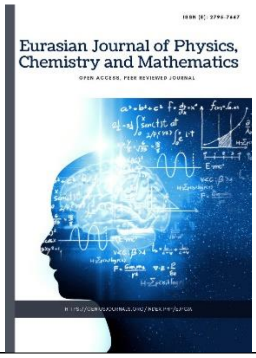

Synthesis and Characterization of some new copolymers as drag reduction agent for study rheology light Basra crude oil

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ABSTRACT

A series methods used to increase the flow of crude oil through the pipes to reduce the economic cost and increase the flow rat of crude oil, the most important of these methods is the addition of small amounts of polymers to reduce the drag reduction flow crude oil, In this study, three polymers of different structures were prepared , P1 linear condensation polyester and different branching functional group by free radical polymerization P2 and P3, This polymers were characterization by using different techniques such as FTIR, ^{1}H-NMR and ^{13}C-NMR, The polymers were added as drag reducing agent for crude oil in different concentrations (100-600 ppm) at 35°C , The percentage drag reduction was calculated by using circulation flow system device with different temperatures(35,45 and 55°C).

Keywords: crude oil, polymers

1. Introduction

Many international reports predicated the growth of crude oil. At least 80% of the world's energy needs will depend on products of petroleum such as oil, natural gas.so because of high viscosity for heavy and light crude oil. This makes it difficult to produce and refine. All exporters of crude oil in the international energy markets are face tough challengers are needs different technology in products refines and transfer. Transporting crude oil through the pipeline is the most economical way to transport crude oil. The rheological properties of petroleum crude oil are very useful for all properties in which liquids are transported from place to another.[1]

Drag reduction can be achieved by using non-additive or by additive technique. The non-additive technique requires use of physical properties of the flow medium to achieve drag reduction, such as riblet, dimples, oscillating walls. compliant surfaces and micro bubbles [2].Additive technique is technique use to add chemical substance to increase flow fluids and that addition lead to drag reduction, However non-use in crude oil, additives technique for drag reduction are less suitable for industries where the chemical and physical of the fluids are important for product quality, such as usage fibers, surfactant, and polymers [3] .the following chart represents the classification of drag reducing method. Polymer drag-reduction agents (DRA) was used to reduce the flow of liquid hydrocarbons in pipes. The use of these additives was very important in the transportation of crude oil pipeline and petroleum product [4]. When fluids are transported through the pipeline, fluid pressure will be decreases due to the friction between the wall of the pipeline and crude oil.

Crude oil must be transported under sufficient pressure to achieve the desired product [5]. The drag reduction agent (DRA) could be polymer with high molecular weight which could suppress the turbulent in the pipeline .The most important feature of polymers is that they have a high molecular weight and chain flexibility [6].

The first discovery of (DRA) by British chemist toms in 1948, while it was first applied by trans Alaskan pipeline 1979 [7].the mechanism of drag reduction agent (DRA) it is believed that they work in some way as turbulent in suppression, extension of laminar rang, close to the flow of the wall and reduce the friction of form the turbulence Fig 1

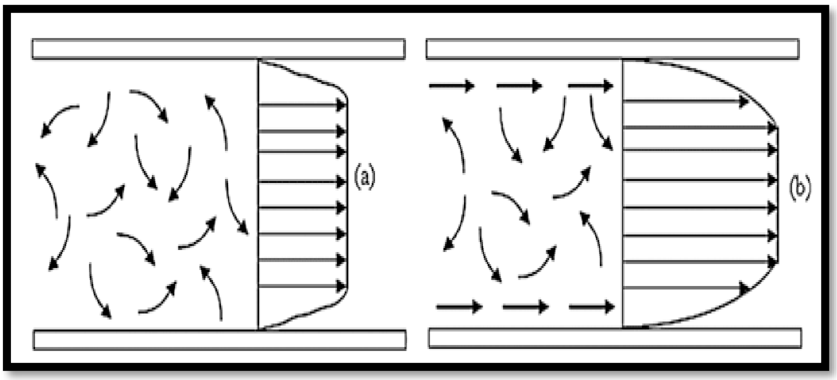


Fig1 Turbulent flow inside the pipe (a) a pure crude oil (b) crude oil contains the additives polymer

The polymers as DRA is affected by several factors such as temperature, pipe diameter, fluid viscosity and the presence of water and paraffin [8]. But when using the flow fluids device the efficiency can be expressed by difference pressure drops use polymer and without polymers, equation 1, [9].

$$\% \, DR = \left[1 - \frac{\Delta p \text{ crude oil} - \Delta p \text{ with polymer}}{\Delta p \text{ fluid}}\right] \quad \ldots\ldots\ldots\ldots 1$$

Where ΔP fluid and ΔP Polymer expressed the pressure drops in the collision in absence and presence of drag reduction, Also the performance of DRA was effected by some factors such as characterization of polymer.

2-Meterials and methods

A-meterials:

Sebacic acid (99%), *p*-toluene sulfonic acid (PTSA), 1,10-decandiol (98%), maleic anhydride, Erucic acid(99%), methyl methacrylate, benzoyl peroxide(74), waxy poly ethylene and toluene, sodium hydroxide (0.01N), argon gas. All materials were purchased from Sigma Aldrich and were used without further purification.

B- Synthesis

1-Synthesis of polyester (Dodecane 1, 10-dioic acid - *CO* -1, 10- decane dioate) P1, [10-11].

(4.6 gm ,22 mmol) of Dodecane dioic acid, 2% w\w of *P*- toluene sulfonic acid and 50 ml of anhydrous toluene were charged into 250 round bottom flask adopted with dean stark apparatus quick fitted separator funnel and inlet class tube for argon gas. ,(4 gm ,22 mmol) of 1,10- decane diol was added to reaction .argon gas allowed to bubble at the bottom of reaction mixture, 5 mint before starting reaction, Then the mixture was heated to its boiling point .the reaction was stopped after water collecting in graduated tube of dean stark flask.. The mixture was cooled and washed with 0.01N solution of sodium hydroxide to extracted residual of *p*- toluene sulfonic acid, also washed with water five times and evaporated by rotary evaporator to obtain (60 %) weight solid yellow product, At the same procedure method synthesis polyester.

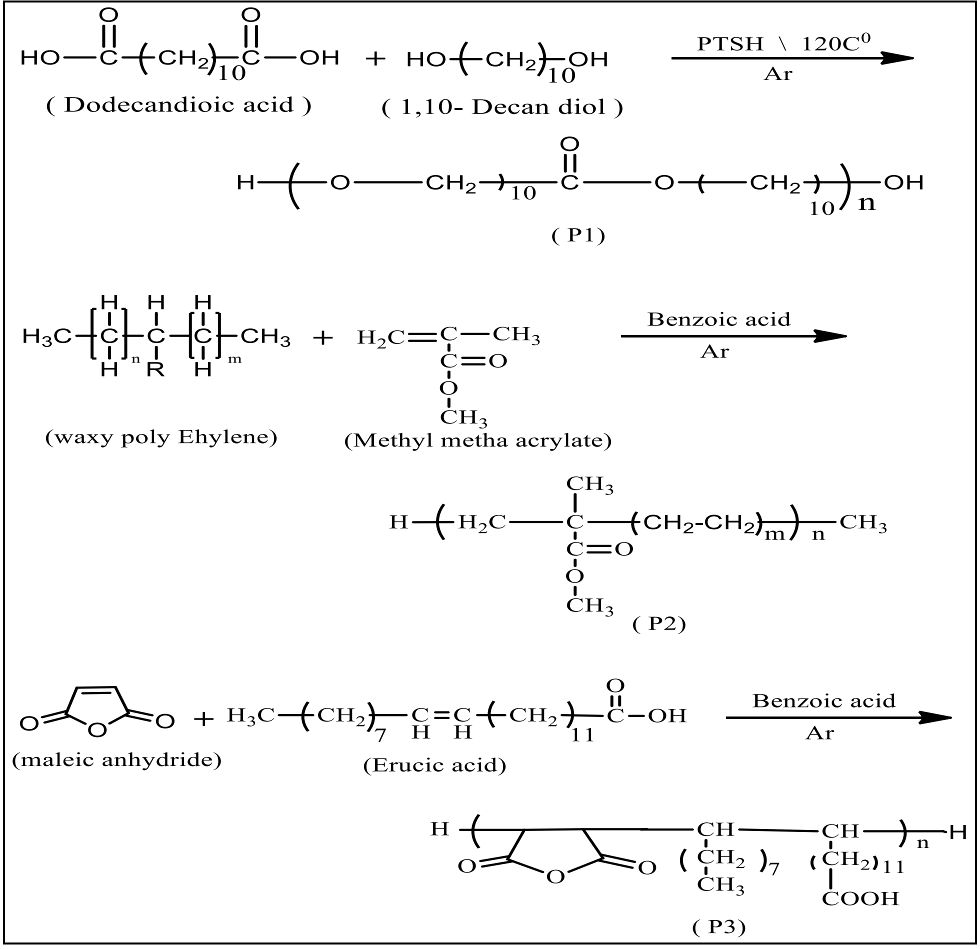
2 - (2-methoxy carbonyl -1-propane – *CO* – poly ethylene) P2.[12-13].

The copolymer P10prepared by (2.7 gm ,96 mmol) of waxy poly ethylene dissolved in 10 ml toluene then added (10 gm, 99 mmol) of methyl methacrylate to the reaction mixture. Heated the mixture for 50 ^{0}C then added 1%

benzoyl peroxide, the reaction time was 1:30 min to obtained (98) whit solid copolymer P2.

3-Synthesis of (Docos-13-enoic - *CO* - furan-2,5-dion) P3.

Copolymer P3 (1 gm, 0.01 mol) of maleic anhydride was dissolved in 50 ml anhydrous toluene at temperature 500C, then added (3.45 gm, 0.01 mol) of Erucic acid and 1% benzoyl peroxide as catalyst ,the reaction mixture heated at (80-100) 0C 90 min .the product copolymer obtained viscos yellow copolymer purification chloroform and ethanol .the copolymer P3 (64%).



Shem 1 Synthesis copolymers P1,P2 and P3

3-Characterization:

The chemical structures of the copolymers were confirmed by nuclear magnetic resonance (NMR) and Fourier transformation infrared spectroscopy (FT-IR). Synthesis of long-chain aliphatic polyester was obtained by direct esterification of dicarboxylic acids with diols by poly condensation through removal of the liberated water. IR were showed assigned to carbonyl group (C=O) at 1732 cm-1 for copolymer P1 also showed a strong band for carbonyl ester group (C-O) at 1168 cm-1 and 1219 cm-1[14-15]. While appearance band for at 3448 cm-1 and 3525 cm-1 for inter carboxylic acid group. Copolymer P2 was showed strong vibration band at 1149 cm-1 for vibration (C-O-C) Stretching. P3 copolymer were showed some bands at district (1774) cm-1 for (C=O) symmetrical coupled stretching, The proximity of the carbonyl group causes the vibration two split this band at 1708 cm-1 is very characteristic of maleic anhydride for C=O symmetry stretching[16-18]. Fig (2-4).

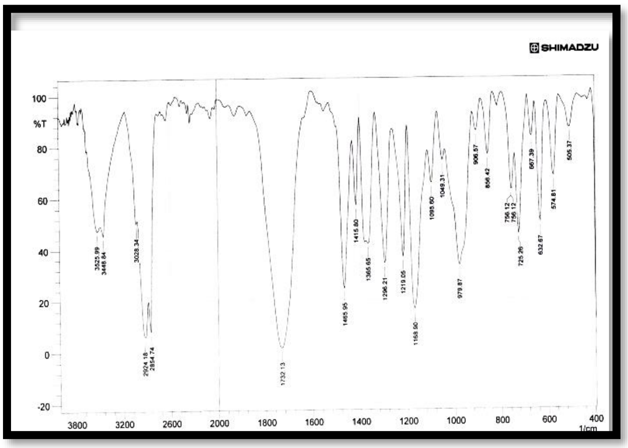


Fig2 Infrared spectra for copolymer P1

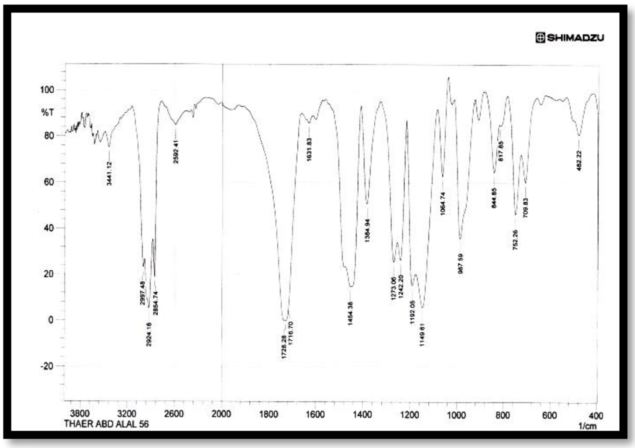


Fig3 Infrared spectra for copolymer P2

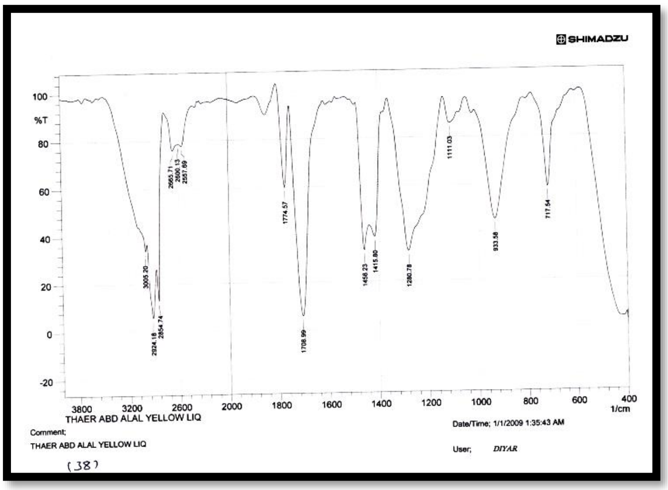
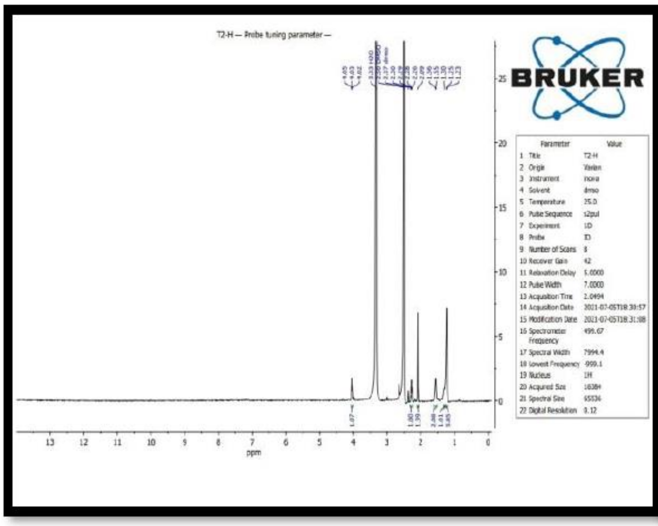


Fig4 Infrared spectra for copolymer P3

^{1}H- and ^{13}C-NMR spectra of the copolymers P1, P2 and P3, The copolymer P1 show signal at 4.5 ppm and 2 ppm for protons methylene group (-CH2 -), the terminal protons as (OH) and (H) was showed tow bands at 2.18 ppm and 4 ppm respectively. P2 copolymer has shown clear band for terminal methyl group at 0.5 ppm and 0.9 ppm, methylene groups signal peaks between (1.4-2.3) ppm can be also attributed increase methylene group at chain polymers, P3 copolymer shown clear peaks at 12.1 ppm for proton carboxylic group (-COOH) and beak at 0.85 ppm for protons methyl group[19-20], while methylene group has shown strong beak at 1.23 ppm[21] Fig(5-7). also ^{13}C-NMR spectra measurement for copolymer P3, it show signal at 176 ppm for carbon carboxylic acid(m) , So carbonyl carbon on the phthalic acid (a) was shows signal at 132ppm.the methyl and methylene carbon groups such as (f),(h),(d) and (e) were shows signals about at 16,31,27 and 32, ppm respectively.Fig8, [22-23]



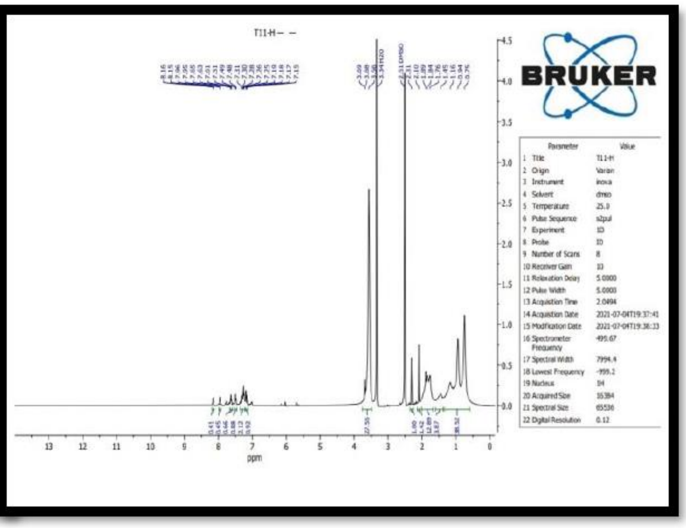
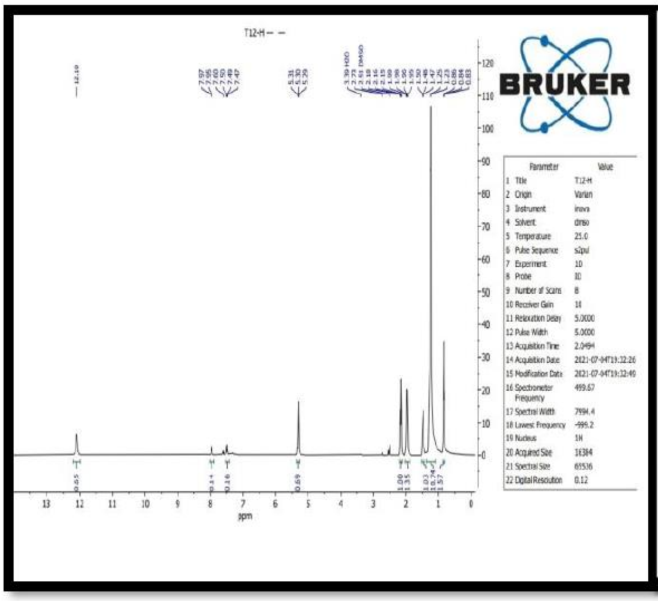


Fig5 ^{1}H-NMR spectra for copolymer P 1

Fig6 ^{1}H-NMR spectra for copolymer P2



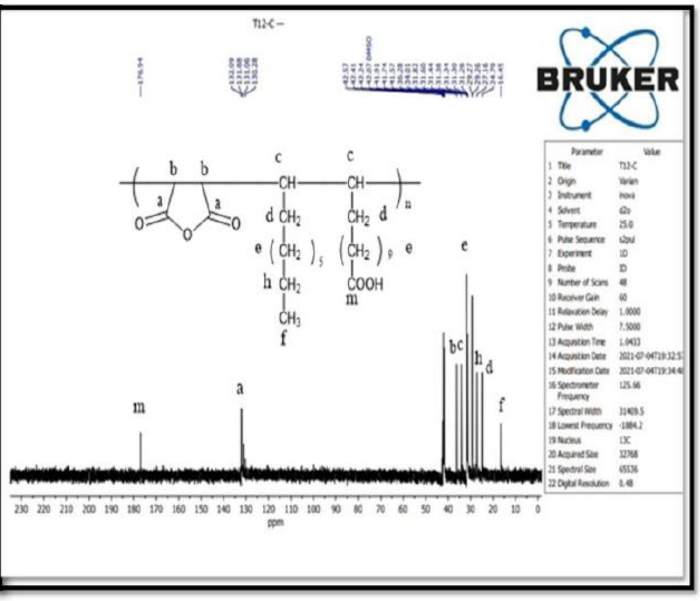


Fig7 ^{1}H-NMR spectra for copolymer P 3

Fig8 ^{13}C-NMR spectra for copolymer P 3

4. Sample preparation and Rheological behavior of crude oil

light Basra crude oil is liquids at room temperature ,the physical properties for crude oil sample obtained in table 1,To study rheology crude oil ,mixed all copolymers prepared with 5 liter crude oil at variable temperatures (35.45 1nd 55 ^{o}C), Experiments were carried out on a steel tube with diameter 15 inch and length 310 centimeter, the tank was filled with crude oil, the difference in pressure drops value (Δp) of the crude oil was between two points by using the oil flow rate device (circulating flow loop system device) using different speed of flow rates from 10 L/min to 90 L/min Fig 9, Reynolds number for each measured speed of flow rate and compare the pressure drops value before and after adding different concentration of drag reduction agent $[C]_{min}$= 100ppm to $[C]_{max}$= 600 ppm.

Table1 physical properties of crude oil

Parameter	Unit	Value
Density	g cm^{-1} at 25 °C	0.901
API	At 16 °C	28.5
Viscosity	cP At 25 °C	60
Wax content	Wt%	1.2
%	Wt %	1.5
Asphaltene%	Wt%	0.1
Water		

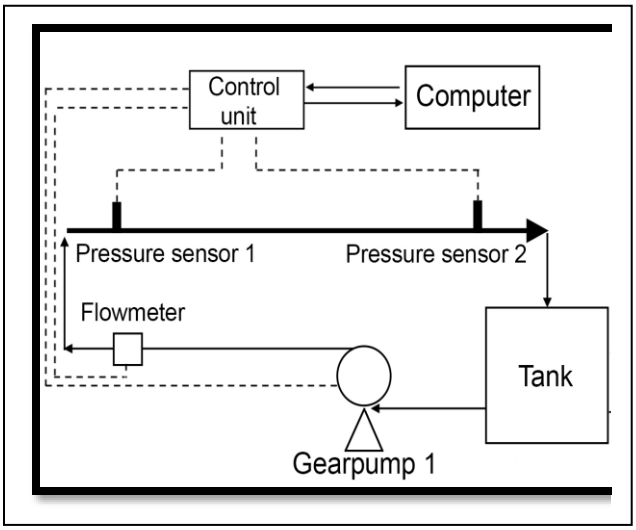


Fig9 Circulating flow loop system device

5 Results and discussion

A. Characterization of percent drag reduction for variable concentrations at 35 °C

The prepared copolymers were assessed as DRA additive in Basra crude oil at different temperatures, The value of the differential pressure was found to increase gradually for crude oil with increasing of the flow rate [24-25], This indicate that the Laminar flow change to turbulent flow motion before polymer additive, The maximum value of percentage drag reduction obtained for copolymer P1 was 39% at the concentration 300ppm, but the minimum percent Drag reduction was 5% at 400 ppm and flow rat 80 L/min, while the copolymers P2 The maximum percentage drag reduction was 50% at concentration (500 and 600) ppm at a flow rate 30 L/min, Copolymer P3 showed maximum percentage of drag reduction was 65% at the concentration 300 ppm but the minimum percentage drag reduction was 7% at 200ppm Fig(10-12).

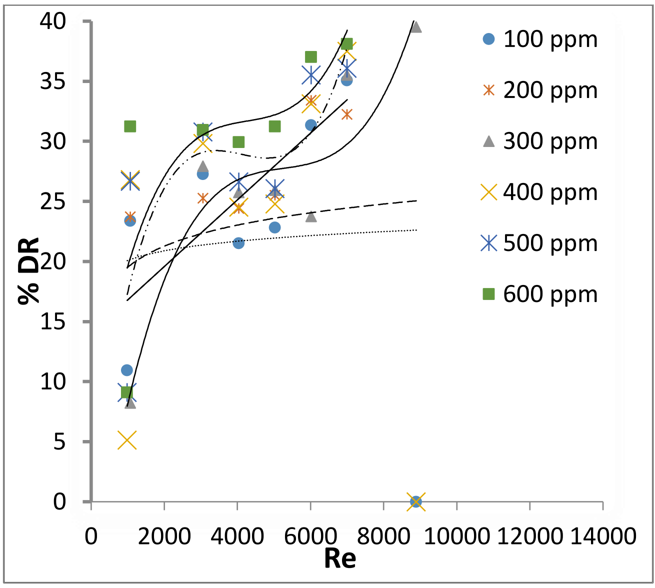


Fig10 percent drag reduction for additive P1

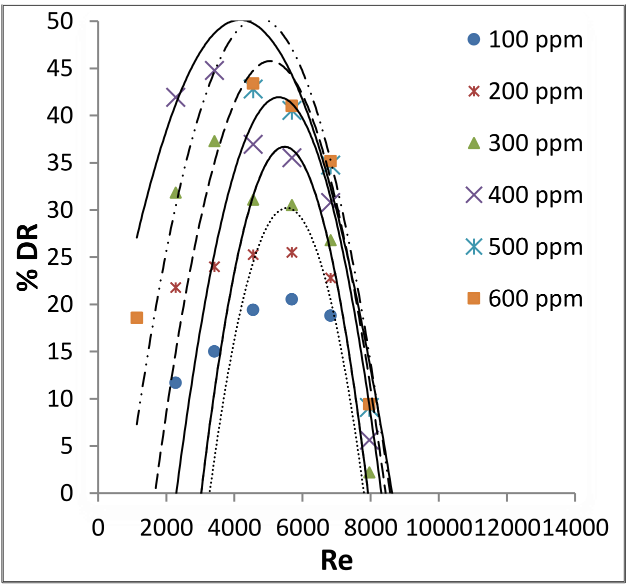


Fig11 percent drag reduction for additive P2

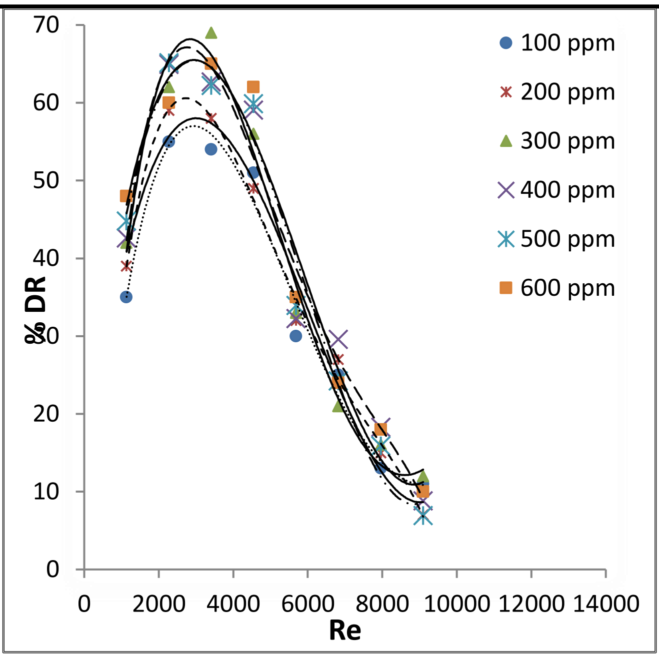


Fig12 percent drag reduction for additive P3

B. Characterization percent drag reduction of 600 ppm at (35, 45 and 55°C)

The effect of temperature is an important in the processes of transporting crude oil, especially in areas that witness a significant change in weather throughout the year. The drag reduction tests at different temperatures were tests in a loop system device to simulate the influence of weather conditions. All copolymers added at the highest concentration (600) ppm were tested at three different temperatures (35, 45, 55°C)

The highest percentage drag reduction for copolymer P1 was 55%, while the % DR decreases at higher temperatures this is due to an increase of crude oil viscosity with increasing the temperature [26-27], while copolymer P2 very close drag reduction at different temperature's and reached 51% at Reynolds number of 2959 and minimum drag reduction was 2% at 45 and 55 °C this could be attributed to the stability of this copolymer from degradation at different temperature, on the other hand , From the pressure change testes, the copolymer P3 recorded a maximum drag reduction of 64% at Reynolds number 2959 and minimum percent drag reduction was 1% at 45°C ,(Fig13-15),also from the results obtain decreases percentage drag reduction with increasing of concentrations because the laminar states becomes unstable resulting a fluctuated flow with the characteristic of drag reducing agent[28],Table 2.

Table2 drags reduction for additives copolymers at different temperatures

Copolymer	% DR_{MIN}			% DR_{MAX}		
	35°C	45°C	55°C	35°C	45°C	55°C
P1	1.6	3	2	38	26	22
P2	3	2	2	52	48	44
P3	5	1	1.3	65	58	15

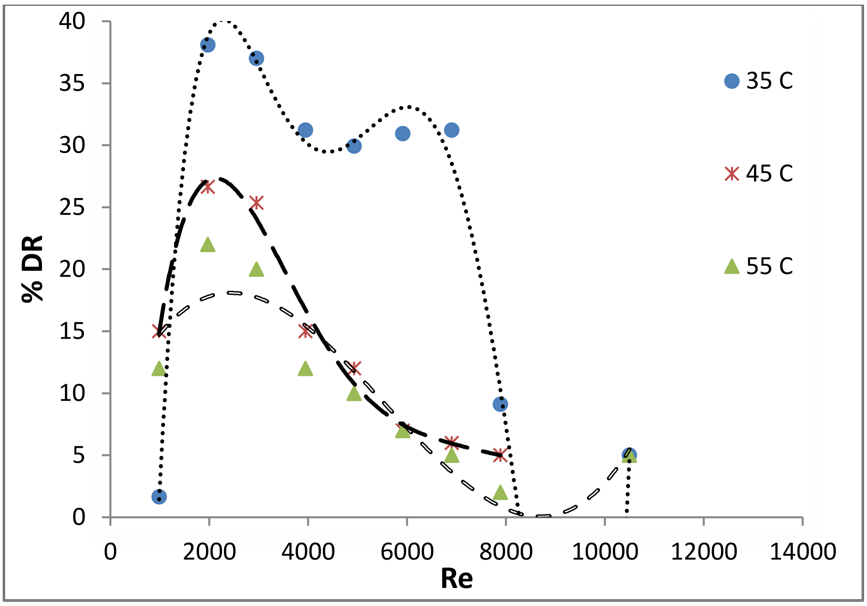


Fig13 percent drag reduction versus Reynolds number for P1 at different temperatures

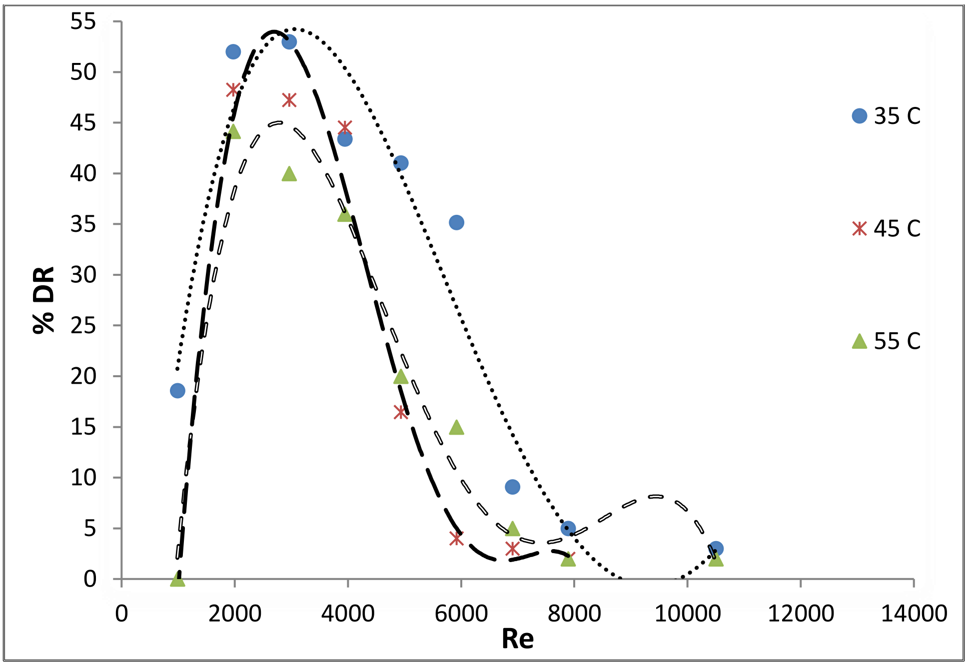


Fig14 percent drag reduction versus Reynolds number for P2 at different temperatures

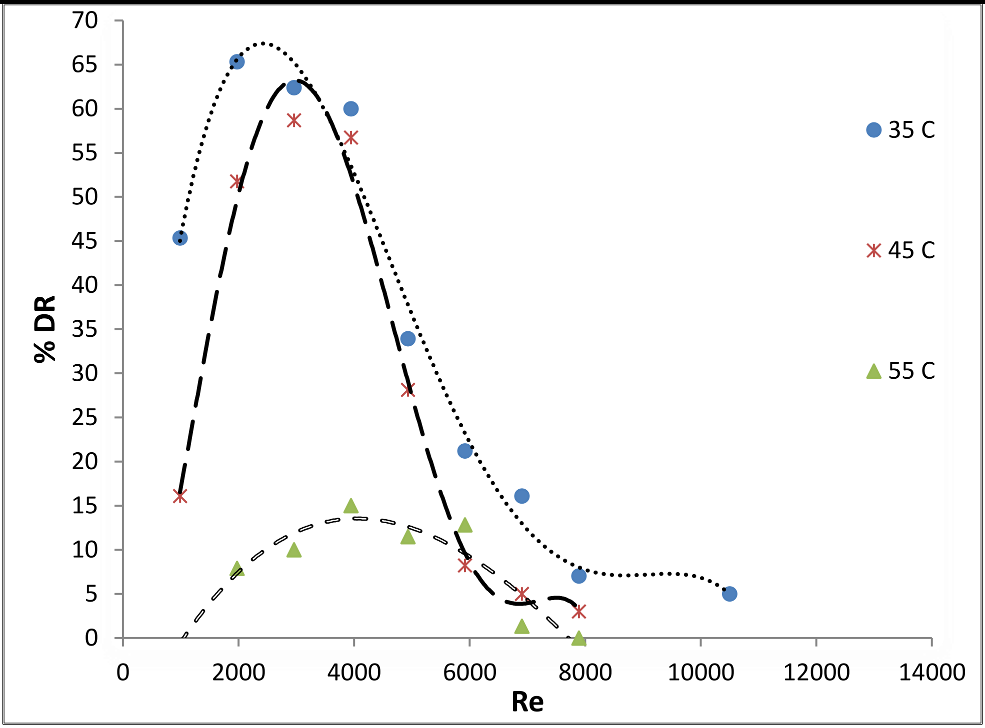


Fig15 percent drag reduction versus Reynolds number for P3 at different temperatures

6 Conclusions

In this work, new copolymers were prepared as drag reducing agent for evaluated Rheology light crude oil of Basra, New linear poly ester (Dodecane 1,10-dioic acid -*CO*-1,10- decane dioate) P1 by condensate polymerization using monomers dicarboxalic acid with diol and *P*-toluene sulfonic acid as catalyst ,also, prepared copolymers by free radical polymerization method contain branching polar chain such as(2-methoxy carbonyl -1-propane – *CO* – poly ethylene) P2 and alkyl side chain as (Docos-13-enoic - *CO*- furan-2,5-dion)P3.

This copolymers characterization by using many techniques such as (FTIR), (^{1}HNMR) and ^{13}C-NMR spectroscopy for copolymer P3, Light Basra crude oil mixed with copolymers at concentration (100-600ppm) to study the percentage of drag reduction and Reynolds number by using circulation flow loop close system device at three temperatures (35, 45 and 55^{o}C).

1. The results showed that the maximum percentage drag reduction at 35^{o}C was 65% for copolymer P3 when the concentration 400 ppm and Reynolds number 2274, in addition, decrease the maximum percentage of drag reduction for copolymers P1 and P2 were 39 and 50% respectively.

2.The results showed an increase in the percentage of drag for all added polymers for crude oil when 100ppm to medium concentrations and this percentage decreases when reaching to highest concentration 600 ppm because the laminar states becomes unstable resulting a fluctuated flow with the characteristic of drag reducing agent.

3. There is a convergence in results percentage drag reduction for copolymers P3 at variable concentration while observed spacing all results for copolymer P1, P2 this Due to stability in turbulent flow rat and compatibility copolymer P3 with crude oil to the presence long alkyl and polarity function group at side chain polymers.

4. The results obtained, the high temperature negatively affects with the percentage of drag reducing and this may be due to the reduction of viscosity at high temperatures, however, thermal stability of polymers at 35^{o}C.

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