



Chemical mitigation technology for wax deposition in submarine oil pipeline systems

Marwa Elkatory^{a,*}, Emad Soliman^a, Mohamed Hassaan^b, Rehab Ali^c, Eslam Hafez^d,
Hesham S. Ibrahim^e, Ahmed Hashem^f



- a. Polymer Materials Research Department, Advanced Technology and New Materials Research Institute, SRTA-City, New Borg El-Arab City 21934, Alexandria, Egypt.*
b. Marine Pollution Lab, National Institute of Oceanography and Fisheries, Bahary 12622, Alexandria, Egypt.
c. Fabrication Technology Department, Advanced Technology and New Materials Research Institute (ATNMRI), City of Scientific Research and Technological Applications (SRTA-City), New Borg El-Arab City 21934, Alexandria, Egypt.
d. petrochemical department Egyptian petroleum research institute
e. Researches and Laboratorial Studies, El-Ameria Petroleum Refining Co. (APRC), Alexandria, Egypt
f. Chemistry Department, Faculty of Science, Ain Shams University, Cairo 11566, Egypt.

Abstract

This study aims to produce a cost-effective pour point depressant (PPD) to mitigate wax deposition of waxy petroleum crude oil (WPCO) in subsea pipelines from free fatty acids which are produced as wastes from sunflower oil refining process. The major constituents of these wastes are unsaturated fatty acids i.e., oleic acid (41.926%) and linoleic acid (38.892%), were first esterified and copolymerized with maleic anhydride. Then the obtained copolymers were then esterified with fatty alcohol (C₁₉H₃₆O₃) to form comb-like poly fatty esters (PFES). The copolymers and its esterified form were structurally characterized by FTIR, XRD spectral analysis and scanning electron microscopy (SEM). Moreover, the potential effects of this PPD on paraffinic waxes, pour point, and waxes crystallization was investigated by (DSC) and (XRD). The measurements showed that the using of PPD has a great impacts on hindering wax formation and on the WPCO pour point reduction from 24 to 3°C by using a dosage of 3000 ppm.

Keywords: Pour point depressant, Agro-industrial wastes, Co-polymerization, Wax crystallization, Petroleum crude oil.

Introduction

The main source of energy until now is the petroleum crude oil, which can be classified into three types; paraffin base, intermediate base and/or naphthenic base. The most problematic kind of these previous types is the paraffinic base that contains long chain normal alkanes which tend to accumulate waxes and obstacle the oil flow ability [1,2]. The temperature is the most dominant and critical factor affecting the paraffinic wax deposition. In deep-water zone with extremely low temperature, below wax appearance temperature (WAT), the motion of the wax molecules in the crude oil are being hindered, due to less energy to move around freely the wax crystals that become closer and aligned showing a strong tendency to crystallize together [3,4]. Such paraffinic waxes agglomerates on the inner surface in submarine pipeline can turn the oil into a particulate gel fluid

which is hardly and costly transported through pipelines and consume much energy to pump such these oils from the reservoir to the refinery causing a number of handling problems [5,6]. Consequently, these problems cause (i) reduction in flow area, (ii) change in wall friction and (iii) blockage of the subsea pipeline that eventually leads to complete shutdown of production processes and the oil industry imposing large costs. Therefore, these waxy crude oils need pre-treatments with chemical additives. The chemical treatment are the predominant and economic method than others ways for the mitigation wax deposition from waxy crude oil as well as they increase its flow ability at lower temperature that are known as flow improvers, crystal modifiers and PPDs [7,8]. Hence they improve the oil's flow and transportation through the pipelines. Polymers such as vinyl acetate copolymer, acrylate copolymer, and their derivatives, terpolymers, and nanocomposite are the main

*Corresponding author e-mail: marwa_elkatory@yahoo.com; (Marwa R.Elkatory).

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additives used in this respect [9,11]. Such comb-like polymers, as previously reported, exhibit higher ability to reduce the pour point of crude oils, due to the non-polar long side alkyl chains that can self-assemble to nucleated the long-chain paraffin crystallization or co-crystallize with paraffin wax to modify the size and shape of wax crystals [4,11-14]. Many types of copolyester were synthesized and utilized as PPDs and viscosity modifiers [4, 15-17], while the high cost of the raw materials and preparation difficulties always obstacle using of these additives in large or industrial scale. Therefore, looking for waste of renewable source as waste vegetable oil used as reliable starting material to access new products with a wide array of structural and functional variations to avoid high cost and address problems in the environment, in waste disposal caused by leakage into marine [18,19]. These oils they are classed as the International Convention for the Prevention of Pollution from Ships (MARPOL) Y ("Noxious liquid substances with if discharge into the sea from tank cleaning of de-ballasting operations, or deemed to present a hazard to either marine resources or human health or cause harm to amenities or other legitimate users of the sea and therefore justify a limitation on the quality and quantity of the discharge into the marine environment"). However, when spilled in significant volumes, and particularly in the spring and summer, they can have adverse effects on the environment or economic activities (tourism, mariculture) and interfere with amenities [20].

This work aims to benefit from the sunflower oil refining free fatty acids which are considered as wastes to be utilized as an abundant, available low cost raw material for producing cost-effective bio-based functional co-polymer. The synthesized co-polymer is full characterized and its performance is assessed as a pour point depressant for WPCO to investigate the potential interactions between such additive and the paraffinic wax.

Experimental

Reagents

Sunflower refining wastes, the source of free fatty acids, were donated from extracted oils and derivatives Co. Egyptian WPCO was obtained from Alamein field that is located in the Egyptian western desert. Maleic anhydride, oleic acid, octadecanol, p-toluene sulphonic acid, and toluene were obtained as analytical reagents from Aldrich Chemicals and used as received. Benzoyl peroxide was supplied from Acros Organics and was used as an initiator after its recrystallization.

WPCO location and characterization

Egypt is one of the oldest energy producers in the Middle East and one of the major oil-producing non-OPEC countries. Figure 1 shows the main oil

production fields and their locations in Egypt. According to the Egyptian General Petroleum Corporation (EGPC), Crude Oil Production in Egypt averaged 705,960 b/d from 1994 until 2018, reaching an all-time high of 930,000 b/d in November of 1996 and a record low of 560,000 b/d in January of 2018. The Western Desert covers about two-thirds of the whole area of Egypt and plays a large role in supporting Egypt's oil and gas sector. In the last few years, the northern half of the Western Desert witnessed a series of major oil discoveries, including new fields of the coastal basins in the Alamein and north Ras-Quattara basins [21] as shown in Fig. 1. Crude oil production from the Western Desert comprised 58% of the total Egyptian oil production in 2018. The coastal basins are characterized by their high oil and gas accumulations, which represents more than one-third of the oil production from the northern Western Desert from 150 producing wells in 16 oil fields. The Alamein Block lies in the Western Desert, around 130 kilometers southwest of Alexandria. Phillips Petroleum Co. discovered the Alamein field in 1966 and brought it on-stream two years later. Alamein field is one of the most prolific petroleum trends which has the third high oil productivity in Egypt after south Mariut and south Ghazalat. The Alamein concession has produced over 130 million BO since discovered [22]. However, the main drawback faces the Alamein field is the production of a paraffinic crude oil which has a relatively high pour point and viscosity. The oil physicochemical properties were analyzed at Amerya petroleum refining Co. according to American society for testing and materials (ASTM) standards.



Fig. 1. The main oil production fields in Egypt.

Sunflower oil FFAs refining wastes characterization

The composition of these wastes, free fatty acids, were qualitatively and quantitatively analyzed using a gas chromatograph-mass spectrometer (GCMS)

(Shimadzu QP 2010/Plus). A high polar fused-silica capillary column (Chrompack CP-Sil88 Varian, Middelburg, Netherlands; 100 m 0.25 mm 0.20 ml) was employed for GC-MS analysis. The temperature program was as follows: initial temperature was set as 100°C, held for 2 min, and increased to 160°C with a speed of 10°C/min, then the speed was set at 5°C/min, the column temperature was increased to 220°C and held for 25 min. Both the detector and injector port temperatures were maintained at 240°C. Helium was used as the carrier gas at a flow rate of 3 mL/min.

Synthesis of comb-like poly fatty esters

Synthesis of comb-like PFES from oleic acid and linolenic acid which are the main components of the sunflower oil free fatty acids wastes was carried out according to the following three steps which are summarized in figure 2.

Esterification of free fatty acids wastes

Free fatty acids were esterified with octadecanol (fatty alcohol of molecular formula $C_{18}H_{38}O$) in the presence of concentrated sulphuric acid as a catalyst. The product of n-alkyl esters was neutralized using $NaHCO_3$ solution [12].

Co-polymerization of fatty esters

The pre-prepared n-alkyl esters were copolymerized with maleic anhydride in toluene with different molar ratios of 1:1, 1:2 and 1:3 using benzoyl peroxide as an initiator (1% w/w). The polymerization was conducted at 90°C for 20 h with constant stirring. The copolymer was precipitated in petroleum ether 40/60, then filtered and washed by petroleum ether 40/60. The product, poly (fatty esters-co-succinic anhydride) (PFECOSA), was dried at 60°C.

Formation of pendant alkyl chains (comb-like structure)

The obtained copolymers were esterified with octadecanol. The esterification reaction was conducted in 100 ml xylene as a solvent in presence of *p*-toluene sulphonic acid as a catalyst in a three-necked bottom flask equipped with a dean-stark. The reaction was carried out at $147 \pm 2^\circ C$ for 15 h and then the temperature was slowly raised to $163 \pm 2^\circ C$ up to end of the reaction. The resultant PFES was precipitated and washed by acetone and then dried and collected, the molecular weight was determined using the gel permeation chromatography (GPC).

Characterization of structural properties of PFECOSA and PFES

Fourier transform infrared spectroscopic analysis was carried out using (FTIR Shimadzu 8400S spectrometer, Japan) to confirm the formation and the structure of the dominant synthesized copolymer and polyester after selecting proper molecular weight which detected by (GPC) to record 12759 MW by using molar ratio 1:2.

X-ray diffractograms of PFECOSA and PFES were obtained using (Shimadzu XRD-7000 diffractometer, Japan), adjusted at 30 kV, 30 mA with Cu $K\alpha$. The specimen was placed in the sample holder and scanned at 2θ from 4 - 100° at a rate of 2°/min.

Performance evaluation of the synthesized polymeric additives

Pour point (PP) measurements

A certain dosage (1000, 2000, 3000 and 5000 ppm) of the synthesized PFES in xylene (30%) active material was injected at 60°C into the WPCO. The treated oils were stirred to be homogenized with complete dissolution of the polymeric additives and then subjected to the pour point test according to the ASTM D97 standard procedure without reheating.

Crystallization behavior

Differential scanning calorimetry (DSC) tests were performed with (Shimadzu DSC-60A calorimeter, Japan). After the waxy oil sample was heated to 70°C to dissolve the wax completely, about 1 mg of waxy oil was placed in a DSC pan equipped with a data processor. The samples allowed to cool to -25°C at a constant cooling rate of 10°C/min and scanned from -20 to 70°C at a constant heating rate of 10°C/min.

X-ray diffraction analysis was carried out by selecting a graphite monochromator, 40 kV, 30 mA with Cu $K\alpha$ radiation and defined a beam with an angular resolution of full-width at half-maximum δ (2θ). Full wave at half maximum = 0.15° in the horizontal direction. The sample was scanned at a rate of 4°C/min in the 2θ range of 4–100°. Data were collected on each sample using a 2θ step size of 0.02° [23].

Results and Discussion

WPCO characterization

Determination of the WPCO physicochemical characteristics is very essential to evaluate the oil and facilitate measuring the improvement of the oil after the depressant addition. Table 1 summarizes the mean of the WPCO physicochemical properties \pm standard deviation (SD).

Sunflower oil FFAs refining wastes characterization

The chemical composition of the sunflower oil FFAs refining wastes was characterized using GCMS and summarized in Table 2.

Structural properties characterization

FTIR spectra

FTIR spectrum of dominant PFECOSA and PFES are shown in Fig. 3. PFECOSA spectrum showed absorption bands at 607.6, and 1680.05 cm^{-1} , which may be attributed to vibration $(CH_2)_n$ and C=O. The bands at 1230.63 and 1438.94 indicate the presence of C-O and CH_2 [24]. Besides, the characteristic CH_3

absorption peak of the alkyl group has appeared at 2906 cm⁻¹[16]. On the other side, the spectrum of PFES displayed the similar absorption bands belonging to vibration of a long chain carbon of the hydrophobic group which is appeared at 719.47 cm⁻¹[24]. Functional groups of C–O, CH₂ and C=O were represented in FECOSA spectrum at 1222.91, 1471.74 and 1726.35 cm⁻¹, respectively [25]. An increase of the intensities of these adsorption bands can confirm introducing more methylene (-CH₂-) groups which are involved in fatty esters. However, absorption bands due to CH symmetric and CH asymmetric stretch have appeared at 2920.32 and 2852.81 cm⁻¹[26].

XRD patterns

X-ray diffractogram for the dominant PFECOSA exhibited some scattering angles extending in 2θ scale where, the diffraction peaks having half-width narrow appeared at 15.06, 17.86, 20.16, 22.52 and 28.54° which are belonging to scattering of the crystalline phase (bigger crystallites) of copolymer matrix. While, the spectrum of dominant PFES was exhibited significant variation in the Bragg angle values where, fewer diffraction peaks of crystallites appeared at 11.93, 13.96 and 16.04° with lower relative scattering intensities as shown in Fig. 4. This result can be explained on the basis that the structure of the crystalline phases is partly transformed by esterification of PFECOSA. These findings prove that nonpolar alkylated branches of such polymeric additives would hinder stacking of the copolymer chains causing lattice distortion and structural disorder producing less crystalline structure compared with that of PFECOSA.

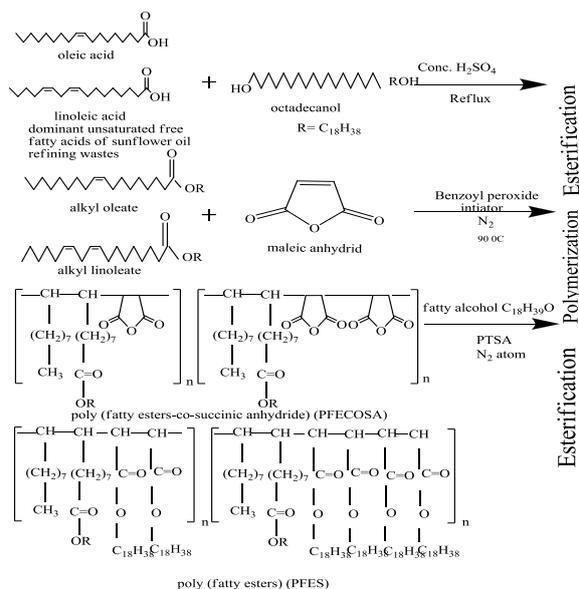


Figure 2 scheme of the three steps of PFES synthesis.

Table 1. Physicochemical characteristics of Alamein crude oil.

| Physico-chemical parameters | Method | Values |
|--------------------------------------|------------|-------------|
| Density (g/cm ³) | ASTM D1298 | 0.818±0.003 |
| API Gravity | ASTM D1298 | 41.38±0.016 |
| Kinematic Viscosity (c.st.) at 40 °C | ASTM D445 | 10.29±0.02 |
| Pour Point, PP (°C) | ASTM D97 | 24±0.2 |
| Wax Content (%) | UOP46 | 12.4±0.1 |
| Asphaltene Content (%) | ASTM D6560 | 1.32±0.02 |
| Water Content (% vol.) | ASTM D4006 | 0.1±0.05 |
| Sediment, %m/m | ASTM D473 | 0.034±0.007 |
| Water and sediment, %vol | ASTM D4007 | 0.15±0.05 |
| Salt content, PT B | ASTM D3230 | 85±1 |
| Ash content, %wt | ASTM D482 | 0.018±0.004 |

Table 2. Fatty acids content of waste sunflower oil.

| Property | Waste Free fatty acids (sunflower oil) |
|------------------------|--|
| Content of fatty acid | wt.% of FA |
| Palmitic acid (C16:0) | 6.095±0.012 |
| Linolenic acid (C18:3) | 0.1919±0.008 |
| Linoleic acid (C18:2c) | 38.892±0.16 |
| Oleic acid (C18:1c) | 41.926±0.25 |
| Stearic acid (C18:0) | 12.994±0.03 |
| Total % of FA | 100.0 |
| Total unsaturated | 80.98 |

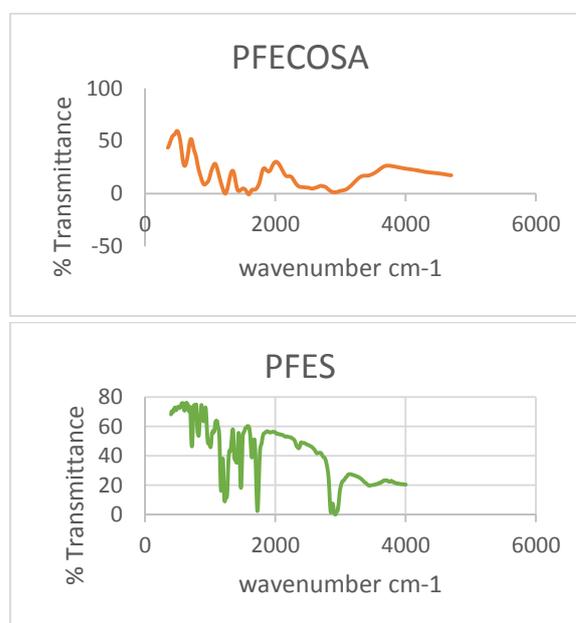


Fig. 3. IR Spectrum of PFECOSA and PFES.

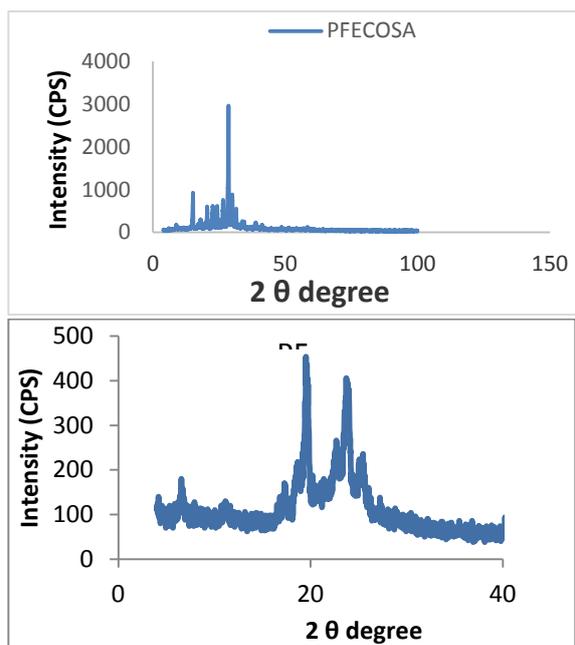


Fig. 4. X-ray diffractograms of FECOSA and PFES.

SEM micrographs

The morphological features of the polymeric additives; PFECOSA and PFES were examined using SEM as shown in Fig. 5. The micrograph of PFECOSA showed that the chains of the copolymer produced from fatty esters with maleic anhydride agglomerated in a large cluster of lamellar flakes or rods having an appearance of broom-like structure similar to wax crystals. Meanwhile, PFES, the esterified form of this copolymer has appeared as a bulky material with a collapsed structure. This structure may be due to the high content of octadecyl side branches which gathered and fold up seemed as mass convergence.

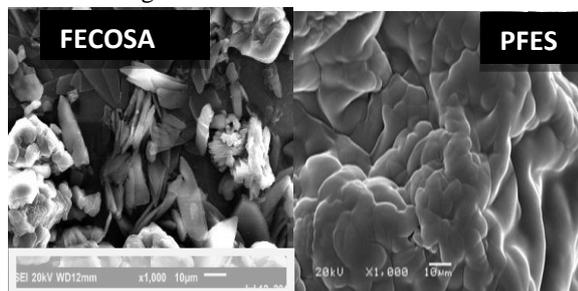


Fig. 5. SEM micrograph of PFECOSA and PFES.

Functional properties characterization

Pour point depression

The results of pour point measurement of plain crude oil and that treated with polyesters at different

dosages of PPD were tabulated in Table 3. The pour point values of the treated waxy crude oil decreased gradually with increasing the PFES concentration. But the higher concentration than 4000 ppm is not commercially acceptable and thus not considered. Thus the highest potency to reduce the pour point of treated waxy crude oil from 24 to 3°C was observed by using 3000 ppm PFES to give the highest pour point depression of 21°C [4]. This can be described on the basis of tethering the PFES polymeric additive with the paraffin wax lamella and therefore form spherulitic crystal instead of the platelet like crystals formation. This reduces the cohesive energy and consequently retards the paraffin crystals growth and agglomerations which are significantly lower the oil pour point [27].

X-ray diffractograms

X-ray diffractograms of untreated WPCO and that treated with PFES are presented in Fig. 6. The XRD patterns of untreated paraffinic wax exhibited two middle-angles scattering at 2θ of 21.0068 and 23.37° which are the typical scattering of the single orthorhombic phase of micro-crystalline paraffin crystals. This type of wax has the ability to retain more oil than macro-crystalline wax [28,29]. On the other side, in the diffractograms of the paraffin wax crystals treated with PFES, the diffraction line intensities of the orthorhombic paraffin mixture, decreased progressively with increasing the additive dosage without any significant variation of the Bragg angle values. This decrease can be explained on the basis of the partial transformation of wax structure from orthorhombic into hexagonal phase accompanying with decreasing the degree of wax crystallinity with increasing the PFES dosage.

DSC thermograms

DSC thermographs of the melting and crystallization intervals of the waxes are measured at the same time for untreated and treated WPCO crystals. The results are summarized in Table 4 and Fig. 7. During the heating cycle, it can be observed that the DSC thermograms of the WPCO before treatment with additives have two endothermic peaks, one of them is broader and the second one is sharper due to the presence of a mixture of paraffin types that have different melting temperatures. After adding PFES, the two endothermic peaks are merged and both the melting range and the peak temperature of solid-liquid transition are decreased gradually with increasing

PFES concentration. Meanwhile, through the cooling cycle, all exothermic peaks of liquid-solid transition corresponding to wax WAT and solid-solid transition are decreased gradually with increasing the PFES dosages [4,18]. These results indicated that doping the paraffin wax with PFES which shifted the phase transition peaks in the wax thermograms to lower temperatures and they were broadened with remarkably less area (ΔH) (lower amount of deposited wax). Thus, the onset temperature and ΔH for wax doped with PFES were decreased with increasing the additive dosage. These results suggest that crystallization was depressed and occurred at lower temperatures and thereby there is a delay in the wax deposition by PFES addition. This may be due to the additive adsorption on the wax crystal surface or co-crystallization with structurally similar alkyl chains in paraffin wax which hinder the crystallization and lead to entropic repulsion between the wax crystals. This repulsion can be enhanced by the polar ester moieties of the co-polymeric additive. In addition, the Van Der Waals interactions between the long alkyl moieties of PPD and paraffinic alkyl chains may improve the wax solubility [27, 28].

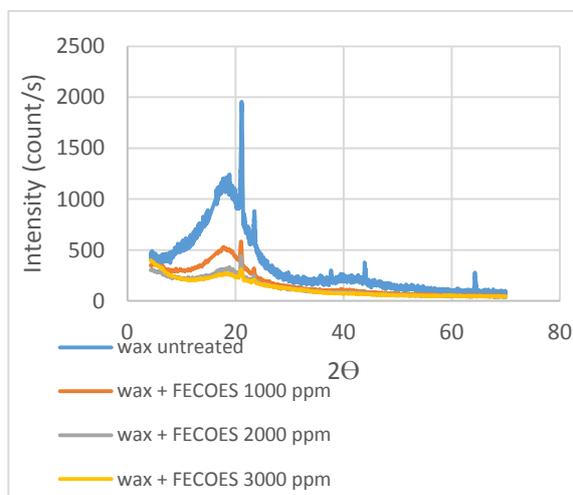


Fig. 6. X-ray diffractograms of untreated WPCO and treated with PFES dosages (1000, 2000 and 3000ppm).

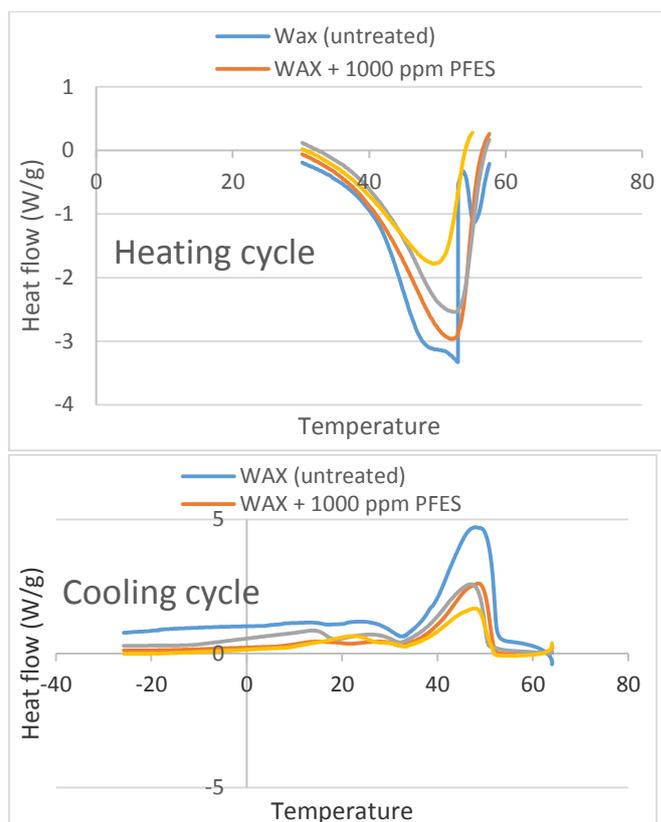


Fig. 7. DSC thermographs of paraffin crystals in untreated WPCO and treated WPCO with different PFES dosages (1000, 2000 and 3000ppm) during two cycles of heating /cooling with rate of 10°C/min.

The interaction mechanism discussion

Figure 8 illustrate under low temperature and without PFES addition, the high content of the wax crystals with short distances facilitates hydrophobic bonds that form wax aggregates as shown in Fig. 11 and convert the WPCO to a two-phase system; the lower phase is wax and the upper phase is oil. Moreover, wax aggregates can be grown due to the interaction of the wax intermolecules, form networks and hamper the crude oil flow ability. These results are consistent with the high pour point of WPCO of 24°C.

Table3 Effect of concentration of polymeric additives on the pour point of crude oil.

| Additive | Pour point (°C) of crude oil by using different additive concentration (ppm) | | | | | Pour point depression (°C) |
|---------------------------|--|------|------|------|------|----------------------------|
| | Blank | 1000 | 2000 | 3000 | 5000 | |
| poly(fatty esters) (PFES) | 24 | 12 | 9 | 3 | 0 | 24 |

Table 4. Effect of PFES additives on pour point and transition temperatures and energies of crude oil (Alamin).

| Conc. of polymeric Additive | Heating cycle | | | | Cooling cycle | | |
|-----------------------------|--------------------|-------|------------------|-----------------------------------|---------------------------------------|---|---|
| | Melting range (°C) | | | $\Delta H_{\text{melting}}$ (J/g) | Wax Appearance Temperature (WAT) (°C) | Solid-solid Phase Transition Temperature (°C) | $\Delta H_{\text{crystallization}}$ (J/g) |
| | Initial | Final | Peak temperature | | | | |
| 0 | 41.55 | 58.53 | 53.66 | - 98.89 | 54.23 | 40.86 | 86.97 |
| PFES 1000 ppm | 38.46 | 57.50 | 52.32 | - 87.41 | 53.75 | 33.72 | 49.38 |
| PFES 2000 ppm | 36.24 | 56.57 | 51.87 | - 68.02 | 51.84 | 33.44 | 47.84 |
| PFES 3000 ppm | 34.87 | 53.43 | 49.14 | - 33.96 | 50.98 | 31.97 | 42.71 |

By using PFES with polar and non-polar groups, the interaction mechanism refers to adsorption or co-crystallization or both [32,33]. The co-crystallization occurs between non-polar alkyl groups of PFES molecules and wax molecules. Meanwhile, PFES is composed of polar ester groups in addition to the non-polar groups. These polar groups exist on the surface of the wax crystals and absorb low molecular weight polar substances to the wax crystal surfaces and form a layer of energy barrier on it, called solvated layer [34]. These solvated layers not only changed the interface properties between the wax crystals and the oil phase but also prevent the connection of the wax crystals and the formation of larger crystals aggregates [35,36].

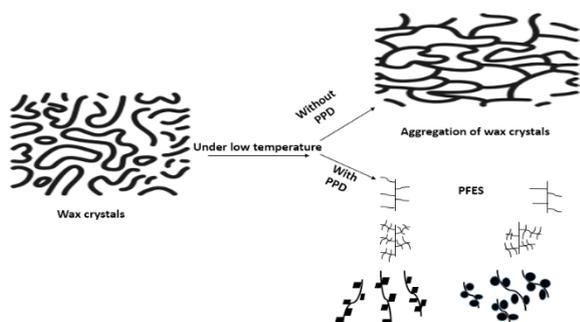


Figure 8: The mechanism of the pour point depressant performance.

Techno-economic analysis of PFES production

The cost of the additives is mainly dependent on the cost of the raw materials that are used in its synthesis. Hence, low cost raw materials such as FFAs are sorely needed to be comparable with the other additives in terms of efficiency, economic feasibility, availability, and eco-friendly. Figure 13 showed that in 2017/2018, the global production of sunflower seeds is 40.34 MT. These seeds are used to produce 17.75 MT of

sunflower edible oil, used for cooking purposes, and produce 0.44 MT of free fatty acids which are non-edible and considered as wastes after the oil refining process. In this study, these wastes are viewed and dealt with as a renewable source of producing valuable products rather than just partially using it in soap production and other minor purposes. In Egypt, supplying of FFAs is available all over the year from oil extraction and refining companies with a reasonable price of about 274 \$/Ton. Using the FFAs wastes can reduce the additive production cost by about 83% than using pure oleic acid of the price of 1600 \$/Ton.

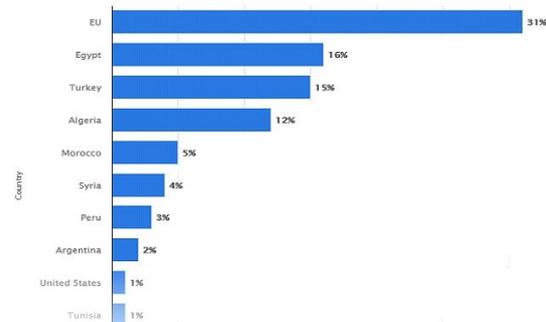


Fig. 9. The worldwide sunflower production distribution by country in 2018/2019.

Conclusions

In this study, comb-shaped PFES is successfully synthesized from free fatty acids obtained as waste from sunflower oil refining industry. Potential feasibility of this polyester as a pour point depressant for WPCO was indicated by measuring its capability for depressing the pour point and improving the cold flow ability. Adding 3000 ppm PFES to the WPCO decreased the pour point from 24 to 3°C and this depression was associated with reducing the paraffin

wax crystal size, suppressing the crystal platelets formation. These results revealed the possibility of producing and using agro-industrial waste (PFES) as a green, efficient, sustainable and cost-effective PPD that can greatly affect the WPCO pour point and viscosity which help to overcome the problems of WPCO transportation and storage.

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