, Brazil, Argentina and some Middle East countries. Jojoba has become an attractive alternative crop because of the promising commercial applications for its seed oil in cosmetics. The oil of jojoba is composed mainly of straight chain monoesters in the range of $C_{20} - C_{22}$ as alcohols and acids, with two double bonds [8]. The use of jojoba oil as a lubricating derivative, or agent in the prior art has been confined to single agent use, jojoba oil and sulfurized derivatives of jojoba oil has been used individually as single agents in the art. There remains, however, much room for improvement of lubricating properties for automotive and marine oils, cutting fluids, pre-coat oils, metalworking oils, gear oils and way lubricants [9]. In the present work, six terpolymers were prepared by free radical chain polymerization using jojoba oil and different alkyalcrylates with molar ratio (1:1:1). The prepared terpolymers were elucidated and evaluated as lubricating oil additives, viscosity index improvers and pour point depressants.

MATERIALS AND METHODS

a) Esterification of acrylic acid with different fatty alcohols.

Four esters were prepared via the esterification reaction of one mole of acrylic acid with one mole of (decanol, 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 an 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 $130^{o}C\pm5^{o}C$ using a well-controlled thermostat. The extent of reaction was followed by monitoring the amount of liberated water to give products decylacrylate, dodecylacrylate, tetradecylacrylate, and hexadecylacrylate [10, 11].

b) Terpolymerization of different monomers with jojoba oil.

Six terpolymers were prepared via free radical chain addition polymerization of jojoba with (decylacrylate, dodecylacrylate, tetradecylacrylate and hexadecylacrylate) alternately using molar ratios (1:1:1). The polymerization was carried out using a 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 $80\pm10^{o}C$. 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 [12, 13, 14].

c) Elucidation of the prepared terpolymers.

- **Infrared Spectroscopic Analysis**

Infrared spectra of the synthesized esters, jojoba terpolymers were measured by using FTIR—Spectrometer Model Type Mattson Infinity Series Bench Top 961 for the purified esters.

- **^{1}H-NMR spectroscopic Analysis.**

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

- **Determination the Molecular Weight of Prepared Esters and Terpolymers.**

The molecular weights of the prepared esters were determined by using a Vapor Pressure Osmometer, while the molecular weights of the prepared terpolymers were determined by using Agilent GPC, Germany Poly Strogel (Germany), particle size 100, 104, 105A°.

- **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.

Evaluation of the Prepared Terpolymers as Lubricating Oil Additives

- **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 (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.

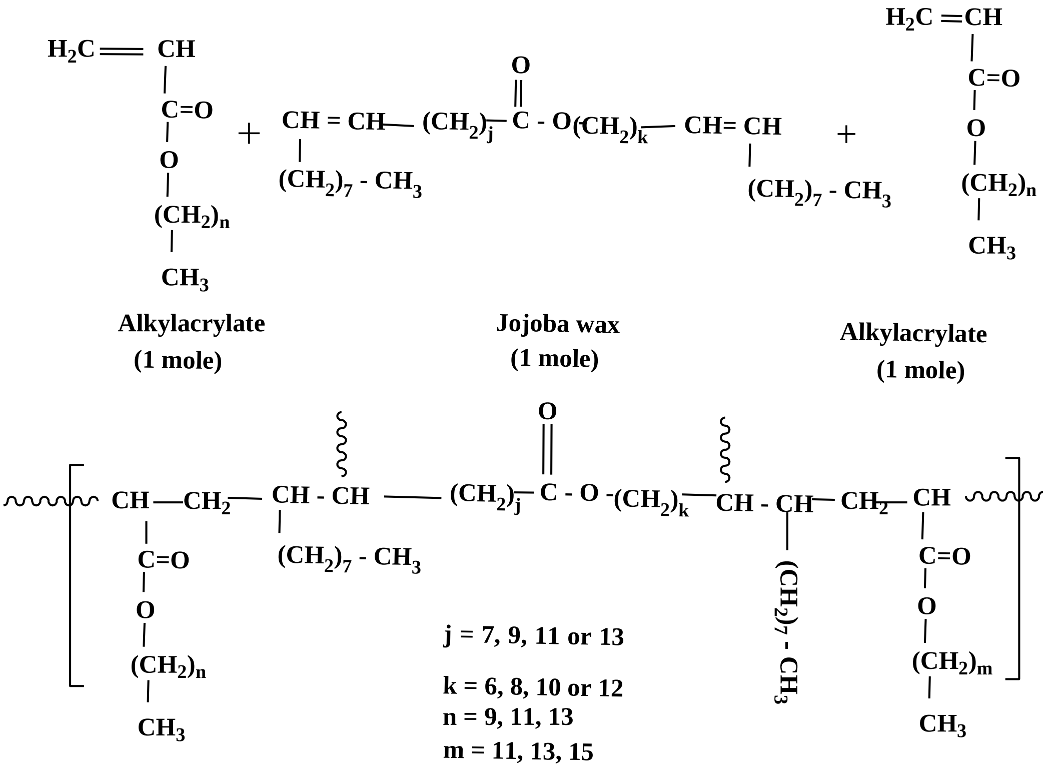
- **As Pour Point Depressants for Lube Oil.**

The evaluation of the prepared terpolymers as pour point depressants was carried out by using the ASTM-D 97-93 for measuring the pour point (PP).

RESULTS AND DISCUSSION

Elucidation of the prepared ester and terpolymers.

Six terpolymers based on jojoba oil –alkylacrylate were prepared via free radical polymerization, **Scheme (1)**. Both esters and terpolymers were elucidated using FTIR. By studying the FTIR spectra of the prepared esters, we noticed the appearance of ester group bands at $1735cm^{-1}$ due to (C = O) group and $1265cm^{-1}$ corresponding to (C – O – C) stretching, respectively [9-11]. The FTIR spectra of the prepared terpolymers assure the disappearance of methylene (CH = CH) group at $1465cm^{-1}$, which confirm the complete formation of the terpolymers.



Scheme 1. Alkylacrylate – jojoba – alkylacrylate terpolymers

The molecular weight of the prepared esters was determined using Vapor Pressure Osmometer, it is obvious from data given in **Table (1)**, that the experimental and theoretical values of molecular weight are in a good accord for the prepared esters. This indicates that the esterification reactions were completed successfully. The weight average molecular weight ***Mw***, number average molecular weight ***Mn***, polydispersity index ***PI***, designation and composition of the prepared terpolymers were given in **Table (1)**, which indicates that the molecular weight increase from **(A-D)** terpolymers while it reversely decreases for **(E and F)** terpolymers. This may be due to the presence of bulky groups (dodecylacrylate with hexadecyacrylate in ***E*** terpolymer and tetradecylacrylate with hexadecyacrylate in ***F*** terpolymer), which lead to steric hindrance, accordingly decrease the rate of polymerization and decrease the molecular weight.

Table 1. Esters molecular weight, terpolymers designation, mean molecular weight (Mn), average molecular weight (Mw) and poly dispersity index (PI)

Ester	Theoretical M.wt.	Experimental M.wt.	symbol	Polymer designation	Mn	Mw	PI
Jojoba oil	324.00	324.66	**A**	**Decylacrylate: Jojoba: dodecylacrylate**	20361	31497	1.55
Decylacrylate	213.00	212.40	**B**	**Decylacrylate: Jojoba: tetradecylacrylate**	23450	34002	1.45
Dodecylacrylate	240.00	243.00	**C**	**Decylacrylate: Jojoba: hexadecylacrylate**	28580	40898	1.43
Tetradecylacrylate	268.45	268.00	**D**	**Dodecylacrylate: Jojoba: tetradecylacrylate**	30460	46299	1.52
Hexadecylacrylate	297.02	298.00	**E**	**Dodecylacrylate: Jojoba: tetradecylacrylate**	27360	37510	1.37
			F	**tetradecylacrylate: Jojoba: hexadecylacrylate**	24475	34632	1.42

The structure of the prepared terpolymers were confirmed by using ^{1}H-NMR, 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, δ-2.254 for – (CO – CH) of alkylacrylate, and a peak signal at δ 3.8 corresponding to - (COO – CH_2) – of jojoba oil.

The thermal stability of the prepared terpolymers was investigated, **Figures (1,2)**, both integral and differential, are shown for all the investigated polymers. It was found that the primary degradation occurs at 354^{o}C, with 15.62% weight loss, while the complete degradation occur at 455^{o}C with a 6.56% weight loss. This confirms the suitability of the prepared terpolymers as lubricating oil additives.

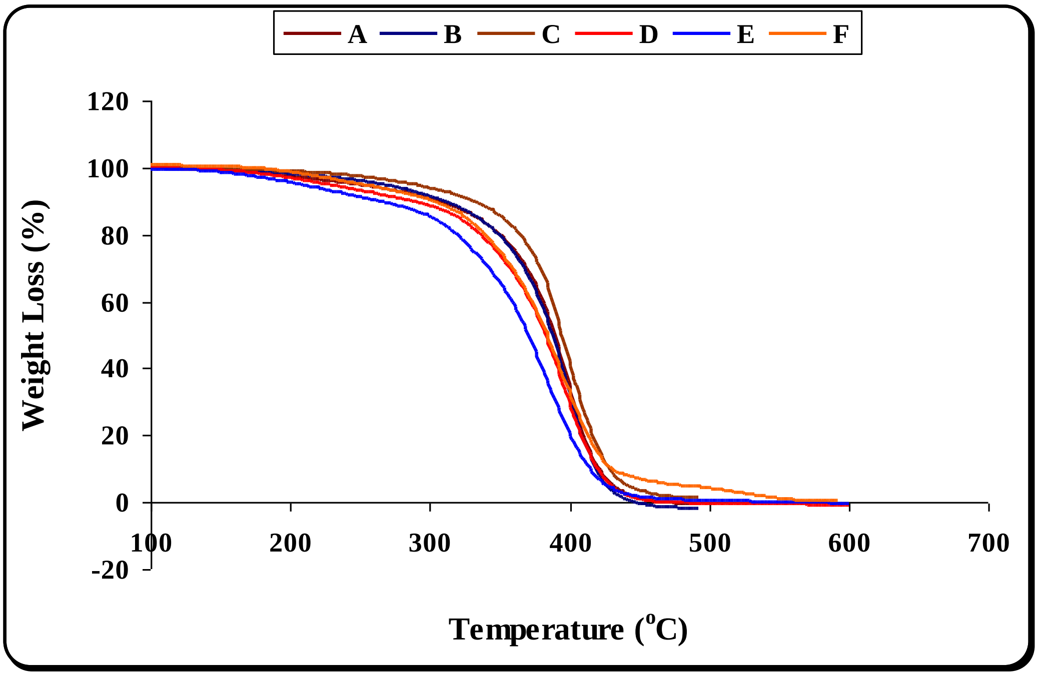


Figure 1.TGA analysis of (A –F) terpolymers.

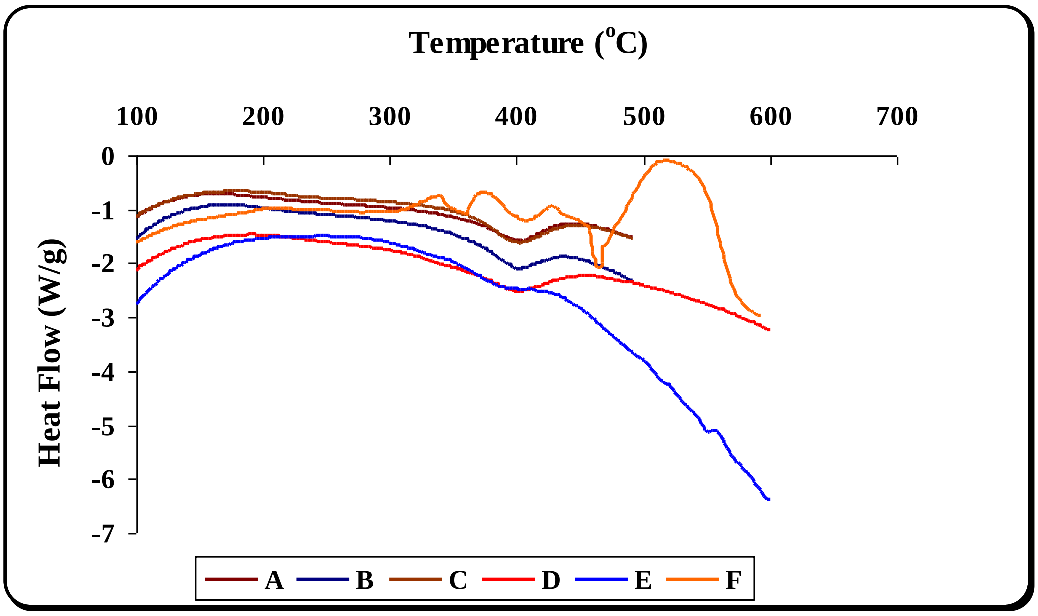


Figure 2. DSC analysis of (A - F) terpolymers.

Evaluation of the Prepared compounds as Lubricating Oil Additives:

In the oil / polymer system, two main interactions operate; polymer with polymer, $\mathbf{I}_{pp}$, leading to the formation of the structure in the oil, and polymer with oil, I_{po}, leading to the solution of the polymer in the oil. If no polymer/oil interaction occurs, the polymer chain tends to form intermolecular aggregates, coiled clusters, as the most likely conformation of the macromolecules, and avoid contact with the oil. In polymer/oil interaction when the oil is a good polymer solvent, the chains interact with the oil and straighten due to solvation, so that the clusters expand, their density decreases and viscosity of the system increase [5].

As Viscosity Index Improvers

Viscosity index improvers affect the rheological properties of the oil, increasing its viscosity at higher temperatures without degrading its other properties, mainly low temperature, flow and pumpability, thermal, chemical stability and without interfering with the effects of other additives. They are mainly used in engine, hydraulic and gear oils, but are also applied in other lubricants. They are mostly linear, non-crystalline or atactic polymers and copolymers, with a variety of chemical compositions, the mean relative molecular weight from 5.000 to 2 million[5].

a) Effect of additives concentration on viscosity index of lubricating oil.

The polymer concentration depends mainly on the solubility of the polymer in oil. Viscosity increases with increasing polymer concentration. The effect of concentration ***c*** on reducing the viscosity can be expressed by the empirical Huggins equation:

$$\eta = [\eta] + k\ \mathrm{H}\ [\eta]^2 c + \ldots\ldots\ldots \qquad (1)$$

where ***k*** **H** is a constant.

Viscosity increase is proportional to concentration at lower polymer concentrations and to as much as the fifth power of the polymer concentration at higher concentrations. Polymers used as viscosity index improvers tend to increase not only the viscosity of the oil, but also its viscosity index. Different concentrations of the prepared additives ranging from 0.25%, 0.50%, 1.00%, 2.00% and 3.0%, were used to study the effect of the additive concentration on viscosity index of lube oil (SAE-30) free of additives, data are tabulated in **Table (2)**, which indicates that the viscosity index of lube oil increases with increasing the concentration of the prepared polymers in solution. This change can be explained by "entangling" of the polymer chains at higher concentrations. Consequently, a high concentration of polymer, till 3.00%, will impart a higher viscosity index than a lower concentration of the same polymer.

b) Effect of terpolymers composition on the viscosity index of lubricating oil.

The thickening power of the prepared terpolymers is influenced by the length, composition and configuration of the alkyl ***R*** substituent; it increases with increasing the length of the alkyl chains, till terpolymer **D**, then the thickening power decrease for terpolymers **E** and **F**, **Figure 3**. The decrease of the thickening power occurs due to the presence of negative power that hinder the effect of terpolymers **E** and **F**, this power is mainly called steric hindrance effect.

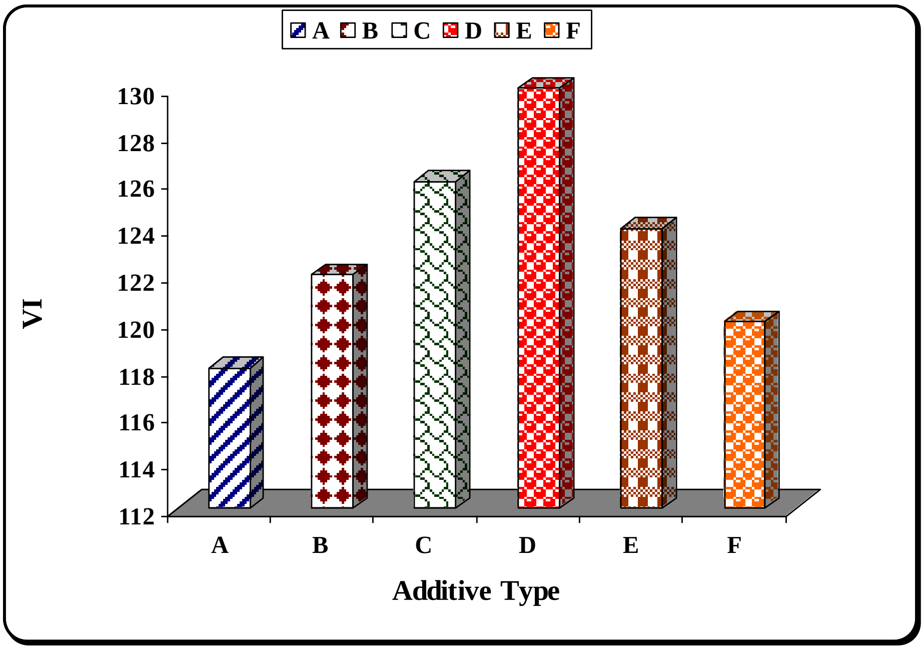


Figure 3. Effect of alkyl chain length of (A-F) terpolymers on VI of lube oil (SAE-30) free of additives.

As Pour Point Depressants.

Pour point depressants are added in order to overcome the effects of residual solid hydrocarbons (waxes, paraffins and ceresines) which have not been separated from the oil in the dewaxing process and so reduce the fluidity limit (true pour point) of the oil. Pour point depressants do not prevent the crystallization of residual paraffins and ceresines, but do prevent them forming interlocking networks and separating from the oil in the form of felt – like lattice.

The mechanism of pour point depressants effect can be explained either by adsorption of a thin film of the pour point depressant onto the surface of the nascent crystals of paraffin and ceresine or by co- crystallization with them. This prevents the formation of undesirable, extended structures of needles and platelets.

a) Effect of terpolymers composition on pour point of lubricating oil.

The reduction of the pour point of an oil depends on the composition and properties of the oil and on the pour point depressant type, its constitution, relative molecular weight and concentration in oil. Different types of pour point depressants influence pour point in different ways. However, in all cases, there is an optimum concentration in oil. If this optimum is exceeded, the pour point increases again. In the region of the optimum, the pour point reduction with increasing dosage decreases. Within a polymer group, the pour point depressant capability depends on the composition of the monomers and their concentration in oil. The distribution of molecules by size has more influence than molecular weight, **Table (2**).

b) Effect of additive concentration on pour point of lubricating oil.

Five different concentrations ranging from (0.25%, 0.50%, 1.00%, 2.00% and 3.00% by weight) of the prepared terpolymers were tested as pour point depressants, the experimental data are tabulated in **Table (2)**, which indicates that the prepared terpolymers are efficient as pour point depressants for lube oil (SAE-30) free of additives, and the efficiency increase by decreasing concentration of the prepared terpolymers. This is explained by that solvation power of any solvent deceases with decreasing temperature and vice versa. The reduction in solvation power becomes more obvious when the molecular weight of the solute and its concentration increases [13].

Table 2. Viscosity Index and Pour Point of Lube Oil (SAE-30) Treated with the Prepared Terolymers

Physical Property	**Viscosity Index (VI)**					**Pour Point (^{o}C)**				
Conc. (g/100ml) **Sample**	***0.25%***	***0.50%***	***1.00%***	***2.00%***	***3.00%***	***0.25%***	***0.50%***	***1.00%***	***2.00%***	***3.00%***
Blank	98					0				
A	104	108	112	114	118	-15	-15	-12	-12	-9
B	106	108	114	116	122	-15	-15	-12	-12	-9
C	108	112	116	120	126	-12	-12	-9	-9	-6
D	112	116	122	126	130	-9	-9	-6	-6	-3
E	110	114	118	120	124	-9	-6	-6	-3	-3
F	108	113	116	118	120	-6	-6	-3	-3	-3

c) Effect of alkyl chain length on pour point of lubricating oil.

The alkyl group should be long enough to ensure good solubility of polymers in oil and their length also affects the efficiency as pour point depressants. If good efficiency is to achieve, the choice of optimum length can be very important. However, the efficiency is still higher if alkyls of different lengths, but whose mean carbon number corresponds to the optimum are employed [5]. The effect of alkyl chain length on the efficiency of the prepared terpolymers as pour point depressants for lubricating oil was studied and it was found that the effect of **(A-C)** terpolymers was excellent, **(D and E)** terpolymers have moderate effect, while **(F)** terpolymer have weak effect. This may be due to the effect of molecular weight, which considerably have a close relationship with steric hindrance.

CONCLUSION

In this article, and with the increasing of the awareness for green lubricants and lubricating oil additives, six terpolymers consisting of (alkylacrylate: Jojoba: alkylacrylate) backbone were synthesized via free radical chain addition polymerization. The alkylacrylates used were (decylacrylate, dodecylacrylate, tetradecylacrylate and hexadecylacrylate), they were used alternately with jojoba using (1: 1: 1) molar ratios. The prepared terpolymers were characterized using FTIR, ^{1}H-NMR and using GPC for determination of weight average molecular. The thermal stability of the prepared terpolymers was determined using TGA and DSC analysis. It was found that the viscosity index increase with increasing molecular weight, concentration and alkyl chain length of the prepared terpolymers from (A-D), then the viscosity index decreases as a result of decreasing molecular weight of (E and F) terpolymers. The prepared terpolymers proved its efficiency as green lubricating oil additives under severe conditions.

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