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ECO-FRIENDLY BIO-BASED LUBE OIL ADDITIVES

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Abstract

Due to increasing the global awareness towards the environment, six eco-friendly bio-based terpolymers based on (jojoba – vinyl acetate - ɑ-olefin) and (Jojoba – vinyl pyrrolidone - α-olefin) were synthesized via free radical polymerization using (1:1:1) molar ratios. They were elucidated using FT-IR, ^{1}H-NMR, GPC and their thermal stabilities were determined. The prepared terpolymers (A_1-A_3) and (B_1-B_3) were evaluated as performance additives for lube oil (SAE-30) free of additives, and it was found that the prepared terpolymers possess a dual effect on untreated lube oil (as viscosity modifiers and pour point depressants).

Keywords: Eco-friendly lube oil additives; bio-based terpolymers; lubricating oil additives; viscosity modifiers; pour point depressants.

1. Introduction

Tribology is the science and technology of friction, wear, and lubrication. It is an interdisciplinary approach that involves a scientific basis to understand surfaces in contact and the lubrication needs of a given tribological system. Friction is the force that hinders or resists the relative motion of the two contacting bodies and, depending on the application, high friction may either be desirable or undesirable. In case of tire traction on pavement and braking, high friction is desirable. However, in applications such as the operation of engines or of equipment with bearing and gears, high friction is undesirable. This is because friction causes wear and generates heat which can lead to premature failure of the functioning machine parts [1]. Minimizing friction is one of the fundamental functions of a lubricant. If friction is not controlled, it can lead to wear and surface damage, and ultimately to catastrophic failure of the equipment. Because of a generally direct correlation between friction and wear [1-3], proper lubrication of the equipment is important if its integrity is to be preserved over its designated lifetime.

A lubricant may be solid, semi-solid, and liquid or gas. Liquid lubricants represent the major branch. Liquid lubricants are classified as, mineral, vegetable, and synthetic. The basic functions of a lubricant are:

1. to prevent the moving interacting surfaces from coming into direct contact,
2. to provide an easily shared interfacial film,
3. to remove the heat evolved in the process, and
4. to reduce wear of the contacted surface [4].

The use of natural plant oils as lubricants has roots in historical antiquity. While these materials have excellent lubrication properties and are biodegradable, they also suffer from limited chemical stability. The presence multiple double bonds and ester linkage make jojoba oil reactive in the presence of oxygen and water at elevated temperatures. Many reactions had been carried out to block the reactivity of the multiple double bonds "hydrogenation, hydroxylation, ozonolysis" [5]. Vegetable oils are carboxylic esters derived from the single alcohol glycerin and are known as triglycerides. Triglycerides derived from many carboxylic acids, and they are different in nature according to the type of alkyl group bound to glycerol. They are traditionally used as a natural raw material in linoleum, paint, lacquers, cosmetics, and laundry powder additives. There is a growing market in the field of lubricants, hydraulic oils, and special applications [6]. Studies have revealed that the presence of jojoba oil in lubricant formulation can enhance or impart certain desirable characteristics like viscosity index, anti-rust, anti-foam, anti-wear and friction reduction to the blend [7].

In the present work, six eco-friendly bio-based terpolymers were synthesized via free radical polymerization; they were characterized using FTIR, ^{1}H-NMR, and GPC. Thermal analyses of the prepared terpolymers were done. The prepared terpolymers were evaluated as viscosity index improvers and pour point depressant for lube oil (SAE-30) free of additives.

2. Materials and Methods

2.1. Materials

Vinyl acetate (99 %), vinyl pyrrolidone (97%), 1-dodecene (99%), 1-tetradecene, (97 %), 1-hexadecene (99 %), benzoyl peroxide (98%) were from Sigma-Aldrich Chemical Company, while jojoba oil was obtained from the Egyptian Company of Natural Oils, Egypt.

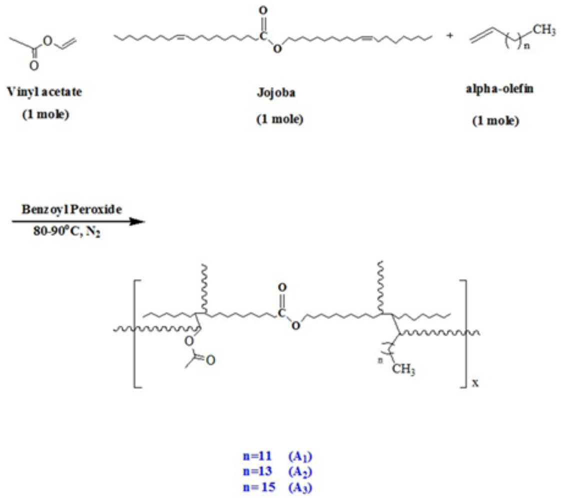
2.2. Instrumentation

Fourier Transform Infrared (FTIR) spectra were determined using FTIR- spectrometer, Model Type Mattson Infinity series Bench Top 961. ^{1}H-NMR Spectrometer Type (300MHz Spectrophotometer- W-P-300, Bruker), using tetra- methyl silane "TMS" as internal standard and dimethyl sulphoxide "DMSO" as a solvent. The molecular weight of the prepared terpolymers was determined by using Agilent GPC, Germany Poly Strogel, particle size 100, 104, 105 A°, using tetrahydrofuran "THF" as a solvent. Differential scanning calorimetric thermosgrams were recorded using Simultaneous Q-600 DSC/TGA (USA). Calculations were made based on the corrected sample weight.

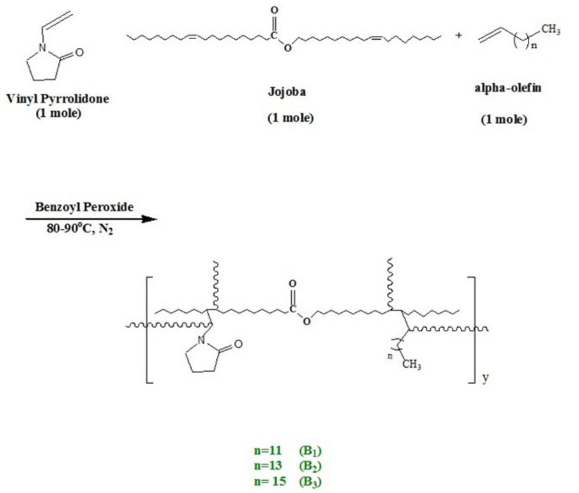
2.3. Methods

2.3.1. Synthesis of bio-based jojoba terpolymers

Two series of eco-friendly bio-based terpolymers were prepared via free radical polymerizetion, using jojoba oil as a bio-based monomer, vinyl acetate, vinyl pyrrolidone, 1-dodecene, 1-tetradecene, and 1-hexadecene. The first series (A_1-A_3) terpolymers was composed of (1: 1: 1) molar ratio from "jojoba: vinyl acetate: ɑ-olefins", Scheme 1; while the second series (B_1-B_3) was composed of (1: 1: 1) molar ratio from " jojoba: vinyl pyrrolidone: ɑ-olefins", Scheme 2.



Scheme 1. (Jojoba: vinyl acetate: α- olefins) terpolymers



Scheme 2. (Jojoba: vinyl pyrrolidone: α- olefins) terpolymers

The polymerization processes were carried out in a three neck flat-bottomed flask equipped with an efficient condenser, thermometer, an inlet for introduction of inert nitrogen and an efficient weight of benzoyl peroxide "1% by weight" was used. The reaction temperature was raised slowly till 80±10°C, and then the temperature was fixed till the reactants converted from liquid state to viscous state. The temperature was allowed to reduce to room temperature, and the reaction mixture was poured slowly into cooled methanol with continuous stirring. The produced polymers were filtered off and dried at room temperature [8-11].

The FTIR spectrum of $\mathbf{A_1}$ terpolymer as an example of the first series gave the following absorbances in cm^{-1}; peak at less than 3000 very strong, 2855 s, 1738 m, 1364 m, 1174 m, 1031 m and 720 m. The ^1H-NMR of $\mathbf{A_1}$ terpolymer (TMS, DMSO) gave δ: 0.96, 1.06, 1.25, 1.29, 1.33, 1.57, 1.64, 1.68, 2.05, 2.25, and 4.08. The FTIR spectrum of $\mathbf{B_1}$ terpolymer as an example of the second series gave the following absorbances in cm^{-1}; peak at less than 3000 cm^{-1} very strong, 2856 s, 1735 m, 1630 w-m, 1427 w, 1364w, 1163 w, 722m. The ^1H-NMR of $\mathbf{B_1}$ terpolymer (TMS, DMSO) gave δ: 0.96, 1.06, 1.25, 1.29, 1.30, 1.33, 1.46, 1.57, 1.64, 1.68, 2.00, 2.08, 2.23, 2.28 and 3.40 ppm.

The weight average molecular weight Mw, the number average molecular weight Mn, poly dispersity index, terpolymers designation and composition were tabulated at Table A_1.

TGA and DSC analysis were carried out using about 0.01g polymer sample were hermetically double-sealed in coated aluminum pans at a heating rate of 10°C min^{-1} from 25 to 600°C, under a flowing (25ml/min) of inert nitrogen.

Table 1. Terpolymers designation, mean molecular weight (Mn), average molecular weight (Mw) and poly- dispersity index (PDI)

Symbol	Polymer designation	Mn	Mw	PDI
A1	Vinyl acetate: Jojoba: dodecene terpolymers	21450	32818.5	1.53
A2	Vinyl acetate: Jojoba: tetradecene terpolymers	22300	34565	1.55
A3	Vinyl acetate: Jojoba: hexadecene terpolymers	24560	39296	1.60
B1	Vinyl pyrrolidone: Jojoba: dodecene terpolymers	18000	26100	1.45
B2	Vinyl pyrrolidone: Jojoba: tetradecene terpolymers	18800	27824	1.48
B3	Vinyl pyrrolidone: Jojoba: hexadecene terpolymers	20000	30000	1.50

2.3.2. Tribological Property Evaluation of the Synthesized Terpolymeric Bio-Based Lube Oil Additives

2.3.2.1. As viscosity index improvers

The prepared terpolymers were evaluated as viscosity index improvers using free additives base oil (SAE 30) through the viscosity index test (V.I.) according to the ASTM D-2270-93 [12]. The kinematic viscosity of the oil containing the tested terpolymer was determined at 40°C and 100°C. Different quantities ranging from (2.5 – 30.00) * 10^3 ppm were used to study the effect of terpolymer concentration on VI. The VI was calculated from equations (1-3).

$$V.I. = [(L-U) / (L-H)] \times 100 \qquad (1)$$

where: **L**- kinematic viscosity, in cSt (mm^2 / s), at 40°C of an oil of 0 viscosity index having the same kinematic viscosity at 100°C as the oil whose viscosity index is to be calculated; **H** - kinematic viscosity, in cSt (mm^2 / s), at 40°C of an oil of 100 viscosity index having the same kinematic viscosity at 100°C as the oil whose viscosity index is to be calculated; **U** - kinematic viscosity, in cSt (mm^2 / s), at 40°C of the oil whose viscosity index is to be calculated.

Values of **L** and **H** were obtained from a special table from the ASTM D-2270-93 at which the basic kinematic viscosity values at 100°C are equal to or more than 2 cSt (mm^2/s) and less than 70 cSt.

When the basic kinematic viscosity value at 100°C was above 70 cSt, the values of L and H were calculated as follows:

$$L=0.8353\ Y^2 + 14.67\ Y - 216 \qquad (2)$$

$$H=0.1684\ Y^2 + 11.85\ Y - 97 \qquad (3)$$

where Y = kinematic viscosity at 100°C.

If the measured kinematic viscosity values at 100°C were not listed in the table but were within the range of 2-70 cSt (the listed values), the corresponding values of [L and H] were obtained by linear interpolation. When the obtained value of the viscosity index was above 100, it was recalculated, as recommended by the ASTM, on the basis that:

$$Y^N = H / U \qquad (4)$$

where Y-kinematic viscosity in cSt (mm^2/s), of the unknown oil at 100°C.

$$N=(\log H - \log U)/\log Y$$

H - kinematic viscosity, in cSt (mm^2/s), at 40°C of an oil of 100 viscosity index using the above-mentioned procedure and having the same kinematic viscosity at 100°C.

$$V.I. = \{[(\text{anti}\log N) - 1] / 0.00715\} + 100 \qquad (5)$$

2.3.2.2. As pour point depressants

The prepared compounds were evaluated as pour point depressants using base oil (SAE 30) through the pour point test according to the ASTM-97-93 [13]. The effect of additive concentration was investigated by using different concentration ranging from $(2.5–30.00)*10^3$ ppm. The instrument used for measuring the pour point was the Cold Filter Plugging Point Automatic Tester (CFPPA-T), model 1st CPP97-2. The specimen is cooled inside a cooling bath to allow the formation of paraffin wax crystals. At about 9°C above the expected pour point, and for every subsequent 3°C, the test jar is removed and tilted to check for surface movement. When the specimen does not flow when tilted, the jar is held horizontally for 5 seconds. If it does not flow, 3°C has added to the corresponding temperature and the result is the pour point.

3. Results and discussion

The polymerization processes take about eight hours. Then polymers were allowed for filtration and drying.

3.1. Characterization of the prepared terpolymers

3.1.1. Jojoba – vinyl acetate – olefins terpolymers

Prominent features of the FTIR spectra of the prepared (Jojoba – vinyl acetate – olefins) terpolymers are the absence of the peak 3008 – 3004cm^{-1} (=C-H) stretch and absence of a peak at 1640 – 1680cm^{-1} (C=C) crossbanding to vinylic bond, indicates the complete conversion of the reacted monomers into terpolymers. The ^{1}H-NMR spectra of the starting materials (Jojoba, vinyl acetate, and α- olefins) shows the presence of vinylic protons at (5.53ppm) that have been replaced by a set of methine protons of the polymer chains at 1.64 and 2.05ppm. The triplet at 2.25 ppm is assignable to methylene protons proximal to a carbonyl group (CH_2-COO); whereas the four proton multiplet at 1.57ppm corresponds to a methylene group adjacent to the methine protons. Peak at 4.08ppm corresponding to (COO-CH_2).

3.1.2. Jojoba – vinyl pyrrolidone – olefins terpolymers

The FTIR spectra of the prepared (Jojoba – vinyl pyrrolidone – olefins) terpolymers are similar to that of (Jojoba – vinyl acetate – olefins) terpolymers, with increasing of a peak at 1630cm^{-1} crossbanding to (C = O) and a peak at 1427cm^{-1} (C – N) of vinyl pyrrolidone. The ^{1}H-NMR spectra of the starting materials (Jojoba, vinyl pyrrolidone and α- olefins) shows the presence of vinylic protons at (5.53ppm) that have been replaced by a set of methine protons of the polymer chains at 1.46, 1.64 and 2.08ppm. The triplet at 2.28ppm is assignable to methylene protons proximal to a carbonyl group (CH_2-COO); 4.08ppm "triplet" is assignable to methylene protons proximal to ether (C – O) bond; whereas the four proton multiplet at 1.57ppm corresponds to a methylene group adjacent to the methine protons. Peaks at 2.00 triplet, 2.23 quartet and 3.4 triplet ppm corresponding to three (-CH_2) of vinyl pyrrolidone.

The designation, composition, weight average molecular weight (Mw), number average molecular weight (Mn), and the polydispersity index of the prepared terpolymers were given in Table 1, which indicate that the molecular weight of the first series based on (Jojoba:Vinyl acetate:α-olefins) is greater than that of the second group based on (Jojoba:Vinyl pyrrolidone: α-olefins); this is a logical consequence due to the presence of steric hindrance in the 2nd series.

3.2. Measurement of terpolymers thermal degradation by TGA and DSC.

The establishment of thermal stability of the prepared terpolymers is an important characteristic with respect to its applications. Data tabulated in Table 2, indicates that the prepared terpolymers possess high thermal stability. Consequently, they have low volatility at higher temperatures.

Table 2. Thermal TGA and DSC analysis of the prepared (A1-A3) and (B1-B3) terpolymers

Sample	Character					
	Tg	Tc	Ti	WLi	Tf	WLf
A1	105	391	289	4.18	415	94.4
A2	106	401	280	4.72	412	94.5
A3	108	401	257	5.4	411	94.52
B1	106	397	257	9.35	408	96.54
B2	106	391	261	10.4	407	97.22
B3	105	393	255	16.39	406	97.41

3.3. Evaluation of the tribological property of the synthesized eco-friendly bio-based terpolymers

3.3.1. As Viscosity modifiers

Some types of polymers are generally used commercially as viscosity modifiers and known to possess certain inherent advantages and disadvantages in performance. Viscosity modifiers (VMs) are commercially available in the form of a solution in oil. Certain polymers are also comercialized in powder or granular form. Polymers commercialized today are classed into two main categories, non-dispersant and dispersant hydrocarbon polymers, and non-dispersant and dispersant ester polymers [14]. Viscosity index is an index designed to emphasize the degree of refinement or chemical composition of the base oil. Dean and Davis, [15] proposed viscosity index for industrial characterization of automotive lubricants. It is an indication of a viscosity-temperature characteristic of oils in terms of its Saybolt Viscosities at 311K and 372K. The kinematic viscosities of the prepared terpolymers were measured at 40°C and 100°C, and viscosity index was calculated according to ASTM D 2270-93, Tables 3 and 4. It was noticed that the thickening power and the viscosity index of the treated oil increased with increasing the kinematic viscosity both at 40°C and 100°C. This may be due to increasing the swelling power of the terpolymer molecule more at high temperatures, which lead to increasing of the hydro-dynamic volume of the terpolymer and continuously counterbalance the normal reduction of oil viscosity as a result of increasing temperature.

The effect of terpolymers concentration on VI was studied by dissolving five different concentrations of the different type of terpolymers (0.25%, 0.50%, 1.00%, 2.00 and 3.00%) on free additive lube oil (SAE -30), Table 3. It was found that the VI of lube oil increase with increasing the concentration of the additives till 3.00% concentration. This was related to the ability of the polymer to form a true solution. By increasing the additives concentration over 3.00%, it was noticed that the polymer converted from enhancing agent into disincentive agent, and continuously restrict the improvement of VI of lube oil.

Table 3. Kinematic viscosities at 40oC and 100oC for lube oil (SAE-30) treated with the prepared terpolymers

Sample conc. (g/100mL)	Kinematic viscosities at 40°C and 100°C for lube oil (SAE-30) treated with (A_1-A_3) and (B_1-B_3) terpolymers											
	A_1		A_2		A_3		B_1		B_2		B_3	
	40°C	100°C	40°C	100°C	40°C	100°C	40°C	100°C	40°C	100°C	40°C	100°C
0.25%	94	11.49	100	12.16	115	13.66	100	11.76	106	12.41	110	12.91
0.50%	97	11.89	110	13.35	127	15.08	110	12.76	114	13.26	116	13.59
1.00%	100	12.43	120	14.43	135	15.81	118	13.61	120	13.94	124	14.46
2.00%	110	13.50	135	16.18	145	17.21	126	14.47	132	15.18	134	15.54
3.00%	130	15.53	150	18.01	150	18.01	134	15.36	138	15.90	140	16.27
Blank	90.35	10.50										

Table 4. Viscosity Index and pour point of lube oil (SAE-30) treated with the prepared terpolymers

Sample conc. (g/100mL)	Physical property											
	Viscosity index (VI)						Pour point (°C)					
	A_1	B_1	A_2	B_2	A_3	B_3	A_1	B_1	A_2	B_2	A_3	B_3
0.25%	110	106	112	108	114	110	-18	-12	-15	-9	-15	-9
0.50%	112	108	116	110	118	112	-18	-12	-15	-9	-15	-6
1.00%	116	110	118	112	122	114	-15	-9	-12	-6	-12	-6
2.00%	118	112	122	114	126	116	-15	-9	-12	-6	-9	-3
3.00%	120	114	126	116	130	118	-12	-6	-9	-3	-6	-3
Blank	98						0					

By studying the effect of alkyl chain length of α- olefin used on viscosity index (VI) of lubricating oil, it was found that the VI increased with increasing the alkyl chain length of the α-olefin used; this may be due to increasing the molecular weight and the solubility character of the α- olefin used, Figure 1.

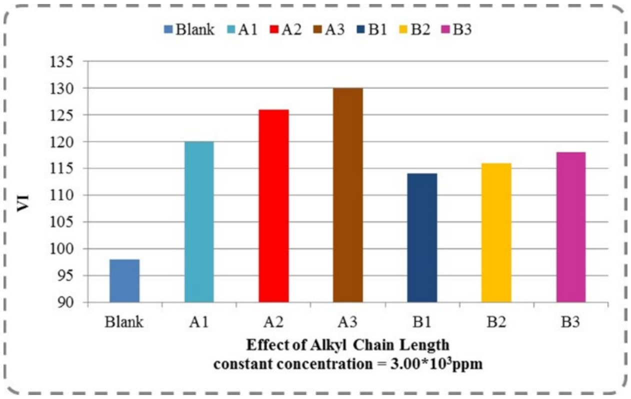


Fig. 1. Effect of alkyl chain length of α- olefin used on VI of lube oil SAE-30 free of Additives

The change of monomer type leads to the change of the terpolymer behavior. Terpolymers based on vinyl acetate possess higher viscosity index compared with vinyl pyrrolidone analogs; this occurs due to the presence of cyclic five-membered ring "vinyl pyrrolidone," which cause the steric hindrance and minimize the effect of its terpolymers derivatives, Figure 2.

3.3.2. As pour point depressants

Waxy oils are producing in many countries around the world. The presence of waxes in these oils causes serious problems for the lubrication process. Crude oils cannot be used directly for engine oil; it should be refined previously, to remove the undesirable wax crystals. However, complete dewaxing of base oils is not practical because of the process limitations, economics, and the desirable presence of wax due to its high VI character [16]. The flow properties of waxy oils are strongly affected by its chemical composition, temperature, pressure condition and previous thermal history. Pretreatment of the waxy oil with the wax inhibitor is necessary. It a process by which the rheological character of the waxy oils changed for easier transportation [17]. Pour point depressant (PPD), alternatively known as wax inhibitor/wax crystal modifier; can reduce the growth of the wax crystal and form smaller crystals of a higher volume to surface ratio.

The effect of polymer composition on pour point of lube oil was studied. It was found that terpolymers prepared from (jojoba: vinyl acetate: α-olefins) improve pour point of lube oil better than that prepared from (jojoba: vinyl pyrrolidone: α-olefins), Figure 3.

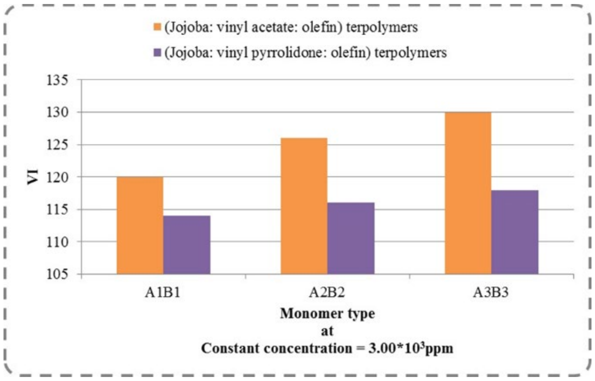


Fig. 2. Effect of Monomer Type on VI of lube oil SAE-30 free of Additives.

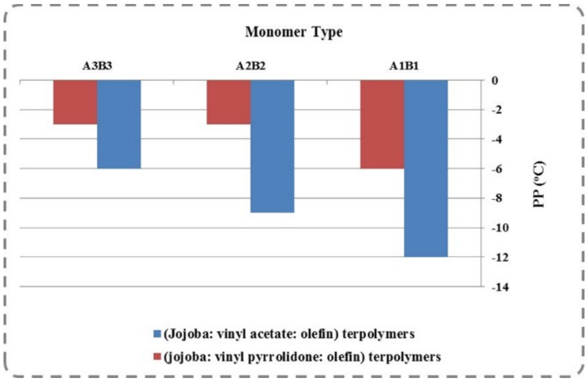


Fig. 3. Effect of Polymer Composition on PP of lube oil SAE-30 Free of Additives

It is well known that the solvation power of the polymer in oil decrease with increasing the polymer concentration. 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 [1]. Data tabulated in Table 4 indicated that the pour point for lube oil improved by decreasing concentration for of the incorporated additive. The effect of alkyl chain length of ɑ- olefin used was determined. It was found that the smaller the alkyl chain length of both series the better the pour point of lube oil.

4. Conclusion

In the present article, and with the increasing of the global awareness toward the green environment, six eco-friendly bio-based lube oil additives based on jojoba oil were synthesized, characterized by FTIR, ^{1}H-NMR, GPC. The thermal stability of the jojoba terpolymers was determined by using TGA and DSC analysis. The prepared terpolymers were evaluated as lube oil additives, and it was found that they possess a dual effect on lube oil (viscosity modifiers and pour point depressants). It was found that terpolymers based on (jojoba: vinyl acetate: ɑ-olefin) improve the viscosity index and pour point for lube oil much better than that prepared from (jojoba: vinyl pyrrolidone: α-olefin).

List of symbols

FT-IR	*Fourier Transform Infrared Spectroscopy,*	*ppm*	Part Per Million,
1H-NMR	*Proton Nuclear Magnetic Resonance,*	*Mw*	Weight average molecular weight,
GPC	*Gel Permeation Chromatography,*	*Mn*	Number average molecular weight.
V.I.	*Viscosity index,*	T_g	*Glass Transition Temperature,*
PP	*Pour point,*	T_c	*Crystallization Temperature,*
PPD	*Pour point depressant,*	T_i	*Initial Degradation Temperature,*
VMs	*Viscosity modifiers,*	T_f	*Final Degradation Temperature,*
ASTM	*American Society for Testing Materials,*	WL_i	*Initial weight loss,*
SAE	*Society of Automotive Engineers,*	WL_f	*Final weight loss,*
cSt	Centistokes,		

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