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Д.В. Сокольский атындағы «Жанармай,
катализ және электрохимия институты» АҚ

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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
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Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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MODIFICATION OF COPOLYMERS BASED ON OLEFIN AND MALEIC ANHYDRIDE AS POUR POINT DEPRESSANT FOR WAXY OILS

Abstract. In this work, we investigated a modification of a copolymer based on α-olefin (octadecene-1) (ODC) and maleic anhydride (MA) synthesized by the method of initiated radical polymerization. In the studies carried out, it was revealed that of all the synthesized copolymers based on maleic anhydride, the copolymer with α-octadecene was the most effective copolymer in reducing the viscosity of oil and TPT. In this work, a copolymer based on maleic anhydride and octadecene-1 (ODC – MA) was modified with primary amines – butylamine (BA), hexylamine (HA), hexadecylamine (HDA), octadecylamine (ODA), benzylamine (BzA). The copolymer was modified in a xylene solution with a Dean – Stark packing; the ratio of the ODC – MA copolymer to amines was 1:1.2 mol. Tololsulfonic acid (TSC) 0.5 wt% was used as a catalyst. Synthesis temperature 140°C, time 8 hours. The degree of completion of the reaction was evaluated by the amount of water formed in the Dean Stark packing. Modified copolymers ODC – MA with amines (ODC – MA – BA, ODC – MA – HA, ODC – MA – HDA, ODC – MA – ODA, ODC – MA – BzA) were characterized by Fourier IR spectroscopy and ^{1}H and ^{13}C NMR spectroscopy, which indicates the transformation of the original anhydride rings into imide ones. Modified copolymers were tested on waxy oil as depressants. Moreover, all modified copolymers exhibit the properties of depressants – they reduce the viscosity and TPT of oil relative to oil without an PPD. The morphology of waxy crystals formed in oil during a decrease in temperature was determined by microscopy; it was shown that modified waxy crystals of small sizes are formed compared to the original oil without PPDs, which indicates the dispersing effect of modified copolymers based on ODC – MA.

Key words: oil, copolymers, modification, waxes, fluidity, rheometry, pour point, viscosity.

Introduction. The transportation of crude waxy oil through pipelines, in tanks and tankers is complicated by the deposition of waxes on the walls of the tank and pipeline, which leads to an increase in the risk of pipeline shutdown and an increase in solid wax deposits in tanks during storage in tanks and transportation by tankers. In order to prevent these negative consequences in world practice, depressants are used, which are polymeric surfactants of various structures [1-3]

The use of polymer PPDs that ensure the transportation of oil and oil products is an urgent problem for countries with a cold climate and long communications like Kazakhstan. The use of these PPDs is constantly increasing and for 2020 the global market prospects for PPDs were estimated at US $ 1.4 billion [4]. The mechanism of action of these PPDs is different. Some PPDs reduce pour point and can be used as a pour point depressant (PPD). Most importantly, these compounds can both prevent the appearance of wax crystals and modify the surface of the wax crystals by changing their morphology and surface properties, preventing the crystals from sticking together. [5,6].

One of the promising directions is the synthesis of copolymers with amphiphilic properties [7].

Amphiphilic copolymers are used in various industries, and one of them is the use as depressants for oil and oil products [8]. In some works, α-olefins and maleic anhydride act as reagents for the synthesis of amphiphilic copolymers [9]. A feature of the use of maleic anhydride and α-olefins for the synthesis of

polymers is the alternating nature of the obtained copolymers [9]. Thus, for modification, a copolymer synthesized in [10] with a ratio of α-olefins and maleic anhydride 1: 1 was chosen.

Modification of the anhydride fragments of the copolymer with primary amines makes it possible to increase the depressant activity of the copolymers [11]. In the works [12-14], effective depressants were obtained based on copolymers of maleic anhydride with α-olefins modified with various amines or alcohols.

Reagents. A copolymer based on maleic anhydride and α-olefin (octadecene-1) (ODC – MA) used for modification was synthesized using the method of initiated radical polymerization. The ratio of maleic anhydride and α-olefin is 1:1.

Toluenesulfonic acid (Sigma – Aldrich) was used as a catalyst, butylamine, hexylamine, hexadecylamine, octadecylamine (Sigma – Aldrich) with a degree of purity (pure grade) were used without additional purification. The solvent was o-xylene (Sigma-Aldrich) with a purity grade (pure grade) was used without additional purification. Methanol with a degree of purity (pure grade) was used without additional purification.

Modification of copolymers. Modification of the ODC-MA copolymer with primary amines was carried out according to the general procedure (figure 1). A two-necked flask equipped with a Dean – Stark attachment with a reflux condenser, stirrer and thermometer was loaded with an ODC – MA copolymer (8.5 mmol), a primary amine (10.2 mmol), and 6 ml of o-xylene. The mixture was heated to a temperature of 150°C and toluenesulfonic acid (0.15 mmol) was added, then the reaction mixture was continuously stirred until the evolution of reaction water ceased, for 10 hours. The resulting mixture was cooled, washed with methanol, and dried in a vacuum oven to remove residual solvent.

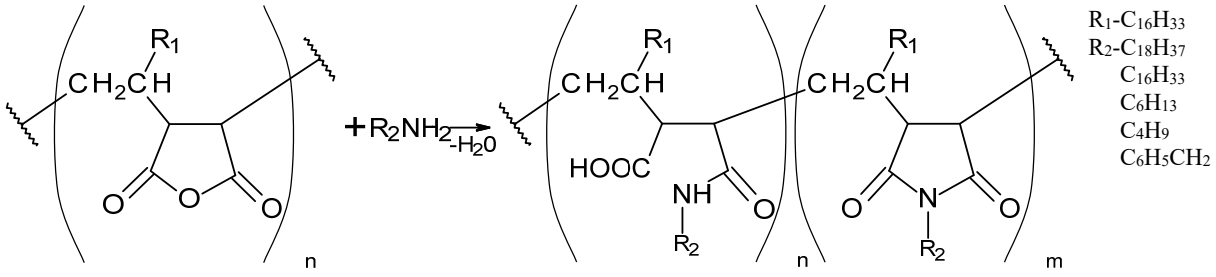


Figure 1 – Scheme of the structure of modified copolymers R_1 - $C_{16}H_{33}$, R_2 - $C_{18}H_{37}$ (octadecylamine), $C_{16}H_{33}$ (hexadecylamine), C_6H_{13} (hexylamine), C_4H_9 (butylamine), $C_6H_5CH_2$ (benzylamine)

Instrumental methods of analysis. The structure of the modified copolymers was analyzed by NMR spectroscopy and IR spectroscopy. ^1H and ^{13}C NMR spectra were recorded on a JNM – ECA Jeol 400 spectrometer (frequencies 399.78 and 100.53 MHz, respectively) using a $CDCl_3$ solvent. Chemical shifts are measured relative to residual protons or carbons of deuterated chloroform. The Nicolet 5700 FT – IR Fourier transform IR spectrometer operated in the range 400–4000 cm^{-1}.

The depressor efficiency of the synthesized copolymers was evaluated for oil from the Akshabulak field. Pour point determined in accordance with ASTM D 5853–09. Rheological measurements were carried out using a RheoLab QC rotary rheometer (Anton Paar, Austria) with Rheoplus 3.0 software equipped with a thermostated cooling system with temperature control. The measurements were carried out using a DG 42 two-slot coaxial cylinder.

The analysis of the wax fraction was carried out in the form of a solution in carbon disulfide on a PerkinElmer AutoSistemXL chromatograph (USA). The components of the wax fraction were identified by chromatography using reference hydrocarbons. The chromatogram of oil from the Akshabulak field is shown in table 2.

The shape and structure of wax crystals were determined using a Nikon ECLIPSE LV150N incident light microscope (Japan). The method for determining the morphology of crystals is standard. A small volume of the test oil was applied to a glass slide, covered with a second layer of glass on top, thermostatted, and purged with a stream of dry nitrogen to prevent condensation. Observation was carried out through a monitor in real time, a picture of wax crystals was taken every degree.

Physico-chemical characteristics of oil. The rheological properties of oil depend on the physical and chemical characteristics of the oil. The fluidity of oil is influenced by such factors as temperature, the content of waxes, asphaltenes and resins in oils [15-17]. Oil from the Akshabulak field is waxy with low resin content and low asphaltene content. The low content of asphalt-resinous substances and the high content of waxes determine high values of the pour point of this oil [18, 19].

The main role that determines the pour point of oil is solid waxes C_{20} and above [20-22]. For oil from the Akshabulak field, the molecular weight distribution of n-alkanes was determined by gas chromatography (table 2). The content of waxes in Akshabulak oil was determined using the program of simulated distillation of hydrocarbons on an AutoSystem XL chromatograph (Perkin Elmer, USA).

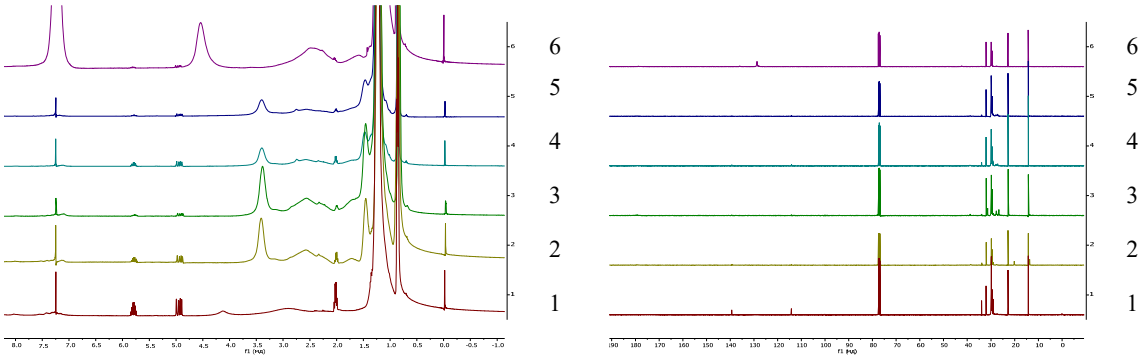
Table 2 – Results of chromatogram distribution of solid waxes in oil Akshabulak

Waxes	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}
%, in oil	1,0704	1,1604	1,0927	1,1640	0,9475	0,9434	0,7442	0,7101
C_{28}	C_{29}	C_{30}	C_{31}	C_{32}	C_{33}	C_{34}	C_{35}	C_{36}
0,5464	0,5477	0,3483	0,2457	0,1476	0,0945	0,0521	0,0266	0,0203
C_{37}	C_{38}	C_{39}	C_{40}	C_{41}	C_{42}	C_{43}	C_{44}	C_{45}
0,0097	0,0066	0,0046	0,0001	0,0004	0,0004	0,0003	0,0001	0,0001

Copolymer structure. The structure of the copolymers was analyzed by ^{1}H and ^{13}C NMR spectroscopy (figure 2) and FTIR spectrometry in the range 400–4000 cm^{-1} (figure 3).

The ^{1}H NMR spectrum of the OD – MA copolymer exhibits multiplet signals at 0.84–0.87 ppm. with a proton integral intensity of 3.0H of the terminal methyl groups of the octadecene fragment. The methylene protons of the octadecene fragment appeared as a broadened signal at 1.10–1.42 ppm. with an integrated intensity of 22.1N. The methine protons of maleic anhydride fragments resonated at 2.5–3.5 ppm. integral intensity 0.4N. Trace amounts of proton signals at 4.09–4.15 and 4.89–4.99 ppm indicate the absence or negligible amounts of unsaturated bonds in the copolymer.

In the ^{13}C NMR spectrum of copolymer 1, the carbon atoms of the terminal methyl groups of the octadecene fragments are observed at 14.27 ppm. The methylene and methine carbon atoms of the copolymer resonate at 22.81, 29.26, 29.86, 31.88 and 33.94 ppmMetinic carbon atoms of the maleic anhydride ring are manifested by broadened signals in the range 41–44 ppm. The carbonyl protons of the above cycle are also manifested by broadened signals in the 170-175 ppm region. In the ^{13}C spectra of the initial OD – MA copolymer, the carbon of the anhydride group resonates at 114.17 and 139.36 ppm, but barely manifests itself or practically disappears in the spectra of copolymers modified with primary amines. For the OD – MA copolymer in the IR spectra, the bands of stretching vibrations of the carbonyl group C = O in the ester range of 1710–1713 cm^{-1} are characteristic. The characteristic vibrations in the region (1770–1775 and 1850–1855cm^{-1}) refer to C=O stretching vibrations in cyclic anhydride units.



1H overlay of samples 1-6 13C overlay samples 1-6

Figure 2 – ^{1}H and ^{13}C NMR spectrum of the ODC – MA[1] copolymer and the modified copolymers ODC – MA – ODA[2], ODC – MA – HDA[3], ODC – MA – HA[4], ODC – MA – BA[5], ODC – MA – BzA[6].

In the modified ODC – MA copolymers with amines (ODC – MA – BA, ODC – MA – HA, ODC – MA – HDA, ODC – MA – ODA, ODC – MA – BzA), the 1H NMR spectrum in the copolymers exhibits multiplet signals at 0.82– 0.89 ppm with a proton integral intensity from 3.0 to 6.0 terminal methyl groups of the octadecene and alkylamine fragments. The methylene protons of the modified copolymers were located in two singlet signals at 1.22–1.25 and 1.45 ppm. with a total integrated intensity from 21.0H to 27.8H. The methine protons of maleic anhydride fragments, as well as the protons of the amide group and the methylene fragment adjacent to it, resonated at 2.0–3.5 ppm. integrated intensity from 1.0H to 2.2N. The opening of maleic anhydride cycles and the formation of cycles with the participation of nitrogen atoms affect the spectrum pattern in this region: it increases at 3.40 ppm. Trace amounts of proton signals of unsaturated bonds are almost not observed. The aromatic protons of the benzylamine fragment of the OD – MA – BzA copolymer resonated with a broadened singlet at 7.20 ppm. with an integrated intensity of 4.0N.

In the ^{13}C NMR spectrum of copolymer 2, the carbon atoms of the terminal methyl groups of the octadecene and alkylamine fragments are observed at 14.21–14.28 and 13.69 ppm. The methylene and methine carbon atoms of the copolymer resonate at 20.17, 22.78, 27.62, 29.85, 32.02, 33.92 and 38.50 ppm.. Two broadened signals at 177.85 and 179.8 ppm correspond to the carbonyl carbon atoms of the copolymer. characterized by Fourier IR spectroscopy, which indicates the transformation of the initial anhydride rings (1780–1850 cm^{-1}) into imide rings (1535, 1690–1700 cm^{-1}). The data presented indicate the presence of the main functional groups in the structure of the copolymers shown in the diagram (figure 1).

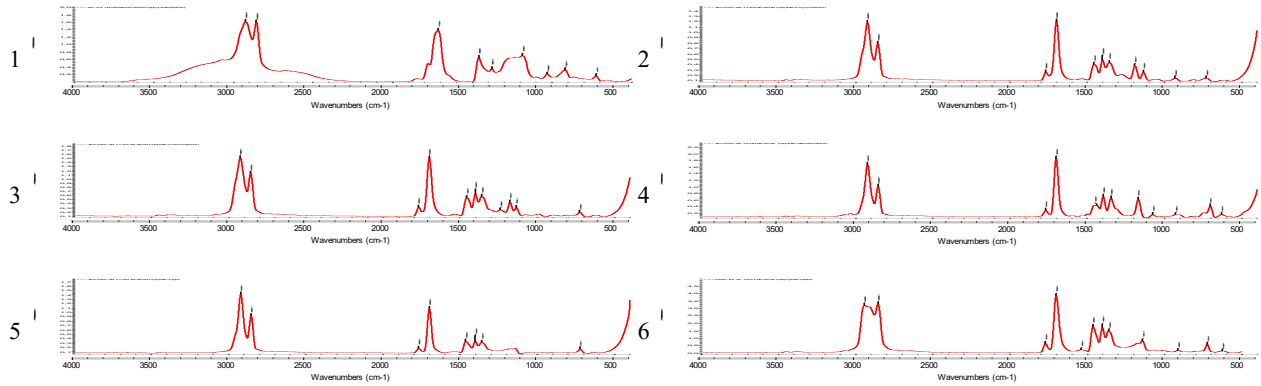


Figure 3 – IR spectrum of the synthesized copolymers ODC – MA[1] and modified copolymers ODC – MA – BA[2], ODC – MA – HA[3], ODC – MA – BzA[4], ODC – MA – HDA[5], ODC – MA – ODA[6] with Fourier transform.

Low temperature oil testing. The determination of the pour point of oil was carried out according to the ASTM D 5853 standard. The results are shown in table 4. From the data presented, it can be seen that the ODC – MA copolymer modified with butylamine[7] shows the best result among the modified copolymers with a pour point of – 6 ° C at a concentration of 300 ppm. A further increase in the concentration of the obtained depressants does not improve the low-temperature properties of oil. Thus, it was determined that the optimal concentration for the obtained depressants was 0.03%. It should be noted that the rheological curve (figure 4) of the modified copolymer ODC – MA – BzA[2] has the lowest rheological efficiency and shows the result lower than that of the ODC – MA[3] on the basis of which it was obtained. The reason for the high efficiency of the copolymer modified with butyl amine is possibly related to the chain length. Short-chain branches in the copolymer, like butylamine, do not prevent the polar portions of the copolymer from accessing the waxes, while the long-chain portions of the copolymers, like octadecylamine, shield the wax crystals from the polar portions. Similar conclusions were made in [23], where the octadecene-maleic anhydride copolymer was modified with primary alcohols of various lengths.

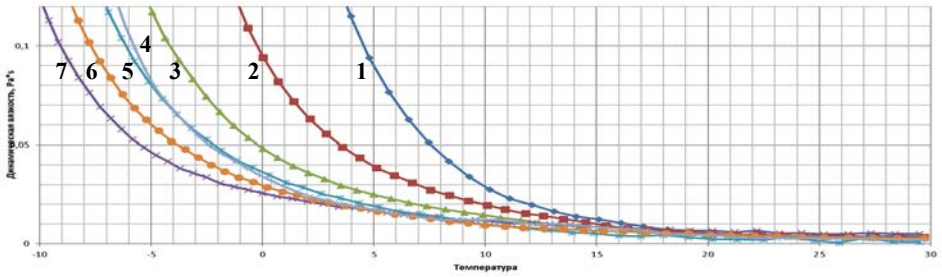
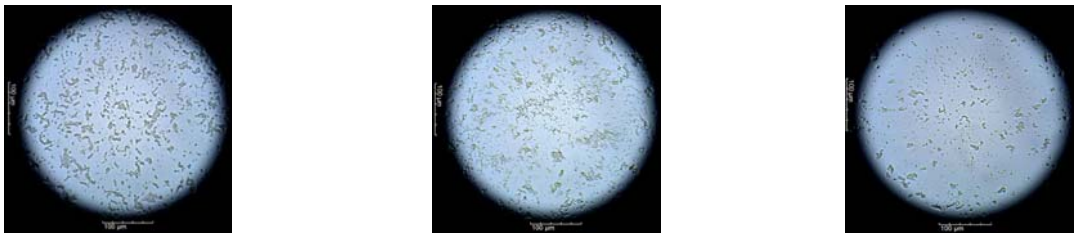


Figure 4 – Curve of the dependence of the dynamic viscosity of Akshabulak oil on temperature with a heat treatment at 60 ° C at a dosage of 300 ppm depressants with the addition of PPD: ODC - MA-BZA[2], ODC - MA[3], ODC - MA-ODA[4], ODC - MA-HA[5], ODC - MA-HDA[6], ODC - MA-BA[7] and without PPD[1]

Table 4 – Dependence of the pour point of Akshabulak oil with and without the addition of depressants

Sample	Pour point temperature		
	300 ppm	500 ppm	1000 ppm
Crude oil without PPD	+6°C		
Crude oil with ODC-MA	–3°C	0°C	0°C
Crude oil from ODC-MA-BA	–6°C	–3°C	0°C
Crude oil from ODC-MA-BzA	+3°C	+3°C	+6°C
Crude oil from ODC-MA-HA	–3°C	0°C	+3°C
Crude oil with ODC-MA-HDA	–6°C	–3°C	0°C
Crude oil from ODC-MA-ODA	–3°C	0°C	+3°C

Morphology of wax crystals. Figure 5 shows micrographs of oil without PPDs and with the addition of ODC-MA copolymer and ODC-MA copolymer modified with butylamine, which showed the highest depressant activity according to the results of rheological tests. It can be seen from the obtained micrographs of Akshabulak oil that at the same temperature (0°C), wax crystals with the addition of an PPD modified with butylamine have a shape and size different from the crystals of wax of a copolymer of non-amines modified maleic anhydride with linear α-olefin and is more different from crystals wax in oil without PPDs.



1 2 3

Figure 5 – Micrograph of Akshabulak oil without PPD[1] with PPD (ODC-MA)[2] and with modified PPD (ODC-MA-BA)[3].

According to the data obtained, we can observe that the modified copolymer does not prevent the appearance of crystals, but prevents their growth, thereby restraining the agglomeration of wax crystals and reducing the pour point of oil. The figure shows that the number of small wax crystals, which are the nuclei for the appearance of large crystals, in oil with an PPD is much less than in oil without an PPD. The formation of large crystals that do not interact with each other is the reason for the effectiveness of the copolymer as a depressant. Hence, it can be concluded that the obtained copolymers exhibit a depressing and dispersing effect.

Conclusion. In this work, the modified copolymers were tested on oil from the Akshabulak field using conventional methods. The copolymer modified with butylamine exhibits the highest depressant activity. The efficiency of the modified copolymers obtained is associated with the dispersing effect arising from the co-crystallization of the additive with paraffin waxes. It was revealed that the copolymer modified with the short primary amine ODC-MA-BA shows better efficiency than the copolymer modified with the long primary amine ODC-MA-ODA.

When studying the structure of wax crystals, it was revealed that wax crystals with the addition of a copolymer modified with butylamine have a shape and size different from the wax crystals of a copolymer not modified with amines. A possible reason for the effectiveness of the butylamine-modified copolymer is the easier access of waxes to polar groups, which provides a high depressant efficiency of copolymers modified with short-chain amines, compared to copolymers modified with amines with a longer chain.

It is shown that, in contrast to the copolymer of maleic anhydride with linear α-olefin, modified copolymers with amines more effectively lower the pour point of oil, which gives rise to further study of copolymers modified with primary amines.

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ПАРФФИНДІ МҰНАЙҒА PPD РЕТІНДЕ ҚОЛДАНЫЛАТЫН ОЛЕФИНДЕР МЕН МАЛЕИН АНГИДРИДІ НЕГІЗІНДЕГІ КОПОЛИМЕРЛЕРДІ ТҮРЛЕНДІРУ

Аннотация. Жұмыста мономер қатынасы 1:1 болатын ауыспалы құрылыммен басталған радикалды полимерлеу әдісімен синтезделген α-олефин (октадецен-1) және малеин ангидриді (ODC-MA) негізіндегі сополимердің түрлендірілуі зерттелді. Алынған сополимерлер метанол арқылы реакцияға түспеген компоненттерден тазартылды. Өткізілген зерттеулерде малеин ангидриді және α-олефиндер негізінде синтезделген сополимерлер арасынан октадецен негізіндегі сополимер мұнай мен ТПТ тұтқырлығын төмендетуде ең тиімді сополимердің болғандығы анықталды. Жұмыста малеин ангидриді мен октадецен-1 негізіндегі сополимер бастапқы аминдермен – бутиламин (BA), гексиламин (HA), гексадециламин (HDA), октадециламин (ODA), бензиламин (BzA) арқылы түрлендірілді. ODC - MA сополимері Дин-Старк қондырмасымен ксилол ерітіндісінде түрледірілді. ODC - MA сополимерінің аминдерге қатынасы 1: 1,2 моль болды. Катализатор ретінде тололсульфо қышқылы (TSC) 0,5% көлемінде қолданылды. Синтез температурасы – 140 °C, уақыты – 8 сағат. Реакцияның аяқталу дәрежесі Дин Старк қондырмасында түзілген су мөлшерімен бағаланды. Аминдермен модификацияланған ODC - MA сополимерлері (ODC - MA - BA, ODC - MA - HA, ODC - MA - HDA, ODC - MA - ODA, ODC - MA - BZA) Фурье ИК спектроскопиясымен және 1H және 13C спектроскопиясымен сипатталды, бұл бастапқы ангидрид сақиналарының имидтік сақиналарға айналуын көрсетеді. 1H және 13C ЯМР спектрлері CDCl3 еріткішін қолдану арқылы JNM - ECA Jeol 400 спектрометрінде (жиіліктері сәйкесінше 399,78 және 100,53 МГц) жазылды. Химиялық ығысулар қалдық протондарға немесе деитериленген хлороформды есепке алу арқылы өлшенді. Nicolet 5700 FT - IR Fourier түрлендіретін ИҚ-спектрометрі 400-4000 $см^{-1}$ аралығында жұмыс істеді. Модификацияланған сополимерлер Ақшабұлақ кен орнынан алынған парафинді мұнайға депрессант ретінде сыналды. Мұнайдың қату температурасы ASTM D 5853-09 сәйкес анықталды.Реологиялық өлшем RheoLab QC ротациялық реометрі (Антон Паар, Австрия) арқылы Rheoplus 3.0 бағдарламалық жасақтамасымен температураны басқаратын термостатталған салқындату жүйесімен жүзеге асырылды. Өлшеу екі ойықталған коаксиалды цилиндр DG 42 негізінде жүргізілді.

Түйін сөздер: мұнай, сополимерлер, түрлендіру, парафиндер, аққыштық, реометрия, аққыштықты жоғалту температурасы, тұтқырлық.

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МОДИФИКАЦИЯ СОПОЛИМЕРОВ НА ОСНОВЕ ОЛЕФИНОВ И МАЛЕИНОВОГО АНГИДРИДА КАК PPD ДЛЯ ПАРАФИНИСТЫХ НЕФТЕЙ

Аннотация. В работе исследована модификация сополимера на основе α–олефина (октадецен–1) и малеинового ангидрида (ОДЦ-МА), синтезированного методом инициированной радикальной полимеризации с чередующейся структурой с соотношением мономеров 1:1. Полученные сополимеры были очищены метанолом от несреагировавших компонентов. В проведенных исследованиях было выявлено, что из всех синтезированных сополимеров на основе малеинового ангидрида наиболее эффективным сополимером по снижению вязкости нефти и ТПТ явился сополимер с α-октадеценом. В этой работе сополимер на основе малеинового ангидрида и октадецена-1 подвергался модификации первичными аминами–бутиламин (БА), гексиламин (ГА), гексадециламин (ГДА), октадециламин (ОДА), бензиламин (БзА). Модификацию сополимера проводили в растворе ксилола с насадкой Дина–Старка, соотношение сополимера ОДЦ–МА к аминам составляло 1:1,2 моля. В качестве катализатора применяли тололсульфокислоту (ТСК) 0,5% вес. Температура синтеза 140°С, время 8 часов. Степень завершения реакции оценивали по количеству воды образующееся в насадке Дина Старка. Модифицированные сополимеры ОДЦ–МА с аминами (ОДЦ–МА–БА, ОДЦ–МА–ГА, ОДЦ–МА–ГДА, ОДЦ–МА–ОДА, ОДЦ–МА–БЗА) охарактеризованы методом Фурье ИК спектроскопии и ЯМР спектроскопии 1Н и 13С, которые свидетельствует о преобразовании исходных ангидридных циклов в имидные. Спектры ЯМР 1Н и 13С снимались на спектрометре JNM–ECA Jeol 400 (частота 399.78 и 100.53 МГц соответственно) с использованием растворителя $CDCl_3$. Химические сдвиги измерены относительно сигналов остаточных протонов или атомов углерода дейтерированного хлороформа. ИК–спектрометр с преобразованием Фурье Nicolet 5700 FT–IR работал в диапазоне 400–4000 $см^{-1}$. Проведены испытания модифицированных сополимеров как депрессорных присадок на парафинистой нефти месторождения Акшабулак. Температура потери текучести определена в соответствии со стандартом ASTM D 5853–09. Реологические измерения проводились с использованием ротационного реометра RheoLab QC ("Anton Paar", Австрия), с программным обеспечением Rheoplus 3.0 оснащенного термостатированной системой охлаждения с контролем температуры. Измерения проводились с применением двухщелевого коаксиального цилиндра DG 42.

Ключевые слова: нефть, сополимеры, модификация, парафины, текучесть, реометрия, температура потери текучести, вязкость.

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