



Pour point depressants for waxy crude oil based on used sun flower oil

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Abstract

The deposition of paraffin wax from crude oil at low temperature is one of the serious problems that induce high viscosity and poor flowability which restrict the processing of crude oil and causes huge economic loss. Pour point depressants (PPDs) has been proved to be an efficient way to inhibit wax deposition. In the present work, six terpolymer pour point depressants comprised of [sunflower oil- octadecane- acrylic acid/vinyl acetate] at different molar ratio were prepared by a facile method. These are coded as SOA and SOV respectively. The chemical transformation of sun flower oil was proved by FTIR spectroscopy and their molecular weights were estimated via GPC. In comparison to composition and operational parameters, the produced additives' effectiveness as pour point depressants for waxy crude was confirmed. Moreover, the surface tensions at dodecane versus different concentrations at 25oC were displayed in order to verify the surface activity of the green terpolymers. The pour point measurements showed that PP temperature of the examined waxy crude was reduced by the addition of the investigated surfactants according the variation of molar ratios comprising the terpolymer. The data revealed that the additive SOA1 displayed maximum reduction in the pour point of crude oil samples.

Keywords: Used Sunflower oil, green surfactant, pour point, terpolymer additive, wax modification, waxy crude oil, surface properties

1. Introduction

Highly viscous crude which now represents considerable fractions of the recently discovered crude oils embodies a problematic issue to the entire petroleum industry [1]. The streaming of waxy oil is dependent on its chemical constitution, surrounding temperature and pressure and on its previous thermal history. Wax (high molecular weight paraffin fraction of crude oil) is one of the problematic components of crude oil which can be deposited when the oil temperature becomes lower than its pour point [2, 3]. Indeed, waxy Oils are highly viscous with high pour points due to their elevated content of high molecular weight fractions. Then, upon cooling, wax particles will crystallize and agglomerate. This phenomenon frequently occurs when the surrounding temperature is lower than the waxy crude oil's pour point. Wax deposition and accumulation restrict the flowability of crude oil and may cause obstruction of the transportation pipelines. Therefore, establishing cost-effective and green solutions is highly encouraged [4]. Indeed, several materials can be added to the

crude oil to induce a specific function. These include demulsifiers [5-8], emulsifiers [9, 10] and dispersants [11-13]. These materials belong to a class of active ingredients known as surfactants. Pour-point depressants (PPDs), flow improvers, and wax inhibitors are also classified as surfactants as they behave similarly and possess relevant chemical construction. As a preventive solution, these materials are added into the crude oil to enhance the fluid viscosity and inhibit the process of crystal growth [14]. The interactions between the PPD molecules and crystal particulates are essential to the overall inhibition mechanism. Wax crystals' surface characteristics, shape, and dynamics of crystal growth are all changed by this interaction. The end result is a decrease in the crude oil's viscosity and pour point temperature. The inherent figures formed via the co-crystallization and adsorption processes cease the inter-growth and inherence of the crystals. However, a model PPD consists of a comb-like polymeric molecule with long straight alkyl chains usually copolymerized with acrylate monomers [15-18]. The

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polar groups and the nonpolar long alkyl chain are both present in the copolymeric PPD in the same chemical architect [19, 20]. The nonpolar long alkyl chain of the PPDs can inhibit wax development via nucleation or adsorption onto the wax crystals thereby altering the growth orientation and crystal morphology [21]. Also, the polar groups can adhere onto the wax crystal. Accordingly, the growth of wax crystal is inhibited and the cold streaming of crude oil is promoted. A number of polymeric PPD categories have been modified to increase crude oil's fluidity in cold environments. The PPDs that are most frequently used are α -olefin copolymer [25], maleic anhydride copolymer (MA), ethylene-vinyl acetate copolymer (EVA) [22], alkyl methacrylate polymer [23], ethylene-butene copolymers (PE-PEB) [24], and their derivatives [22], alkyl methacrylate polymer [23], ethylene-butene copolymers (PE-PEB) [24], α -olefin copolymer [25], maleic anhydride copolymer (MA), and their derivatives [26]. These works have proved that the suitable ratio between polar and nonpolar groups in the PPD molecule is of particular importance in establishing a proper arrangement of these entities around the wax crystals and consequently in achieving crude oil fluidity at low temperature. Generally, the optimum PPD is designed and optimized based on the polarity- matching principle. The polarity of PPDs can be reformed by presenting various polar moieties or controlling the ratio between nonpolar and polar components. Therefore, PPDs can be applied to improve the flow properties of different waxy crude oil systems. The primary method for assessing the enhanced operability of the treated crude oil is the use of cloud point and pour point tests to determine the flow parameter. Additionally, photo-analysis is employed as a quick and simple screening method to validate various experimental protocols for assessing the cold flow characteristics of treated and untreated lubricant [27].

On the other hand, green chemistry approach has been established to encourage employment of environmentally friendly materials as sustainable and cost-effective alternatives in different industrial applications [28-30]. Thus, the present work deals with preparation of six terpolymer additives based on modified used sunflower oil (categorized in two groups [sun flower oil- octadecane- acrylic acid] and [sun flower oil- octadecane- vinyl acetate]) with different molar ratio of monomers and their evaluation as flow improvers and pour point depressants for waxy crude oil. Studying the rheological characteristics of crude oil in relation to shear rate, shear stress, and viscosity was done both with and without additives.

2. Experimental

2.1. Materials:

All chemicals are of analytical grade (Vinyl acetate, octadecane, acrylic acid) and purchased from Sigma-Aldrich. The crude oil sample that was obtained from Qarun Petroleum Company is an Egyptian waxy crude oil. In Table 1, the physicochemical characteristics are listed. By using gas chromatography analysis in accordance with ASTM D-2887, the n-paraffin distribution of the separated waxes was calculated and is also provided in Table 1. Used cooking sunflower oil was filtered and distilled twice to remove the contaminants and the ignited fractions.

Table 1: Waxy crude oil (Qarun crude oil) physicochemical characteristics

Test	Method	Result
Density at 20°C Kg/L	ASTM D1298	0.8621
Kinematic viscosity, (c.st.) At 40°C At 100°C	ASTM D445	10.440 02.510
Pour point (PP), °C	ASTM D97	24
Asphaltene content, wt. %	IP143	0.829
Wax content, wt. %	UOP46/64	10.820
Total sulfur content, wt. %	ASTM D4294	0.890
n-paraffins, wt%	GLC	90.13
Iso- paraffin, wt%	GLC	05.01
Total paraffins content, wt%	Urea adducts	95.14
Average carbon number (n)	GLC	22.013

2.2.

ynthesis of surfactant

The tertiary polymers were prepared by a facile methodology using the following ingredients; used cooking sunflower oil, Octadecane and vinyl acetate (or acrylic acid) in different molar ratios. Simply, the assigned molar percentages of the reactants were mixed thoroughly using magnetic stirrer and then introduced into the three-necked flask fitted with nitrogen inlet, thermometer and condenser. . After that, the flask was submerged in an oil bath, and the temperature was raised to and kept at 80 ± 2 °C to guarantee a decent polymerization. At 500 rpm, the reaction was agitated to achieve total homogeneity. Subsequently, the flask was gradually filled with the

initiator solution, which was benzoyl peroxide (0.3 weight percent of monomers) diluted in 20 mL of toluene. For eight hours, the reaction was maintained at a consistent temperature and input. Once the reaction was finished, a viscous, thick liquid mass was created, and the reaction system was allowed to cool to room temperature. Through the use of the solvent/non-solvent method, the terpolymers were purified. In this case, methanol was used as the non-solvent and toluene as the solvent. In a beaker, the prepared polymer/toluene solution was added dropwise at a 5:1 methanol to polymer solution ratio while being continuously stirred. After being collected at the beaker's bottom, the polymer was dried and put to use in additional research. Table 2 lists the codes and compositions of the prepared terpolymers.

Table 2: The codes and the compositions of the prepared terpolymers

Code	waste cooking oil (mol%)	Octadecane (mol%)	Acrylic acid (mol%)
S OA1	1	1	1
S OA2	1	1	2
S OA3	1	2	1
Code	waste cooking oil (mol%)	(Octadecane mol%)	Vinyl acetate (mol%)
S OV1	1	1	1
S OV2	1	1	2
S OV3	1	2	1

2.3.

Characterization of terpolymers

2.3.1.

Molecular weight determination:

The molecular weight was ascertained by means of Gel permeation chromatography (GPC) mounted with a Waters 515 HPLC pump, Waters temperature control module, and 2410 refractive index detector from Water company, the measured values are tabulated in Table 3. 2410 refractive index detector from Water company, the measured values are tabulated in Table 3.

2.3.2. IR characterization:

The IR analysis was conducted to confirm the chemical modification of the used sunflower oil. The

spectra of the prepared surfactants were recorded by using Perkin-Elmer spectrometer at range 4000-400 cm^{-1} .

2.3.3. Cloud Point (C.P.):

The cloud point of the prepared surfactants was measured by heating a solution of 1% of the prepared pour point depressants in dodecane and recording the temperature at which the solution starts to become turbid. The value of C.P. was taken as an average of three repeated measurements.

2.3.4. Surface tension measurement:

The surface tension measurements of different concentrations of the prepared PPDs in dodecane solution at 25°C were conducted with a KRÜSS K9 tensiometer by the ring method. The values were used to present the S.T. concentration isotherms of the prepared surfactants. These graphs were used to calculate some surface properties for the prepared surfactants. The surface tension of dodecane @ 20 °C is 25.35 mN/m.

2.4. Evaluation of the prepared terpolymer additives

2.4.1. As pour point measurement (ASTMD97)

The prepared terpolymers were evaluated as pour point depressants for waxy crude oil by measuring the pour point of crude oil upon the addition of different concentrations of the prepared surfactants (250, 500, 750, 1000 and 2000 ppm) according to the ASTM-97 test procedures.

2.4.2. Dynamic viscosity measurements

The dynamic viscosity for the original and treated crude oil sample (Containing 2000 ppm of PPD) was measured at different temperatures (15, 20 and 30°C) by using (Brookfield viscometer USA), (DVII). Then, research has also been done on the flow modes that are known to appropriately identify the Non-Newtonian rheological flow characteristics of crude oil at temperatures near and below the pour point. These equations can be used to estimate the viscosity, shear rate, and shear stress.[31]:

$$\text{Shear rate (D): } D = M \times n \text{ (s}^{-1}\text{)} \quad [1]$$

where; M is the Shear rate factor, dependent on the viscometer structure, and n is the actual test speed. The actual test speed can be obtained from the Rheometer device.

$$\text{Shear stress } (\tau): \tau = A \times S \text{ (Pa)} \quad [2]$$

where S: is the measuring value (torque), and A is the shear-stress factor based on the type of measuring drive unit and sensor structure.

Apparent viscosity (η):

$$\eta = (G \times S)/n \text{ (mPa. s)} \quad [3]$$

Where G is an instrumental factor, depending on the type of measuring drive unit and sensor system.

2.4.3. Photo- micrographic analysis:

The images displaying the behaviour of wax crystallisation in both treated and untreated crude oil (CO) samples with 200 ppm of SOA1 and SOV1 have been photographed by using an Olympus polarizing microscope model BHSP mounted with an automatic camera with a 35mm format at temperature of 0°C below the pour point. A cooling thermostat that was attached allowed the temperature of the tested crude oil sample to be regulated on the microscope slide. A 100X magnification was chosen.

3. Results and discussion

3.1. Verification of chemical modification of the used sunflower oil:

The process of terpolymer creation is merely a polymerization process started with free radical formation initiated by thermal decomposition of benzoyl peroxide. Basically, the sunflower oil mainly contains about 15% saturated acid (stearic acid) and 85% unsaturated acids (14–43% oleic and 44–75% linoleic acids). Green tertiary polymer is created when these fatty acids combine with octadecane, acrylic acid, or vinyl acetate [3]. The end result is a tertiary polymer called poly (sunflower oil, octadecane, acrylic acid, and vinyl acetate). Figure 1a illustrates the suggested reaction and chemical formula of the prepared terpolymers. The chemical transformation was assessed by the IR analysis. Figure 1b displays the FTIR spectra of acrylate group and Figure 1c illustrates the spectra of vinyl acetate group. Stretch vibration peaks at $\sim 1720 \text{ cm}^{-1}$ are assigned to the carbonyl group of esters present in sunflower oil – acrylic acid/vinyl acetate – octadecane terpolymers, and those appear at 1626 cm^{-1} to 1662 cm^{-1} are assigned for the stretching vibration of alkene groups kept in the terpolymer [2]. In a synthetic polymer, the peaks at 1463 cm^{-1} correspond to alkane groups. Some other important observations can be picked up: the absence of the strong peak distinguishing O-H (at $3200\text{--}3500 \text{ cm}^{-1}$) from all the spectra of vinyl acetate group (Figure 1c) while its appearance in all the spectra of the acrylate group (Figure 1b). Also, the intensity of the peak at $1737\text{--}1750 \text{ cm}^{-1}$ characterizing the carbonyl group delocalized upfield according to the ratio of the acrylate monomer in the recipe.

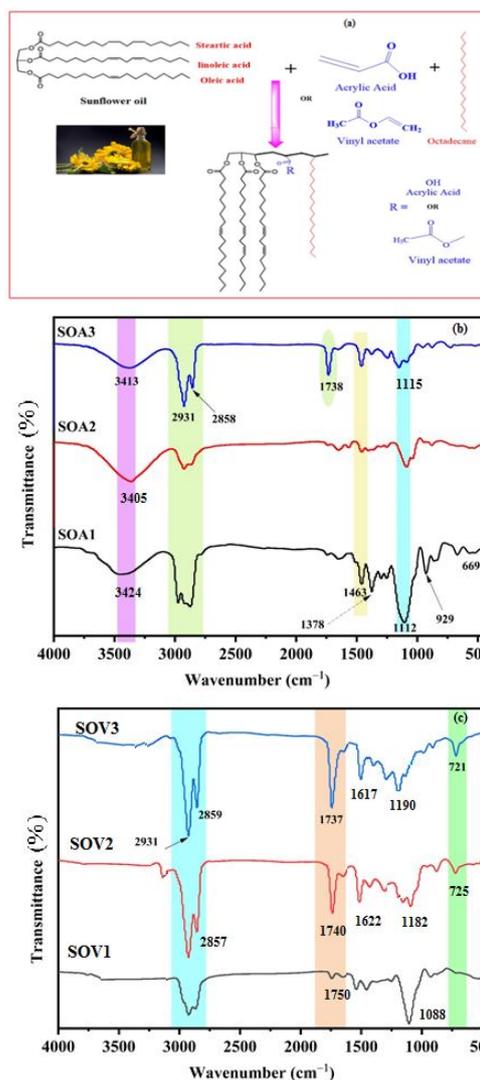


Figure 1: a- Schematic representation of the polymerization reaction, b- IR spectra of SOA group and c- IR spectra of SOV group

3.2. Characterizations of the prepared surfactants:

Molecular weights of the prepared PPDs -as measured by GPC- are given in table 3. It can be seen that the formulations based on acrylic acid display higher average molecular weights and greater heterogeneity. On the other hand, the polymers based on vinyl acetate are of lower molecular weights and more uniformity. This may be attributed to the higher reactivity of acrylic acid when compared to vinyl acetate which leads to higher randomness. This interpretation runs parallel to Plutalova and Chernikova [32]. Therefore, longer hydrophobic chains are highly favored for inducing effective steric inhibition of the crystal growth [33]. Indeed, the cloud points are very important features that judge the solubility of the solute in the solvent versus the

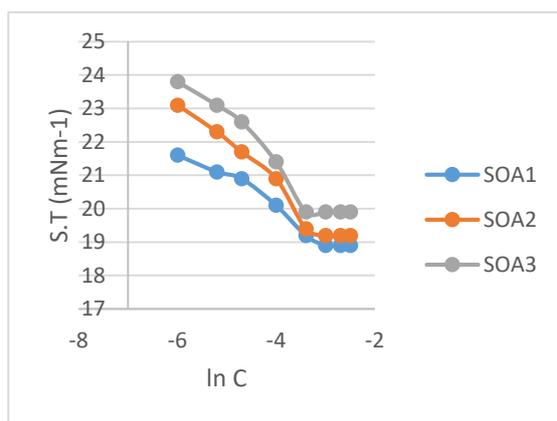
temperature factor. Therefore, the cloud points of the PPDs in dodecane (b.p 216.2°C) are also given in Table 3. It can be seen that the values of the cloud points run parallel to the determined molecular weights. This observation is very reasonable regarding the increased solubility of the PPD molecule by increasing the hydrophobic contents constituting this molecule [34]. This reflects better miscibility of the prepared compounds with the crude oil and reveals enhanced pour point depression effect as will be seen in the next sections.

Table 3: Characterization of the synthesized terpolymeric additives

Additive designation	C.P. (in dodecane) (°C)	M. wt (g. mol)	Poly dispersity index
SOA1	55.4	33000	1.82
SOA2	50.8	31000	1.80
SOA3	48.5	28000	1.60
SOV1	46.7	25000	1.56
SOV2	44.2	22000	1.41
SOV3	41.8	20000	1.32

3.3. Surface activity of the green PPDs

Figure 2 (a and b) illustrates the surface tension curves of the prepared surfactants as a function of the



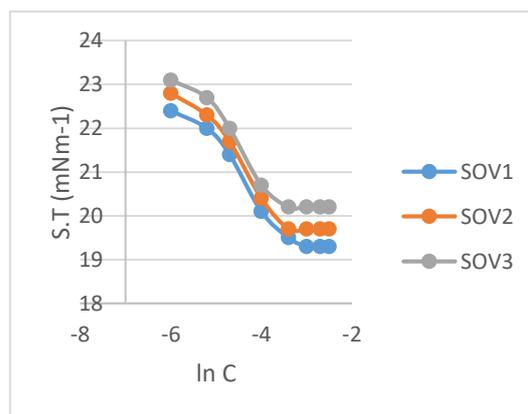
(a)

logarithm of their concentrations in dodecane at 25°C for the acrylic acid and vinyl acetate groups respectively. It can be seen that the surface tension of surfactant solutions decreased with increasing concentrations, reaching clear break points, which were taken as CMC. Careful investigation of these figures, the following observations can be listed out:

- The surface activity of the first group is more pronounced than the second group.
- The order of surface activity runs parallel to the molecular weight of the molecule. This can be well understood on the basis of the distribution of the hydrophobic chains on the surface of the octadecane.
- The maximum surface reduction was achieved by SOA1 which reduced the surface tension of octadecane from 25 to 19 mNm⁻¹. This value of reduction is reasonable regarding the weak Van der Waal forces between the non-polar octadecane molecules.

3.4. Evaluation of the prepared terpolymers as pour point depressant

The temperature at which the flow of crude oil ceases due to gravity is known as the pour point. Waxy petroleum crude oil with a high pour point is particularly problematic during transportation in cold weather. The hardness of cold oil is mainly due to the crystalline paraffin wax. Pour point depressants diminish the size of crystal structures and lessen the cohesion between them resulting in reduced pour point and increased flux at lower temperatures [35].



(b)

Figure 2: Surface tension-concentration isotherms of the prepared PPDs in octadecane at 25°C.

3.4.1. Effect of the synthesised terpolymers' average molecular weights on their pour point depressant efficacy

Pour point depressant was used to evaluate the green terpolymers (SOA1, SOA2, SOA3, SOV1, SOV2, and SOV3) at a concentration of 2000 ppm in crude oil and the experimental findings are given in Table 4. The molecular weight variation can be observed from the data of molecular weights mentioned in Table 3, where the molecular weights ranging from 33000 to 20000 and that the optimum performance is achieved within the range of 33000 to 31000 (SOA1 and SOA2). Moreover, it is shown that (SOA1 and SOA2) with the highest polydispersity index (1.82 and 1.80 respectively) reached the ideal

pour point depression $\Delta pp = 24$ and 18 °C at 2000 ppm with respect to the other terpolymers, Figure 3.

On the other hand, terpolymers SOV2 and SOV3, with the minimal polydispersity (1.41 and 1.32 respectively), achieved the least pour point depression $\Delta pp = 12$ and 9 °C at the same dose. Consequently, it can be said that these terpolymers' performance is nearly better than the polydispersity index. This outcome is consistent with what we previously published about this point [36]. Overall, it has been shown that the polydispersity index and average molecular weights are key factors influencing how effective the terpolymeric additives that are used are.

Table 4: Impact of the environmentally friendly additives on the waxy crude oil's pour point.

Additive design		Crude oil									
		Concentration of Additive, ppm									
		Nil	250		500		750		1000		2000
	pp	Δpp	pp	Δpp	pp	Δpp	pp	Δpp	pp	Δpp	
SOA1	24	18	6	9	15	6	18	6	18	0	24
SOA2	24	18	6	12	12	12	12	9	15	6	18
SOA3	24	21	3	12	12	12	9	12	12	9	15
SOV1	24	24	0	18	6	18	9	12	12	9	15
SOV2	24	24	0	18	6	18	9	15	9	12	12
SOV3	24	24	0	21	3	18	6	18	6	15	9

3.4.2. Impact of the terpolymer concentration on the pour point depression efficiency of the samples studied.

The data of pour point measurement of untreated and treated crude oil (at different dosages of PPD additive 250, 500, 750, 1000 and 2000ppm) were tabulated in Table 4 and presented in Figure 1. As the concentration of terpolymer increased, the treated waxy crude oil's pour point values gradually decreased. Therefore, it was found that utilising 2000 ppm SOA1 had the greatest potency for lowering the treated waxy crude oil's pour point from 24 to 0°C. This indicates that the additive co-crystallizes with the paraffins at this concentration, changing their crystal surface to inhibit accumulation and growth. It is possible to attribute the decreased efficiency at lower concentrations to either wax crystallisation with terpolymer-induced nucleation or to the precipitation of pure terpolymer [26].

3.4.3. Validation of the green terpolymers' molar ratios for their efficacy as pour point depressants.

Additionally, the usefulness of the pour point depression in relation to the component molar ratio is examined. The data presented in Table 4 reveals that the effectiveness of terpolymers increases in the order SOA1 > SOA2 > SOA3 in group acrylic acid and in the same order in the group of vinyl acetate. While the acrylic group is better than the group vinyl acetate as pour point depressants. This observation may be due to the higher polarity of acrylic acid with respect to vinyl acetate as feasible generation of intermolecular hydrogen bonding between acrylic acid molecules. This finding is consistent with previous research on the benefit of slightly polar groups over non-polar or highly polar groups for enhancing flow behaviour and improving interaction with precipitating paraffin [37].

3.4.4. Properties of rheology and flow dynamics

The streaming readiness of a waxy crude was found strongly dependent on the shear rate applied during cooling (shear history effect), i.e., the viscosity and rheological behaviour of crude oils are significantly influenced by their shear history. As a result, there is a minimum operating point below which waxy crude oil pipeline flow is impeded. When crude oil is subjected to shear, the interaction between the polymeric molecule and the wax particulates causes the crystal to break easily, producing particles with varying sizes, shapes, and rheological behaviors. Therefore, overcoming these challenges—especially in a clod environment—requires a thorough understanding of the rheology of crude oil. Generally, compositional factors like the kind, quantity, and nature of wax, as well as its crystallisation behaviours, influence the flow behaviour of the waxy crude. It is also dependent on surrounding environments such as the applied shear rate, time of shearing, temperature and rate of cooling [38].

Dynamic viscosity measurements at 15, 20, and 30 °C were used to confirm the rheological behaviour of both treated and untreated crude oil in the presence of the most effective concentration (2000 ppm), as shown in Figure 3. At all temperatures, it is evident that shear stress rises as shear rate does as well. As seen in Figure 4-6, the cold flow pattern for the untreated crude oil exhibits a non-Newtonian yield pseudoplastic rheological behaviour due to an abrupt increase in shear stress as shear rate increases. The rheological data displayed in Figures 7-10 show that the viscosity of the treated crude oil decreases linearly with the increase of the shear rate under all the applied temperatures and the rate of decrease was reduced at higher shear rates where the viscosity attained a constant value. The obtained data reveal that SOA1 was superior over other counterparts. The following explanations could be given for this behaviour: Wax crystals tend to be partially destroyed by the energy applied by shear and debauched energy in the matrix at temperatures close to the pour point and at reduced shear rates. Conversely, a greater shear rate increases the energy dissipated, which overcomes the yield stress and starts the oil flowing. Additionally, the clustered masses shrank at high shear rates, allowing some of the continuous phase that had been trapped inside the agglomerates to escape. Finally, the viscosity is reduced because the effective dispersed phase concentration declines. More increases in the shear rate are applied to this process until most agglomerates have completely broken down to their original size. Consequently, non-Newtonian

characteristics are displayed by the waxy crude oil system [39]. Thus, the reduction the rheological parameters after adding the green terpolymers can be referred to their amphiphilic nature. Therefore, one important factor preventing the agglomeration of wax crystals in the crude oil is the higher polarity of acrylic acid in the terpolymer chains compared to vinyl acetate. The sample crude oil treated with 2000 ppm SOA1 displayed a distinguished rheology performance over crude oil treated with 2000ppm SOV1.

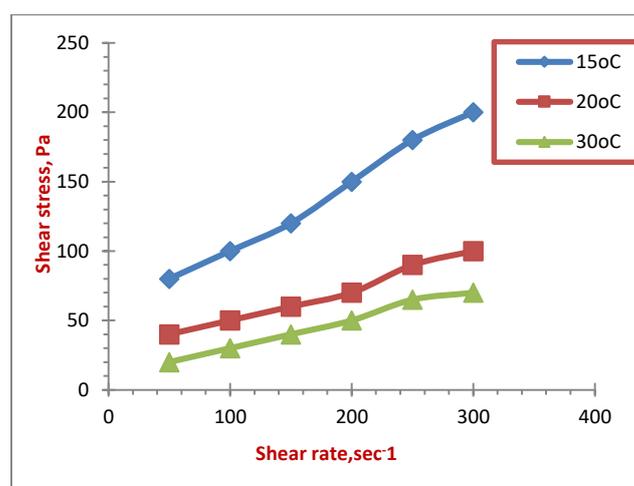


Figure 3: Shear stress and shear rate in relation to untreated crude oil

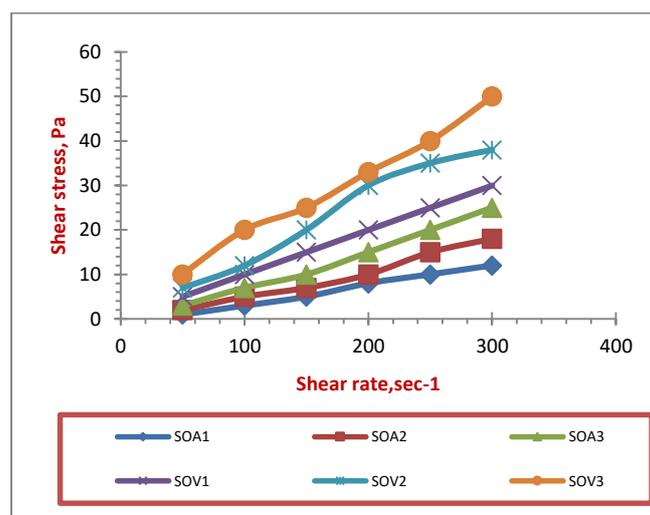


Figure 4: Relationship between shear stress and shear rate for crude oil treated at 15 °C with 2000 ppm of various additives

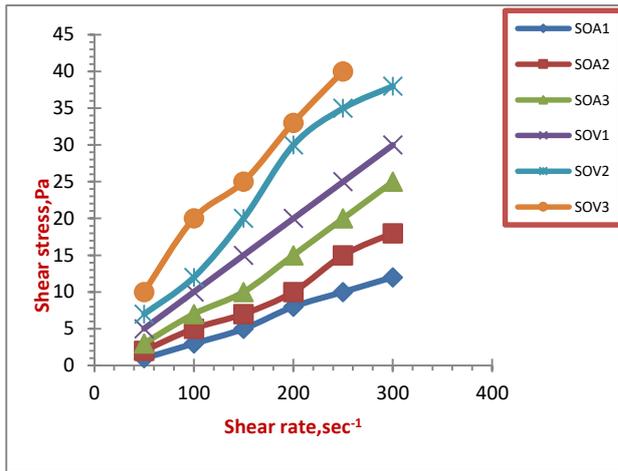
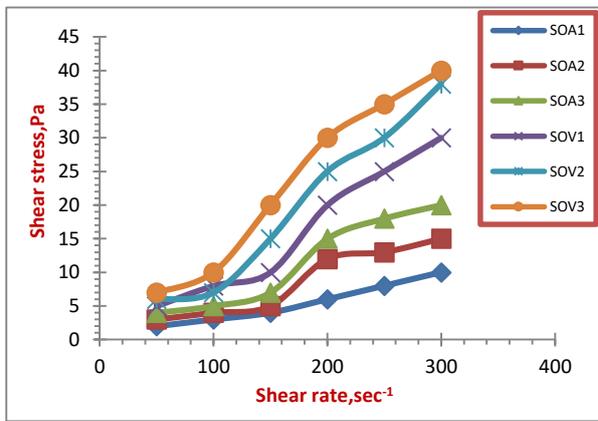


Figure 5: Shear rate and shear stress relationship for crude oil



treated with 2000 ppm of various additives at 20 °C

Figure 6: Relationship between shear stress and shear rate for crude oil treated at 30 °C with 2000 parts per million of various additives

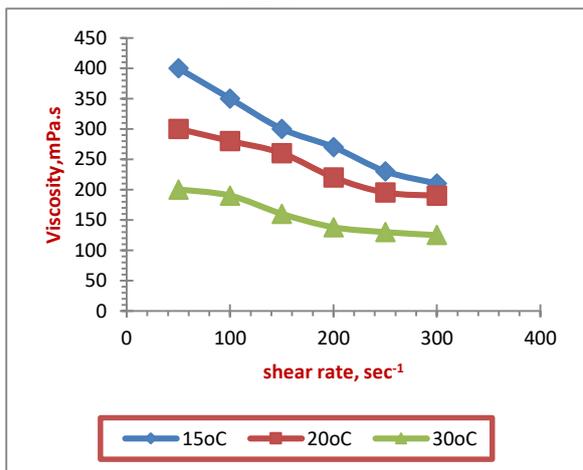


Figure 7: Relation between viscosity and shear rate at different temperatures for untreated crude oil

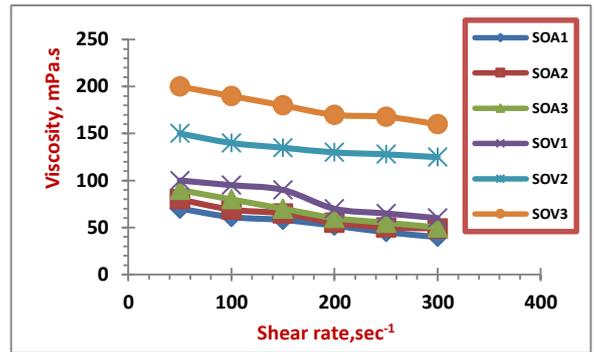


Figure 8: Relation between viscosity and shear rate with 2000ppm from different additives at 15oC for crude oil treated

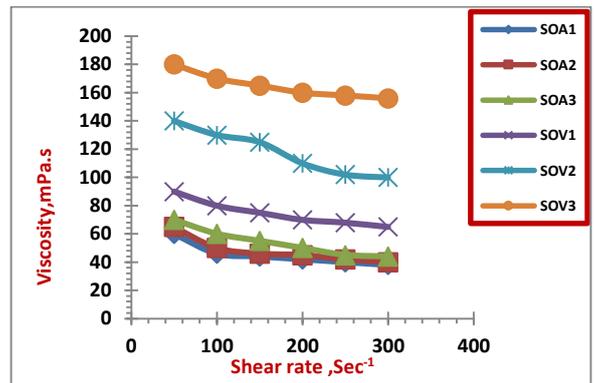


Figure 9: Relation between viscosity and shear rate for treated crude oil with 2000ppm of different additives at 20°C

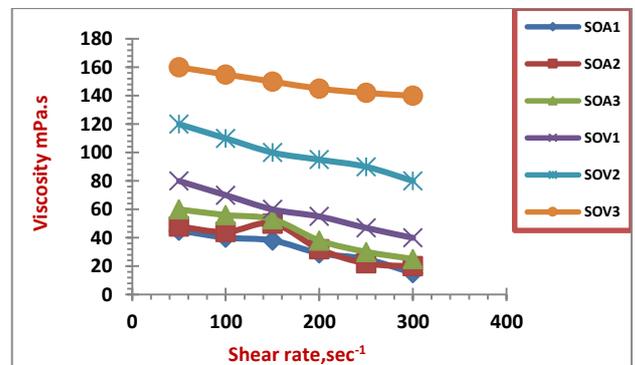


Figure 10. shows the relationship between shear rate and viscosity for crude oil treated at 30°C with 2000 ppm of different additives

3.5. Kind of additive and wax modification

Photomicrographs depicted in Figure 11(a–c) demonstrate how the type of additive can alter the morphology of variant wax. In figure 11a, the untreated crude oil showed large collected lumps of wax (PP= 24 °C) of approximate size of 100 μm which were reduced upon treated with 2000 ppm of SOV1 into PP= 12°C. However, Figure 11b's data suggested a significant decrease in the size of wax crystals and the formation of a large number of finely dispersed crystals. When adding the SOA1 (PP₂₀₀₀

ppm = 0°C), finely dispersed wax crystals started to appear, Figure 11c. In reference to the flow parameter measurements, it is observed that a higher degree of wax modification occurs in the order POA1>POS1 with an increase in additive activity in terms of Δ PP; that is, there is a satisfactory correlation between the measured flow parameter and wax modification.

3.6. Proposed mechanism of preventing wax deposition

The wax crystals in crude oil can be dissolved by the oil reservoir's high temperature and pressure. Then, the abrupt drop in temperature during the oil movement from deep to surface levels leads to the precipitation of paraffin [40]. The non-Newtonian behaviour of crude oil and its extremely high viscosity limit the oil flow as it approaches the pour point. The paraffinic fraction of crude oil that consists of cycloalkane, branched chain alkane, and normal alkane is known as wax molecules. Some or all of these fractions readily crystallize under specific conditions and creels the movement of crude oil [41].

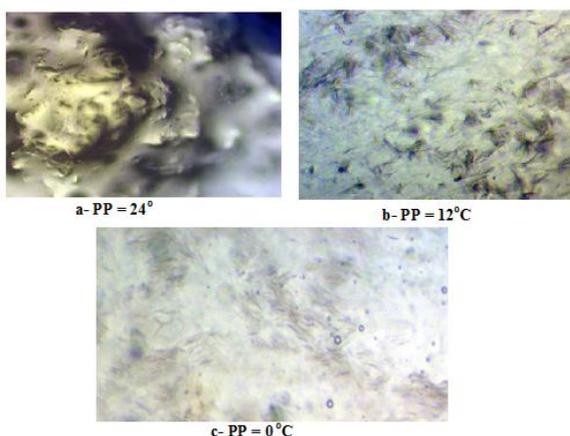


Figure 11: Photomicrographs of a: Crude oil (CO) untreated, b: (CO)+2000ppm SOA1 and, c: (CO)+2000ppm SOV1. (The field scale is 100µm)

Therefore, the mechanism of wax deposition involves the following steps [42]:

- Formation of wax crystals under certain conditions.
- Wax crystals tend to form a network structure (Crystal growth).
- Entrapping the liquid fractions within the cage like structure when the temperature decreases.
- When crude oil reaches the pour point, it stops moving altogether, clogging the pipelines.

The chemical additives play very crucial role in inhibition of wax crystal growth and enhancing creation of smaller crystals, where volume to surface

ratio is high. The wax crystallization is usually inhibited or deferred by different mechanisms involve nucleation, co-crystallization or adsorption of these additives onto the tiny crystals preventing them from accumulation [43]. According to another theory, surface modification phenomena and thermodynamic solubility work together to improve flowability in crude oil that has been benefited by polymeric additives [44]. In the present work, we assume that the prepared additives are adsorbed onto the wax crystals via Van Der Waal forces and arrange themselves in a manner that restrict crystal growth by strong steric interaction, Figure 12.

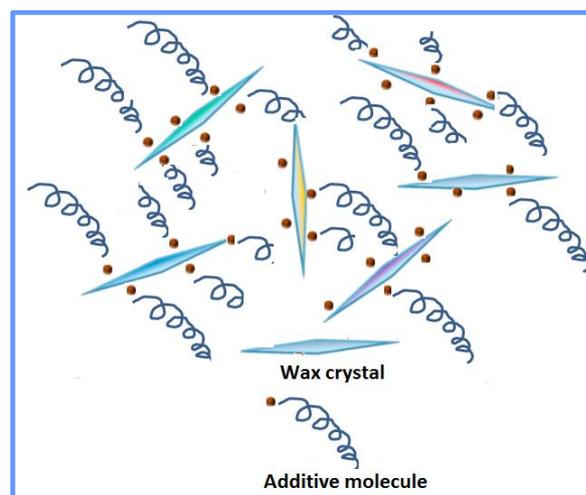


Figure 12: Proposed mechanism of prevention of crystal growth by the green additives

4. Conclusions

The overall conclusions of this the work can be addressed in following points:

- ❖ Six green sunflower-based terpolymers (namely; SOA1, SOA2, SOA3, SOV1, SOV2 and SOV3) were prepared and assessed as waxy crude oil pour point depressants.
- ❖ The monomer ratios were varied in order to investigate the effect of structure variation on the efficiency of the additives' purported ability to lower waxy crude oil's pour point.
- ❖ The prepared additives were characterized by FTIR, GPC and their effect on pour point and rheological properties of the crude oil was investigated.
- ❖ The surface activity of the prepared additives in reducing the surface tension of dodecane reveal that these materials can adsorb onto the surface of hydrocarbon by Van der Waal forces and this is an indication for their suitability for this application.

❖ The effect of average molecular weights, poly dispersity index of these additive on their performance as pour point depressants/ flow improvers was verified.

❖ The data reveal that the depression activity increased as the molecular weight and polydispersity increased.

❖ It was found that the reduction in the pour point runs parallel to the concentration of the additive and that the maximum reduction was attained at 2000 ppm.

❖ Moreover, the impact of these terpolymer additions on the waxy crude oil's pour point and rheological characteristics was confirmed.

❖ The wax modification induced by the effective pour point depressant can be monitored by the photo analysis. It is evident that the pour point depressant changed the irregular large size crystals into finely dispersed wax crystals and generally affected crystal growth.

Finally, this research reduced the deposition of the wax crystal structure, resulting in very affordable promising products that can be used to improve crude oil transportation, particularly in cold weather. Also, the green chemistry approach is being applied by introducing green and cost-effective materials based on used sunflower oil.

5. Ethical Approval

No Ethical approval required for this article.

6. Consent to Participate

The study's authors attest that all of the data and conclusions presented in it are accurate experimental results.

7. Consent to Publish

The authors authorize the publication of the information contained therein.

8. Funding

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9. Competing Interests

The authors declare no conflict of interest.

10. Accessibility of information and resources

The manuscript contains the data that back up the study's conclusions.

11. References

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