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Amidation of Polyethylene-Acrylic Acid Copolymer as Pour Point Depressants for Waxy Crude Oils

The present work aims to provide amine-modified polyethylene-acrylic acid (PEAA) copolymers as a pour point depressant (PPD) that will be evaluated for lower pour point of crude oil. For this, PEAA was amidated with butylamine and octadecylamine in the presence of xylene as a solvent at 150 °C for 10 hours to obtain copolymers PEAA/ODA and PEAA/BA. The copolymers were modified by amidation using the carboxyl groups of an ethylene-acrylic acid copolymer as reaction sites in reactions with RNH_2. The resulting copolymers were purified and analyzed by FTIR spectroscopy. The modified PEAA copolymers were evaluated for their effectiveness as depressants for crude oils by pour point measurements at 50 ppm, 100 ppm and 200 ppm and rheological measurements at 100 ppm. The pour point measurements of the crude oil showed that octadecylamine-modified PEAA copolymer performed better than butylamine-modified and unmodified PEAA copolymer. The effectiveness of the modified copolymers compared to unmodified PEAA can be explained by the polarity of the monoalkylamide groups in the peripheral substituents along the copolymer backbone, which plays a crucial role in preventing the agglomeration of wax crystals in crude oil.

Keywords: polyethylene-acrylic acid (PEAA), crude oil, pour point depressant (PPD), wax crude oil, copolymers, pour point, flow, modification, primary amines.

Introduction

The global petroleum industry is experiencing significant material costs, as well as technical and technological difficulties, due to the current trend of an increase in the share of heavy and highly waxy crude oil. According to forecasts this share is already 37–56 %, which is especially typical for crude oils from Kazakhstan fields (fields of the Mangyshlak Peninsula, South-Turgai trough, and other regions). In general, the anomalous properties of crude oils from Kazakhstan fields allow us to class them as solidifying at positive temperatures, highly waxy and high-viscosity ones. Even under standard conditions the viscosity of crude oils fluctuates within several hundred and sometimes thousands of centipoises. At low temperatures highly waxy crude oils show the pronounced non-Newtonian (viscous-plastic, viscoelastic, thixotropic) properties, without which it is impossible to organize rational well operation and crude oil transportation through pipelines. When the pumping process is stopped, crystalline structures are formed in crude oil, the strength of which depends on the content of wax fractions, the dormant time of the crude oils, and the conditions for their formation. From a scientific point of view, the most effective way to regulate the fluidity of crude oil is chemical action, that is, to achieve a significant change in the structural organization and phase state of crude oil dispersed systems. Thus, a chemical additive known as PPD is used to reduce the viscosity and pour point of crude oils [1–5]. These supplements are most recognized for their simplicity and cost effectiveness. When used in manufacturing processes, these PPDs minimize the problems associated with wax deposition on manufacturing equipment. Pour point depressants (PPDs) are polymeric compounds consisting of a hydrocarbon chain that interacts between the additive and wax, as well as a polar part that repels the wax crystals from each other, preventing the growth of wax crystals [6, 7]. Pour point depressants include poly (ethylene-vinyl acetate) (PEVA) copolymers, which have good PPD performance for crude oil, an alkyl ester, a copolymer of unsaturated carboxylic acid and olefin, olefin and maleic anhydride [8–11]. Thus, the development of new PPDs that can solve or minimize such problems is of great interest to the petroleum industry around the world.

Crude oil from the Akshabulak field (Kazakhstan) with high wax content is characterized by a high pour point, high viscosity, high gel strength, and a large amount of wax deposits. An increase in the wax con-

tent of crude oil leads to a deterioration in the solubility of the wax in the crude oil, in some cases with the formation of a separate solid phase.

Experimental

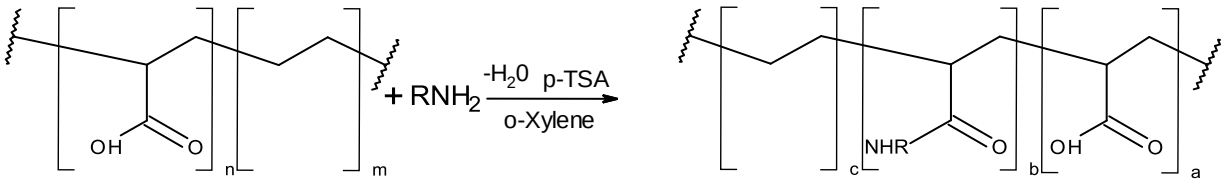
In the work, the PEAA modification was carried out. The characteristics of PEAA copolymers were investigated. The molecular weight and polydispersity index were determined. PEAA copolymers were characterized by FTIR spectroscopy. The effectiveness of the modified copolymers as a pour point depressant was shown. A rheological study of highly wax crude oil from the Akshabulak field was carried out.

Reagents

Poly(ethylene-co-acrylic acid) (acrylic acid 20 %, t = 99–101 °C, density = 0.96), octadecylamine, butylamine, *o*-xylene, THF, toluenesulfonic acid from Sigma-Aldrich.

Amidation of poly(ethylene-co-acrylic acid)

Modification of the poly(ethylene-co-acrylic acid) copolymer with butylamine (mass ratio PEAA-BA was 1–0.4), octadecylamine (mass ratio PEAA-ODA was 1–1.5) was carried out according to the general procedure (Figure 1). A two-necked flask equipped with a Dean-Stark head with a reflux condenser, stirrer and thermometer was loaded with an poly(ethylene-co-acrylic acid) copolymer, a primary amine and *o*-xylene. The mixture was heated to a temperature of 150 °C and toluenesulfonic acid dissolved in *o*-xylene (1 % wt based on total mass of reactants) was added. Then the reaction mixture was continuously stirred until the evolution of reaction water ceased, namely for 10 hours. The resulting mixture was cooled, washed with methanol and dried in a vacuum oven to remove residual solvent.



R = $C_{18}H_{37}$ (octadecylamine) or C_4H_9 (butylamine)

Figure 1. Structure of modified copolymers

Instrumental methods of analysis

The structure of the modified copolymers was analyzed using FTIR spectroscopy. The FTIR spectra of the copolymer samples were recorded on a Nicolet 5700 FTIR spectrometer in the range of 400–4000 cm^{-1}.

The depression efficiency of the synthesized copolymers was evaluated for crude oil from the Akshabulak field. The pour point was determined following ASTM D 5853.

Rheological measurements were carried out using a RheoLab QC rheometer (Anton Paar, Austria) with Rheoplus 3.0 software equipped with a thermostated cooling system with a temperature control.

The chromatogram of crude oil from the Akshabulak field is presented in Figure 2. The analysis of the wax fraction was conducted in the form of a solution in carbon disulfide using a simulation program for the distillation of hydrocarbons on a PerkinElmer AutoSystemXL chromatograph (USA). The components of the waxy fraction were identified by chromatography using reference hydrocarbons.

The Gel Permeation Chromatography (GPC) method was used to determine the molecular weight and polydispersity index of the obtained copolymers. The measurements were carried out on an Agress 1100 instrument with Elitapex software. In measurements, tetrahydrofuran was used as a mobile phase at a flow rate of 0.7 ml/min, and polystyrene of various molecular weights was used as a standard.

Results and Discussion

Physical and Chemical Characteristics of Akshabulak Crude Oil

The rheological properties of crude oil depend on the physical and chemical characteristics of the crude oil (Table 1). Several factors affect the fluidity of a crude oil, including temperature, wax, asphaltene and tar content in the crude oil. Crude oil from the Akshabulak field is wax and low in resins and asphaltenes. The low tar content and the high wax content determine the high pour point values of this crude oil.

The main role in determining the pour point of crude oil is played by hard waxes C_{20} and above. For crude oil from the Akshabulak field, the molecular weight distribution of n-alkanes was determined using

gas chromatography (Fig. 2). The presented data show that the bulk of *n*-alkanes in crude oil are C_{20}–C_{34} waxes. In turn, among this group, the largest percentage is accounted for by C_{20}–C_{30} waxes, and the smallest one — by C_{31}–C_{45}. Waxes of the C_{20}–C_{34} group melt in the temperature range of 36–70 °C.

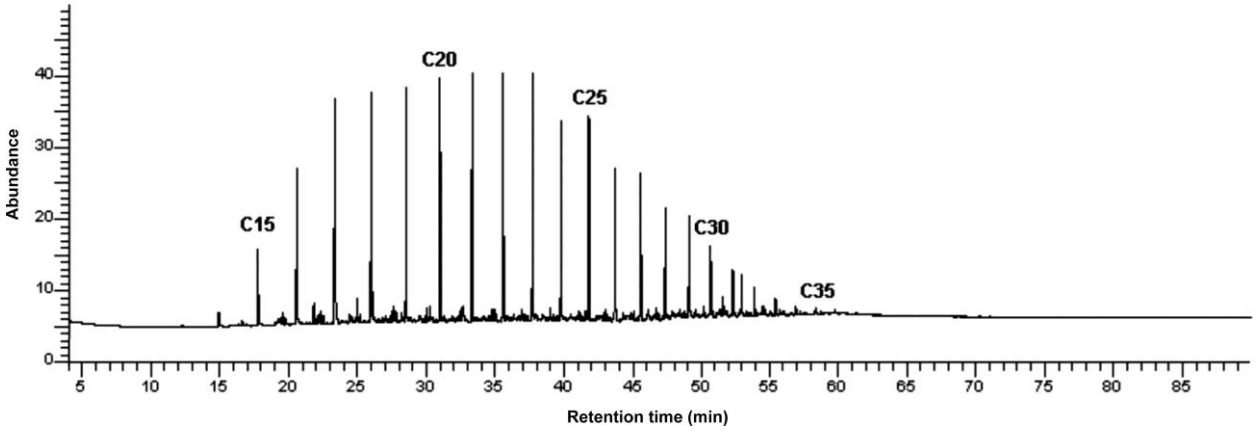


Figure 2. Chromatogram of the distribution of *n*-alkanes in Akshabulak crude oil

Table 1

Physical and chemical characteristics of Akshabulak crude oil

No.	Determined characteristics	Example	Test method
1	Density at 20°C, kg/m^3	813.3	ASTM D 1298
2	Water content, %	0.1	ASTM D 95
3	Concentration of chloride salts, mg/dm^3	20	ASTM D 3230
4	Pour point, °C	+15	ASTM D 97
		+9	ASTM D 5853
5	Mass fraction of wax, %	14.3	ASTM 3235-06
6	Mass fraction of silica gel resins, %	8.6	ASTM D 6560–00
7	Mass fraction of asphaltenes, %	0.6	ASTM D 6560–00
8	Kinematic viscosity at 40°C, mm^2/s	4.2	ASTM D 445–96

Characterization of the copolymers

The structure of the copolymers was analyzed using FTIR spectrometry in the range of 400–4000 cm^{-1}.

FTIR spectra of a copolymer of ethylene and acrylic acid are shown in Figure 3, where vibration bands are observed for ν_{as} methylene group in the region of 2918.5 cm^{-1} and ν_s vibrations of methylene group in the region of 2849.9 cm^{-1}.

A wide band in the range of 3400–2800 cm^{-1} is due to amino groups' ν vibrations in primary amides. The characteristic fluctuations in the 1703 cm^{-1} range refer to the ν_s vibrations of acrylic acid carbonyl group. After modifications the peak at 1703 cm^{-1} disappears, which indicates the conversion of carboxylic group of acrylic acid into amide. δ-vibrations of methyl and methylene group appear in the region of 1463.9 cm^{-1} for aliphatic groups. The absorption at about 1409.7 cm^{-1} is partly attributed to the hydroxy group of the COOH fragment [12]. The presented data indicate the presence of the main functional groups in the structure of the copolymers shown in the diagram (Fig. 1).

In Figure 3, all FTIR spectra of poly (ethylene-co-acrylic acid) copolymers modified with amines contain ν_{as} of methyl and methylene groups in the region of 2918–2920 cm^{-1}, as well as ν_s of methyl and methylene group in the region of 2850 cm^{-1}. Stretching vibrations of the carbonyl group in the amide and imide rings are in the range of 1640-1645 cm^{-1}. δ-vibrations of methyl and methylene group for aliphatic groups are presented in all spectra in the range of 1450–1460 cm^{-1}. δ vibrations of the hydroxy group of acrylic acid are presented in the region of 940 cm^{-1} and practically completely disappears after modifications with amines [12].

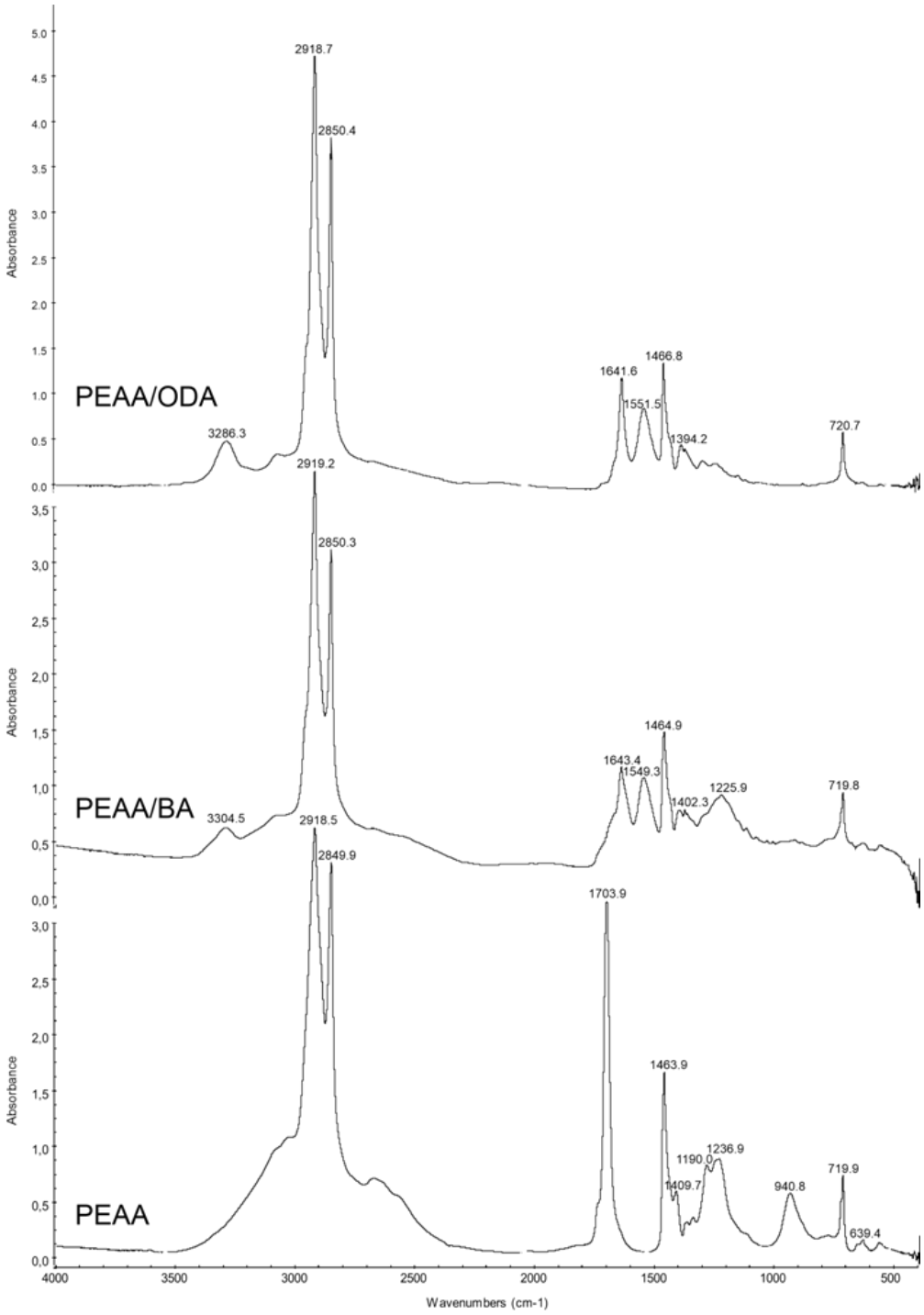


Figure 3. FTIR spectrum of the synthesized copolymers PEAA, PEAA/BA, PEAA/ODA

The Results of Measuring the Molecular Weight of the Copolymers

The measurement results showed that the molecular weight of PEAA (Mw is 2.21×10^5 g/mol) is lower than the molecular weight of PEAA modified with butylamine (Mw is 2.49×10^5 g/mol) and the molecular weight of PEAA modified with butylamine is lower than the molecular weight of PEAA modified with octadecylamine (Mw is 3.83×10^5 g/mol). The polydispersity index (Mw/Mn) ranges from 1.211 to 1.287 (Table 2). Comparing and analyzing the molecular weight and polydispersity index of the synthesized and modified copolymers improving the pour point of crude oil in various studies in similar directions, it was found that the molecular weight and polydispersity index of the modified copolymers were within the regulated norms. Therefore, it is possible to use modified copolymers as potential PPDs.

Table 2

Molecular weight of PEAA copolymers

Sample	M_W, g/mol	Mn, g/mol	M_W/ Mn
Poly(ethylene-co-acrylic acid)	221.315	182.754	1.211
Poly(ethylene-co-acrylic acid)/butylamine	249.412	199.051	1.253
Poly(ethylene-co-acrylic acid)/octadecylamine	383.124	297.687	1.287

Pour Point and Rheological Measurements

From the obtained data, we can observe that the PEAA copolymer modified with octadecylamine shows the best efficiency at lowering the pour point of crude oil to –3 °C at an additive concentration in crude oil of 100 ppm. Increasing or decreasing concentration of an additive, the pour point of the crude oil is 0 °C. The same trend is observed for PEAA copolymer, where the pour point of crude oil at 100 ppm is 0 °C, and with decreasing or increasing pour point concentration, it increases to 3 °C and PEAA copolymer modified with butylamine, where the pour point of crude oil at 100 ppm is 3 °C, and with a decrease or increase in the concentration of pour point, it increases to 6 °C. Therefore, the most effective dosage for PEAA-based additives for Akshabulak crude oil is 100 ppm and when dosage changes, the achieved effectiveness deteriorates.

A 12 °C decrease in pour point of crude oil (from 9 °C to –3 °C) of modified PEAA copolymer, compared to unmodified PEAA copolymer by 6 °C (from 9 °C to 3 °C) indicates that PEAA grafts have the ability to disperse wax crystals and reduce their nucleation (Table 3). According to the obtained data, the deposition and coagulation of wax crystals decrease with an increase in the length of the side group of the modified PEAA copolymers, which, in turn, shows the effect of the length of the pendant groups on the effectiveness of the depressant additive.

Table 3

Pour point of crude oil with the addition of PEAA copolymers and blank crude oil

Sample	Pour point temperature, °C			ΔT, °C
	50 ppm	100 ppm	200 ppm	
Crude oil blank 45 °C	+18			–
Crude oil blank 60 °C	+9			–
Crude oil with PEAA	6	3	6	6
Crude oil with PEAA/BA	3	0	3	9
Crude oil with PEAA/ODA	0	–3	0	12

The rheological properties of crude oil from the Akshabulak field were measured with and without the addition of PEAA copolymers at a concentration of 100 ppm. The PEAA copolymer and modified PEAA copolymers having octadecylamine and butylamine side chains show an improvement in the rheology curve (Fig. 4).

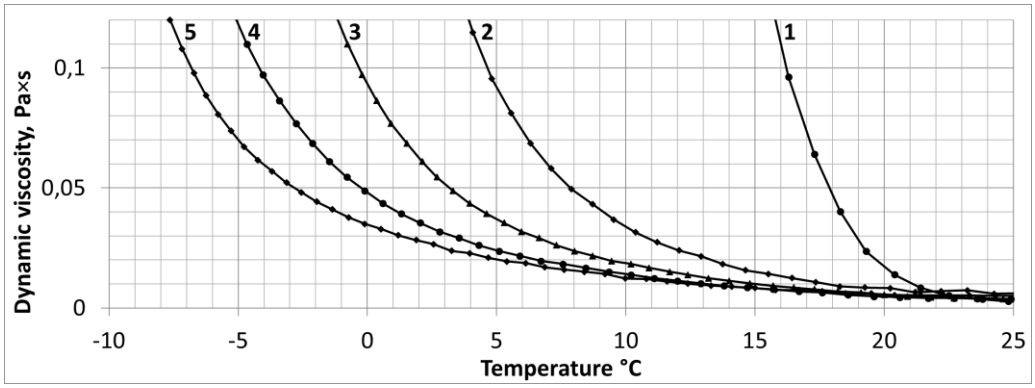


Figure 4. Curve of the dependence of the dynamic viscosity of Akshabulak crude oil on temperature with a heat treatment at 45 °C[1] and 60°C[2] without PPD, and heat treatment at 60 °C with dosage of 100 ppm depressants: PEAA[3], PEAA-BA[4], PEAA-ODA[5]

The addition of unmodified PEAA copolymer to crude oil is less effective than modified PEAA. The most effective additive for rheological measurements and for measuring the pour point of crude oil is PEAA copolymer modified with octadecylamine. The rheological data also show the dependence of the rheological curve on the heat treatment temperature. Crude oil heat treated at 60 °C performs better than crude oil heat treated at 45 °C.

The effectiveness of modified copolymers compared to unmodified PEAA can be explained by the polarity of nitrogen in the amide group along the copolymer chain, which plays a role in preventing the agglomeration of wax crystals in crude oil.

Conclusions

Modification of the PEAA copolymer was carried out using primary amines, namely long-chain octadecylamine and short-chain butylamine. The most effective concentration for copolymers based on PEAA as a pour point depressant for Akshabulak crude oil is 100 ppm. Octadecylamine-modified PEAA copolymer shows the best performance as Pout Point Depressant for Akshabulak crude oil. Rheological measurements demonstrate that the viscosity properties of the treated crude oil depend on the structure of the modified PEAA copolymers. The longer the pendant group is, the higher the effectiveness of the pour point depressants is.

The rheological properties and pour point of crude oil were found to decrease with the addition of modified PEAA even at low concentrations (50 ppm).

Acknowledgments

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Полиэтилен акрил қышқылының сополимерін парафинді шикі мұнайларға депрессант ретінде қолдану үшін амидациялау

Осы жұмыс депрессорлық қоспа ретінде пайдалану үшін модификацияланған аминдермен полиэтилен-акрил қышқылының (PEAA) сополимерлерін алуға және оларды шикі мұнайдың аққыштығының жоғалу температурасын жақсарту үшін бағалауға бағытталған. Ол үшін PEAA/ODA және PEAA/BA сополимерлерін алу үшін 150°C температурада 10 сағат бойы еріткіш ретінде ксилол қатысуымен PEAA бутиламинмен және октадесиламинмен амидирленді. Сополимерлер RNH_2 реакцияларында реакция орталықтары ретінде этилен мен акрил қышқылы сополимерінің карбон қышқылының топтарын қолдана отырып, амидирлеу арқылы модификацияланды. Модификацияда негіз ретінде пайдаланылатын PEAA сополимері 20 моль акрил қышқылына ие. Алынған сополимерлер FTIR-спектроскопия әдісімен тазартылып, талданды. Модификацияланған PEAA сополимерлері 50 ppm, 100 ppm және 200 ppm концентрациялары кезінде аққыштықтың жоғалу температурасын өлшеу, сондай-ақ 100 ppm концентрациясы жағдайында реологиялық өлшеу арқылы шикі мұнайға арналған депрессорлық қоспалар ретінде олардың тиімділігі үшін бағаланды. Шикі мұнайдың аққыштығының жоғалу температурасын өлшеу нәтижелері октадециламинмен модификацияланған PEAA сополимерінің модификацияланған бутиламинге және модификацияланбаған PEAA сополимеріне қарағанда тиімділігі жоғары екенін көрсетті. Модификацияланбаған PEAA-мен салыстырғанда модификацияланған сополимерлердің тиімділігін шикі мұнайдағы парафин кристалдарының агломерациясын болдырмауда маңызды рөл атқаратын сополимер тізбегі бойындағы амидтер тобындағы азоттың полярлығымен түсіндіруге болады.

Кілт сөздер: полиэтилен-акрил қышқылы (PEAA), шикі мұнай, депрессорлық қоспалар (PPD), парафиндік мұнай, сополимерлер, қату температурасы, аққыштық, модификация, бастапқы аминдер.

А.А. Жубанов, В.Г. Бондалетов, С.С. Кожабеков, А.З. Галымжан

Амидирование сополимера полиэтилен-акриловой кислоты для использования в качестве депрессорных присадок для сырых парафинистых нефтей

Настоящая работа направлена на получение сополимеров полиэтилен-акриловой кислоты (PEAA), модифицированных аминами, для применения в качестве депрессорных присадок и оценку их на предмет улучшения температуры потери текучести сырой нефти. Для этого PEAA амидировали бутиламином и октадециламином в присутствии ксилола в качестве растворителя при 150 °C в течение 10 часов с получением сополимеров PEAA/ODA и PEAA/BA. Сополимеры были модифицированы путем амидирования с использованием групп карбоновой кислоты сополимера этилена и акриловой кислоты в качестве реакционных центров в реакциях с RNH_2. Полученные сополимеры очищали и анализировали методом FTIR-спектроскопии. Модифицированные сополимеры PEAA были оценены на предмет их эффективности в качестве депрессорных присадок для сырой нефти посредством измерений температуры потери текучести при концентрациях 50 ppm, 100 ppm и 200 ppm, а также реологических измерений при концентрации 100 ppm. Результаты измерения температуры потери текучести сырой нефти показали, что большую эффективность показывает сополимер PEAA, модифицированный октадециламином, чем модифицированный бутиламином и не модифицированный сополимер PEAA. Эффективность модифицированных сополимеров по сравнению с немодифицированным PEAA можно объяснить полярностью азота в амидной группе вдоль цепи сополимера, которая играет роль в предотвращении агломерации кристаллов парафина в сырой нефти.

Ключевые слова: полиэтилен-акриловая кислота, сырая нефть, депрессорная присадка, парафиновая нефть, сополимеры, температура застывания, текучесть, модификация, первичные амины.

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