RESEARCH ARTICLE   OPEN ACCESS

The Effect of Some Additives on the Rheological Properties of Engine Lubricating Oil

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ABSTRACT
The present work deals with the evaluation of some viscosity index improving additives. Three esters were prepared by esterification of acrylic acid with alcohols having different alkyl chain length. The structures of the prepared compounds were confirmed by Infra Red Spectroscopy. Three polymeric compounds were prepared by free radical polymerization of the different acrylates with vinyl acetate. The molecular weights of the prepared compounds were determined by Gel Permeation Chromatography. The prepared copolymers were evaluated as viscosity index improvers for lube oil and the rheological properties of lube oil were studied. It was found that the efficiency of the prepared additives as viscosity index improvers increases with increasing the molecular weight and concentration of the prepared copolymers and it was found that the apparent viscosity decreases with an increase in temperature.
Key words: Lubricating Oil, Lubricating Oil Additives, Viscosity Index, Rheological properties.

I. INTRODUCTION

Tribology is the science and technology of interacting surfaces in relative motion and of related subjects and practices [1]. Tribology mainly focuses on friction, and wear, which are normally improved by the presence of oil [2, 3]. Reduction of friction and wear leads to increase in service life, less downtime and lower operating costs [2,4]. The engine tribologist is required to achieve effective lubrication of all moving engine components. Lubrication is simply the use of a material to improve the smoothness of movement of one surface over another, and the material which is used in this way called a lubricant [5]. An additive is a chemical substance added to a lubricant base stock to impart specific properties by enhancing the desirable properties already present in the lubricants oil [6], the most important is viscosity index improvers. (VI) improvers are used to limit the rate of change in viscosity with temperature. Performance of viscosity index improvers depends on the behavior of the polymer molecules in the oil, polymer solubility, molecular weight, and resistance to shear degradation [7, 8]. The VI improvement increases regularly with the increase in the molecular weight of the synthesized additives [9].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 [10]. Fluids may be classified into Newtonian and non–Newtonian according to their flow character. Another important classification is whether they are time

dependent or not [11].There are several types of non-Newtonian flow behavior, characterized by the way a fluid's viscosity changes in response to variation in shear rate. The most common types of non-Newtonian fluids may encounter include: A Bingham plastic material, the apparent viscosity indicates the sum of the shear resistance of the liquid of Newtonian behavior and the shear resistance of the particle structure which decreases with increasing shear rate [12].A third type of time independent flow is the decrease of apparent viscosity with shear rate. A Fourth type of time independent flow behavior is that exhibited by the Shear Thickening (or Dilatant) fluid. In this case, the apparent viscosity increases reversibly as the shear rate increases [12].

II. EXPERIMENTAL

1. Esterification of Acrylic Acid with different types of Alcohols

The esters were prepared by reacting 1 mole of acrylic acid with 1 mole of different types of alcohol (1-decanol or dodecanol or 1-tetradecanol). The reactions were carried out in a resin kettle in presence of 0.5% p-toluene sulfonic acid as a catalyst and 0.25% hydroquinone as inhibitor for the polymerization of acrylic acid and xylene as a solvent(to aid water removel). The esterification reactions were carried out under a slow stream of deoxygenated nitrogen; the reaction mixture was agitated using mechanical stirrer at 500 rpm. The reactants which were mixed with an equal weight of

xylene were gradually heated from room temperature to 130o C ± 5o C using awell controlled thermostat. The extent of reaction was followed by monitoring the amount of liberated water to give products: [decyl acrylate (A) or dodecyl acrylate (B) or tetradecyl acrylate (C)].

2.   Purification of Prepared Esters

The prepared esters were purified according to the following procedures:

- Suitable amount of charcoal was added to the esters and allowed to reflux for 4 hours and filtered.
- Unreacted acid was neutralized by 0.5 N sodium hydroxide in separating funnel and shake well. The entire process was repeated several times to ensure complete removel of unreacted acid.
- The purified ester was then washed several times with distilled water to remove any traces of sodium hydroxide then the ester was left overnight on calcium chloride anhydrous for drying. It was then removed by filtration and xylene was removed by distillation. The ester is ready to use in the copolymerization.

3.   Infra Red Spectroscopic Analysis

I.R Spectra of the synthesized esters were measured by using F.T.I.R. Spectrometer Model Type Mattson- Infinity Series Bench top 961 for the purified esters.

4.   Synthesis of Polymeric Additives Based on Alkylacrylate

Polymeric additives were prepared by free radical copolymerization of vinyl acetate monomer with the prepared esters, the polymerization was carried out in a 4- necked round bottom flask equipped with a stirrer, efficient condenser, thermometer, an inlet for the introduction of nitrogen, the nitrogen was dried by passing it through silica gel. In the flask was placed 1 mole of the prepared esters and 1 mole of vinyl acetate monomer, the desired weight of initiator (benzoyl peroxide), then heated for 8 hours at 60°C   5°C in the presence of toluene as a solvent. When the reaction was completed, the temperature was allowed to reduce at room temperature, then the reaction mixture was poured drop by drop in cooled methanol with continuous stirring, filtered off and dried.

5.   Determination of the Mean Molecular Weight of the Prepared Copolymers

Molecular weights of the prepared copolymers were determined by using Gel Permeation Chromatography (GPC), Water 600E.

6.   Evaluation of the Prepared Copolymers as Lube Oil Additives

The soluble copolymers were evaluated as viscosity index improver for lube oil and rheology using base oil (SAE 30) through the viscosity index test (V.I.) according to the ASTM D-2270-87.The kinematic viscosity of the oil containing the tested copolymer was determined at 40°C and 100°C. Different quantities ranging between 0.00 and 30.00x103 ppm were used to study the effect of copolymer concentration on V.I.

7.   Investigation of Rheological Properties of Lube Oil

Rheological studies were performed on an oil samples using Brookfield Rheometer (Model DV-III+).The following are the specifications of this rheometer:

- Shear Rate (Sec-1)
- Shear Stress (N/m2)
- Viscosity (mPa.s)

Also the effect of temperature increase on the rheological properties of the oil was investigated by using controlled oil path unit attached to the Brookfield Apparatus. Then, series of experimental was performed to determine the effect of prepared additives on the rheological properties of the engine oil.

To study the effect of additive concentration of another series of the experimental was performed using different concentrations starting from (0.25-3.00) % by weight.

To illustrate the effect of temperature on the performance of different additives, one fixed concentration was used and the rheological properties were measured at different temperatures (40oC, 60oC and 100oC).

III. RESULTS AND DISCUSSIONS

Three esters were prepared via esterification reactions of acrylic acid with C10, C12, and C14 alkanols. The IR spectroscopy was used to elucidate the completion of the esterification reactions. All esters [A, B, and C] afforded similar I.R spectrum. Figure (1) represented IR spectrum of ester (C) which shows that:

1) No sign for the presence of strong absorption band at 3200 cm-1of aliphatic
(-OH) group or the characteristic absorption bands of the carboxylic acids. These bands are broad peak extending from 3300 cm-1 to 2500 cm-1 due to hydrogen bonded (-OH) and the (-CH) stretching vibrations.
2) Appearance of the ester group bands at 1720±10 cm-1 and 1250±100 cm-1 due to (C=O) and (C – O – C) stretching respectively.
3) The band for methylene group (-CH = CH-) appear near 1465 cm-1.

4) The bands for methyl group, which appear, near 1370 cm-1to1465 cm-¹.
5) The band for (- C – H) aliphatic appears near 2840 cm-1 & 2950 cm-1.

Disappearance of the strong band at 3200 cm-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 reactions. On the other hand, the formation of the bands, which represents the ester group, i.e., (C=O) and (C – O – C) vibration reveals that the esterification reaction is complete. The polymeric additives were prepared by addition polymerization of vinyl acetate and prepared alkyl acrylate. The mean molecular weight of copolymers is given in Table (1) which indicates that the molecular weight of copolymer increases with increasing the alkyl chain length of alcohol used.

1.   Effect of Molecular Weights of Additives on Kinematic Viscosity and Viscosity Index of Lube Oil

The first experimental series was performed to investigate the effect of the molecular weights of the additives on both kinematic viscosity (υ) and viscosity index (VI) this was done by measuring υ and the calculated VI for each sample shown on Figure (2), which indicates that VI of lube oil is in direct proportionality with the molecular weight of additives. Physically this can be attributed to the friction between oil layers increasing with increasing the molecular weight of additives.

The sensitivity of viscosity index improvers to mechanical stresses increases with increasing the molecular weight of the prepared additives. To clarifying this point the sensitivity of VI to addition was calculated in each case.
This is defined as:

$$S = \frac{C}{VI}\frac{d(VI)}{dC} = \frac{d\ln(VI)}{d\ln(C)} \quad (1)$$

Where C' ….. is the Concentration of polymer,(ppm)
Plots of ln VI against ln C are shown in Figure (3); the slopes of the fitted straight lines represent the sensitivity of VI to addition in each case. Figure (4) shows that the copolymer C display the highest sensitivity.

2.   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 concentrations (0.25 % up to 3.00 % by wt.) of each type of polymer additives to the blank oil (SAE 30) at temperatures (40 oC, 60 oC and 100oC) , the rheological results at were plotted on Figures (5 – 13).

By studying these data were drawn to fit the linear Bingham model in the form:

$$\tau = \tau o + K\gamma\bullet \quad (2)$$

Where
τ ……...is the shear stress acting on the fluid [Pa]
τo……..is the yield value or yield stress.
K……..is the Consistency Index
γ•……..is the shear rate [s-l].

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 simple-Bingham fluid with yield values and consistency indices.

3.   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 Figures (14-22), the curves show that the viscosity slightly decreases with the increase of shear rate, which was concluded by calculating of μapp as = τ / γ• from this equation are obtained:

$$\mu app = \tau / \gamma\bullet = \tau o / \gamma\bullet + K \quad (3)$$

Where
μapp …....is the apparent viscosity.

These waves showed that for the A and B additives, the viscosity tends to reach a constant value at about 30 S-1 shear rate at 40o C and 60oC and above 100 S-1 at 100oC, on the other hand, the additive C displays a Newtonian behavior at 40oCand 60oC as evidenced by the nearly constant values of μapp or all shear rates [13].

IV. CONCLUSIONS
The following conclusions could be derived from the results of this study:
1. All the prepared copolymers were soluble in lube oil.
2. All the prepared polymeric additives improved the viscosity index of the lubricating oil engine.
3. Almost all treated oil samples show a simple Bingham behavior except for some concentrations of C additive which show a Newtonian behavior.
4. The apparent viscosity of the treated oil samples decreases by the temperature increasing. The rate of this decrease is different according to the type of the polymeric additive.

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edition, Amsterdam: Elsevier, Pages 2, 12,22, 52, 62-67, 77.

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Table (1) The mean Molecular Weight of the prepared Copolymers

Components	Mean M. wt.
A	139,831
B	255,949
C	272,352

Figure (1) I.R. Spectrum of C

Effect of concentration on VI for lube oil doped with (A-C)additives
VI of Blank =98
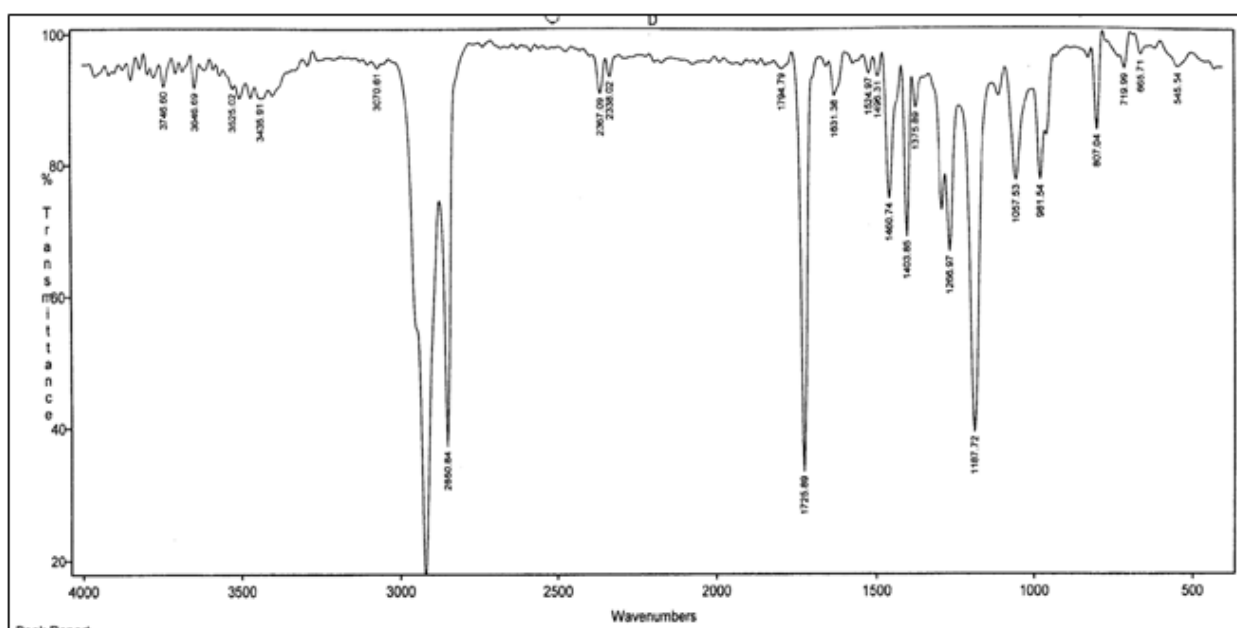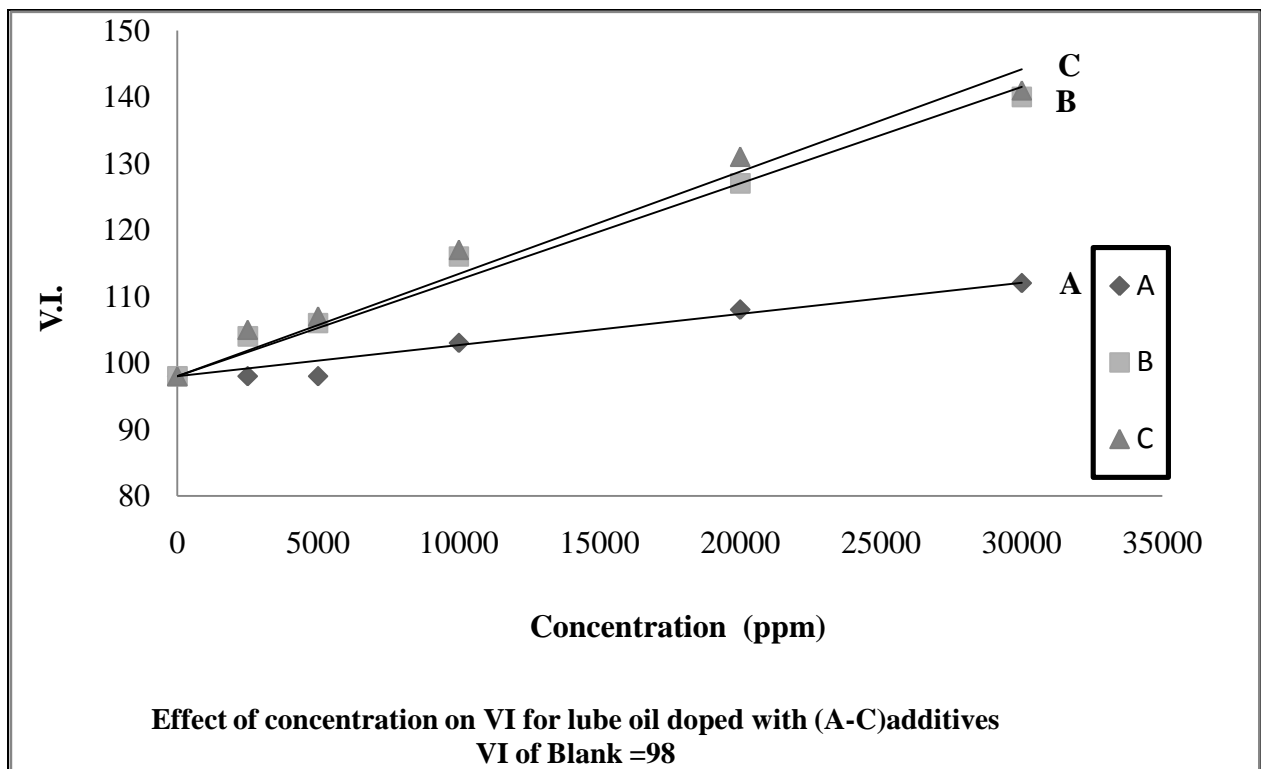
Figure (2) Effect of concentration on VI for Lube oil doped with (A-C) additives

$$y = 0.073x + 3.958$$

$$y = 0.119x + 3.673$$

$$y = 0.123x + 3.656$$
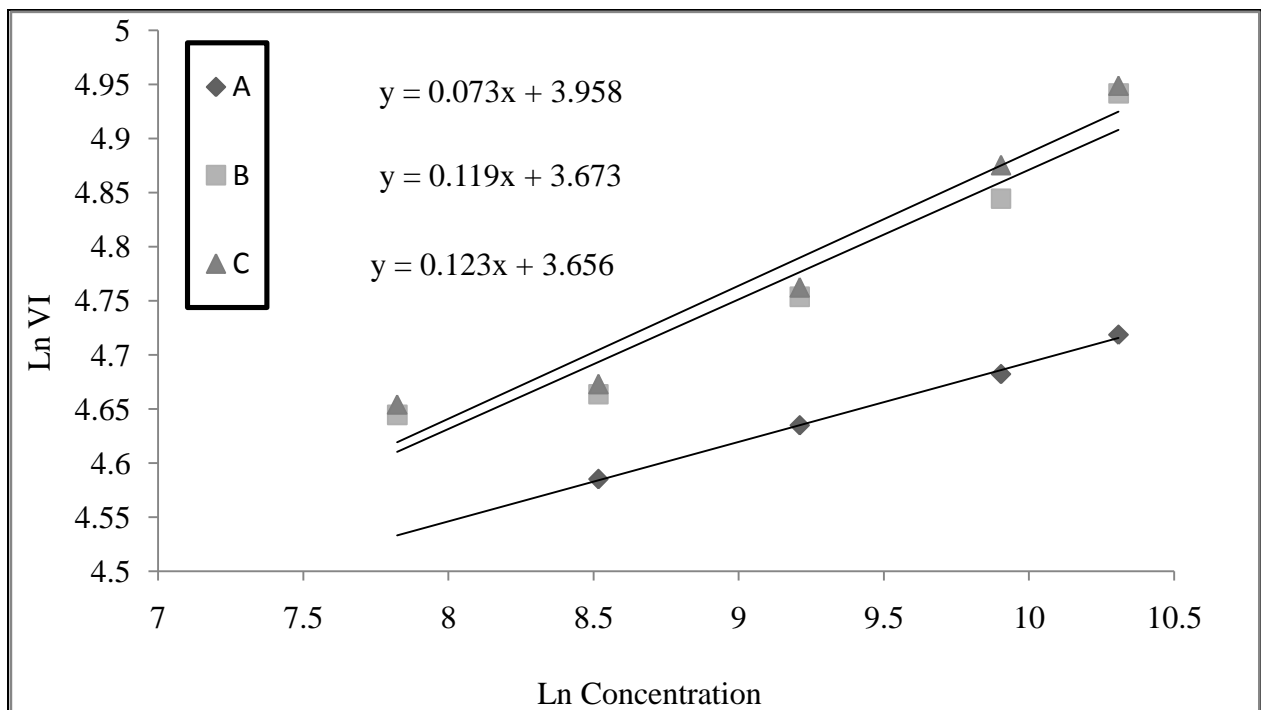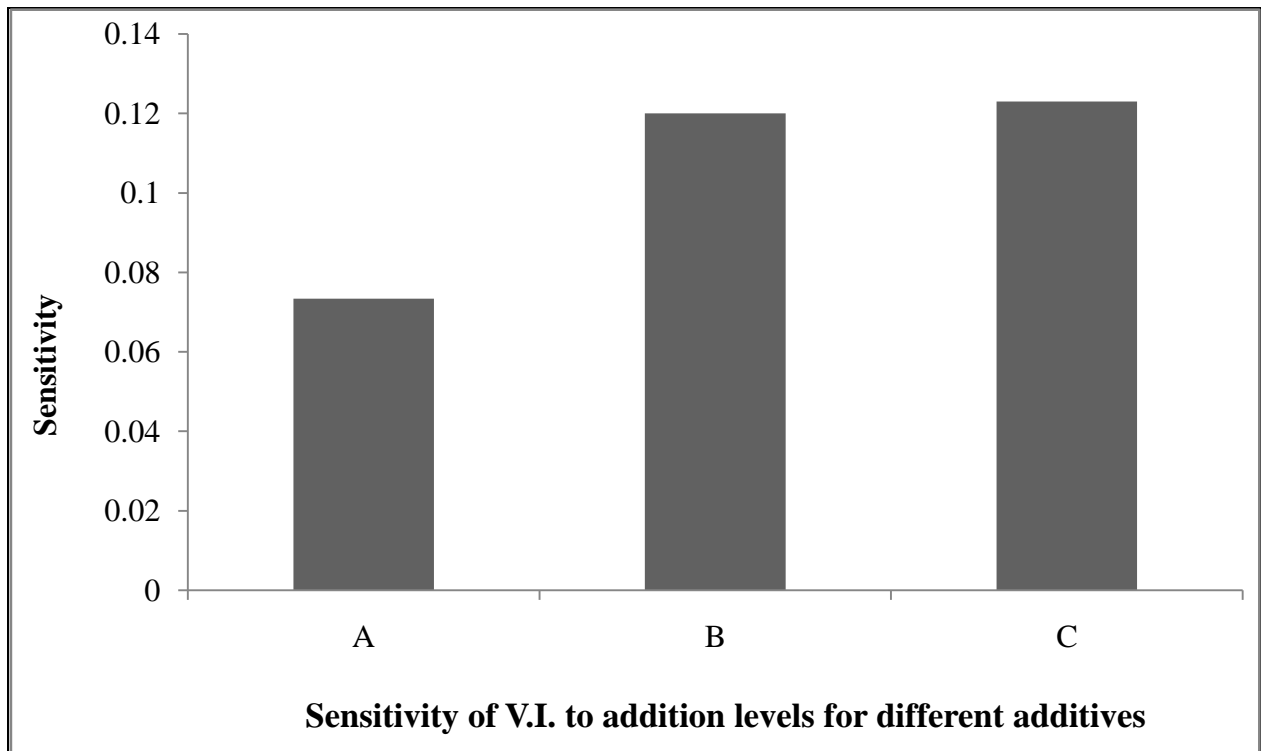
Figure (3) Ln VI against Ln Concentration

Figure (4) Sensitivity of VI to addition levels for different additives
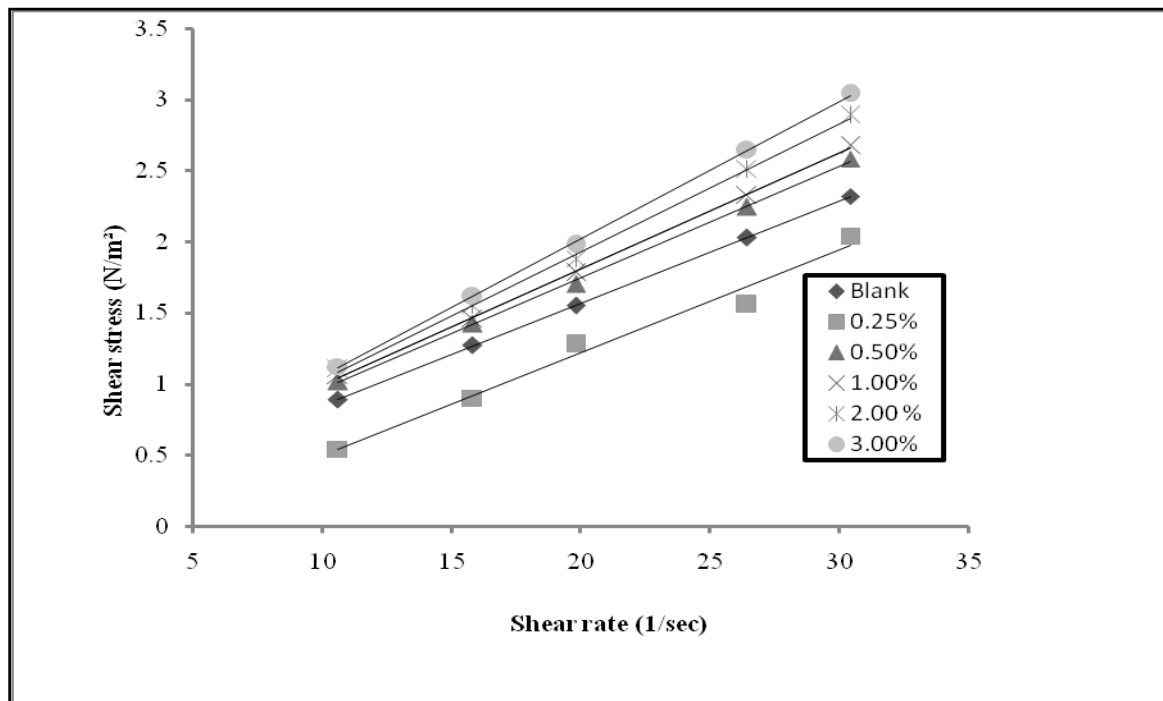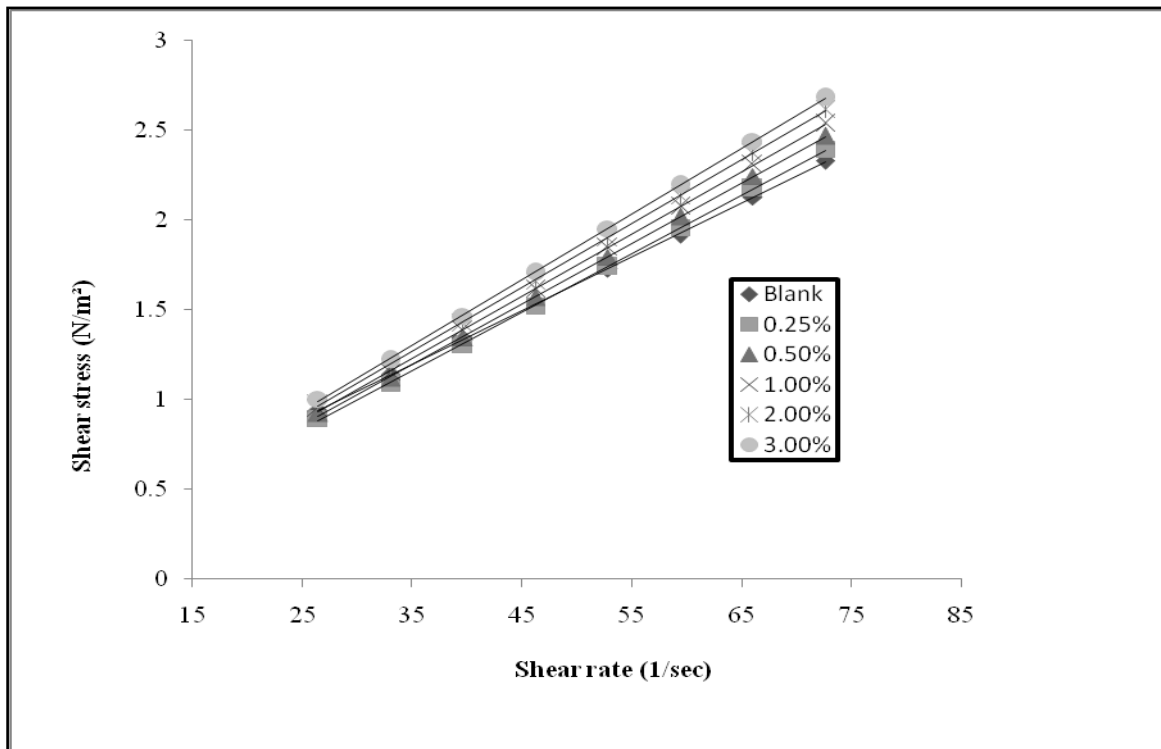

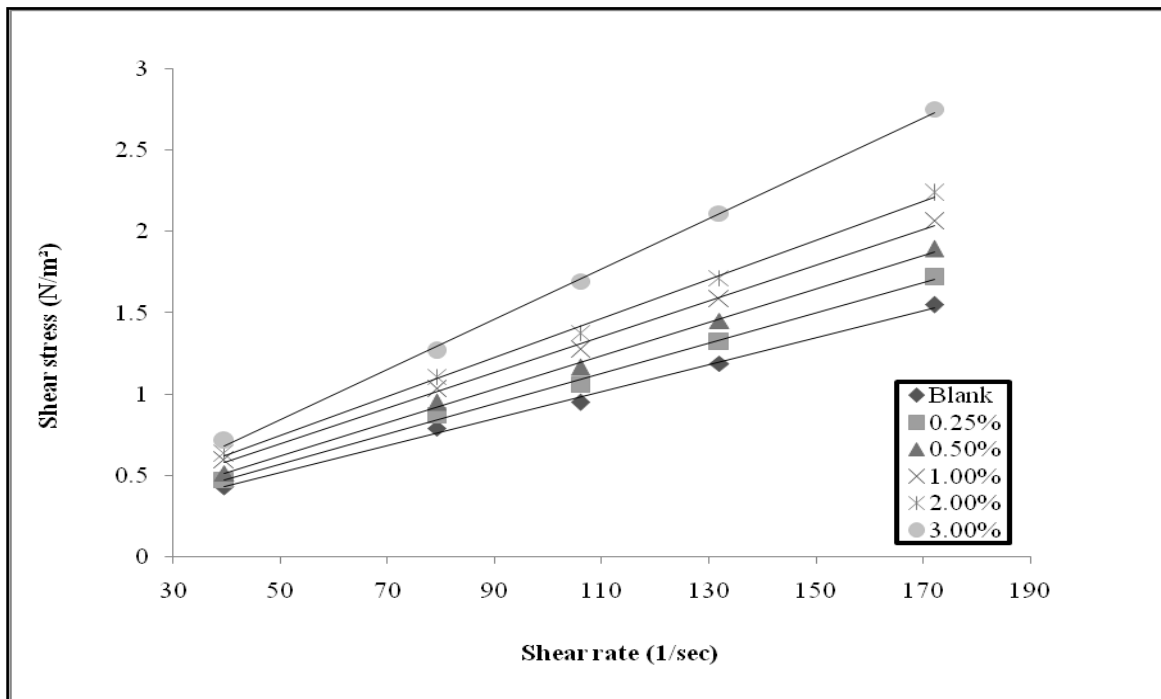**Figure (5) Flow curve of A additive at 40°C**

Figure (6) Flow curve of A additive at 60°C

Figure (7) Flow curve of A additive at 100°C
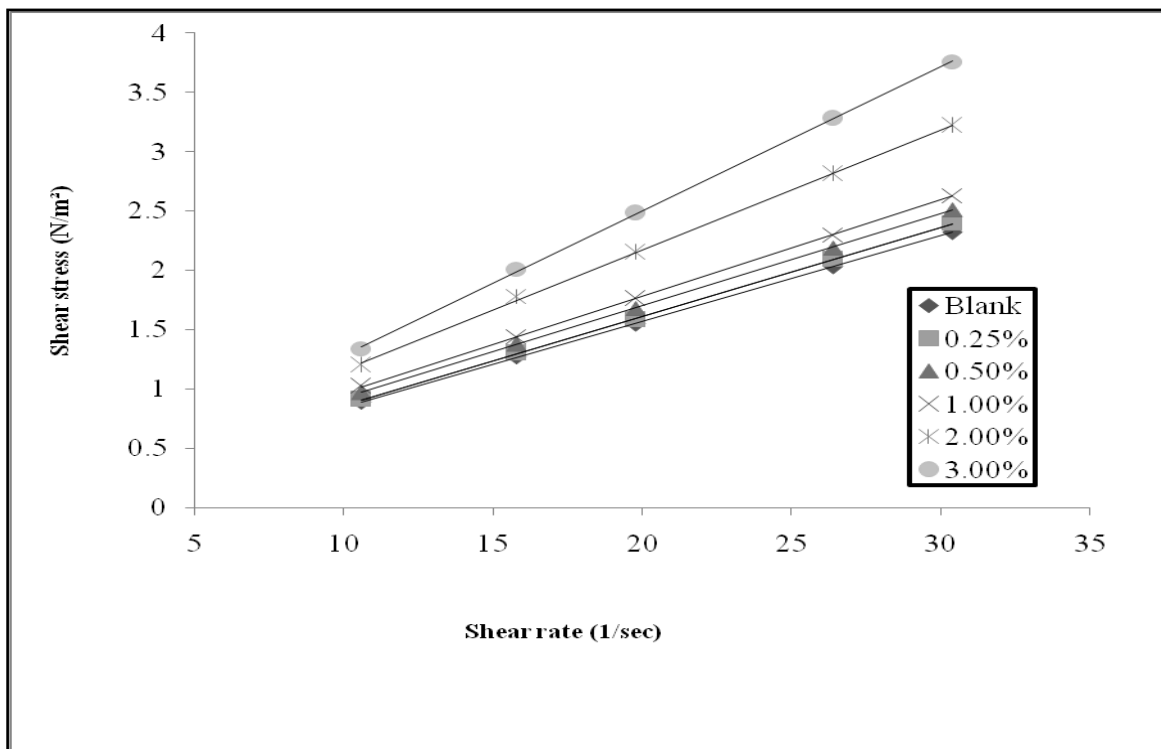
Figure (8) Flow curve of B additive at 40°C
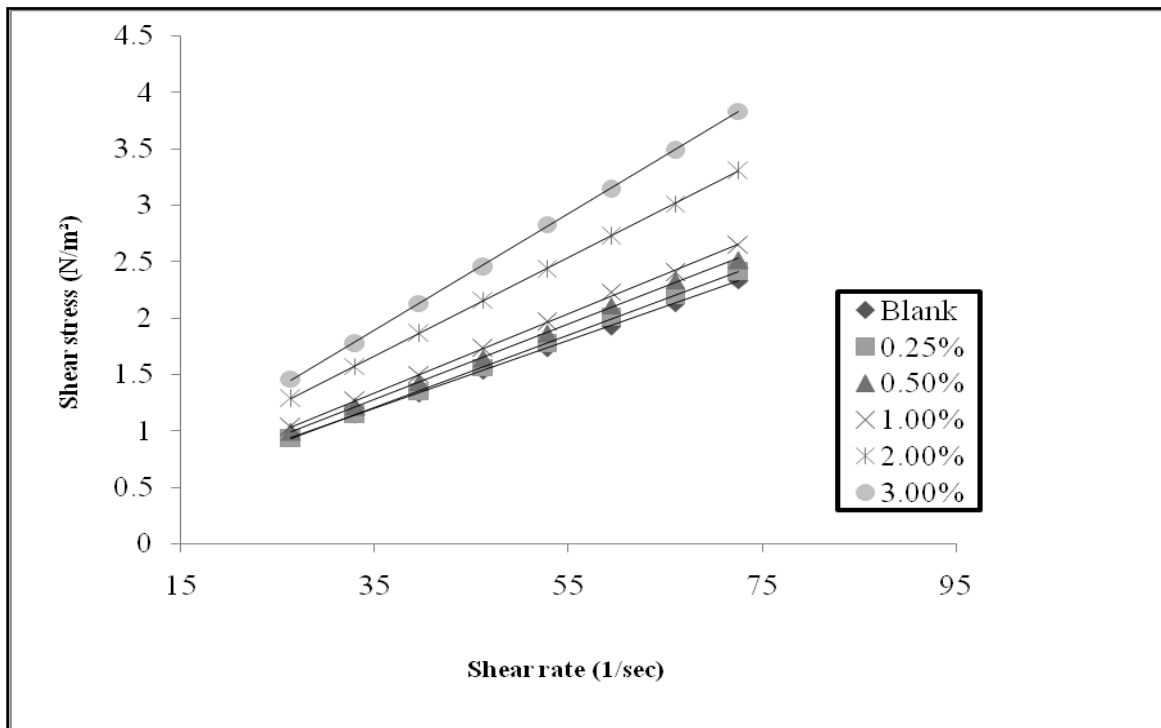
Figure (9) Flow curve of B additive at 60°C
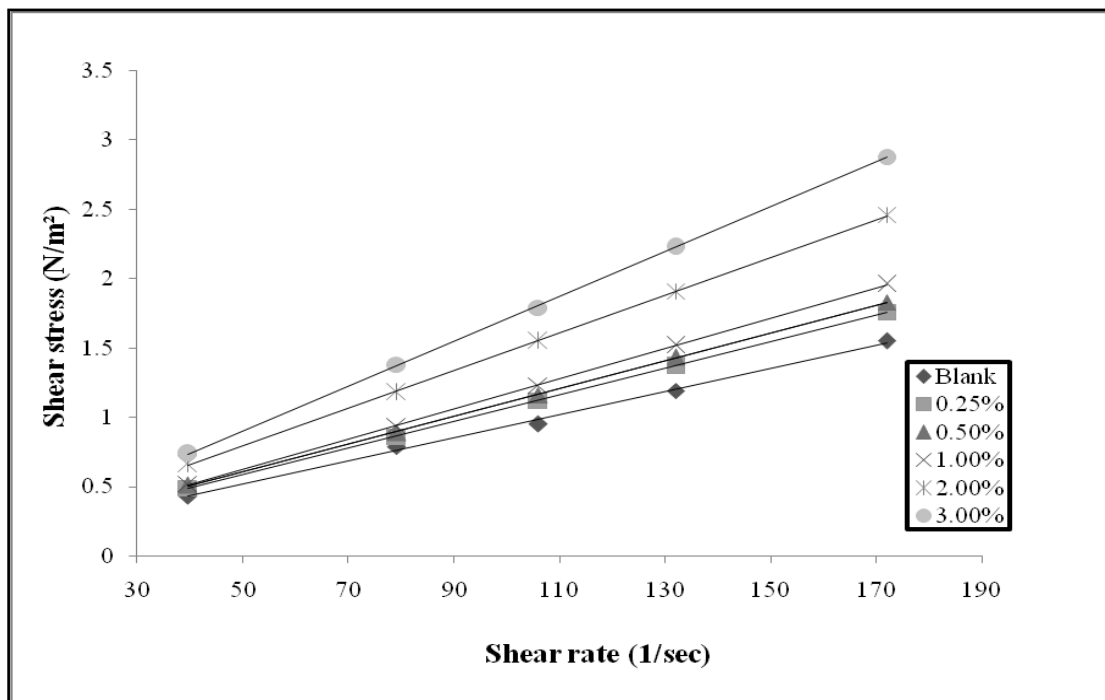
Figure (10) Flow curve of B additive at 100°C
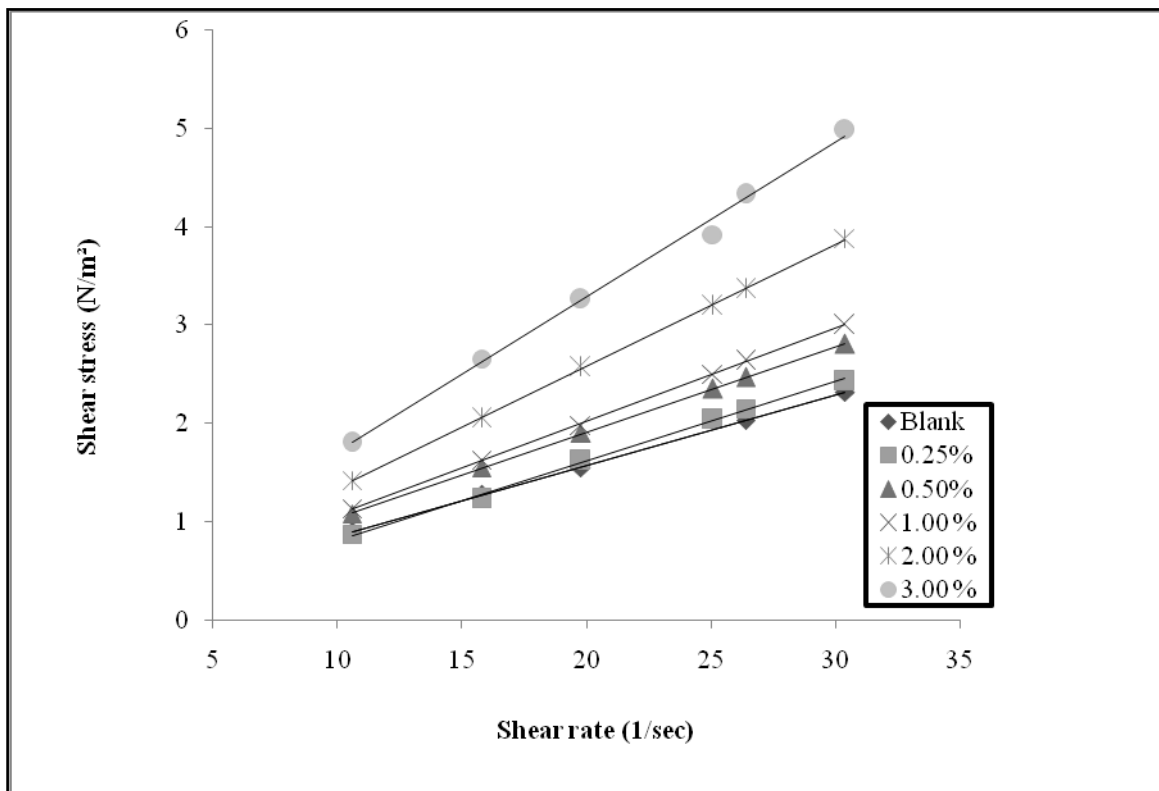
Figure (11) Flow curve of C additive at 40°C
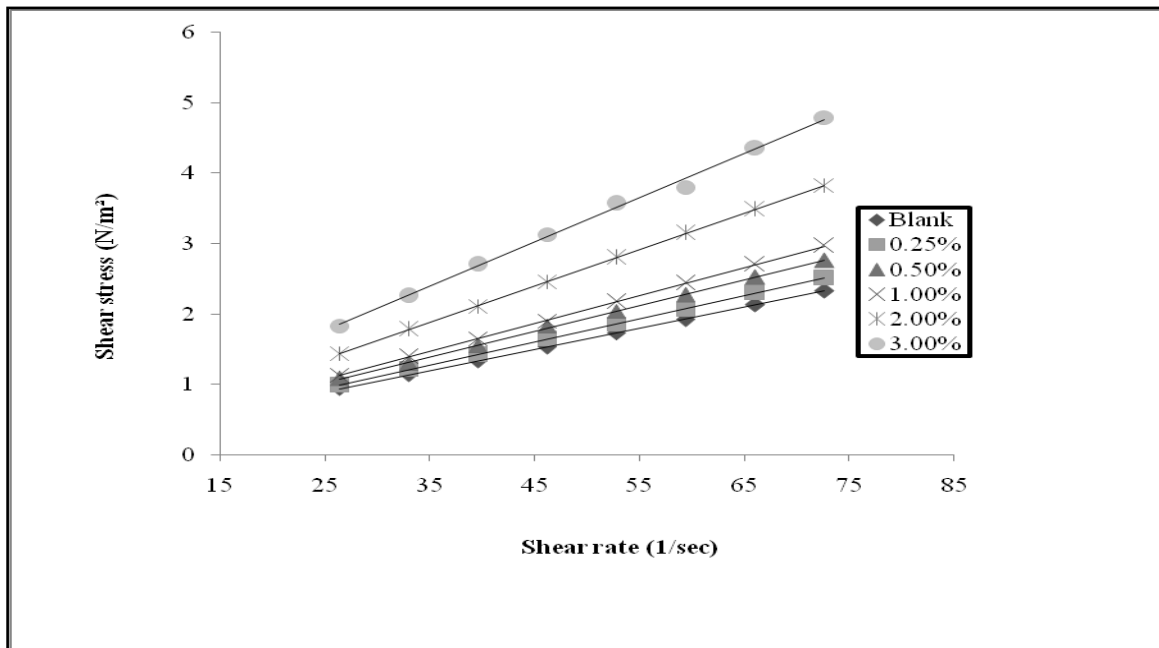
Figure (12) Flow curve of C additive at 60ºC
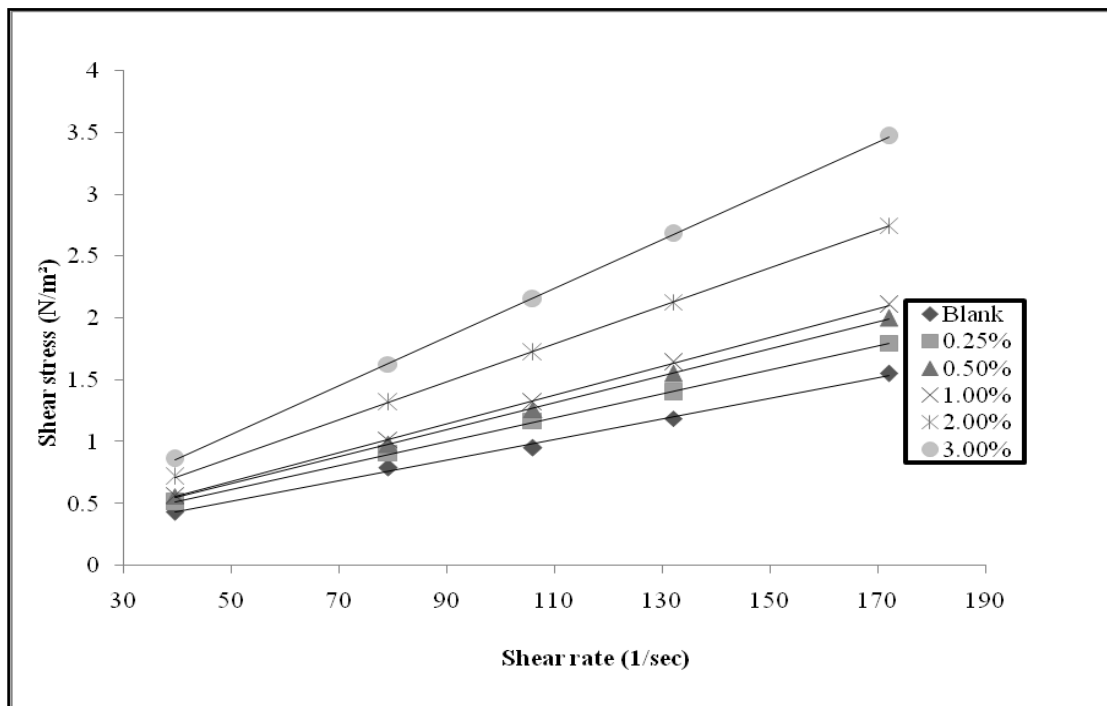
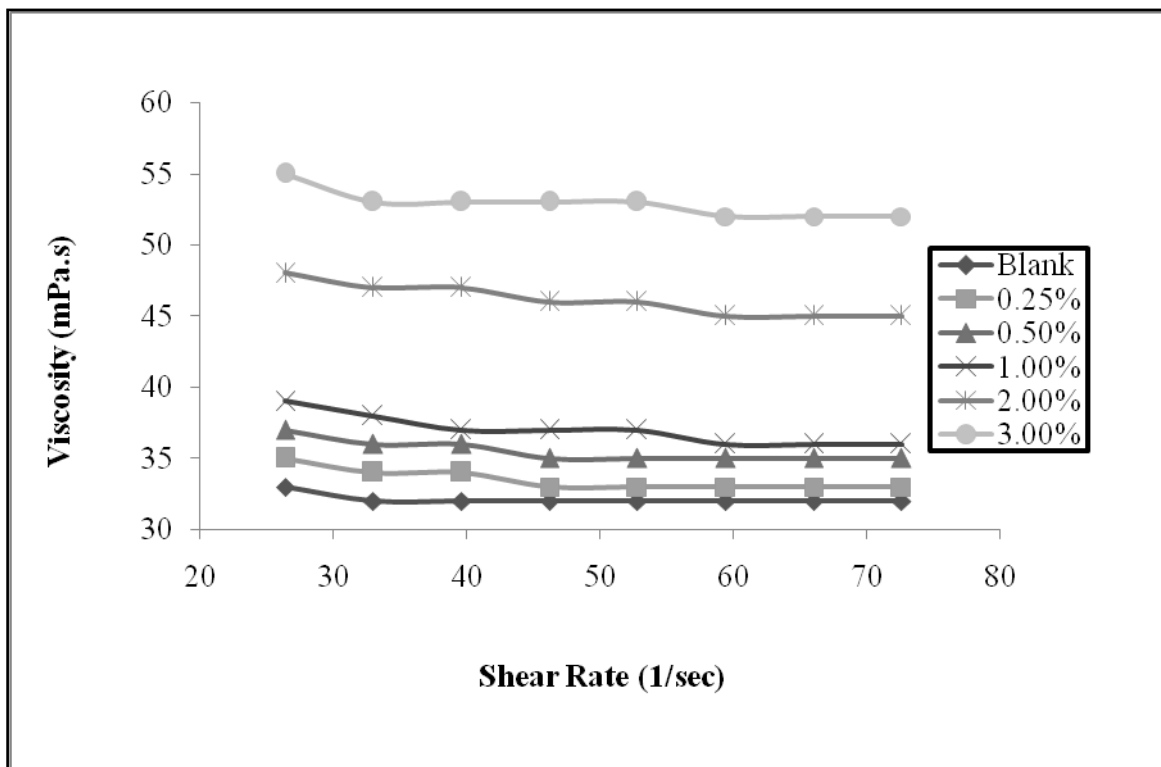

Figure (13) Flow curve of C additive at 100ºC
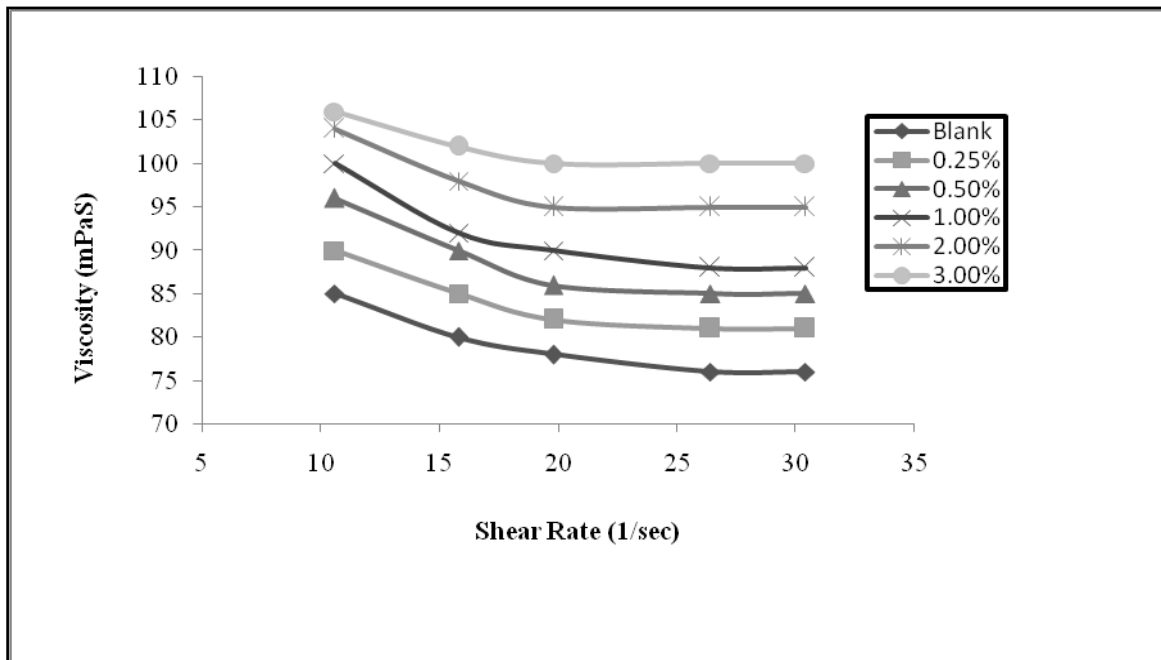
Figure (14) Viscosity-Shear rate curve of A additive at 40°C
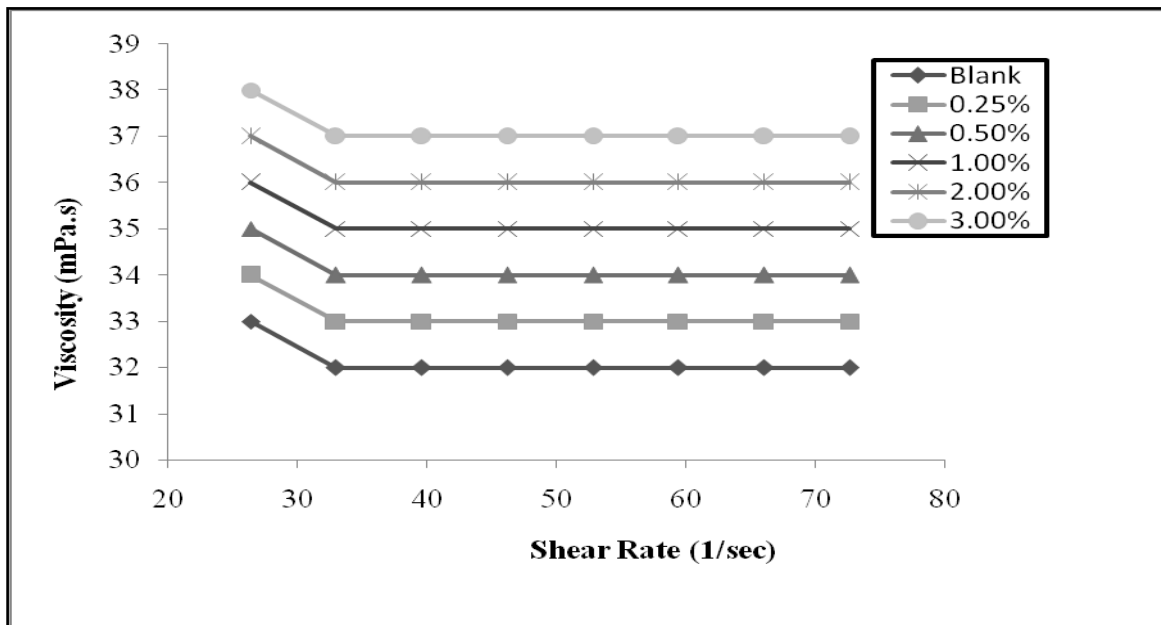
Figure (15) Viscosity-Shear rate curve of A additive at 60°C
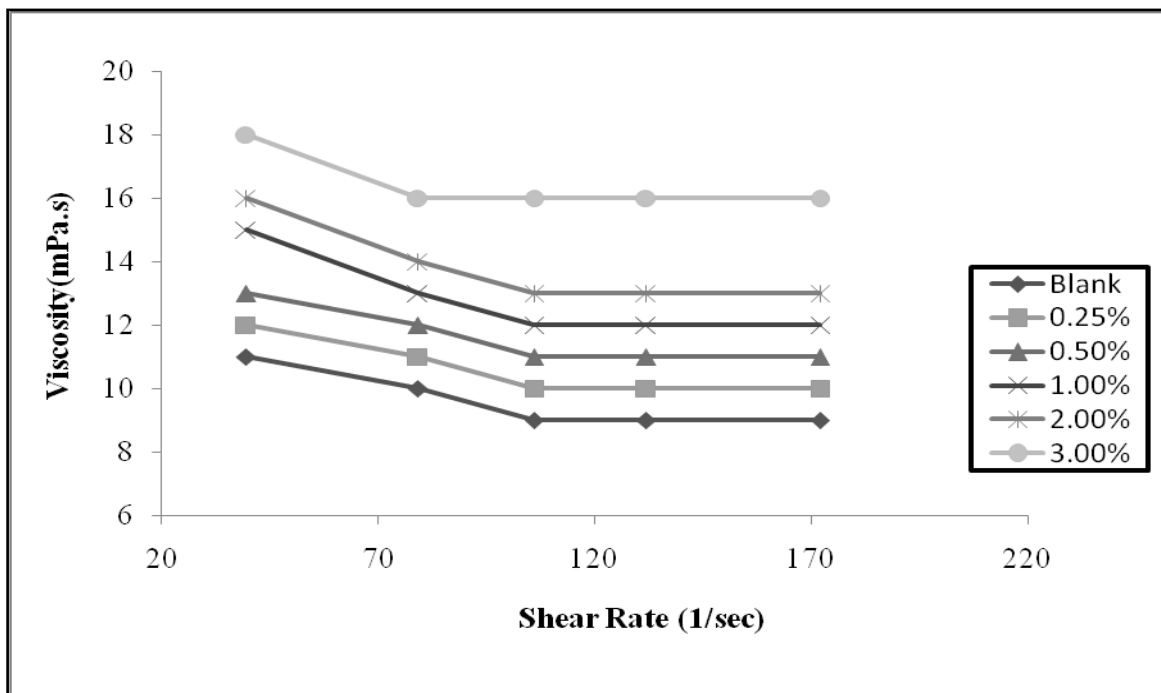
Figure (16) Viscosity-Shear rate curve of A additive at 100°C
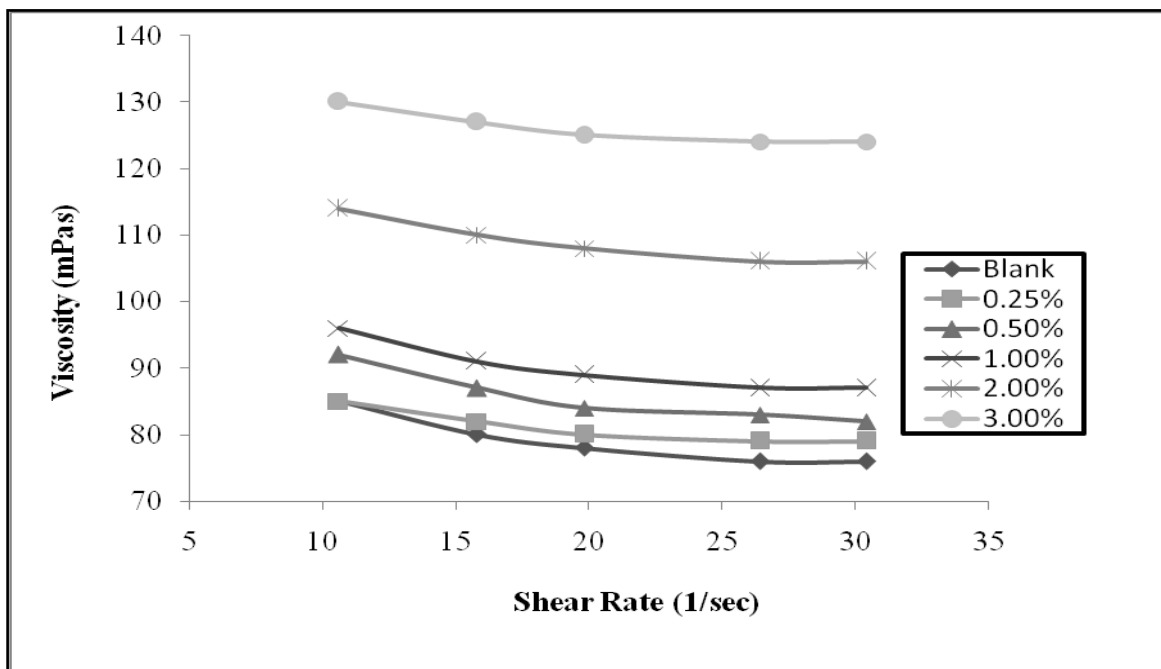
Figure (17) Viscosity-Shear rate curve of B additive at 40°C
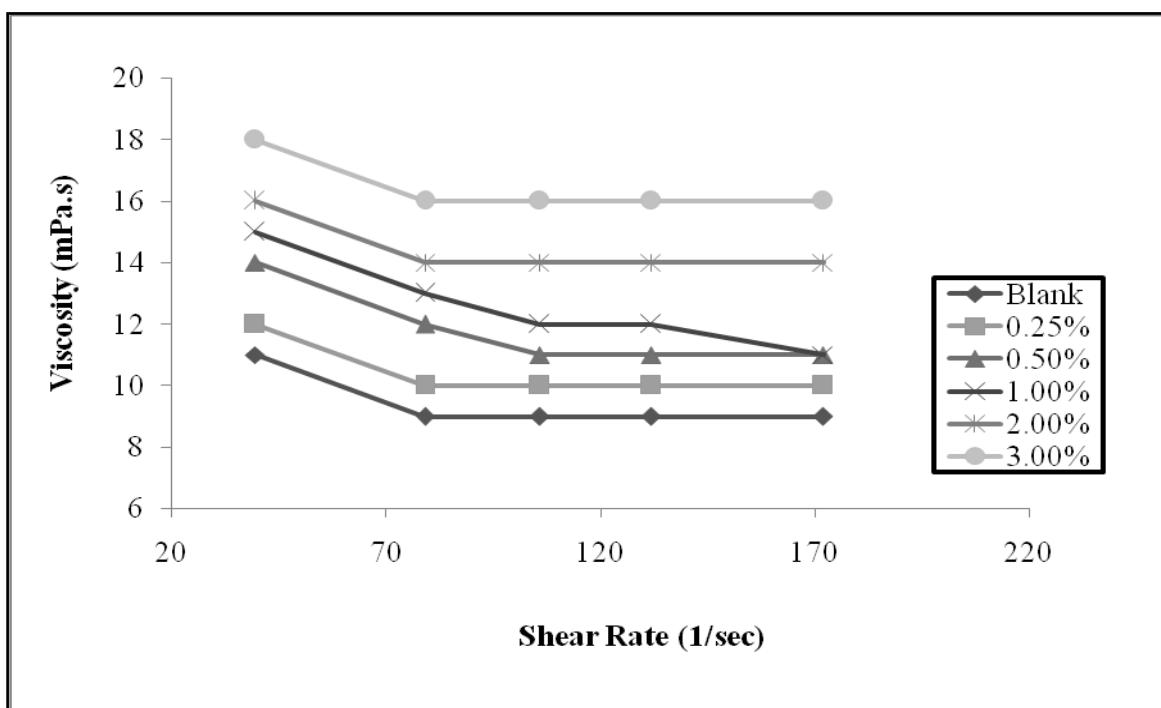
Figure (18) Viscosity-Shear rate curve of B additive at 60°C

Figure (19) Viscosity-Shear rate curve of B additive at 100°C
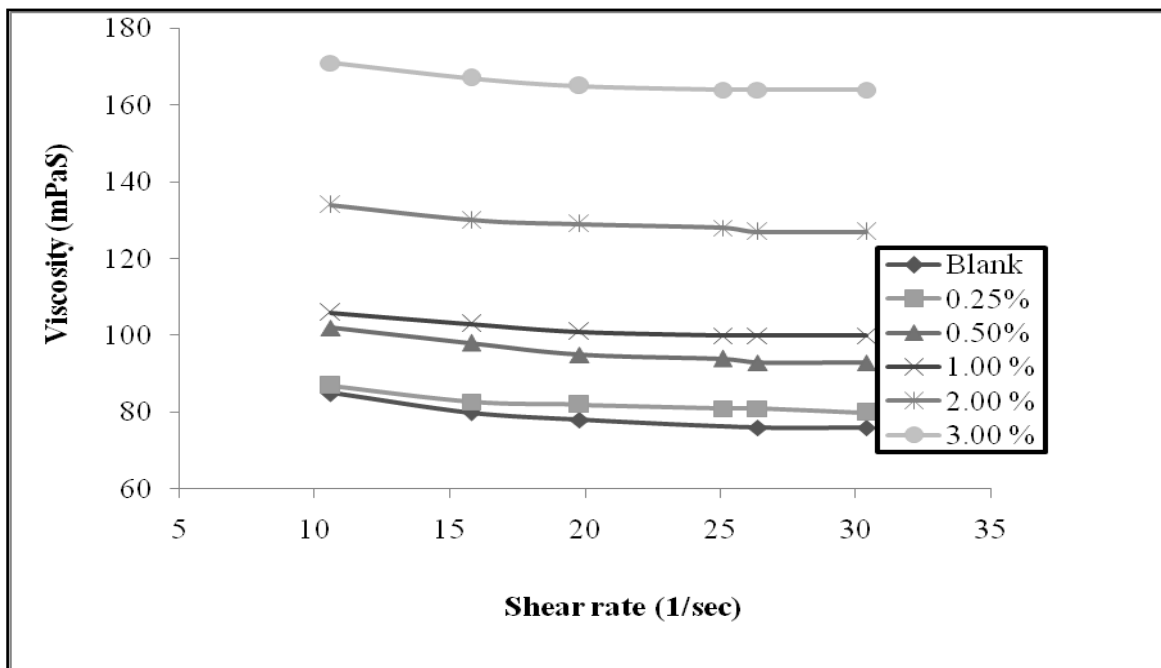
Figure (20) Viscosity-Shear rate curve of C additive at 40°C
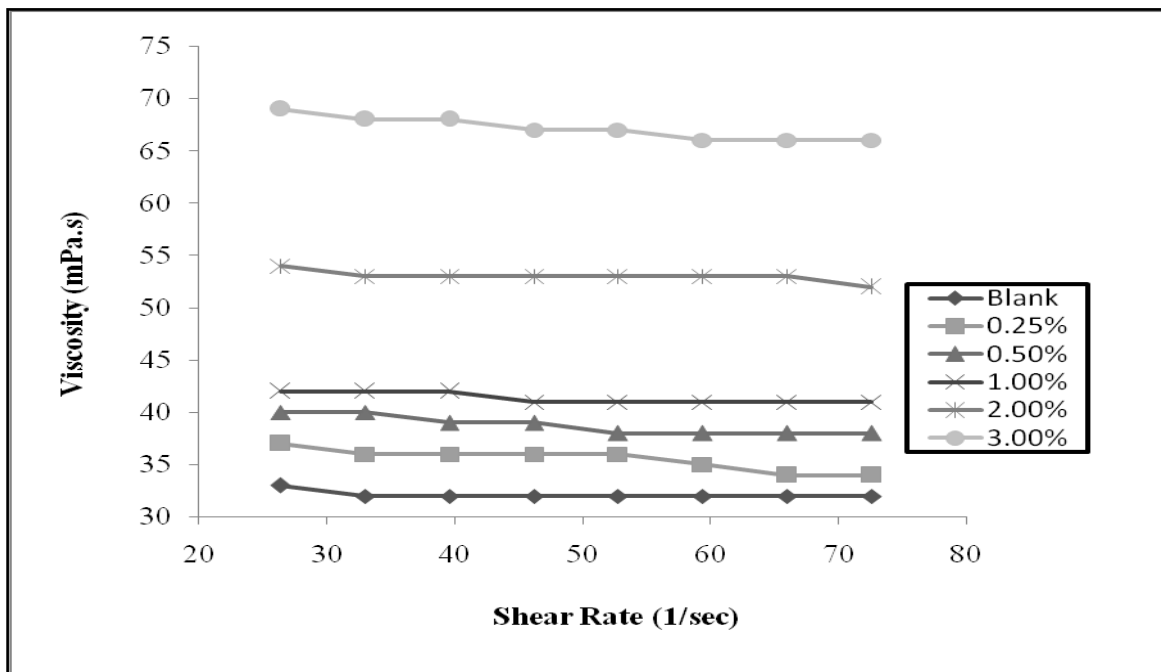

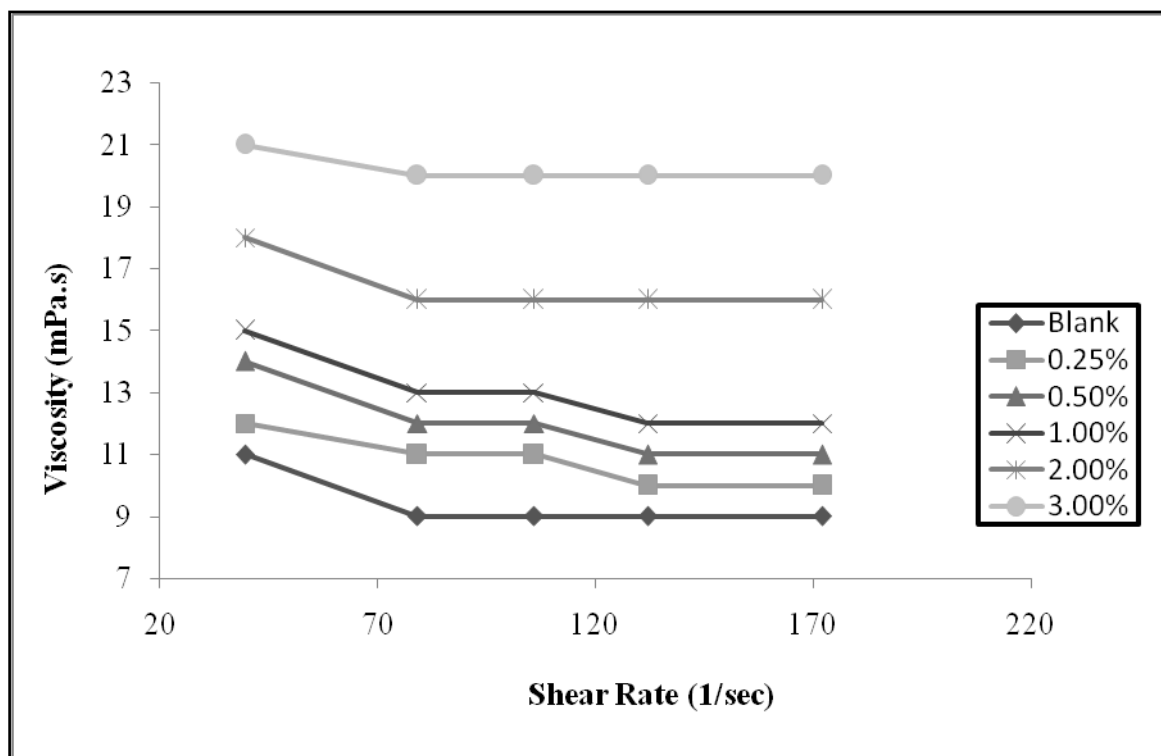**Figure (21) Viscosity-Shear rate curve of C additive at 60°C**

Figure (22) Viscosity-Shear rate curve of C additive at 100°C