Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Paraffin Inhibition and Pour Point Depression of Waxy Crude Oil Using Newly Synthesized Terpolymeric Additives

Sameh A. Elbanna [1] *, Abdellatief M. M. Abd El Rhman [1], Ayman S. Al-Hussaini [2], and Salah A. Khalil [1]

[1]Egyptian Petroleum Research Institute (EPRI), Nasr City, Cairo, Egypt
[2]Faculty of Science, Port Said University, Port Said City, Egypt

Abstract

Wax deposition under low temperature conditions is a serious problem observed in pipelines transporting crude oil. Herein, three terpolymeric additives; styrene octadecyl acrylate maleic anhydride terpolymer, and the corresponding ester and imide were synthesized through the free radical polymerization technique for the first time. The above mentioned terpolymers were assessed as pour point depressors and paraffin inhibitors for Egyptian waxy crude oil with different concentrations ranging between 50 ppm and 200 ppm. The characteristics of the synthesized terpolymers were investigated using FTIR, ^{1}H-NMR, and GPC techniques. The FTIR and ^{1}H-NMR results demonstrated the successful synthesis of the mentioned terpolymers via confirming their structures. Also, the GPC results revealed the high average molecular weights of the ester and imide terpolymers compared to the corresponding terpolymer. Reasonable depression effects were achieved by the addition of lower concentrations of the synthesized terpolymers to the Egyptian waxy crude oil. The N-containing terpolymer; styrene octadecyl acrylate maleic anhydride imide, with a low concentration of 200 ppm exhibited the highest effect on the waxy crude as it was able to depress the pour point by 15 °C from the initial blank (27 °C to 12 °C), and a paraffin inhibition of 88 %. Thus, the synthesized terpolymers can be considered as promising and applicable additives for depressing the pour points and inhibiting the paraffinic precipitates for the waxy crude oil.

Keywords: Pour point depressant, Paraffin inhibition, Waxy crude oil, Terpolymers, Synthesis and characterization

1. Introduction

One of the major petroleum flow insurance problems is the deposition of wax [1]. When the appearance temperature of wax (WAT) reduces, the crystal usually is divided into a three-dimensional network from crude oil [2, 3]. Many mechanisms, such as molecular, Brownian diffusion, and dispersion shearing exist to reduce wax problems [4]. Chemical treatment [5, 6] with pour point depressant (PPD) [7] or wax inhibitor (WI) [8, 9] is the viable solution for avoiding wax deposition [10, 11]. Pretreatment with a small dosage of PPDs [12] is a cost-effective way to decrease paraffinic wax deposition problems [13, 14]. Comb copolymers are the most promising pour point depressors which consist of a polyvinyl backbone [15] and have amorphous moieties [8, 16] with different pendant chains [17] to enhance the solubility of waxy crude oil [18]. Traditional polymeric PPDs containing waxy-like paraffin parts with a polar part are homogenous copolymers and monomers [19-21]. According to terpolymerization strategies, we designed a new type of acrylate terpolymer which contains and affords the desired properties such as absorption ability, charge mobility, and solubility. By introducing functional monomers as maleic anhydride (MA), styrene (S) into its molecular structure, the structure of octadecyl acrylate can be well adjusted. Styrene with a benzene polar group was selected to synthesize a series of styrene maleic terpolymers. In particular, to improve compatibility with oil components MA has been grafted onto the acrylate. Both double bond electron acceptor and an anhydride in maleic anhydride make it able to polymerization [22]. Styrene maleic anhydride copolymer has strong durability and low cost for

*Corresponding author e-mail: elbannasameh@yahoo.com.; (Sameh A. Elbanna).
Receive Date: 08 April 2022, **Revise Date:** 01 May 2022, **Accept Date:** 13 June 2022, **First Publish Date:** 13 June 2022
DOI: 10.21608/EJCHEM.2022.132291.5838

various applications including adhesives and coatings [23, 24] as starting materials. Chemical modification is our strategy for synthesizing new polymeric materials with synergistic features by esterification and imidation of the synthesized terpolymer. Herein, we have synthesized a novel styrene octadecyl acrylate maleic anhydride terpolymer. Then, it was chemically modified by esterification and imidation reactions to synthesize two newly styrene octadecyl acrylate maleic anhydride ester EDA and imide IDA. The synthetic pristine and modified terpolymers were investigated with various characteristics as FTIR, ^{1}H-NMR, and GPC. In addition the synthesized modified terpolymer efficiency at various dosages as pour point depressors and paraffin inhibitors was evaluated.

2. Experimental

2.1. Materials

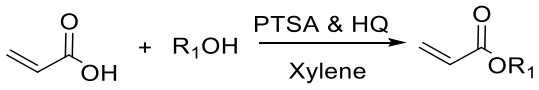
Acrylic acid, styrene, maleic anhydride, octadecanol, octadecyl amine, p-toluene sulphonic acid (PTSA), hydroquinone (HQ), methanol, and xylene were obtained and used as received from Aldrich chemical, while benzoyl peroxide (BPO) was recrystallized from methanol.

2.2. Collected crude oil

Tut waxy crude oil was obtained from Khalda Petroleum Company fields (western desert, Egypt). The physicochemical features of the waxy crude oil investigated and fingerprinted data were established and listed below. The distribution of n-paraffin waxes was determined according to the ASTM D 2887 gas chromatographic analysis and illustrated in (Figure 1). First, the collected crude oil has shaken for an hour to ensure that all measurements have the same physical characteristics.

2.3. Esterification of acrylic acid

One mole of acrylic acid was esterified with one mole of 1-octadecanol in the presence of 1% PTSA as a catalyst and 0.6% HQ as an inhibitor and xylene as the solvent with Dean-Stark. The octadecyl acrylate (ODA) received was light yellow. The synthesis scheme of octadecyl acrylates was illustrated in Scheme 1. A stream of nitrogen was performed for the esterification; the refluxing continued with continuous stirring at 130 °C for 6 h [25-29]. The obtained ester was purified and filtered off repeatedly to ensure the complete removal of unreacted acid then the produced ester was left on $CaCl_2$ overnight for drying [29]. The octadecyl acrylate monomer is now ready to be used in the terpolymerization reactions.

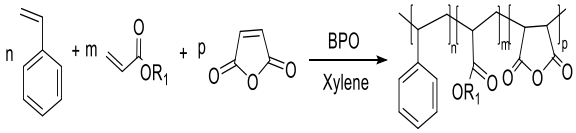


$R_1 = C_{18}H_{37}$

Scheme 1. Esterification of acrylic acid with octadecanol.

2.4. Synthesis of styrene octadecyl acrylate maleic anhydride terpolymer (TOA)

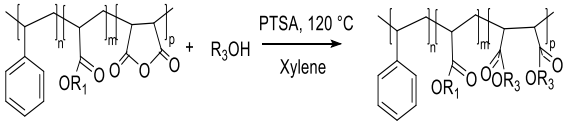
The terpolymer was synthesized by using one mole of the synthesized octadecyl acrylate, one mole of styrene, and one mole of maleic anhydride with the desired weight of initiator benzoyl peroxide (BPO, 1 wt %) in the 3-necked flask using an inert medium of N_2 and xylene as a solvent and heated for 8 h at 80 ^{o}C as indicated in Scheme 2. The temperature was reduced to room temperature when the reaction was completed, then the mixture was poured dropwise into cooled methanol with continuous mixing and stirring, flittered off, and dried. The produced terpolymer was designated as TOA.



Scheme 2. Terpolymerization of styrene octadecyl acrylate maleic anhydride.

2.4.1. Esterification of the synthesized terpolymer

Esterification was directly performed by reacting 1 mole of the synthesized terpolymer with 1 mole of octadecyl alcohol at 120 °C for 6 h in the presence of xylene as a solvent, 1 wt% PTSA as a catalyst, and hydroquinone as an inhibitor (Scheme 3). In a three-necked flask, the ingredients were placed and fitted with the Dean-Stark trap until the theoretical amount of water was separated. The ester was collected and washed with 5% NaOH solution and distilled water then dried in air. This esterified sample was named EOA.



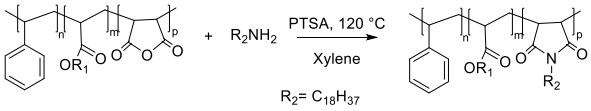
$R_3 = C_{18}H_{37}$

Scheme 3. Esterification of styrene octadecyl acrylate maleic anhydride terpolymer.

2.4.2. Imidation of the synthesized terpolymer

Imidation of the obtained terpolymer was performed by directly reacting one mole of the synthesized terpolymer with one mole of octadecyl amine in a three-necked flask containing toluene as a solvent with constant stirring at 120 °C (see Scheme 4). The obtained product purification was executed

by pouring in an excess volume of methanol then filtration, vacuum drying, and washing with hot water three times. The synthesized imide was denoted as IOA.



Scheme 4. Imidation of styrene octadecyl acrylate maleic anhydride.

2.5. Characterization of the synthesized terpolymers

2.5.1. Infra-Red (FTIR) spectroscopy

The FTIR spectra of the synthesized terpolymers were examined using a Nicolet IS-10 FTIR spectrometer [30-33].

2.5.2. ^{1}H-NMR spectroscopic analysis

To confirm the structure of the synthesized terpolymer, a Bruker-NMR spectrometer operating at 300 MHz with CDCL3 as a solvent was used [34].

2.5.3. Gel Permeation Chromatography (GPC)

The average molecular weights of the synthesized terpolymers were determined at 40 ºC using a GPC-Water 2410 coupled with a 515 HPLC pump and styragel HR THF 7.8X300 mm column. The eluent used was tetrahydrofuran at a flow rate of 1 mL/min.

2.6. Evaluation of the synthesized terpolymers as pour point depressants

The synthesized additives were tested as PPDs at various concentrations (50, 100, 150, and 200 ppm) and injected into crude oil samples collected at 60 °C. The crude oil samples, both treated and untreated, were then evaluated by (ASTM D97) [35]. In addition, the aforementioned additives were tested in the Egyptian Petroleum Research Institute's (EPRI), Chemical Services and Development Center (CSDC) against commercially available PPD products (EPRI-J25 and EPRI-65J).

2.6.1. Evaluation of the synthesized terpolymers as paraffin inhibitors (PI %)

The improvement in the flowability of the treated crude oil via the synthesized additives was evaluated using a laboratory designed cold Finger experiment. This experiment would simulate wax precipitation within oil pipelines [36]. 400 mL of waxy crude oil samples were heated above WAT for thermal treatment for 1 h to dissolve any precipitated wax. The experiments were performed for 3 h. The experimental runs have been replicated three times to find accurate data. Then, the amount of deposit was scraped off from surface tube of the cold finger and then weighed to estimate the paraffin inhibition.

2.7. Crude oil component analysis

A wax deposit was isolated and measured from crude oil using the UOP procedure (46/64). And the standard procedure (IP 143/84) was used to isolate asphaltene [37].

3. Results and Discussion

3.1. Characterization of the collected crude oil

Tut waxy crude oil's physicochemical properties were analyzed using standard ASTM methods to establish the average molecular weight distribution of wax. The gas chromatography technique according to the IP/372/85 system is used. Data presented in Figure 1 and Table 1, respectively indicate that the average distribution of carbon numbers is 12.34 for the collected crude oil and represented its physical characteristics. Also, the wax content data obtained show that the collected crude oil is waxy and may lead to wax network build-up in the pipelines [38].

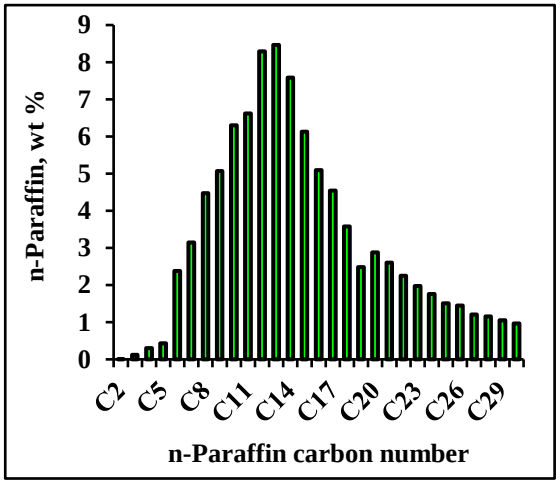


Fig. 1 Carbon number distribution of n-paraffin in Tut waxy crude oil

Table 1 Physical characteristics of the evaluated Tut waxy crude oil

Properties	Method	Result
Density at 20 ºC (g/cm^3)	ASTM D1298	0.8301
Kinematic viscosity at 40ºC cst	ASTM D445	2.77
Dynamic viscosity at 40ºC cp	ASTM D2196-18	2.30
Pour point (PP), ºC	ASTM D 97	27.0
Wax content, (wt %)	UOP 46/64	13.0
Asphaltene content, (wt %)	IP 143/84	2.00
Average carbon number (n)	IP 372/85	12.34
Water content, (wt %)	IP 74/70	0.35
Ash content, (wt %)	ASTM D 482	0.02
API gravity at 60° F	ASTMD-1298	38.96

3.2. Characterization of the synthesized octadecyl acrylate (ODA)

3.2.1. FTIR spectroscopy

The completion of the esterification reaction and the successful synthesis of octadecyl acrylate (ODA) were elucidated by FTIR spectroscopy (Figure 2). From Figure 2, At about 3200 cm^{-1}, the absence of the carboxylic acid's characteristic band can be observed, the appearance of the ester carbonyl group band at 1722 cm^{-1} [39]. At 1183 cm^{-1} and 1227 cm^{-1}, there are two bands that are characteristic of the (C-O-C) group, scissoring CH_2 group vibration band at 1471 cm^{-1} and two strong alkyl group bands for both (CH_3- and -CH_2-) at 2920 and 2849 cm^{-1}, respectively [40]. Furthermore, the strong band recorded at 1630 cm^{-1} indicates the presence of a non-conjugated alkene's double bond (C=C str). The -CH_2- absorption bands of long-chain alkyl groups are detected at 717 cm^{-1} [41].

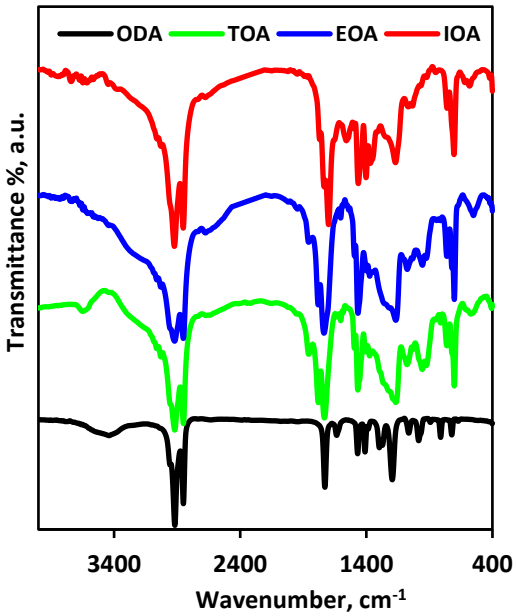


Fig. 2 Collective FTIR spectra of ODA, TOA, EOA, and IOA

FTIR spectroscopy was also used to elucidate the structure of the synthesized styrene octadecyl acrylate maleic anhydride terpolymer (Figure 2). Figure 2 shows that in addition to the (-C=C-) stretching vibration band absence of octadecyl acrylate esters, which was shown at 1630 cm^{-1} in the TOA terpolymer spectrum, The octadecyl acrylate ester groups are located at 1722 and 1183 cm^{-1}. In addition, the stretching band caused by the benzene skeleton of styrene is recorded at 1492 cm^{-1} [42]. Because the FTIR band located at 1462 cm^{-1} represents the aromatic C─C bond stretching vibrational bands at the range of 650–1350 are attributed to aromatic C─H vibration deforming in the benzene ring of styrene unit [43, 44] indicating that styrene was successfully involved in the terpolymerization reaction. Furthermore, Two new bands located 1829 cm^{-1} and 1773 cm^{-1} that was attributed to the asymmetrical and stretching vibrations of C = O of maleic anhydride [11, 45], respectively as shown in Figure 2. In addition to the FTIR bands mentioned above, two strong bands at 2849 and 2920 cm^{-1} were detected due to the terpolymer's (-C-H) aliphatic alkyl groups [46].

Figure 2 displayed the FTIR spectrum of the esterified terpolymer EOA in comparison with the pristine terpolymer TOA. The EOA exhibits the same characteristic bands as the TOA terpolymer, with slight variations in their intensity Moreover, the disappearance of the anhydride (-C=O, str) bands recorded at 1773 cm^{-1} and 1829 cm^{-1} in the TOA spectrum indicates the successful esterification of the TOA terpolymer [47].

Furthermore, FTIR spectroscopy was used to elucidate the structure of the imidated terpolymer IOA (Figure 2). When comparing the IOA spectrum to that of the pristine TOA terpolymer, the anhydride -C=O bands were completely absent [48]. Aside from the presence of a new band at 1344 cm^{-1} correspond to the C-N stretching vibrations of the imide group [49]. The results demonstrated successful terpolymeric imide formation.

3.2.2.^{1}H-NMR spectroscopy

To complement the detailed characterization information of the synthesized additives acquired from the FTIR, ^{1}H NMR spectroscopic analysis was performed. The signals at chemical shifts of 0.9, 1.3, and 1.6 ppm in the ^{1}H-NMR spectrum of octadecyl acrylate (ODA; Figure 3a) were attributed to the terminal –CH_3, –CH_2 proton of the acrylate alkyl chain, as well as the –CH_2 (acrylate backbone) groups, respectively.

The protons of the acrylate O-CH_2 are represented by the signal at 4.2 ppm. Acrylate olefinic proton signals were detected at =5.8, 6.15, and 6.43 ppm, respectively. The structure of octadecyl acrylate was revealed by all of the above signals. Figure 3b shows ^{1}H-NMR spectra of the synthesized styrene octadecyl acrylate maleic anhydride terpolymer intermediate (TOA). In addition to the previously mentioned ODA characteristic signals, a new signal at a chemical shift of 3.71 ppm due to the –CH_2– group (polymer backbone) of maleic anhydride was detected [50]. Furthermore, the signal at 2.7 ppm in the ^{1}H-NMR spectrum of TOA terpolymer is attributed to the H of the polymerized maleic anhydride [51]. Furthermore, the presence of new peaks at = 3.5–3.75 ppm related to the protons of a carbon-carbon single bond confirms the involvement of maleic anhydride in the formation of TOA terpolymers via its double bonds. The aromatic protons (-CH- of the benzene ring)

produced multiplate signals centered at 7.25 ppm (Figure 3b), confirming the incorporation of styrene in the TOA terpolymer structure [52]. Similarly, ^{1}H-NMR spectroscopy was used to demonstrate the successful synthesis of esterified EOA (Figure 3c) and imidated IOA (Figure 3d) terpolymers. Their structures exhibit the same signals as the TOA terpolymer but with a higher intensity.

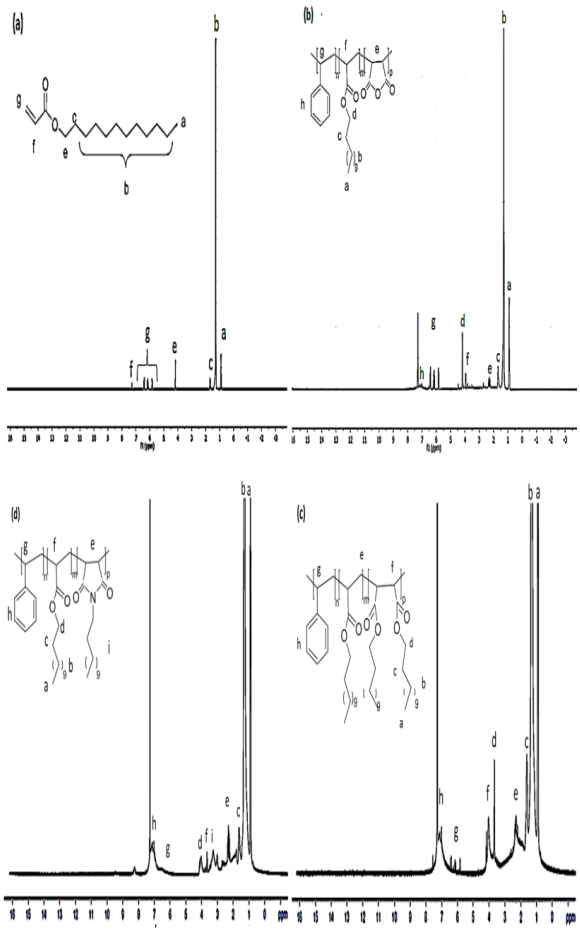


Fig. 3 ^{1}H-NMR spectra of (a) ODA, (b) TOA, (c) EOA, and (d) IOA

3.3. GPC of the synthesized terpolymers

Molecular weight is an important polymeric feature used to assess polymer additive efficiency. The mean molecular weights (Mw and Mn) and polydispersity (PD) of the synthesized terpolymers are tabulated in Table 2. It was found that the styrene octadecyl acrylate imide additive (IOA) has a higher molecular weight than the esterified terpolymer (EOA) and the corresponding terpolymer (TOA) (Table 2). Elbanna et al. reported that the higher molecular weight of the synthesized polymers had a good impact on reducing the waxy crude oil PPD and PI which coincided with the obtained GPC data of the current study [36]. So, the synthesized terpolymers may be highly applicable as PPDs and PI for the waxy crude oil.

Table 2 Average molecular weights for the synthesized terpolymer, ester, and imide

Terpolymer Designation	M_n (g/moL)	M_W (g/moL)	PD
TOA	10450	34074	3.261
EOA	16337	69031	4.225
IOA	18761	92139	4.911

3.4. Performance evaluation of the synthesized additives as pour point depressors

The synthesized terpolymeric additives were evaluated as pour point depressors for waxy crude oil with various concentrations (50, 100, 150, and 200 ppm). The resultant data of the synthesized additive's effect on the PPD of the waxy crude oil samples showed in Figure 4. This shows that the increase in their concentrations enhances the pour point depression of the treated crude oil compared with blank. This is because when the additional PPD concentration is low; it is difficult for the co-crystallization to occur between the PPD molecules and crude oil paraffin. Whereas at high concentrations, the excess PPD molecules form small particles, thus inhibiting co-crystallization between crude oil paraffin molecules which resulted in enhancing the dispersion of the wax aggregates. This concludes that the additive alkyl side chains (C18) can co-crystallize with the paraffin crude oil molecules.

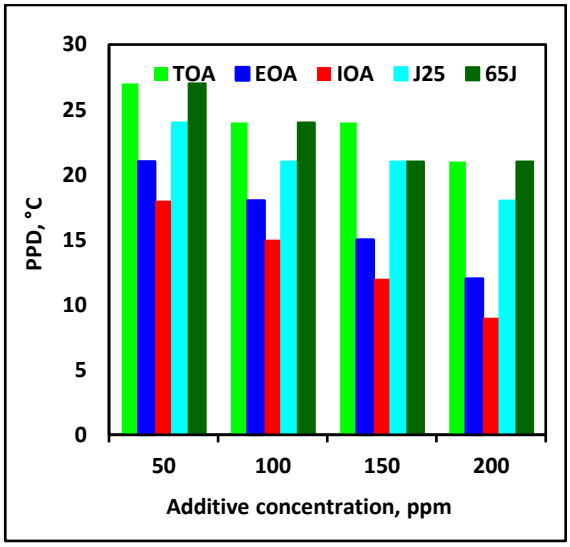


Fig. 4 Effect of the synthesized terpolymers and commercial products as PPDs on the waxy crude oil

Also, the results indicate that the produced terpolymeric imide (IOA) is better than the produced ester (EOA) and terpolymer (TOA) as pour point depressor which may be due to the high polarity of the nitrogen of the imide (-NH_2) group compared to the oxygen of the ester (-C=O-) group which

increases the electronegativity of the produced imide. Additionally, the delocalized lone pair of electrons of nitrogen can enhance the adsorption on the wax surface, improve the wax crystals matching with the PPDs, and increase their dispersion [53, 54]. Moreover, the precipitated wax crystals' nature can be changed due to the presence of the nonpolar group bonded to the imide group which hinders the wax aggregation. Finally, the introduction of organic modifications (esterification and imidation) in the terpolymer backbone can reduce the pour point temperature of the waxy crude oil [17, 55]. Finally, the pour point depression results of the synthesized terpolymers were compared with two commercial products at various concentrations (50-200 ppm) as presented in Figure 4. The results showed that the synthesized terpolymers exhibited an enhanced performance and have shown the best results as PPDs than that of the commercial products.

3.5. Performance evaluation of the synthesized additives as paraffin inhibitor (PI)

The effect of the synthesized terpolymers as paraffin inhibitors was studied and the results are shown in Figure 5. This Figure declares that a 9.5 g of the wax deposit was separated from the Tut crude oil showing its waxy nature. After treating the crude oil with the optimum dosage; 200 ppm, of TOA, EOA, and IOA terpolymers, the wax deposition was decreased to 6.48 g, 1.52 g, and 1.04 g respectively. These results can be assigned to the presence of polar ester and imide groups in the synthesized additives indicating that they can be considered highly efficient and promising paraffin inhibitors [56].

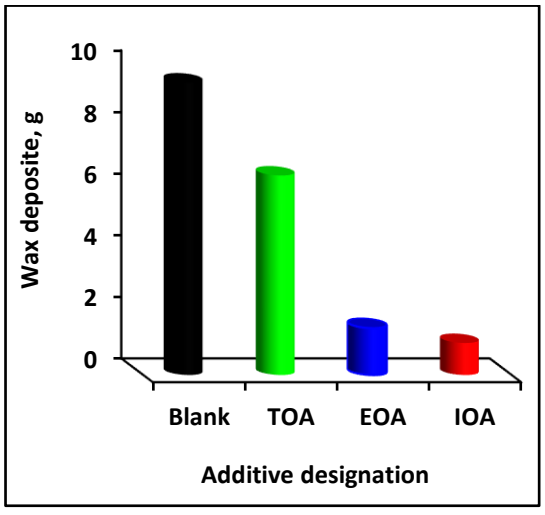


Fig. 5 Wax deposition for the untreated and treated crude oil

4. Conclusion

In summary, three new styrene-based terpolymeric additives; styrene octadecyl acrylate maleic anhydride terpolymer TOA, styrene octadecyl acrylate maleic anhydride ester EOA and styrene octadecyl acrylate maleic anhydride imide IOA were successfully synthesized and their characteristics were investigated using FTIR, ^{1}H-NMR and GPC techniques. These three terpolymers were injected with different concentrations (50 ppm, 100 ppm, 150 ppm, and 200 ppm) on Egyptian waxy crude oil to evaluate their impact as wax dispersants and paraffin inhibitors. Additionally, the pour point depression results of the synthesized terpolymers were compared with those of two commercial products. With the addition of lower concentrations of the synthesized terpolymers for Egyptian waxy crude oil, reasonable depressive effects were achieved while the imide additive (IOA) with the optimum dosage of 200 ppm exhibited the highest effect as it was capable of depressing the pour point temperature to 12 °C and the paraffin inhibition by 88 %. Thus, the synthesized terpolymers can be considered as promising and applicable polymeric additives for depressing the pour points and inhibiting the paraffinic precipitates for the waxy crude oils.

Conflict of interests

There are no known competing interests to declare.

Funding sources

None.

References

[1] G.T. Chala, S.A. Sulaiman, A. Japper-Jaafar, Flow start-up and transportation of waxy crude oil in pipelines-A review, Journal of Non-Newtonian Fluid Mechanics 251 (2018) 69-87.

[2] M. Kurniawan, S. Subramanian, J. Norrman, K. Paso, Influence of Microcrystalline Wax on the Properties of Model Wax-Oil Gels, Energy Fuels 32(5) (2018) 5857-5867.

[3] Y. Li, S. Han, Y. Lu, J. Zhang, Influence of Asphaltene Polarity on Crystallization and Gelation of Waxy Oils, Energy Fuels 32(2) (2018) 1491-1497.

[4] B. Deka, R. Sharma, A. Mandal, V. Mahto, Synthesis and evaluation of oleic acid based polymeric additive as pour point depressant to improve flow properties of Indian waxy crude oil, J. Pet. Sci. Eng. 170 (2018) 105-111.

[5] B.F. Alves, P.H.R. Pereira, R.d.C.P. Nunes, E.F. Lucas, Influence of solvent solubility parameter on the performance of EVA copolymers as pour point modifiers of waxy model-systems, Fuel 258 (2019) 116196.

[6] R. Sharma, B. Deka, A. Mandal, V. Mahto, Study the influence of sodium dodecyl sulfate on emulsification of heavy and waxy crude oils to improve their flow ability in low temperature conditions, Asia-Pac. J. Chem. Eng. 14(1) (2018) e2279.

[7] J. Ruwoldt, G. Humborstad Sørland, S. Simon, H.-J. Oschmann, J. Sjöblom, Inhibitor-wax interactions and PPD effect on wax crystallization: New approaches for GC/MS and NMR, and comparison with DSC, CPM, and rheometry, J. Pet. Sci. Eng. 177 (2019) 53-68.

[8] M. Xie, F. Chen, J. Liu, T. Yang, S. Yin, H. Lin, Y. Xue, S. Han, Synthesis and evaluation of benzyl methacrylate-methacrylate copolymers as pour point depressant in diesel fuel, Fuel 255 (2019) 115880.

[9] H. Zhu, C. Li, F. Yang, H. Liu, D. Liu, G. Sun, B. Yao, G. Liu, Y. Zhao, Effect of Thermal Treatment Temperature on the Flowability and Wax Deposition Characteristics of Changqing Waxy Crude Oil, Energy Fuels 32(10) (2018) 10605-10615.

[10] X. Gu, F. Zhang, Y. Li, J. Zhang, S. Chen, C. Qu, G. Chen, Investigation of cationic surfactants as clean flow improvers for crude oil and a mechanism study, J. Pet. Sci.and Eng. 164 (2018) 87-90.

[11] B. Yao, Z. Mu, C. Li, F. Yang, X. Zhang, Effective flow improving agents for waxy crude oil, Pet. Sci. Technol. 35(17) (2017) 1775-1783.

[12] F. Zhang, J. Ouyang, X. Feng, H. Zhang, L. Xu, Paraffin Deposition Mechanism and Paraffin Inhibition Technology for High-carbon Paraffin Crude Oil From the Kazakhstan PK Oilfield, Pet. Sci. Technol. 32(4) (2013) 488-496.

[13] J. Taheri-Shakib, A. Shekarifard, E. Kazemzadeh, H. Naderi, M. Rajabi-Kochi, Characterization of the wax precipitation in Iranian crude oil based on wax appearance temperature (WAT): The influence of ultrasonic waves, J. Mol. Struct. 1202 (2020) 127239.

[14] J.F. Tinsley, J.P. Jahnke, D.H. Adamson, X. Guo, D. Amin, R. Kriegel, R. Saini, H.D. Dettman, R.K. Prud'home, Waxy Gels with Asphaltenes 2: Use of Wax Control Polymers, Energy Fuels 23(4) (2009) 2065-2074.

[15] W. Jin, J. Jing, H. Wu, L. Yang, Y. Li, X. Shu, Y. Wang, Study on the Inherent Factors Affecting the Modification Effect of EVA on Waxy Crude Oils and the Mechanism of Pour Point Depression, J. Dispersion Sci. Technol. 35(10) (2014) 1434-1441.

[16] J. Xu, S. Xing, H. Qian, S. Chen, X. Wei, R. Zhang, L. Li, X. Guo, Effect of polar/nonpolar groups in comb-type copolymers on cold flowability and paraffin crystallization of waxy oils, Fuel 103 (2013) 600-605.

[17] B. Yao, C. Li, F. Yang, Y. Zhang, Z. Xiao, G. Sun, Structural properties of gelled Changqing waxy crude oil benefitted with nanocomposite pour point depressant, Fuel 184 (2016) 544-554.

[18] B.C. Lemos, V. Gilles, G.R. Gonçalves, E.V.R. de Castro, M. Delarmelina, J.W.d.M. Carneiro, S.J. Greco, Synthesis, structure-activity relationship and evaluation of new non-polymeric chemical additives based on naphthoquinone derivatives as wax precipitation inhibitors and pour point depressants to petroleum, Fuel 220 (2018) 200-209.

[19] T. Liu, L. Fang, X. Liu, X. Zhang, Preparation of a kind of reactive pour point depressant and its action mechanism, Fuel 143 (2015) 448-454.

[20] F. Yang, K. Paso, J. Norrman, C. Li, H. Oschmann, J. Sjöblom, Hydrophilic Nanoparticles Facilitate Wax Inhibition, Energy Fuels 29(3) (2015) 1368-1374.

[21] J. Zhang, C. Wu, W. Li, Y. Wang, H. Cao, DFT and MM calculation: the performance mechanism of pour point depressants study, Fuel 83(3) (2004) 315-326.

[22] Y.M. Al-Roomi, K.F. Hussain, Homo-oligomerization of maleic anhydride in nonpolar solvents: A kinetic study of deviations from nonlinear behavior, J. Appl. Polym. Sci. 102(4) (2006) 3404-3412.

[23] K. Banshoya, Y. Kaneo, T. Tanaka, S. Yamamoto, H. Maeda, Synthesis and evaluation of styrene-maleic acid copolymer conjugated amphotericin B, Int. J. Pharm. 572 (2019) 118719.

[24] A.H. Kopf, M.C. Koorengevel, C.A. van Walree, T.R. Dafforn, J.A. Killian, A simple and convenient method for the hydrolysis of styrene-maleic anhydride copolymers to styrene-maleic acid copolymers, Chem. Phys. Lipids 218 (2019) 85-90.

[25] D.R.S. Alvares, S.M.C. Menezes, E.F. Lucas, Kinetic study of the synthesis of a methacrylic ester copolymer by nuclear magnetic resonance, Polym. Int. 53(11) (2004) 1639-1643.

[26] S. Han, Y. Song, T. Ren, Impact of Alkyl Methacrylate−Maleic Anhydride Copolymers as Pour Point Depressant on Crystallization Behavior of Diesel Fuel, Energy Fuels 23(5) (2009) 2576-2580.

[27] K.-M. Jung, B.-H. Chun, S.H. Park, C.H. Lee, S.H. Kim, Synthesis of methacrylate copolymers and their effects as pour point depressants for lubricant oil, J. Appl. Polym. Sci. 120(5) (2010) 2579-2586.

[28] Y.-W. Kim, G.T. Eom, J.-S. Hong, K.-W. Chung, Fatty Acid Alkyl Esters as Feedstocks for the Enzymatic Synthesis of Alkyl Methacrylates and Polystyrene-co-alkyl Methacrylates for use as Cold Flow Improvers in Diesel Fuels, J. Am. Oil Chem. Soc. 88(11) (2011) 1727-1736.

[29] M. Zhou, Y. He, Y. Chen, Y. Yang, H. Lin, S. Han, Synthesis and Evaluation of Terpolymers Consist of Methacrylates with Maleic Anhydride and Methacrylic Morpholine and

Their Amine Compound as Pour Point Depressants in Diesel Fuels, Energy Fuels 29(9) (2015) 5618-5624.
[30] H.A. Ahmed, M.F. Mubarak, Adsorption of Cationic Dye Using A newly Synthesized CaNiFe2O4/Chitosan Magnetic Nanocomposite: Kinetic and Isotherm Studies, Journal of Polymers and the Environment 29(6) (2021) 1835-1851.
[31] M.F. Mubarak, A.H. Ragab, R. Hosny, I.A. Ahmed, H.A. Ahmed, S.M. El-Bahy, A. El Shahawy, Enhanced Performance of Chitosan via a Novel Quaternary Magnetic Nanocomposite Chitosan/Grafted Halloysitenanotubes@ZnγFe(3)O(4) for Uptake of Cr (III), Fe (III), and Mn (II) from Wastewater, Polymers (Basel) 13(16) (2021) 2714.
[32] M.F. Mubarak, A.M. Zayed, H.A. Ahmed, Activated Carbon/Carborundum@Microcrystalline Cellulose core shell nano-composite: Synthesis, characterization and application for heavy metals adsorption from aqueous solutions, Industrial Crops and Products 182 (2022) 114896.
[33] S. Solyman, H.A. Ahmed, Treatment of Industrial Dye Effluent by Photo-Catalytic Process Using Modified Egyptian Bentonite, Egyptian Journal of Chemistry 0(0) (2021) 0-0.
[34] N.E.A. Abd El-Sattar, K. El‐Adl, M.A. El-Hashash, S.A. Salama, M.M. Elhady, Design, synthesis, molecular docking and in silico ADMET profile of pyrano[2,3-d]pyrimidine derivatives as antimicrobial and anticancer agents, Bioorganic Chemistry 115 (2021) 105186.
[35] H.A. Ahmed, A.A. Altalhi, S.A. Elbanna, H.A. El-Saied, A.A. Farag, N.A. Negm, E.A. Mohamed, Effect of Reaction Parameters on Catalytic Pyrolysis of Waste Cooking Oil for Production of Sustainable Biodiesel and Biojet by Functionalized Montmorillonite/Chitosan Nanocomposites, ACS Omega 7(5) (2022) 4585-4594.
[36] S.A. Elbanna, A.M.M. Abd El Rhman, A.S. Al-Hussaini, S.A. Khalil, Synthesis and characterization of polymeric additives based on α-Olefin as pour point depressant for Egyptian waxy crude oil, Pet. Sci. Technol. 35(10) (2017) 1047-1054.
[37] H.A. Ahmed, R.A. Geioushy, S.A. Elbanna, R. A. A, I.M. Nassar, H.A.a. El‐saied, Facile Synthesis and Characterization of Magnetic Biopolymer Nanocomposite and Its Application for Preparing Novel Bioasphalt Coating Binder, Egyptian Journal of Chemistry 0(0) (2022) 0-0.
[38] S.A. Elbanna, A.M.M. Abd El Rhman, A.S. Al-Hussaini, S.A. Khalil, Synthesis, characterization, and performance evaluation of novel terpolymers as pour point depressors and paraffin inhibitors for Egyptian waxy crude oil, Petroleum Science and Technology (2022) 1-21.
[39] E.A. Soliman, M.R. Elkatory, A.I. Hashem, H.S. Ibrahim, Synthesis and performance of maleic anhydride copolymers with alkyl linoleate or tetra-esters as pour point depressants for waxy crude oil, Fuel 211 (2018) 535-547.
[40] A. Ercegkuzmic, M. Radosevic, G. Bogdanic, V. Srica, R. Vukovic, Studies on the influence of long chain acrylic esters polymers with polar monomers as crude oil flow improver additives, Fuel 87(13-14) (2008) 2943-2950.
[41] R. A. A, M. A. Sayed, S.A. Elbanna, E. Hafez, M. Roushdi, a. abdelrahaman, Effect of solid contents and the ratio of EVA/ Octadecylacrylate blends on Paraffin Inhibition and pour point temperature of waxy crude oil, Egyptian Journal of Chemistry 0(0) (2021) 0-0.
[42] H. Ren, J. Sun, B. Wu, Q. Zhou, Synthesis and characterization of a novel epoxy resin containing naphthyl/dicyclopentadiene moieties and its cured polymer, Polym. 47(25) (2006) 8309-8316.
[43] S. Gou, S. Luo, T. Liu, H. Xia, D. Jing, Q. Zhang, S. Li, Z. Li, Q. Guo, Thermally stable imidazoline-based sulfonate copolymers for enhanced oil recovery, RSC Adv. 5(104) (2015) 85165-85173.
[44] N. Lai, W. Dong, Z. Ye, J. Dong, X. Qin, W. Chen, K. Chen, A water-soluble acrylamide hydrophobically associating polymer: Synthesis, characterization, and properties as EOR chemical, J. Appl. Polym. Sci. 129(4) (2012) 1888-1896.
[45] Y. Wu, G. Ni, F. Yang, C. Li, G. Dong, Modified Maleic Anhydride Co-polymers as Pour-Point Depressants and Their Effects on Waxy Crude Oil Rheology, Energy Fuels 26(2) (2012) 995-1001.
[46] S.A. Elbanna, A.M.M. Abd El Rhman, A.S. Al-Hussaini, S.A. Khalil, Development of Novel Terpolymes and Evaluating Their Performance as Pour Point Depressants and Paraffin Inhibitors for Waxy Crude Oil, Egyptian Journal of Chemistry (2022) -.
[47] S. Deshmukh, D.P. Bharambe, Synthesis of polymeric pour point depressants for Nada crude oil (Gujarat, India) and its impact on oil rheology, Fuel Process. Technol. 89(3) (2008) 227-233.
[48] L. Fang, X. Zhang, J. Ma, B. Zhang, Investigation into a Pour Point Depressant for

Shengli Crude Oil, Ind. Eng. Chem. Res. 51(36) (2012) 11605-11612.

[49] H. Shang, J. Liu, Y. Zheng, L. Wang, Synthesis, characterization, and flocculation properties of poly(acrylamide-methacryloxyethyltrimethyl ammonium chloride-methacryloxypropyltrimethoxy silane), J. Appl. Polym. Sci. 111(3) (2009) 1594-1599.

[50] R. Qi, Z. Chen, C. Zhou, Solvothermal preparation of maleic anhydride grafted onto acrylonitrile–butadiene–styrene terpolymer (ABS), Polym. 46(12) (2005) 4098-4104.

[51] J. Xu, H. Jiang, T. Li, X. Wei, T. Wang, J. Huang, W. Wang, A.L. Smith, J. Wang, R. Zhang, Y. Xu, L. Li, R.K. Prud'homme, X. Guo, Effect of Comb-type Copolymers with Various Pendants on Flow Ability of Heavy Crude Oil, Ind. Eng. Chem. Res. 54(19) (2015) 5204-5212.

[52] E. Faujdar, H. Negi, A. Kukrety, R.K. Singh, Study of alkyl acrylate-co-maleic anhydride-based novel amide copolymers as multifunctional lubricant additives, Polym. Bull. 78(4) (2020) 2085-2102.

[53] W.G. Hunter, R. Mezaki, CATALYST SELECTION BY GROUP SCREENING, Ind. Eng. Chem. 56(3) (1964) 38-40.

[54] H. Zhu, T.-l. Liu, C.-h. Liu, J. Wang, H. Zhang, B. Dong, J. Shen, C.-k. Zhao, Z.-f. Li, Z. Cheng, Z. Yang, Evaluation of a novel monoclonal antibody mAb109 by immuno-PET/fluorescent imaging for noninvasive lung adenocarcinoma diagnosis, Acta Pharmacol. Sin. 41(1) (2019) 101-109.

[55] E. Torres, N. Dutta, N.R. Choudhury, J. Matisons, Effect of composition on the solution rheology of stearyl methacrylate-co-styrene-co-vinyl pyrrolidinone in paraffinic base oil, Polym. Eng. Sci. 44(4) (2004) 736-748.

[56] P. Sivakumar, A. Sircar, B. Deka, A. Silviya Anumegalai, P. Suresh Moorthi, N. Yasvanthrajan, Flow improvers for assured flow of crude oil in midstream pipeline - A review, J. Pet. Sci. Eng. 164 (2018) 24-30.