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RESEARCH ARTICLE

THE RHEOLOGICAL PROPERTIES OF LUBE OIL WITH SOME ADDITIVES

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ABSTRACT

In the present work, some polymeric additives were prepared via copolymerization of hexadecylacrylate and dodecylacrylate with styrene. Structure of the prepared compounds was confirmed by Fourier Transform Infrared Spectroscopy (F.T.I.R.), Proton Nuclear Magnetic Resonance (¹H-NMR), and Gel Permeation Chromatography (GPC). The rheological properties of lube oil (SAE-30) with and without additives were studied at different temperatures (40°C, 60°C and 100°C) and it was found that they behave as Bingham fluids. The sensitivity of the prepared terpolymers to mechanical stresses was studied. It was found that the sensitivity increases with increasing the molecular weight of the prepared additives.

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INTRODUCTION

In metal-forming operations, friction increases tool wear and the power required to work a piece. The engine tribologist is required to achieve effective lubrication of all moving engine components. In order to reduce friction and wear, with a minimum adverse impact on the environment (Leslie R. Rudnick 2003). This task is particularly tough given the wide range of operating conditions of speed, load, and temperature in an engine. Lubrication reduces both friction and wear. The lubricant is designed to act to prevent direct contact between surfaces in relative mutual motion, and thus reduce both the frictional force between these surfaces and wear (Theo Mang and Wilfried Dresel 2001). Viscosity is a fundamental property of engine oil. If the oil is too thin (i.e., low viscosity), oil film thickness between components is reduced enough to cause asperity contact, resulting in mixed or boundary friction. Viscosity is often thought of as the fluid's friction, resistance to flow or the fluid's resistance to shear when the fluid is in motion. The viscosity of a fluid is often represented as a coefficient, which describes the diffusion of momentum in the fluid. Shear rate - the rate at which adjacent layers of a fluid move with respect to each other, usually expressed as reciprocal seconds (also see shear stress) (Hassanean *et al.*, 1997). The shear stress of petroleum oil or other Newtonian fluid at a given temperature varies directly with shear rate (velocity). The ratio between shear stress and shear rate is constant; this ratio is termed viscosity (Barnes 1989; Gwidon

et al., 2006; David B. Braun and Meyer R. Rosen 2000). The higher the viscosity of Newtonian fluid, the greater the shear stress as a function of rate of shear (Chhabra and Richardson 2008). In the present work we prepared some terpolymers to be used as lube oil additives based on esterification of acrylic acid with dodecyl alcohol and hexadecyl alcohol then copolymerization of the prepared esters with styrene by constant ratio of styrene and different ratio of esters. The prepared terpolymers were evaluated as rheology modifiers for lubricating oil.

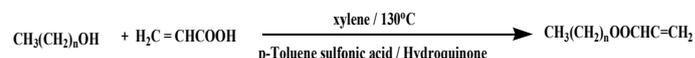
EXPERIMENTAL

1. Preparation of Ester

The esters of acrylic acid were prepared by reacting 1 mole of acrylic acid with 1 mole of different type of alcohols (1- dodecyl and hexadecyl). The reactions were carried out in a resin kettle flask in presence of 0.5wt % p-toluene sulfonic acid as a catalyst and 0.25wt % 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 mechanical stirrer at 500 rpm. The reactants which were mixed with an equal weight of xylene were heated gradually from room temperature to 130° C ± 0.5° C using a well-controlled thermostat. The extent of reaction was followed by monitoring the amount of liberated water to give products dodecylacrylate and hexadecylacrylate (Amal M. Nasser *et al.*, 2011).

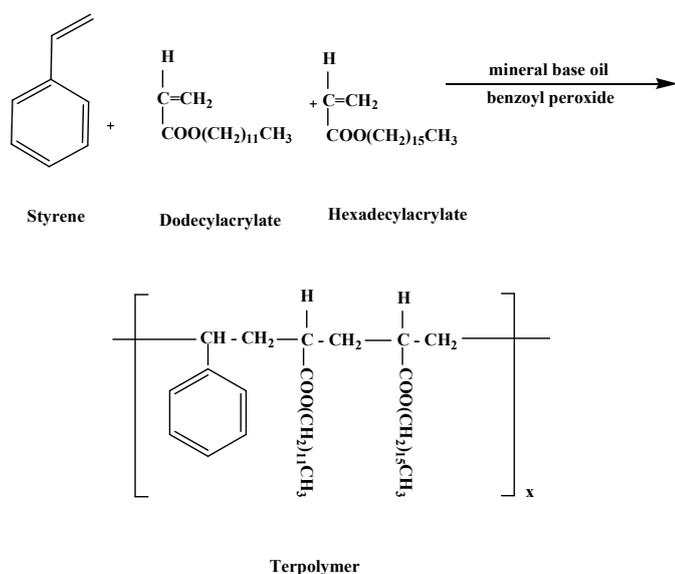
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2. Preparation of Terpolymers

In four-neck round flask fitted with a mechanical stirrer, condenser, thermometer and inlet for the introduction of nitrogen, the nitrogen was dried by passing it through silica gel. The three monomer (dodecylacrylate, hexadecylacrylate and styrene) were placed with different constituents in presence of benzoyl peroxide as an initiator and acetone as solvent the reaction was continued at 60-80°C for 6 h. The prepared terpolymers were purified by precipitation in an excess volume of methanol and then separated. Further purification was carried out by dissolution in acetone and reprecipitation with methanol, the process was repeated for several times, and the polymer was vacuum dried at 50°C for 5 h (Amal M. Nasser et al., 2011).



3. I.R. spectroscopic analysis

I.R. spectra of the prepared esters were determined by using F.T.I.R. spectrometer Model Type Mattson Infinity Series Top 961.

4. ¹H.NMR spectroscopic analysis.

The HNMR spectra of synthesized terpolymers were measured by using 300 MHS spectrometer W.P. 300, Bruker.

5. Determination of the molecular weights

The molecular weights of the prepared terpolymers were determined by using gel permeation chromatography (GPC), Water 600 E.

6. Evaluation of the prepared terpolymers as rheology modifiers for lubricating oil.

Rheological studies were performed on an oil samples containing (2.50-30.00*10³ppm) additives, using Brookfield Rheometer (Model DV-III+). Shear Rate (s⁻¹), Shear Stress (N/m²), and 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.

RESULTS AND DISCUSSION

Dodecyl alcohol and hexadecyl alcohol were esterified by using acrylic acid and the I.R.spectroscopy was used to elucidate the completion of the esterification reactions. Both esters afford similar I.R spectrum, so one spectrum give in Fig. (1) which indicate the following: absence of strong absorption band at 3200cm⁻¹ of aliphatic (OH) group of the characteristic absorption bands of the carboxylic acid and alcohols.

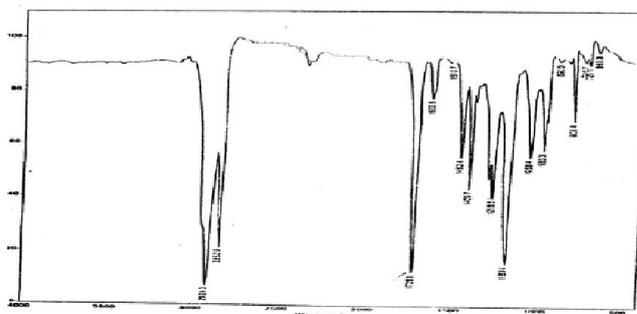


Figure 1. I.R. Spectrum of Dodecyl Acrylate

Appearance of the ester group bands at 1720 ± 10cm⁻¹ and 1250 ± 100cm⁻¹ due to (C=O) and (C-O-C) stretching respectively. The band for (-CH = CH-) appear near 1465 cm⁻¹. The band for (C-H) aliphatic appears near 2840cm⁻¹ & 2950cm⁻¹. This indicates that the esterification process is carried out successfully (9). The reaction of tercopolymer is carried out and confirmed by the ¹HNMR as in Fig. (2) which indicate the presence of proton of aromatic ring at 7 ppm, presence of proton of (CH₂)_n-O-C=O at 3.4 ppm, presence of protons of CH₂ at 2.6 ppm and finally presence of protons of CH₃ at 1.4 ppm. The percentage components of each tercopolymer given in Table (1). The mean molecular weights of the prepared copolymers were determined and given in Table (2).

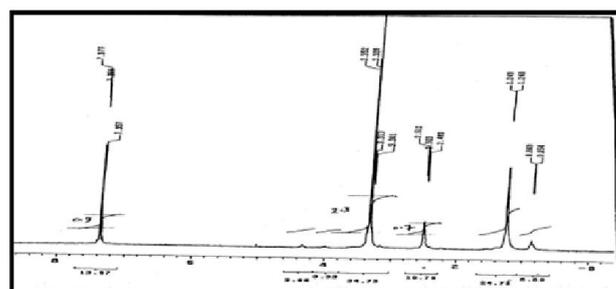


Figure 2. ¹HNMR spectrum of the prepared compound (C).

Table 1. The percentage component of each terpolymer

Copolymer designed	Dodecyl acrylate ester %	Styrene %	Hexadecyl acrylate ester %
A	80	10	10
B	70	10	20
C	60	10	30
D	40	10	50
E	20	10	70
F	10	10	80

Table 2. The mean molecular weight of designed terpolymers

Terpolymer designed	The mean molecular weight	Terpolymer designed	The mean molecular weight
A	226 617	D	273 370
B	255 220	E	290 074
C	265 664	F	126 330

a) Sensitivity of the prepared viscosity modifiers to mechanical stresses

To investigate the effect of the molecular weights of the additives on V.I this was done by calculating V.I for each sample. The results were plotted in Fig. (3).

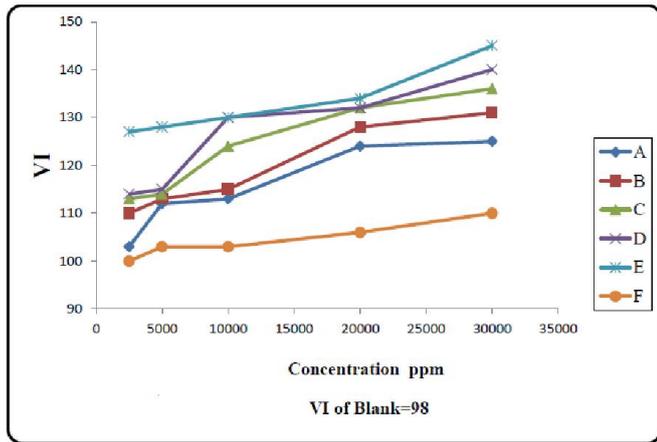


Figure 3. Effect of concentration on VI for lube oil doped with (A, B, C, D, E and F) additives

By studying this figure, it is clear that V.I is directly proportional with the molecular weight of additives. Physically this can be attributed to the increase of the friction between oil layers by increasing the molecular weight. Also it is clear that this effect is highest by the use of D additive. This means that additives D is more efficient as viscosity index improves for lube oil than other prepared additives. The sensitivity of viscosity index (VI) improves 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:

$$s = \frac{C \frac{d(VI)}{d(C)}}{VI \frac{d(C)}} = \frac{d \ln(VI)}{d \ln(C)}$$

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

Plots of [ln VI] against [ln C], are given at Fig. (4), the slopes of the fitted straight lines represent the sensitivity of VI to addition in each case. Fig. (5), the additive (D) displays the highest sensitivity.

b) Study 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*10³ppm-30.00*10³ppm) of each type of polymer additives to the blank oil (SAE 30) at temperatures (40°C, 60°C and

100°C), the rheological results were plotted in Fig. (6). By studying the flow curve (Hongying *et al.*, 2003) of the oil doped with different prepared additives, it obvious that the oil samples behave like simple-Bingham fluids.

$$\tau = \tau_0 + K\gamma^n$$

Where:

- τ.....is the shear stress acting on the fluid [Pa]
- τ₀is the yield value or yield stress
- K.....is the consistency index
- γⁿ.....is the shear rate [s⁻¹].

The degree of correlation was very close to unity. This means that this formula describes the rheological properties of the tested oil samples; namely each one of these samples is a Bingham fluid.

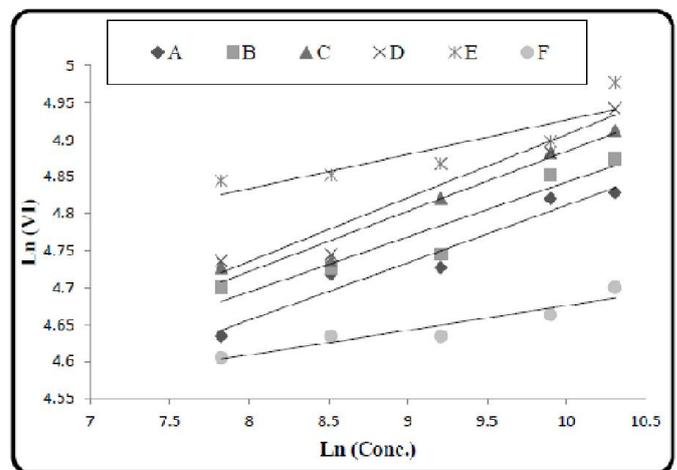


Figure 4. Ln (VI) against Ln (C.) of Additives (A, B, C, D, E and F).

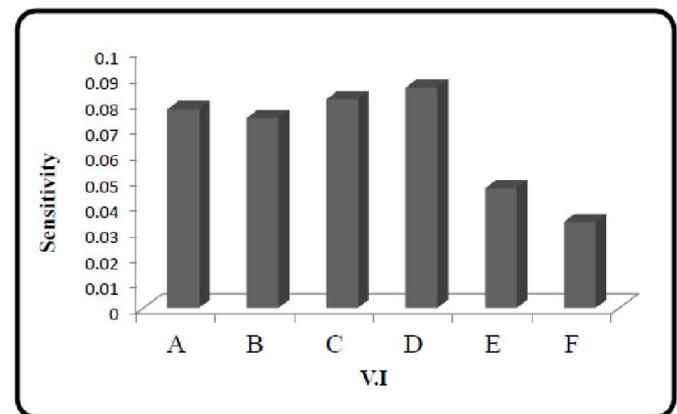


Figure 5. Sensitivity against V.I. for (A, B, C, D, E and F) Additives

c) Studying viscosity shear rate curve

The apparent viscosity (Christopher J. Seeton 2006; Bezot *et al.*, 2000) of each oil sample was measured by the same Brookfield rheometer at different temperatures. The data were

plotted in Table (3) and in Fig. (7) for all samples. The curves shows that the viscosity slightly decreases with the increase of shear rate. Which was concluded by calculating of μ_{app} as

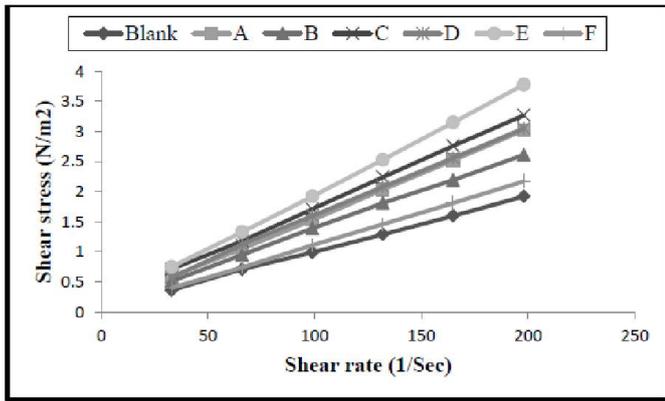


Figure 6. Flow Curve of Additives (A, B, C, D, E and F) with Constant Concentration 30.00*10³ ppm at 100°C

Table 3. Dynamic viscosity with increasing shear rate for lube oil with different additives (A-F) at constant concentration 3.00%

Shear rate (s ⁻¹)	Measurement temperatures	Dynamic Viscosity (m.Pas)						
		Blank	A	B	C	D	E	F
5.02	40°C	85.20	131.8	107.2	135.8	142.1	166.5	98.7
10.00		80.10	125.1	105.4	127.9	134.6	151.9	97.1
15.00		77.10	122.9	101.6	124.2	127.6	148.1	94.5
20.10		75.60	120.4	99.60	122.3	123.1	146.8	91.6
25.10		75.30	118.7	99.50	121.2	120.8	146	88.4
30.00		75.10	118.3	99.40	119.7	114.8	140	88.3
32.70		80.30	117.9	99.30	120	114.2	136	87.9
26.40		34.2	51.1	47.7	60.7	50.2	63.3	40.2
39.60		32.8	50.4	46	57.6	48.9	62.2	38.5
52.80		31.9	50.2	44.8	55.6	48.3	61.6	37.7
59.40	31.7	50.1	44.5	54.6	48.3	61.7	37.5	
66.00	31.7	50	44.1	54.2	48.2	61.7	37.3	
33	60°C	10.7	17.6	15.4	21.7	19.7	22.6	14.4
66		10.2	16.1	14.3	18.7	17.1	20.2	11.3
99		9.92	15.5	14	17.3	16.2	19.3	11.1
132		9.81	15.4	13.7	17	15.8	19.2	11
165		9.72	15.3	13.2	16.7	15.5	19.1	10.9
198		9.66	15.3	13.2	16.5	15.4	19.1	10.8
		100°C						

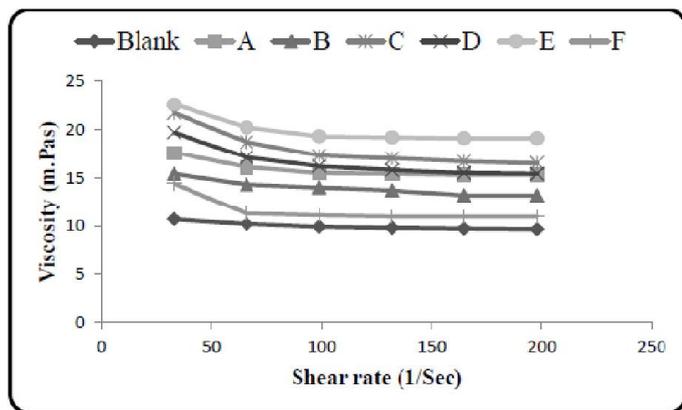


Figure 7. Viscosity – Shear Rate Curve of (A, B, C, D, E and F) Additives at 100°C

$$\mu_{app} = \tau / \dot{\gamma} = \tau_0 / \dot{\gamma} + K$$

Where

μ_{app} is the apparent viscosity.

For oil samples with additives, it is clear that, at low shear rates, all blends have weak non-Newtonian ^(13, 14) behavior represented as shear thinning which is described as pseudo plastic behavior. As shear rate increases, the non-Newtonian ⁽¹⁵⁻¹⁷⁾ behavior disappears and all blends behave as a Newtonian fluid. 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, and by changing the temperature (40°C, 60°C, and 100°C), it was found that all the samples have the same behavior as simple Bingham.

Conclusion

1. All prepared terpolymers were found to be soluble in lube oil SAE-30 free of additives.
2. The structures of the prepared terpolymers were elucidated by Fourier Transform Infrared Spectroscopy (F.T.I.R.), Proton Nuclear Magnetic Resonance (¹H-NMR), and Gel Permeation Chromatography (GPC).
3. The rheological behavior of lube oil (SAE-30) was studied and it was found that they behave as Bingham fluids.
4. The sensitivity of the prepared terpolymers to mechanical stresses was studied and it was found that the sensitivity increase with increasing the molecular weight of the prepared additives.

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