

Effect of Terpolymer Additive as Pour Point Depressant and Flow Improvers for Crude Oil

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Received April 6, 2023; Accepted July 19, 2023

Abstract

The aim of the current study is to synthesize a terpolymer of (Nafol 1822C acrylate-co- maleic anhydride -co-Hexadecyl methacrylate (NA-co-MA-co-HDM) to improve the pour point of crude oil. The structures of the Nafol 1822C acrylate and hexadecyl methacrylate monomers were confirmed by FTIR spectra. The effect of polymerization parameters, such as reaction temperature, initiator concentration, experimental duration, and monomer concentration on the yield of the synthesized terpolymer was evaluated as pour point depressant for crude oil. The experimental results showed that the optimum conditions to obtain the highest yield were at the reaction time of 8 hours, initiator concentration of 1wt%, reaction temperature of 90°C, and monomers ratio of (NA: MA: HDM) 2:1:1. The efficiency pour point depepressan for crude oil was increased by increasing the concentration of terpolymer. Rheological properties of crude oil (with and without additives) were studied. Comparison of structures of wax crystals in untreated and treated crude oil was also done by photo micrographic analysis.

Keywords: Terpolymer additives; Crude oil; Pour point depressant; Optimum condition; Wax modification.

1. Introduction

Crude oil transportation is considered as a difficult and extremely technical operation. More efficient and commercial methods are required to deal with the high viscosity which represents the main difficulties in the pipeline transportation [1-5]. Its well-known that, wax crude oils carries a high viscosity and a high pour point make the production, transportation and refining operations more difficult, especially at a low temperature.

Furthermore, cooling process causes formation of the crystal networks that dispersion of wax crystal with higher saturated crude oil. Indeed, the heavy fraction likes wax, asphaltenes, and resin associated with formation the solid phase. These wax crystals grow in size until the whole inner wall of the pipeline is covered with wax layers, causing reduction of flow and extra burden on the pumping system.

Wax if not removed can affect the effective production of oil by choking and clogging the operation and production lines [6]. Oil and gas industries commonly uses mechanical, thermal and chemical methods or the combinations of these methods to address the wax deposition issue [7]. Mechanical method involves scrapers and pigs to remove the wax formed in the pipelines while thermal method ensures the pipeline temperature is maintained above wax appearance temperature by the means of insulation or electrical heating. The chemical method involves the treatment of the crude oil with solvents, dispersants or inhibitors. The right selection of a wax deposition handling is able to avoid expensive production cost and in efficient 'trial-and-error' procedures, as well as severe formation damages due to wax deposition in the reservoir. The usage of chemical inhibitor is much preferred as chemical inhibitor is much more economical and provides better outcomes four categories, pour point depressants (PPD), crystal modifiers, dispersants and solvents [8]. These four chemical addition is further classified into two, wax inhibitors and wax removal. Wax inhibitors, pour point depressants and crystal

modifiers prevent the wax molecules from agglomerating thus reduces the wax deposition to the surfaces of pipelines while dispersants or surfactants and solvents are responsible for breaking down the larger wax molecules to much smaller particles thus lowering the amount of wax deposited. Wax inhibitors have proven to reduce wax deposition rate significantly which in turn increases production level and reduces remediation cost [9-11]. Pre-treatment by polymeric additives known as flow improvers or pour point depressants (PPD) is the most practical solution to this issue. Polymeric remediation with PPDs are commonly used in the pipeline industry in a limited dose to reduce the pour point and gelation point and improve the low-temperature flow properties of crude and promote pipeline transport [12-14]. These polymeric PPDs are polymerization of homo or different monomers that must be distinguished by high oil solubility and have a flexible structure comprising a wax-like paraffin element. Also, characterized by having long linear alkyl chains with a polar portion such as acetate, acrylate, and methacrylate which has a high potential to interfere with crystals wax of crude oil beneath its cloud point. This possible interaction involves nucleation, co-crystallization and adsorption if such materials are available in a comb-like shape polymer, the pendant chains serve as a wax-like paraffin element that affords nucleation locations and co-crystallizes with oil's paraffin forming component. In contrast, the polar end groups obstruct the wide-ranging growth of wax matrices and restrict any crystallization. Afterward, polymers that adsorbed on the rising wax crystals sterically impeded their development, resulting in small crystals by changing morphology and growth patterns of wax crystals which are typically range from orthorhombic to compact cubic or pyramidal shape, inhibiting wax crystals to agglomerate and creating a gel-like structure [15-16]. There are several polymeric additives with these structural properties, of which different forms are available as commercial PPDs such as alkyl acrylate polymers, alkyl methacrylate, alkyl esters, and particularly ethylene vinyl acetate polymers which are utilized in large amounts in the oil field. Comb-like shaped polymers of maleic anhydride with different monomers like alkyl esters and styrene are also revealed as great PPDs. One of the long chain alkyl groups is stearyl methacrylate in particular. It is a type of acrylic monomer that has a strong association with non-polar solvents, also dispersed widely in synthesizing the PPDs. Nevertheless, poly stearyl methacrylate appears to be in the crystalline phase, and as a result, the long chain in the alkyl groups will crystallize in spite of an amorphous backbone that inhibits oil absorption [17-18].

The first object of this work were synthesis and application of a terpolymer [NA-co-MA-HDM] compound as wax dispersant (WD) to promote the flow ability of waxy crude oil and to decrease its pour point degree. Moreover, illustrative mechanism was used to understand the effect of operating parameters, such as reaction temperature, monomers ratio, initiator concentration and reaction time on pour point depressant for crude oil was the second object The effect of additive concentration on wax crystal modification are studied.

2. Experimental

2.1. Materials

The following chemicals were used, acrylic acid, methacrylic acid, hexadecylalcohol and linear saturated long chain alcohol blends Nafol 1822 C were supplied from Condeu Chemical Company, the typical analysis is listed in Table 1. P-toluene sulfonic acid, hydroquinone, dibenzoyl peroxide were purified by recrystallization before use, maleic anhydride, toluene and other common chemicals used were of laboratory grade reagents. Chemicals used were purchased from International Company with high grade illustrated in Table 1. The crude oil used was obtained from the western desert (Qarun Company QN field) illustrated in Table 2.

2.2. Preparation of additives

2.2.1. Esterification of acrylic acid/ methacrylic acid

Alkyl acrylate/alkyl methacrylate is prepared by the reaction of 1 mol of acrylic acid with 1 mol of Nafol 1822C alcohol/1 mol of methacrylic acid with 1 mol of hexadecanol. The reactions were carried out with toluene as a solvent and in the presence of 0.5% of p-toluene sulfonic

acid as a catalyst and 0.25% of hydroquinone as a polymerization inhibitor. The reactants, were heated gradually to 100°C-110°C, using a well-controlled thermostat to give products Nafol 1822C acrylate(NA)/ hexadecyl methacrylate (HDM) illustrated in Scheme 1.

Table 1. Typical analysis of linear long chain alcohol blends (Nafol 1822C)

Analysis	NAFOL	1822C
Alcohol composition (wt.%)	C ₁₆ - OH	0.9
	C ₁₈ - OH	24.3
	C ₂₀ - OH	24.4
	C ₂₂ - OH	38.2
	C ₂₄ - OH	9.9
	C ₂₆ - OH	2.3
Average carbon number (calculated)	C _{av} = 20.8~21	
Density (g/cm ³) approx.	at 80°C = 0.803	
Solidification point (°C) approx.	56-60	
Flash point (°C) approx.	208	
Ester No. (mg KOH/g)	9.9	
Acid No. (mg KOH/g)	0.05	
Iodine No. (mg I ₂ /100 mg)	0.31	
Water (Wt.%)	0.04	

Table 2. Physicochemical properties of the investigated crude oil

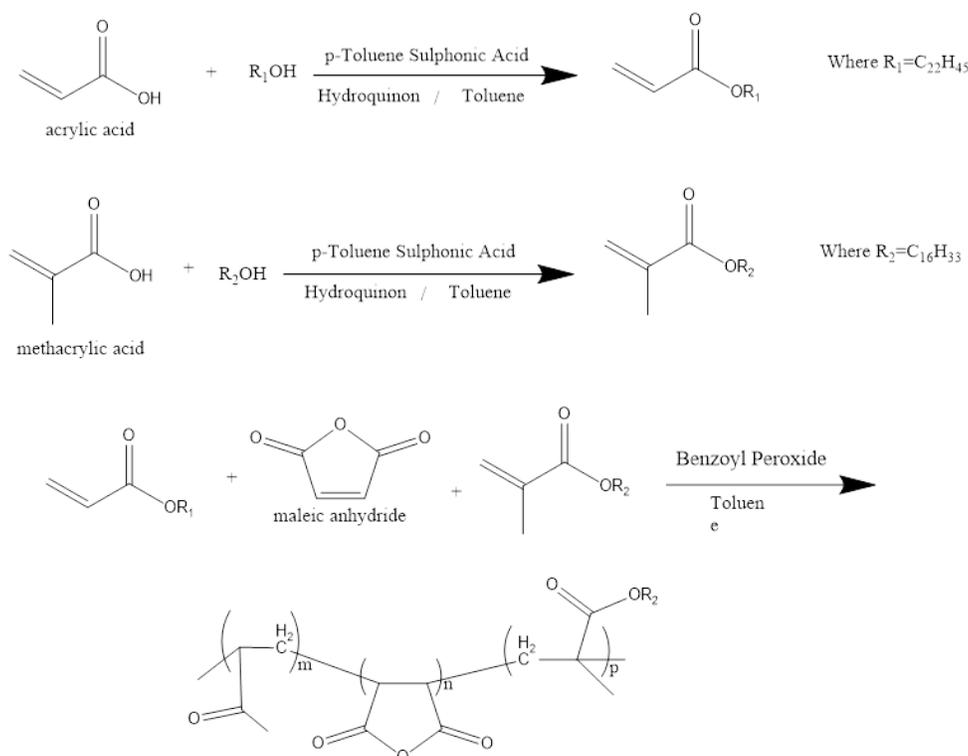
Properties	Method	Crude oil
Specific gravity at 60/60°F	IP 160/87	0.8557
Kinematics viscosity at 35°C (cSt)	IP 71/80	15
Pour point (pp), °C	IP 15/67(80)	21
Sulfur content (wt%)	IP 266/87	0.21
Total paraffins content (wt%)	Urea adduct	20.75
n-paraffin (wt%)	GLC	20.05
iso-paraffins (wt%)	GLC	0.70
Asphaltene content, wt.%	IP 143	00.728
Water content wt%	IP74/70	-
Wax content, wt%	UOP 46/64	10.920

2.2.2. Preparation of terpolymer

Nafol 1822c acrylate- co-maleic anhydride -co-hexadecyl methacrylate was polymerized using free radical polymerization technique in a 250 mL three-necked glass flask at different ratios of monomers concentration, as shown in Table 3. The reactor was equipped with a thermometer, nitrogen gas inlet (for the first 30 min) to eradicate the presence of O₂ in the reaction, and magnetic stirrer. Under a constant stirring, the monomers mixture was dissolved in 50 mL of toluene at a range of reaction time from 4 to 9 h and polymerization temperature from 60 to 100°C. Besides, benzoyl peroxide was used as the initiator for the reaction in the range of 0.3 to 2.0 wt% (of the total of monomers) and dissolved in an appropriate amount of toluene. Then, the initiator solution was added drop-by-drop to the reaction mixture every 15 min for the first hour of reaction. At end of the reaction, the solution was kept at room temperature to cool and then washed by methanol three times; after that vacuum filtered, dried, and weighed to acquire the terpolymer illustrated in Scheme1.

Table 3. Effect of monomer ratio on wax dispersion (WD) yield

Polymer sample	Monomer ratio, [NA-co-MA-co-HDM]	Yield wt%
WD1	1:1:1	80
WD2	0:1:1	50
WD3	1:2:1	73
WD4	2:1:1	85
WD5	1:1:2	69



Scheme 1. Synthetic of [Nafol 1822C acrylate- Maleic anhydride-Hexadecyl methacrylate] terpolymer

2.3. Characterization of the prepared compounds

The prepared compounds (NA, HADM) are characterized by FTIR spectra were recorded by FTIR Spectrometer Model Spectrum 100 (PerkinElmer, UK).

2.4. Evaluation tests

2.4.1. Pour point measurement (ASTM D 97)

The effect of the terpolymer prepared on the Egyptian waxy crude oil on pour-point depression (PPD) was measured according to the ASTM D-97 test procedure at different concentrations of the prepared compounds, namely 250, 500, 750, 1000 and 2000 ppm.

2.4.2. Dynamic viscosity measurements

The dynamic viscosity using Brookfield DV-II + programmable viscometer operating instructions manual No. M/97-164-D1000. The experimental procedure starts when the additives were mixed with crude oil at the prescribed concentration at 60°C. Meanwhile, the viscometer cup is preheated to the same temperature, then loaded with 25 ml of the sample and then the temperature is brought down to a constant temperature. Shearing was continued for 15 min at the test temperature for evaluation. The shear stress-shear rate relationship was recorded for untreated and treated crude oil with some selected pour point depressant (NA:MA:HDM) at concentration 1000 ppm and different temperatures (15, 20 and 30°C) have been studied. In addition, the common flow modes that reasonably identify the non-Newtonian rheological flow properties of crude oil at temperatures around and lower than the pour point have been also studied. The shear rate, shear stress and viscosity can be calculated by the following equations:

Shear-rate (D)

$$D = M \cdot n \text{ (S}^{-1}\text{)} \quad (1)$$

where; M is the shear-rate factor, depending on sensor system and n is the actual test speed. calculated as following = set test speed/reduction factor "R"

Shear-stress (τ) :

$$\tau = A \cdot S \text{ (Pa)} \quad (2)$$

where; A is the shear-stress factor, depending on time of the measuring drive unit and the sensor system, and S is the measuring value (scale grade).

Apparent viscosity (η) :

$$\eta = G \cdot S / n \text{ (m Pa. s)} \quad (3)$$

where; G is the instrument factor, depending on the type of the measuring drive unit and the sensor system.

2.4.3. Photo micrographic analysis

The photomicrographs showing wax crystallization behavior of the untreated and treated crude oil (CO) sample with the synthesized additives at different concentrations have been recorded. An Olympus polarizing microscope model BHSP fitted with an automatic camera with a 35 mm format was used for photo micrographic analysis. The light source was a helium lamp. The temperature of the tested crude oil sample was controlled on the microscope slide by an attached cooling thermostat. All photos were taken at 0°C. The adopted magnification was 100x.

3. Result and discussion

The chemical structure was studied by infrared spectral analysis which showed similar patterns for the Nafol 1822C acrylate and hexadecyl methacrylate. A representative IR pattern for the two monomers did not detected strong absorption Peaks at 3600-3200 cm^{-1} , indicating the monomers did not contain alcoholic hydroxyl groups $-(\text{OH})-$ and acid hydroxyl groups $(-\text{COO}-)$.

The C-H stretching vibration of CH₃ and CH₂ groups absorbed strongly at 2840 – 2910 cm^{-1} , the ester C=O appeared as a strong absorption band at 1705 cm^{-1} and the presence of the ester functionality was further supported by appearance of a C-O stretching vibration at 1154–1188 cm^{-1} . The characteristic C=C stretching band appeared at 1636 cm^{-1} , whereas the CH in plane deformation vibrations of Nafol 1822C acrylate ester monomers appeared at 1323 cm^{-1} . A strong absorption of the bending vibration of C-(CH₂)-C of long alkyl chain of the ester appeared at 713 cm^{-1} .

The optimum condition of the polymerization reaction to acquire high yield polymer has been investigated. The terpolymerization wax dispersant (WD) of Nafol 1822C acrylate -co- maleic anhydride hexadecyl methacrylate has been conducted to study the optimal reaction conditions.

3.1. Effect of monomers ratio

A series of polymers have been synthesized at the conditions of 85°C reaction temperature, 6 hours of reaction time, and 0.5 wt% concentration of initiator (from the total of monomers) with different monomers ratio and the yield for each wax dispersant (WD) was calculated as shown in experimental results in Table 3.

Table 3 demonstrates that the effect of terpolymer yield is diverse when the polymerization process is achieved at various monomer ratios. Molar ratio of [NA-co- MA -co-HDM] polymer has a significant effect on the yield because of the acrylate groups which act as a feedstock for a chemical additive. As seen in Table 3, WD4 (mole ratio 2:1:1) had a significant effect on increasing the yield of the prepared polymer due to increasing concentration of high molecular weight monomer of NA in the feed. The long hydrocarbon chains with polar ends of NA molecules are the key reasons for exhibiting better yield of the synthesized polymeric additives, the optimal condition of polymerization reaction in terms of monomer ratios was at a concentration of 2:1:1. From this result, it is evident that the two molar ratios of Nafol 1822C acrylate, one mole ratio maleic anhydride and one mole ratio hexadecylmethacrylate gives the optimal yield of the prepared polymer.

3.2. Effect of concentration of initiator

To comprehend the effectiveness of the initiator concentration on the yield of the synthesized terpolymer, a chain of reactions was conducted with different amount of benzoyl peroxide between 0.3 and 2 wt% at 90°C for 8h and the [NA-co-MA- co- HDM] ratio of 2:1:1 as

shown in the experimental data in Table 4 below. As it can be seen from Table 4, the yield of terpolymer start to increase from 75% to 90% when the concentration of initiator increased from 0.3 wt% to 2 wt%. when the concentration of increasing the initiator to 2 wt% the aggregation process between the monomer chains reached the point that is sufficient to react with the radicals. Consequently, the optimum condition of initiator concentration is 1 wt%, which the highest yield was achieved at 90%.

Table 4. Effect of concentration on the yield wax dispersion (WD)

Polymer sample	Concentration of initiator, %	Yield, wt%
WD1	0.3	75
WD2	0.5	83
WD3	1	90
WD4	1.5	85
WD5	2	80

3.3. Effect of reaction temperature

At a varying range of reaction temperature from 60 to 100 °C, a series of terpolymer was prepared to investigate the effect of polymerization temperature on the yield of the terpolymer, as shown in Table 5. The other reaction conditions which were reaction time, monomers ratio, and concentration of initiator were kept constant at 8 h, [NA-co- MA -co-HAM] 2:1:1, and 1 wt% (from the total of monomers) respectively. It can be seen from the data in Table 5, the yield of synthesized terpolymer continues to increase with increasing reaction temperature. Besides, the yield stayed stable after increasing the temperature more than 90 °C, this is possibly because of a portion of the initiating species have being destroyed at higher temperatures. As a result, the optimal condition for the polymerization temperature to be completed and achieve the highest yield of terpolymer was found to be at 90°C.

Table 5. Effect of temperature on the yield wax dispersion (WD)

Polymer sample	Reaction temperature (°C)	Yield wt%
WD1	60	65
WD2	70	75
WD3	80	80
WD4	90	85
WD5	100	83

3.4. Effect of reaction time

Under the condition of monomer ratio of 2:1:1, at reaction temperature of 90°C, 1 wt% concentration of initiator (from the total of monomers) and varying reaction time, a series of terpolymer has been synthesized, and the yield of the prepared polymer computed from experimental results is shown in Table 6. As it can be observed from Table 6, the yield of the synthesized terpolymer increased from 65% to 85% by increasing the time from 4 to 8 h, and after that, the yield of terpolymer remained stagnant at 85%. Therefore, the optimum condition for the time of polymerization in terms of reaction yield is 8 h, which achieved the highest yield of 85%. However, after 8 h of reaction, the yield no longer increases over time. It is indicating that the polymerization process is completed after 8 h of reaction.

Table 6. Effect of reaction time on the yield wax dispersion (WD)

Polymer sample	Reaction time, (h)	Yield wt%
WD1	4	65
WD2	5	70
WD3	6	80
WD4	8	85

3.5. Evaluation of the prepared compound

3.5.1. Pour point as pour point depressant (PPD)

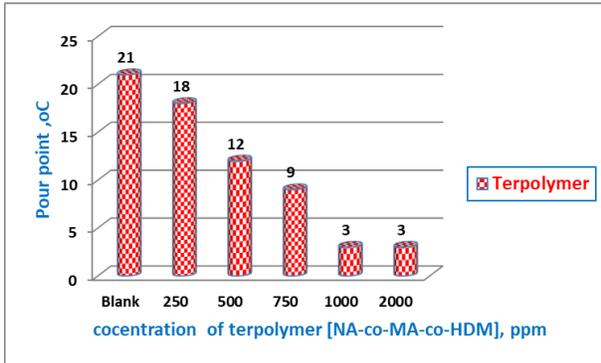


Figure 1. Effect concentration of the terpolymer on the pour point for crude oil

Pour-point measurements were determined using modified ASTM D-97 method with different concentrations of the prepared additives, namely 250, 500, 750, 1000 and 2000 ppm. Figure 1 shows that the pour-point depression is directly proportional to the additive concentration [19], as the additive concentration increased from 1000 to 2000 ppm and the pour point decreases. the concentration of the additives increase an increase in the pour-point depression is achieved this means that, at these concentrations range the additives may co-crystallize with the paraffin wax and modify their crystal structure.

The prepared additives reduced the pour-point temperatures from 21°C to 3°C (ΔPP) = 18 °C at concentration 1000 ppm of terpolymer [NA-co-HAM-co-MA] 2:1:1 which exhibited the maximum pour-point reduction Figure 1. The reduction of pour point [20] was calculated according to the following equation: pour point reduction (ΔPP) = $PP_{pure} - PP_{add}$; where PP_{pure} is the pour point of the crude oil without additive (blank) and PP_{add} is the pour point of the treated crude oil.

3.5.2. Rheological properties and flow behavior

If the oil is cooled during transportation the wax crystals tend to deposit on the cold pipe wall. If these deposits get too thick, they can reduce the capacity of the pipeline transportation and cause problems during pigging. Wax deposition in process equipment may lead to more frequent shutdowns and operational problems. In extreme cases, wax crystals may also cause oil to gel and lead to problems of restarting the pipeline. A thorough understanding of the rheology of the crude oil is therefore necessary for tackling these problems particularly at low temperatures. The nature, the type and the quantity of wax, as well as its crystallization habits influence flow properties to a large extent. The flow properties of the crude oil depend strongly on the shear rate, temperature, rate of cooling, time of shearing and composition of the crude oil [21]. Rheological behavior of the untreated and treated crude oil using [NA-co- MA -co-HDM] 2:1:1 terpolymer sample have been determined in the most efficient concentration (1000 ppm) via dynamic viscosity measurements at 15, 20 and 30°C. From the representative examples in Figures 2 and 3, it can be noticed that the shear noticed stress increases with increase in the shear rate at all temperatures.

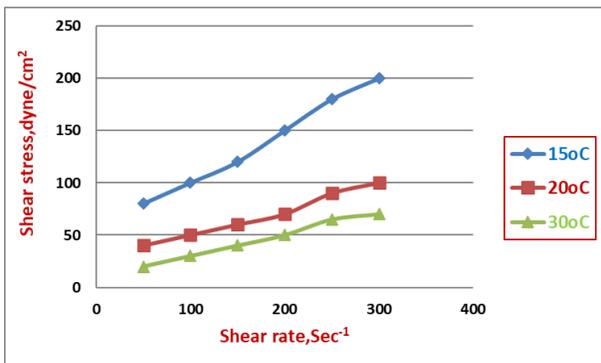


Figure 2. Relation between shear rate and shear stress for untreated crude oil

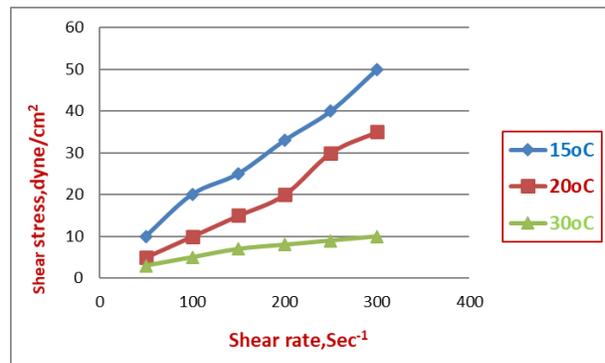


Figure 3. Relation between shear rate and shear stress for crude oil treated with 1000ppm terpolymer

Rheological study of [NA-co- MA -co- HDM] 2:1:1 additive (WD) beneficiated crude oil is performed by maintaining the concentration of 1000 ppm for [NA-co- MA -co- HDM] 2:1:1 additive, as these are the optimum concentration obtained for the lowest pour point of the crude oil. It can be observed from the rheograms (Figures (4-5) that at any particular shear rate there is sharp viscosity increase with decreasing temperature for virgin crude oil.

The apparent viscosity is varying inversely with temperature i.e. decrease in temperature causes increase in viscosity because of crystallization of wax molecules and thus the fluid attains the complex flow behaviour showing non-Newtonian characteristics.

Shear rate variation also effects viscosity and from the Figures 4,5 it is observed that viscosity decreases with increasing shear rate. Moreover, at higher shear rate the crude oil sample was exhibiting almost constant viscosity.

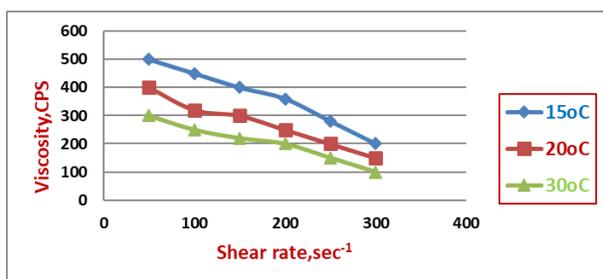


Figure 4. Relation between shear rate and viscosity for untreated crude oil

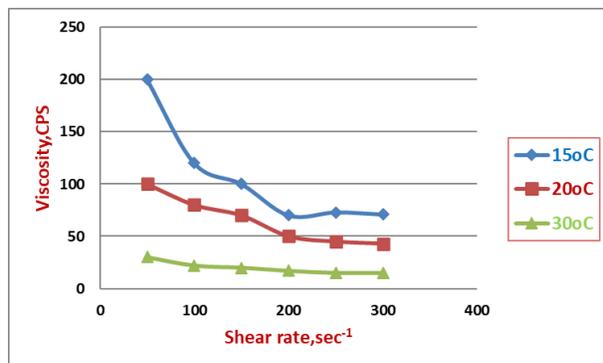


Figure 5. Relation between shear rate and viscosity for crude oil treated with 1000ppm terpolymer

This behavior may be explained by the following reasons: At temperature around the pour point and at low shear rate, the energy exerted by shear and dissipated energy in the matrix tends to break down the wax crystals partially. But by increasing the shear rate, the dissipated energy is high enough to overcome the yield stress and start flow. Upon increasing the shear rate, the size of the agglomerates decreases and this process releases some of the continuous phase originally immobilized within the agglomerates. As a result the effective dispersed phase concentration decreases and leads to decrease of viscosity. The viscosity decreases with increasing the shear rate until the agglomerates are completely broken down into the basic particles. So the crude oil system shows non-Newtonian characteristics [22]. The behavior of decreasing the rheological parameters after addition of the prepared terpolymer can thus be attributed to their chemical structures. The presence of high polarity of oxygen in the ester groups along polymer chain play a role in preventing the agglomeration of wax crystals in crude oil. In addition, the interaction of the alkyl chain with the paraffin fraction in the oil occurs through a good match of the alkyl chain length, as the alkyl chain length decreases a better match occurs.

3.5.3. Photomicrography analysis

Photomicrography is a fast and simple evaluation tool that can clearly reveal the wax modification induced by wax dispersants and pour point depressant according to the type of waxy crude oil. When waxy crude oil cooled below its cloud point, the wax constituent tends to separate from the liquid phase and crystallize. Photomicrography of untreated waxy crude oil shows large wax crystals. Figure 6 (a) shows dark and black wax-crystal blocks. By the addition of different concentration terpolymer, the shape and morphology of wax crystals differ as compared with untreated. Figure 6e also show that the effect of 1000ppm is more effective in crystal morphology and shape comparing with 250ppm, 500 ppm and 750 ppm illustrated in Figures 6b,6c,6d respectively. The paraffin crystals became to be small- and- uniformly distributed particles due to different attachment points, thus preventing paraffin from further crystallization and reducing the pour point of crude oil. The decrease in size and morphology

of wax crystals is due to the action of terpolymer additive that act as centers for nucleation in a way that can cause the formation of a large number of small crystals.

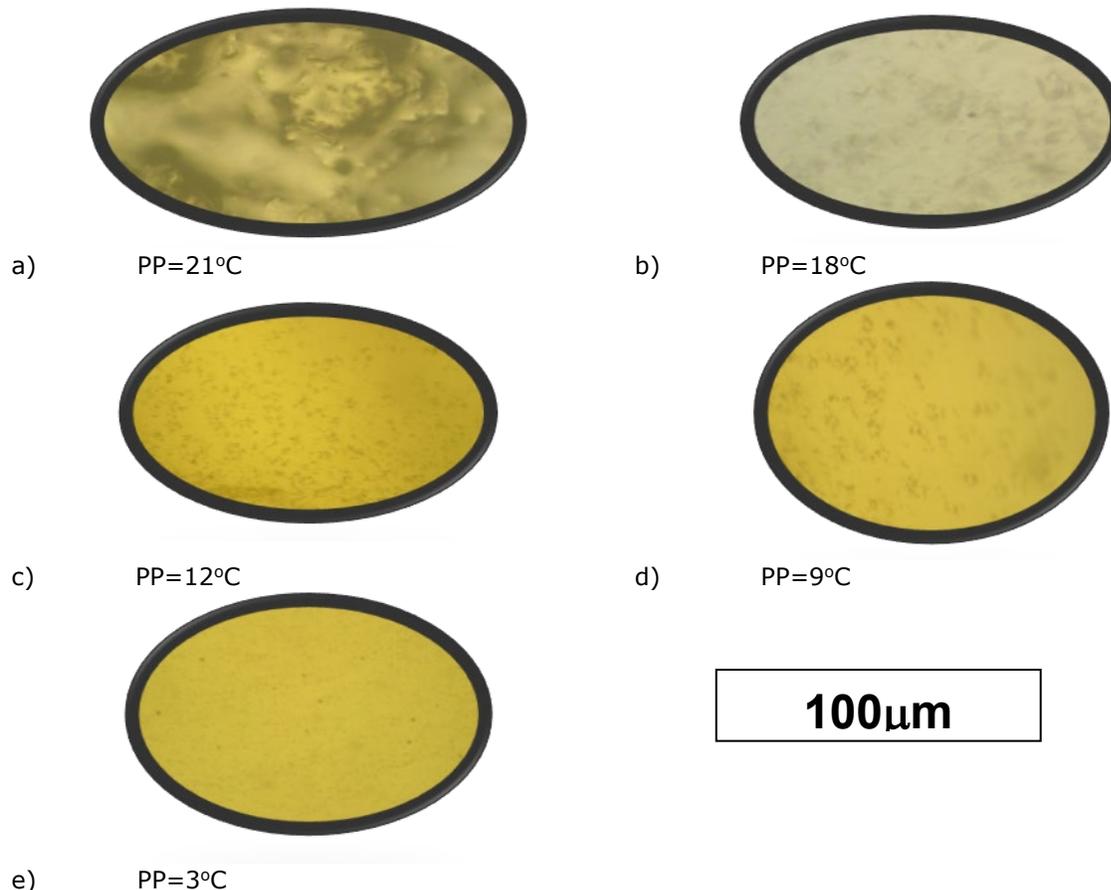


Figure 6. Photomicrographs of a: Crude oil (CO) untreated, b:(CO)+250 ppm terpolymer, c: (CO) + 500ppm terpolymer , d: (CO)+750ppm terpolymer and e: (CO)+1000ppm terpolymer

4. Conclusion

Pour point depressant of [NA-co-MA-co-HDM] 2:1:1 terpolymer was synthesized as pour point depressant in the crude oil. Highest yield of the[NA-co-MA-co-HDM] 2:1:1 was 85 wt%, which was obtained at the optimal polymerization reaction conditions of 8 h of reaction time, 90°C reaction temperature, 1wt% of concentration of initiator and monomers ratio [NA-co-MA-co-HDM] 2:1:1.

The performance evaluation of the prepared terpolymer additive was studied for the pour point depressant of the crude oil. The data reveal that the most effective concentration in case of terpolymer is 1000 ppm. Considering the effect of the prepared compounds on the pour point, it was noted that these properties were enhanced as the concentration increased. As the additive concentration increases, the size of crystals decreases and the number of crystals increases.

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