

Research Article

Ethylene-Vinyl Acetate Copolymer/Crude Gossypol Compositions as Pour Point Depressants for Waxy Oil

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Wax deposition from crude oil that blocks the pipeline and increases the viscosity of the fluid is considered as a serious challenge for petroleum transportation. Employment of chemical additives, the so-called pour point depressants (PPDs), is widely used to solve this problem. Among them are the ethylene-vinyl acetate (EVA) copolymers (EVAc), containing a polyethylene segment along the backbone with vinyl acetate. To improve the performance of EVAc as PPD, the compositions of this polymer with crude gossypol (CG), isolated from the refined cottonseed oil soapstock, were prepared by joint milling in a ball mill. Prepared compositions were characterized by Fourier transform infrared (FTIR), ultraviolet (UV), and nuclear magnetic resonance (NMR) spectroscopy. The pour point and viscosity of the crude oil from the Akshabulak oil field (Kazakhstan) were studied. The compositions with 10, 20, and 25 wt% of CG demonstrate better efficiency as PPD for crude oil than EVAc at the dosage of PPD of 50, 100, 250, and 500 ppm. The improved properties of the obtained PPD in comparison with the commercial EVAc is explained by the appearance of additional nonpolar and polar groups caused by the formation of the EVAc/CG composition.

1. Introduction

Wax or paraffin deposition from crude oils at low temperature that may block the pipelines and increase the viscosity of the fluid is a complex and expensive challenge for the petroleum transportation industry [1–4]. Wax is mainly composed of n-alkanes, which are predominantly responsible for the wax deposition process in crude oils [5–8]. One of the well-recognized solutions of this problem is the employment of chemicals that can prevent wax deposition and wax gelation and/or remove wax deposits; these chemicals act as wax crystal modifiers, pour point depressants (PPDs), or flow improvers and reduce the ability of wax crystals to interconnect [9–13]. Among the various types of chemical additives used as PPDs in crude oil transportation, polymers are mostly used [13–15]. Ethylene-vinyl acetate (EVA) copolymers are the most commonly used chemicals for preventing paraffin deposition in the pipeline [16–20]. The chemical structure of the EVA copolymer (EVAc) is presented in Figure 1.

EVAc consists of a crystalline polyethylene segment along the backbone with vinyl acetate; generally, EVAc with 18–30 wt% of vinyl acetate is used as PPDs. The modern theories of action mechanism of EVAc as PPDs include adsorption, cocrystallization, nucleation, and improving wax solubility [21–24]. The increase in the vinyl acetate content increases the polarity of the polymer and its solubility in the oil; however, the increase in the vinyl acetate content decreases the cocrystallization of the PPD with the wax.

One way to improve the properties of polymeric additives as PPDs is through polymer modification. Jing with coworkers developed new nanohybrid PPDs by organically modified nano-SiO₂ in EVA copolymers; the resulting PPD reduces a pour point of model oil from 34 to 5°C [25].

An attractive idea is to use industrial waste to modify the original polymers to promote their properties as PPDs. This paper explores the possibility of using technical gossypol for

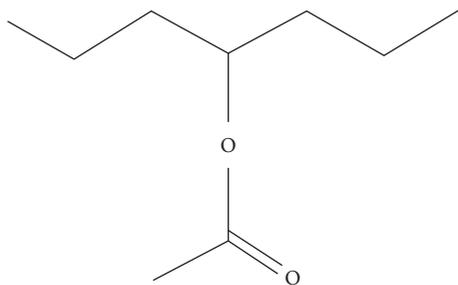


FIGURE 1: The structural formula of the EVA copolymer.

this purpose. Being a complex polyphenolic compound, gossypol contributed to cottonseed oil's toxicity; therefore, this substance is recovered from the soapstock or the byproduct formed during the process of cottonseed oil refining. Gossypol contains a number of polar and nonpolar groups, is highly soluble in oil, and is also a reactive substance. We assumed that the EVAc/CG composition could exhibit better performance as PPD in comparison with the commercial EVAc. Since both gossypol and EVAc are solids under normal conditions, they were comilled in a ball mill to prepare a composition of both reactants.

2. Materials and Methods

2.1. Materials. Crude oil sample used in this work was received from the Akshabulak oil field (Kazakhstan). The density of the crude oil was obtained by the pycnometer method. Wax content was determined according to the SY/T 7550-2004 procedure.

Refined cottonseed oil soapstock was received from *Shymkentmay JCS* (Shymkent, South Kazakhstan). The composition of the soapstock, determined using a gas chromatography-mass spectrometer (*GCMS-QP2010 Ultra, Shimadzu*), was as follows (wt%): fatty acids: 47.4, neutral oil: 11.2, moisture: 39.5, and others: 1.9.

Aviation gasoline, sulfuric acid, and ethylene-vinyl acetate (EVA) copolymer (25 wt% of vinyl acetate) were purchased from *Sigma-Aldrich*.

2.2. Isolation of Gossypol from Refined Cottonseed Oil Soapstock. 150 ml of the soapstock was placed in a flask with a volume of 500 ml, and 5% solution of sulfuric acid was added, until pH = 4.5–5.0 was reached. The resulting suspension was separated by centrifugation using a *Hettich-Mikro 220 R* centrifuge at 4500 rpm. The solid part was treated with aviation gasoline at a solid-liquid ratio of 1 : 1 (wt.) with magnetic stirring for 30 minutes; the resulting mixture was settled for 2 hours until a clear separation of the liquid portion into three layers was obtained. The middle layer, containing yellow flakes (solid part), was neatly separated from the upper and lower layers. The solid part was separated by filtration, washed twice with aviation gasoline, and dried under vacuum (100–150 mmHg) at a temperature of 60–65°C. The resulting product is referred to as crude gossypol (CG).

2.3. Preparation of EVAc/CG Compositions as PPDs. The compositions of EVAc/CG were prepared by milling the determined amounts of the starting components in a laboratory ball mill *HT Machinery IBMT-30*, equipped with a 0.5 L ceramic drum and ceramic balls of 8 mm in diameter, at a ball-to-powder ratio of 6, for 70 min. The resulting compositions were used as PPDs in further experiments.

2.4. Spectroscopic Analysis. Fourier transform infrared (FTIR) spectroscopy was performed by using a *Shimadzu IR Prestige-21* infrared spectrometer.

UV-Vis spectroscopic studies were conducted by using a *Shimadzu UV 2600* spectrophotometer.

¹H NMR spectra were recorded on a *Fourier-300 (Bruker)* NMR spectrometer. The samples were run as a 20% solution in CDCl₃.

2.5. Differential Scanning Calorimetry (DSC) Measurements. DSC analysis was performed using the *DSC 1 (Mettler Toledo)* in the temperature range from 46 to 20°C at a cooling rate of 5°C/min.

2.6. Evaluating Tests of Pour Point. Before the pour point evaluation, oil samples were conditioned at 60°C for 2.5 h and left to cool. The pour points of the treated and untreated crude oil were determined according to the ACTM Standard D-97.

2.7. Rheological Measurements. The viscosity of the untreated and treated crude oil was measured by using a *Rheotek RUV 2(2)* viscometer. The untreated and treated crude oil samples were heated to a predetermined temperature and then used in the experiments to obtain the viscosity of the fluid.

3. Results and Discussion

3.1. Analysis of the Crude Oil Sample. Characterisation experiments were conducted for the crude oil sample, and results of density, wax content, pour point, and kinematic viscosity are presented in Table 1.

The value of density obtained for the crude oil sample indicates that the oil is of medium-heavy. The high wax content allows us to consider the oil sample as highly waxy.

3.2. Spectroscopic Analysis of EVAc and CG. For the spectroscopic analysis, the composition containing the highest amount of CG, i.e., 35 wt%, has been used to stress the effect of CG present in the composition.

3.2.1. FTIR Spectroscopic Study. To obtain information on the alleged new bonds formed by milling the EVAc and CG, FTIR spectra of the starting components and the composition were recorded. The obtained spectra are shown in Figure 2.

TABLE 1: Physical characteristics of the crude oil sample.

Property	Value
Density at 20°C (g/cm ³)	0.8427
Wax content (wt%)	17.1
Pour point (°C)	19
Kinematic viscosity (mm ² /s)	218.46

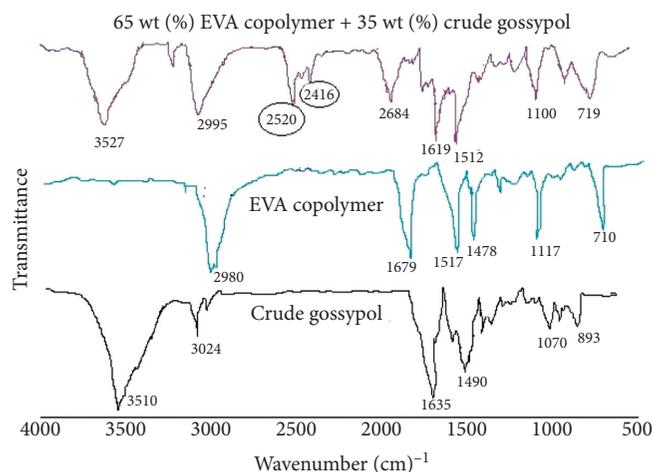


FIGURE 2: FTIR spectra of pure EVAc, CG, and EVAc/CG (65:35 wt%) composition.

In the spectrum of CG, there is a band at 3510 cm⁻¹, for the hydroxyl group associated with phenol, and a band at 3024 cm⁻¹ is assigned as aromatic -CH vibrations. The bands at 1635 and 1490 cm⁻¹ are associated with aromatic C=C and methyl bending vibrations, respectively. In-plane -CH of 1,2-substituted phenyl and out-of-plane -CH and ring bending are observed at 1070 and 893 cm⁻¹, respectively.

In the spectrum of EVAc, a band at 2980 cm⁻¹ is associated with -OH group vibrations and bands at 1679, 1517, and 1478 cm⁻¹ reflect C=O, -CH₂ (ethylene), and -CH₃ vibrations. Bands at 1117 and 710 cm⁻¹ reflect the vibrations of C-O and O-C-O groups, respectively.

All the characteristic peaks of EVAc and CG remain in the spectra of their composition; besides, new peaks appear at 2520 and 2416 cm⁻¹. Slisenko and coauthors demonstrated the possibility of hydrogen bond forming in the blends based on polymers and additives [26]. We assume that these peaks are associated with the formation of intermolecular O-H hydrogen bonds between the components of the mixture.

3.2.2. ¹H NMR Study. To confirm (or refute) the hypothesis of intermolecular hydrogen bond formation in the EVAc/CG composition, an ¹H NMR study was conducted.

Our hypothesis was as follows. If the spectra of the composition retain the same signals of hydrogen protons as in the starting materials, then it represents the absence of the formation of any new intermolecular bonds. The appearance of new signals (or a shift of existing ones to a stronger or

weaker field) will indicate the formation of new bonds. The data obtained from the ¹H NMR study of the copolymer/crude gossypol composition are presented in Table 2.

All the signals of protons present in the starting substances retain their values; at the same time, a new signal appears for the composition, at 4.46 (no. 8 in Table 2). It is known that the formation of a hydrogen bond shifts the resonant signal of the proton to a weak field. We suggest that one of the protons of the hydroxyl groups (H-O₁ or H-O₁) is involved in the formation of a hydrogen bond with the oxygen of vinyl acetate. The fact that the signals of all protons are conserved indicates that only one of the symmetric protons of gossypol (H-O₁ or H-O₁) forms a hydrogen bond.

3.2.3. UV-Visible Spectroscopic Study. The UV-visible absorption spectra of both initial EVAc and CG, as well as the spectrum of EVAc/CG composition in toluene, are presented in Figure 3.

It can be observed that CG has a sharp absorption peak at 284 nm as well as a broad peak at 370 nm, and for EVAc, an absorption peak is found at 301 nm. The spectrum of the EVAc/CG composition demonstrates one relatively sharp peak at 295 nm and a broad peak at the wavelength the same as for CG. The shift of the maximum absorption in the UV spectrum of the composition can be explained by the inclusion of molecularly dispersed gossypol in the EVAc due to the formation of hydrogen bonds between the functional groups of the reactants [27-29].

3.3. Pour Point Depression. Table 3 demonstrates the pour point depressing effect of the EVAc and EVAc/CG composition.

It can be noted that the presence of EVAc in crude oil depresses the pour point, and the higher value of depression is achieved at the concentration of 100 ppm. Milling crude gossypol with a commercial PPD (10-20 wt% of CG in the composition) leads to an increase in depression in comparison with pure EVAc. The composition containing 20 wt % of the CG demonstrated the best performance at 100 ppm of dosage. Using PPD in the concentration of more than 250 ppm reduced the depressing effect for all of the additives studied in these tests.

3.4. Determination of Wax Appearance Temperature (WAT). DSC was conducted to determine the temperature at which the first wax crystal appears in the oil (wax appearance temperature, WAT). The thermograms of the virgin crude oil and the oil benefited with 100 ppm of PPD are shown in Figure 4.

DSC thermograms recorded during the cooling process in the range of the 46-20°C indicate two exothermic peaks in all three cases. According to the DSC analysis, WAT corresponds to the temperature at which the curve deviates from the baseline on the thermogram. As it can be observed from Figure 5, there are no differences between the WAT of virgin oil sample and the WAT of oil sample benefited

TABLE 2: Assignments of proton resonances in the EVAc/CG (65:35 wt%) composition.

Peak number	ppm	Assignments of ^1H resonances	
		Crude gossypol	EVA copolymer
1	1.19 (quint)		$-\text{CH}_2-\text{CH}_2-\text{CH}_2-$
2	1.41 (q)		$-\text{CH}-\text{OCOCH}_3-\text{CH}_2-\text{CH}_2-$
3	1.55 (d)	$(\text{CH}_3)_2\text{C}$	
4	1.76 (t)		$-\text{CH}-\text{OCOCH}_3-\text{CH}_2-\text{OCOCH}_3-$
5	1.93 (s)		$-\text{OCOCH}_3-$
6	2.16 (s)	CH_3	
7	3.90 (sept)	$\text{H}-\text{C}(\text{CH}_3)_2$	
8	4.46 (s)		
9	5.24 (quint)		$-\text{CHOCOCH}_3-$
10	5.73 (s)	$\text{H}-\text{O}_1$	
11	6.46 (s)	$\text{H}-\text{O}_6$	
12	7.79 (s)	$\text{H}-\text{C}_4$	
13	11.13 (s)	CHO	
14	15.19 (s)	$\text{H}-\text{O}_7$	

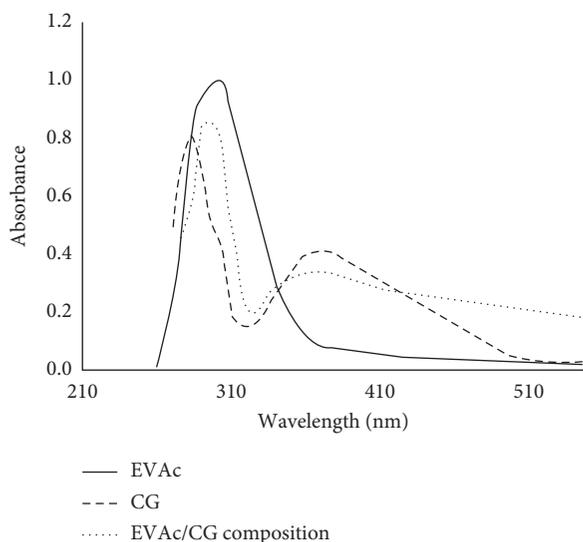


FIGURE 3: UV-visible spectra of EVAc, CG, and the EVAc/CG (65:35 wt%) composition in toluene.

with 100 ppm of EVAc (WAT 1, 40°C), whereas adding EVAc/CG (80:20 wt%) composition reduces the WAT by 2 degrees (WAT 2, 38°C).

As it was demonstrated by Liu and coworkers [23], the first peak can be attributed to asphaltene precipitation, and the second peak appears due to wax crystallisation from the oil. Taking this circumstance into account, it can be assumed that adding crude gossypol to the PPD (EVAc) makes it difficult to precipitate asphaltenes but does not change the temperature of the appearance of paraffin crystals.

3.5. Rheological Study. The viscosities of untreated crude oil and crude oil beneficiated with EVAc/CG (80:20 wt%) composition and EVAc itself (both as PPDs) are presented in Figure 5.

It can be seen that when the temperature exceeded 35°C, the viscosity of all three samples of crude oil (untreated and treated with PPDs) was lower and have almost

the same values. At temperatures below 35°C, the viscosity of untreated oil increased in comparison with the oils treated with PPDs. From the temperature of 31°C, the viscosity of the oil treated with the EVAc/CG composition becomes higher than the viscosity of the oil treated with EVAc. For example, at 10°C, the viscosities of both beneficiated oil samples were 430 and 384 MPa × s. Thus, EVAc/CG composition improves the low-temperature flow properties of the crude oil more effectively than EVAc at the same dosage (100 ppm).

3.6. Proposed Working Mechanism. In order to explain the mechanism of the EVAc/CG composition acting as PPD, let us consider the structure of both substances.

The chemical structure of gossypol is presented in Figure 6.

As demonstrated in Figure 6, gossypol's structure consists of two naphthalene rings joined by a single bond between the 2- and 2'-carbon atoms. Six hydroxyl groups are present in the gossypol's framework, two of which (1- and 1'-positions) are more reactive than the remaining four. Hydroxyl groups as well as two aldehyde (8- and 8'-positions) groups characterize the lipophobic region of the molecule, whereas two methyl (3- and 3'-positions) and two isopropyl (5- and 5'-positions) groups define the lipophilic region of the gossypol [30].

Because of its high reactivity, gossypol when milling with EVAc forms a hydrogen bond with it, as it was concluded from the UV-visible spectroscopic study. The possibility of the hydrogen bond formation between the reactants during their joint milling in a ball mill is indicated in the papers [31–33].

If the content of vinyl acetate in the copolymer is 25 wt%, then it can be calculated that vinyl acetate groups are located in every 5 $-\text{CH}_2$ groups. Since the signal of one of the two protons located at positions 1- and 1'-is stored in the spectrum of the composition, it can be assumed that only one of these protons forms a hydrogen bond with the EVA copolymer. The estimated resulting composition is presented in Figure 7.

TABLE 3: Pour point depression of crude oil sample treated with commercial EVAc and EVAc/CG composition.

Additive concentration (ppm)	Pour point depression (°C)					
	EVAc	EVAc/CG composition (wt%)				
		90:10	80:20	75:25	70:30	65:35
50	6	8	8	6	3	1
100	9	11	12	9	4	2
250	8	10	10	11	5	4
500	6	7	7	7	6	4

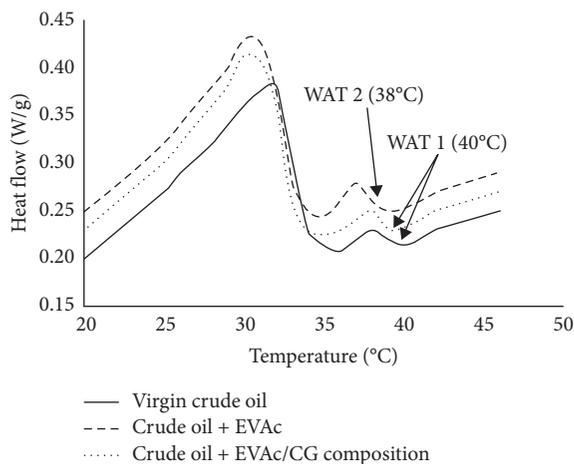


FIGURE 4: DSC curves of virgin crude oil and crude oil benefited with 100 ppm concentration of EVAc and EVAc/CG (80:20 wt%) composition.

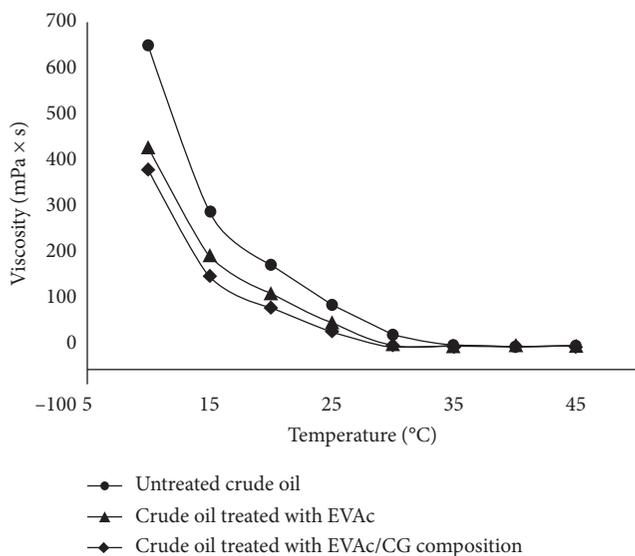


FIGURE 5: Viscosity-temperature relationships between untreated and treated (100 ppm of PPD) crude oil.

This composition has both a nonpolar (alkyl) and polar (vinyl acetate and hydroxyl and aldehyde) groups that positively affect wax inhibition performance [34]. As has been stated in the review [34], the alkyl side chain is the critical factor influencing the PPD's efficiency, especially, for

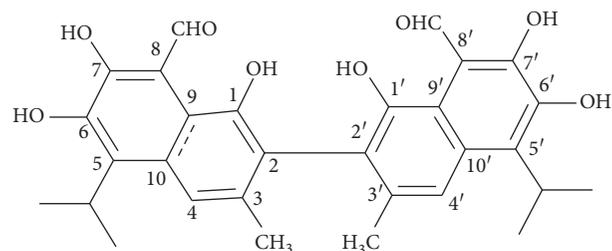


FIGURE 6: The chemical structure of gossypol.

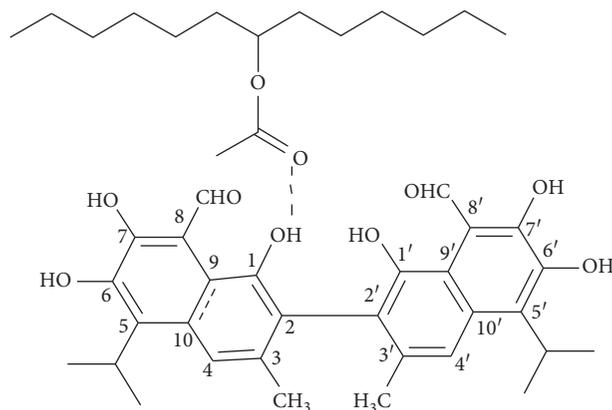


FIGURE 7: Estimated EVAc/CG composition.

comb-shaped copolymers. Thus, introducing alkyl groups into the initial PPD may increase its performance on wax inhibition.

Hereby, H-bonds, promoting the formation of the EVA/CG composition, contribute to EVA performance as PPD.

The EVAc either cocrystallizes with wax molecules or incorporates on the growing wax crystals. The similarity of the ethylene segment of EVAc to wax molecules leads to the interaction between them during the crystal growth. The presence of gossypol's part increases the part that is dissimilar to the wax crystal. This part is responsible for preventing and destructing the wax crystal growth that eventually makes the wax deposition weaker.

4. Conclusions

By joint milling the commercial ethylene-vinyl acetate copolymer (EVAc) and crude gossypol (CG), EVAc/CG

compositions have been obtained and tested as pour point depressants (PPDs) for waxy crude oil. According to the experimental results, the compositions containing 10, 20, and 25 wt% of CG exhibit better efficiency as PPD for crude oil than EVAc at the PPD dosage of 50, 100, 250, and 500 ppm. The best performance has been identified for the composition containing 20 wt% of CG that can depress the pour point by 12°C at the dosage of 100 ppm, while EVAc depresses the pour point by 9°C at the same dosage. Besides, the compositions have a better performance as a flow improver than EVAc itself.

The improved properties of the composite in comparison with the commercial EVAc is explained by the appearance of additional nonpolar and polar groups in the starting copolymer caused by the formation of the EVAc/CG composition. This part of the composition is dissimilar to the wax crystals and can prevent and destruct wax crystal growth.

Data Availability

The data supporting the results reported in the paper are at the disposal of the authors.

Conflicts of Interest

All authors declare no conflicts of interest.

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