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## Development of Novel Terpolymes and Evaluating Their Performance as Pour Point Depressants and Paraffin Inhibitors for Waxy Crude Oil

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**Abstract**

In this work, novel styrene-based terpolymer styrene hexadecyl acrylate maleic anhydride was synthesized and modified via esterification and imidation reactions through the free radical polymerization technique. The synthesized terpolymers were characterized by FTIR, ^{1}H-NMR, and GPC techniques. Also, their impact as pour point depressants and paraffin inhibitors for the Egyptian waxy crude oil were assessed using different concentrations (50-200 ppm). The results showed that all the synthesized additives have great impacts on depressing the pour point temperature and hindering the wax deposits formation. The best performance was achieved by injecting 200 ppm of styrene hexadecyl acrylate maleic anhydride imide which was able to depress the pour point from 27 °C to 9 °C and achieve a paraffin inhibition of 90%. Thus, the synthesized terpolymers can be considered as promising and applicable additives for depressing the pour point and inhibiting the paraffinic precipitates for the waxy crude oil.

*Keywords:* Synthesis, Characterization, Terpolymers, Pour point depressant, Paraffin inhibition, Waxy crude oil

## 1. Introduction

Paraffinic crude oil is desirable due to ease of ++refining but its production and transportation are often encumbered by flow assurance problems resulting from wax precipitation [1-4]. Paraffinic wax is a major component in some hydrocarbons extracted from special reservoirs which are composed mainly of the linear and branched hydrocarbon molecules that have more than 16 carbons and less than 40 carbons [5, 6]. The temperature is the most dominant and critical factor affecting the paraffinic wax deposition. Waxes crystallize from oil when the temperature falls below the wax appearance temperature (WAT) [7-10]. Below this temperature, the wax crystals grow and agglomerate in the crude oil forming a large three-dimensional network that changes oil flow behavior [11-13]. Consequently, the wax formation would cause a reduction in flow area, change in wall friction, blockage of the pipelines and complete shutdown of production processes [13-17]. Millions of dollars are invested to diminish the output problems with paraffinic wax deposition in production, storage, and transportation [14, 18, 19]. A preventive and economic strategy using chemical additives [20-22] represents one of the most viable solutions to depress the wax deposition problems [23, 24] by serving as wax crystals modifiers [25, 26] and pour point depressants (PPDs) [6, 25, 27-29]. Industrial PPDs [30, 31] may be produced by adding and varying the polar and nonpolar group ratios [32, 33] that enhance the cold flow properties [34]. The nonpolar carbon chains have a high chemical affinity for the paraffin molecule [35, 36] while the polar groups can suppress the growth of paraffin crystals [37, 38]. Polymers are amongst the main additives

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used as PPDs in crude oil [25, 39, 40] and wax dispersants [27] 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 [41]. Various polymeric additives were synthesized by the combination of different monomers to be used as wax dispersants [42, 43]. The acrylate monomers have been utilized for the synthesis of polymeric PPDs because their structure possesses non-polar alkyl portions (wax-like), which interact with the wax crystals, and extremely reactive vinyl bonds [44]. Also, the unique characteristics of maleic anhydride (MA) such as its low cost, the presence of electron acceptor double bond, and an anhydride moiety in its structure make it susceptible to free radical addition for improving its compatibility with the oil components [45, 46]. Moreover, styrene is a functional monomer that can react easily with other monomers via the methylene group linked to the phenyl group beside the phenyl group polarity which is easily adsorbed on the surface of wax crystals enhancing its dispersion [47]. The mentioned assumptions provide us the direction to develop more effective and economical additives via polymerizing the three monomers styrene, hexadecyl acrylate, and maleic anhydride to integrate a novel terpolymer. Herein, we have synthesized a novel styrene hexadecyl acrylate maleic anhydride terpolymer. Then, it was chemically modified by esterification and imidation reactions to synthesize two newly styrene hexadecyl acrylate maleic anhydride ester EHA and the corresponding imide IHA. The various characteristics of the synthesized terpolymers were investigated by FTIR, $^1$H-NMR, and GPC techniques. In addition, their efficiency as pour point depressors and paraffin inhibitors for the Egyptian waxy crude oil were assessed using different concentrations (50-200 ppm).

## 2. Materials and Methods
### 2.1. Materials
Styrene, acrylic acid, maleic anhydride, hexadecanol, hexadecyl amine, p-toluene sulphonic acid (PTSA), hydroquinone (HQ), methanol, and xylene were obtained and used as received from Aldrich. Benzoyl peroxide (BPO) was recrystallized from methanol.

### 2.2. Crude oil specification
The physicochemical features of the Tut waxy crude oil; collected from Khalda Petroleum Company fields, western desert, Egypt, were investigated and the fingerprinted data were established and listed in Table 1. Also, the n-paraffin waxes distribution was determined according to the ASTM D2887 and the gas chromatographic analysis was monitored as illustrated in Figure 1.

### 2.3. Esterification of acrylic acid
The ester; hexadecyl acrylate, was prepared by mixing acrylic acid and 1-hexadecanol in a molar ratio of 1: 1 in the presence of PTSA (1%) as a catalyst and HQ (0.6%) as an inhibitor and xylene as the solvent with Dean-Stark. The refluxing was continued with stirring at 130 °C for 6 h in a stream of $N_2$ [48-52]. After removing the unreacted acid, the obtained ester was left on $CaCl_2$ overnight for drying [52]. The prepared hexadecyl acrylate (HDA) monomer is now ready to be used in the polymerization reaction. The synthesis Scheme of hexadecyl acrylates was illustrated in Scheme 1.



R₁= [C₁₆H₃₃]
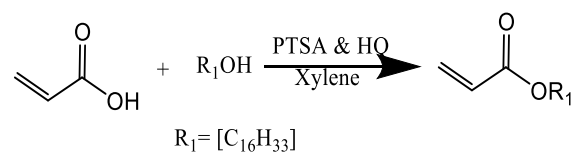
**Scheme 1.** Esterification of acrylic acid with hexadecanol.

### 2.4. Synthesis of styrene hexadecyl acrylate maleic anhydride terpolymer (THA)
The terpolymer was synthesized by using equal molar ratios of hexadecyl acrylate, styrene, and maleic anhydride with the desired weight of BPO (1 wt%) in a 3-necked flask using an inert medium of $N_2$ and xylene as a solvent and heating for 8 h at 80 °C as shown in Scheme 2. After completing the reaction, the temperature was reduced to 25 °C then; the mixture was dropped into cooled methanol under stirring, filtered off, and dried. The produced terpolymer was named as THA.

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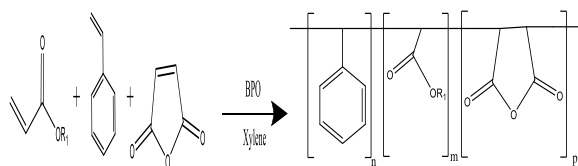
**Scheme 2.** Terpolymerization of styrene hexadecyl acrylate maleic anhydride.

### 2.4.1. Esterification of the synthesized terpolymer

One mole of the synthesized terpolymer was directly esterified by reacting with one mole of hexadecyl alcohol at 120 °C for 6 h in the presence of PTSA (1 wt%) and xylene as a catalyst and solvent, respectively. The ingredients were charged in a three-necked flask fitted with the Dean-Stark trap until the theoretical amount of water was separated. The collected ester was washed with 5% NaOH solution and distilled water then dried in air. The obtained ester was named as EHA.

### 2.4.2. Imidation of the synthesized terpolymer

Imidation reaction was performed by reacting equal molar ratios of the THA terpolymer and hexadecyl amine in a three-necked flask containing toluene as a solvent with constant stirring at 120 °C. The obtained product was purified by pouring in an excess volume of methanol then filtered, vacuum dried, and washed with hot water three times. The synthesized imide was denoted as IHA.

### 2.5. Characterization of the synthesized materials

### 2.5.1. Infra-Red (FTIR) spectroscopy

Nicolet IS-10 FTIR spectrometer was used to investigate the FTIR spectra of the synthesized materials over the wavenumber range of 400-4000 cm$^{-1}$.

### 2.5.2. $^1$H-NMR spectroscopic analysis

Bruker-NMR spectrometer operated at 300 MHz using CDCL3 as a solvent was used to follow the structure of the synthesized polymeric additives.

### 2.5.3. Gel Permeation Chromatography (GPC)

GPC-Water 2410 connected with a 515 HPLC pump and styragel HR THF 7.8X300 mm column was used to determine the mean molecular weights of the synthesized terpolymers at 40 °C. Tetrahydrofuran of 1 mL/min flowing rate was used as the eluent.

### 2.6. Evaluation of the synthesized terpolymers

### 2.6.1. As pour point depressants (PPDs)

The synthesized terpolymer, ester, and imide were tested as PPDs with the different concentrations of 50, 100, 150 and 200 ppm and injected into the collected crude oil sample at 60 °C. The treated and untreated crude oil samples were then evaluated following the ASTM D97. Additionally, the mentioned additives were evaluated in comparison with the commercially currently produced PPDs (EPRI-J25 and EPRI-65J) in the Chemical Services and Development Center (CSDC), Egyptian Petroleum Research Institute (EPRI)..

### 2.6.2. As paraffin inhibitors (PI %)

The efficiency of the synthesized terpolymer, ester, and imide was evaluated by the "Cold Finger experiment" at PPD laboratory, CSDC, EPRI that models used as a simple means to simulate the wax precipitation within oil pipeline [53, 54]. The rest of the wax was finally was removed and weighed carefully from the cold finger.

### 2.7. Crude oil component analysis

The UOP procedure (46/64) was used to measure the wax deposits insulated from crude oil. Also, the IP 143/84 standard procedure was used to isolate the asphaltene.

## 3. Results and Discussion

### 3.1. Characterization of crude oil

The average molecular weight distribution of waxes was established by analyzing the physicochemical properties of Tut waxy crude oil. 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 obtained data of wax and asphaltene contents reveal that the collected crude oil has a waxy nature.
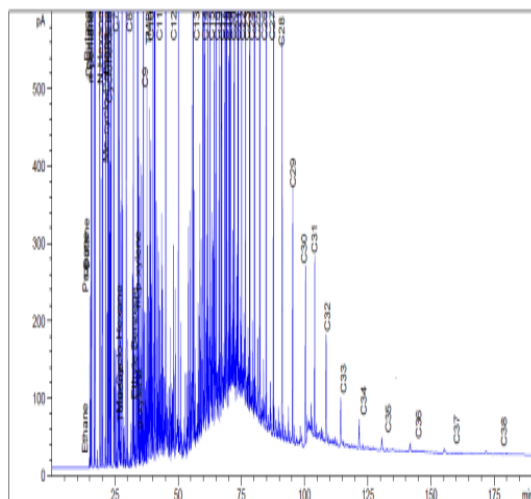
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**Fig. 1** Carbon number distribution of n-paraffin in Tut     waxy crude oil

**Table 1** Physical characteristics of the evaluated Tut waxy crude oil

| Properties | Method | Result |
|---|---|---|
| Density at 20 °C (g/cm³) | ASTM D1298 | 0.8301 |
| Kinematic viscosity at 40 °C cst | ASTM  D445 | 2.77 |
| Dynamic viscosity at 40 °C cp | ASTM D2196-18 | 2.30 |
| Pour point (PP), °C | 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 hexadecyl acrylate (HDA)*
*3.2.1. FTIR spectroscopy*
The successful synthesis of hexadecyl acrylate (HDA) was elucidated by FTIR spectroscopy as shown in Figure 2.
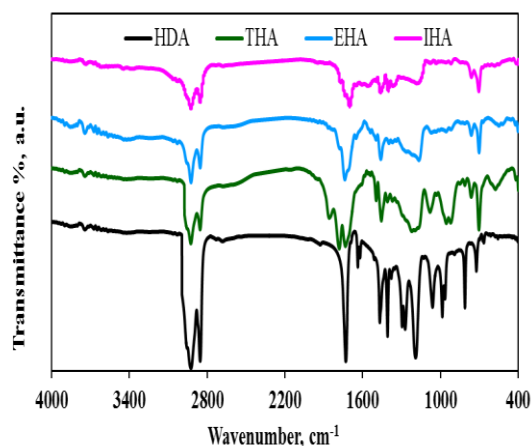


**Fig. 2** Collective FTIR spectra of HDA, THA, EHA, and IHA

From Figure 2, the absence of the characteristic band of the carboxylic acid at about 3200 cm⁻¹, the appearance of the ester carbonyl group band at 1726 cm⁻¹ [55], two bands characteristic for (C-O-C) group at 1153 cm⁻¹ and 1265cm⁻¹, scissoring $CH_2$ group vibration band at 1465 cm⁻¹ and two strong alkyl group feature bands for both ($CH_3$- and -$CH_2$-) at 2910 and 2846 cm⁻¹, respectively were observed [56]. Furthermore, the strong band recorded at 1636 cm⁻¹ indicates the double bond presence of the non-conjugated alkene (C=C str). The absorption bands of the -$CH_2$- of the long-chain alkyl groups are detected at 715 cm⁻¹.

Also, the synthesized styrene hexadecyl acrylate maleic anhydride terpolymer structure was elucidated by FTIR spectroscopy (Figure 2). From Figure 2, besides the (-C=C-) stretching vibration band absence of hexadecyl acrylate esters which was shown at 1630 cm⁻¹ in the spectrum of the THA terpolymer, the ester groups of hexadecyl acrylate are located at 1726 cm⁻¹ and 1153 cm⁻¹. Also, the stretching band due to the benzene skeleton of styrene is recorded at 1471 cm⁻¹ [57]. As the FTIR band located at 1462 cm⁻¹ represents the aromatic C—C bond stretching vibrational bands at the range of 690–1348 are attributed to aromatic C—H vibration deforming in the benzene ring of styrene unit [58, 59] implying the successful involvement of styrene in the terpolymerization reaction. Additionally, two new bands located 1827 cm⁻¹ and 1745cm⁻¹ attributed to the asymmetrical and stretching vibrations of C = O of maleic anhydride [26, 60], respectively as shown

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in Figure 2. In addition to all the mentioned FTIR bands, there are two strong bands detected at 2846 and 2910 cm$^{-1}$ due to (-C-H) aliphatic alkyl groups of the terpolymer.

Figure 2 displayed the FTIR spectrum of the esterified terpolymer EHA which shows the same characteristic bands of the THA terpolymer with some changes in their intensity in addition to the disappearance of the anhydride (-C=O, str) bands recorded at 1745 cm$^{-1}$ and 1827 cm$^{-1}$ in the THA spectrum indicating the successful esterification of the THA terpolymer [61].

Moreover, the structure of the imidated terpolymer IHA was elucidated by using FTIR spectroscopy (Figure 2). By comparing the IHA spectrum with that of the pristine THA terpolymer, complete disappearance for the anhydride -C=O bands was observed [62] besides the existence of a new band at 1346 cm$^{-1}$ correspond to the C-N stretching vibrations of the imide group [63]. The mentioned findings proved the successful terpolymer imide formation.

### 3.2.2. $^{1}$H-NMR spectroscopy

As shown, the $^{1}$H-NMR spectrum of hexadecyl acrylate (HDA; Figure 3a) showed the signals at chemical shifts of 0.9, 1.3, and 1.6 ppm that attributed to the terminal –CH$_3$, -CH$_2$ proton of the acrylate alkyl chain, and the –CH$_2$ (acrylate backbone) groups, respectively. The signal at $\delta= 4.2$ ppm is corresponding to the protons of the acrylate O-CH$_2$. The signals of acrylate olefinic protons were detected at $\delta=5.8$, 6.15, and 6.43 ppm, respectively. All the mentioned signals elucidated the structure of hexadecyl acrylate. The structure of the obtained styrene hexadecyl acrylate maleic anhydride terpolymer intermediate (THA) can be illustrated by $^{1}$H-NMR spectra in Figure 3b. In addition to the mentioned characteristic signals of the HDA, there is a new signal detected at a chemical shift of 3.71 ppm due to the –CH$_2$– group (polymer backbone) of the maleic anhydride [64]. Also, the signal at 2.7 ppm in the $^{1}$H-NMR of THA terpolymer is assigned to the H of the polymerized maleic anhydride [65]. Additionally, the involvement of maleic anhydride in the THA terpolymer formation through its double bonds can be confirmed via the existence of new peaks at $\delta= 3.5–3.75$ ppm related to the protons of carbon-carbon single bond. Multiplate signals due to the aromatic protons (-CH- of benzene ring) centered

at 7.25 ppm were recorded (Figure 3b) confirming the incorporation of styrene in the THA terpolymer structure [66]. Similarly, the successful synthesis of esterified EHA (Figure 3c) and imidated IHA (Figure 3d) terpolymers was revealed by using $^{1}$H-NMR spectroscopy. Their structures show the presence of the same signals as those of the THA terpolymer with an increase in their intensity.
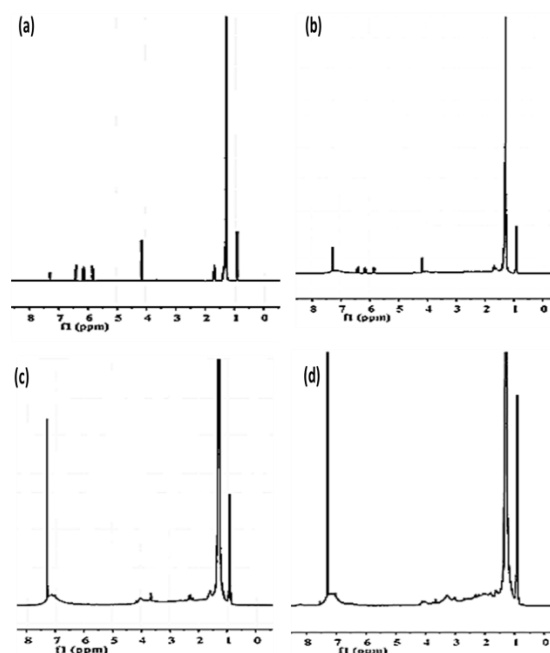


**Fig. 3** $^{1}$H-NMR spectra of (a) HDA, (b) THA, (c) EHA, and (d) IHA

### 3.3. GPC of the synthesized terpolymers

The average molecular weights (Mw and Mn) and polydispersity (PD) of the synthesized terpolymers are tabulated in Table 2. It was found that the styrene hexadecyl acrylate imide additive (IHA) has a higher weight average molecular weight than the esterified terpolymer (EHA) and the corresponding terpolymer (THA) (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 is coincided with the obtained GPC data of the current study [67]. So, the synthesized terpolymers may be highly applicable as PPDs and PI for the waxy crude oil.

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

| Terpolymer Designation | $M_n$ (g/moL) | $M_W$ (g/moL) | PD |
|---|---|---|---|
| THA | 10116 | 31278 | 3.092 |
| EHA | 19201 | 48199 | 2.510 |
| IHA | 15111 | 61840 | 4.092 |

### 3.4. Performance evaluation of the synthesized additives

#### 3.4.1. As pour point depressors

The synthesized terpolymeric additives were evaluated as pour point depressors and added at the injection temperature of 60 °C for waxy crude oil with various concentrations (50, 100, 150, and 200 ppm). The resultant data of the synthesized terpolymer's effect on the PPD of the waxy crude oil samples showed in Figure 4 which shows that the increase in their concentrations up to 200 ppm enhances the pour point depression of the treated crude oil compared with blank. However, by adding the synthesized additives to the crude oil samples at concentrations above 200 ppm, they exhibited the same pour point depression results as that of the 200 ppm. Hence, from the economic point of view, the lower concentration of 200 ppm should be considered as the optimal dosage of the synthesized additives. This is because when the concentration of the added PPD is low, there is a difficulty for the co-crystallization to occur between the PPD molecules and crude oil paraffin. Whereas at high concentrations, the excess PPD molecules themselves form smaller grains which inhibit the co-crystallization between the molecules of crude oil paraffins which resulted in enhancing the dispersion of the wax aggregates. Also, the results indicate that the produced imide (IHA) is better than the produced ester (EHA) as a PPD for the waxy crude oil which may be because of the high polarity of the nitrogen of the imide (-NH$_2$) group than the oxygen of the ester (-C=O-) group which increases the electronegativity of the produced imide. Additionally, the lone pair of electrons on nitrogen can adsorb on the surface of wax by delocalization, make the wax crystal with the same charge and mutual exclusion and hinder the wax crystal aggregation [68, 69] which facilitates the dispersion

of the wax crystals into smaller particles. Therefore, the mentioned factors facilitate the dispersions of wax crystals in the oil phase. 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 as PPDs than that of the commercial products due to the abovementioned advantages of the synthesized additives as PPDs.
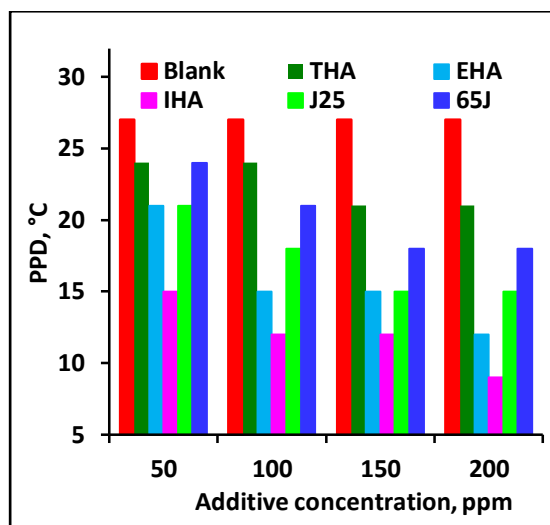


**Fig. 4** Effect of the synthesized terpolymers as PPDs on the waxy crude oil compared with commercial additives

#### 3.4.2. 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 the synthesized terpolymers, the wax deposition was decreased to 6.24 g, 1.37 g, and 0.95 g respectively. These improved results can be assigned to the presence of polar ester and imide groups in the modified terpolymers indicating that they can be considered as highly efficient and promising paraffin inhibitors [70].
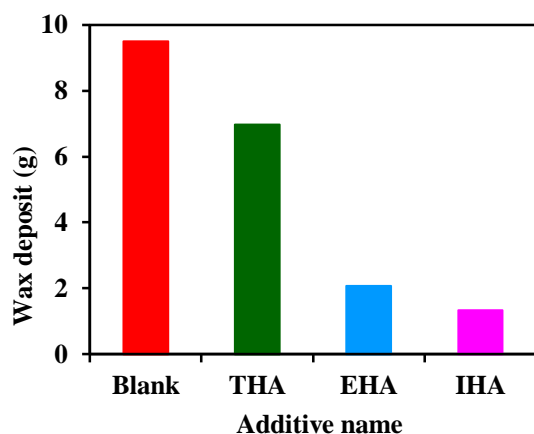
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**Fig. 5** Wax deposition for the untreated and treated crude oil

## 4. Conclusion

In summary, novel styrene hexadecyl acrylate maleic anhydride terpolymer was successfully synthesized via the free radical polymerization route. Then, it was subjected to chemical modifications by esterification and imidation reactions to synthesize two new terpolymeric additives; EHA and IHA. The synthesized terpolymers were characterized by different techniques including FTIR, $^1$H-NMR, and GPC. Also, the performance of the modified terpolymers as PPDs and PI on the Egyptian waxy crude oil had evaluated. The results demonstrated the dual function of the synthesized ester and imide terpolymers as PPDs and PI simultaneously. Their performance as PPDs was increased with the increase in their concentration. The IHA revealed the best results as it reduced the PPD from 27 °C to 9 °C (ΔPP = 18 °C) at a concentration of 200 ppm and achieved a PI of 90%. Moreover, the addition of EHA and IHA to the waxy crude oil played a significant role in dispersing the wax crystals, delaying their precipitation and reducing their number. So, the current study provides new synthetic terpolymers that can be considered as promising and efficient additives for depressing the pour point and inhibiting the waxy crude oil paraffinic precipitates.

### Conflict of interests

There are no known competing interests to declare.

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