



Modified graft copolymers based on ethylene vinyl acetate as depressants for waxy crude oil and their effect on the rheological properties of oil

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ABSTRACT

In this work, modified ethylene-vinyl acetate (EVA)-based copolymers were synthesized by graft copolymerization of hydrophobic monomers onto commercial EVA using a low energy electron beam (EB). The mechanism of graft copolymerization was studied by the spin trap method using a model reaction of the interaction of a tert-butoxy radical with an EVA copolymer. The results show that the main contribution to the initiation of graft copolymerization is made by the reactions of hydrogen abstraction from the methine CH groups of the vinyl acetate units. Oil from the Kumkol region treated with PPD showed better rheological properties, lower pour point temperatures, as well as lower wax content when tested on a cold finger, and better performance on the transportation route of the Kumkol - Karakoin - Shymkent. Moreover, EVA-based graft copolymers (gEVAp) performed better PPD than those obtained for commercial pour-point depressant (PPD). The rheological parameters of oil have been dramatically improved, which can be characterized as better oil pumpability in the cold season, which reduces the load on mainline pumps and saves energy for the transporting company. The pour point of the tested oil dropped from 12 to -3 °C, which led to the formation of wax crystals of the regular, compact platelet shape. Field tests using pigs showed significantly less wax deposited along the pipeline.

1. Introduction

Oil transportation is one of the main problems aside from production in the oil industry (Chala et al., 2018). Kazakhstan oilfields generally have waxy oil that forms deposits and creates rheological problems during transportation (Nadirov et al., 2021; Zhang et al., 2014). When Kazakhstani crude oil is transported by pipeline over long distances, paraffin precipitates, which can block the pipeline and cause additional pressure drops, further increasing transportation costs and in some cases requiring large repair costs (El-Dalatony et al., 2019; Frenier and Ziauddin, 2008; Gluyas and Underhill, 2003; Huang et al., 2011; Sayakhov et al., 2004). One approach that has been used is heaters along the pipeline, for example, on the main pipeline from the Dzhumagaliyev (former Karakoin) pumping station to the south (Pavlodar). Heating stations are located along the pipe and help maintain oil temperatures

suitable for winter transportation. In addition to heating, pigging is also used for mechanical cleaning to scrape off the deposited wax (Li et al., 2021). However, Kazakhstani oil can be so viscous (for example, Uzen oil) that its pour point can be around $+30$ °C (Kozhabekov et al., 2019; Makhmotov et al., 2008). This means that the heaters had to work all year round (Sayakhov et al., 2004). These are additional energy expenses for oil transporters (Rehan et al., 2016). The problem of oil flow in the cold season through a pipeline without heating systems is an urgent problem for Kazakhstan and the Kumkol region in particular. Moreover, given that winter temperatures in Central Kazakhstan can reach an average of -10 to -20 °C, and oil transportation pipes are laid deep underground, where negative temperatures can persist much longer, and if wax deposits accumulate rather quickly and solidify, the “pig” can get stuck in the pipe, as happened with the pipeline in the Gulf of Mexico (Fung et al., 2006). Besides, in many oilfields, the wax

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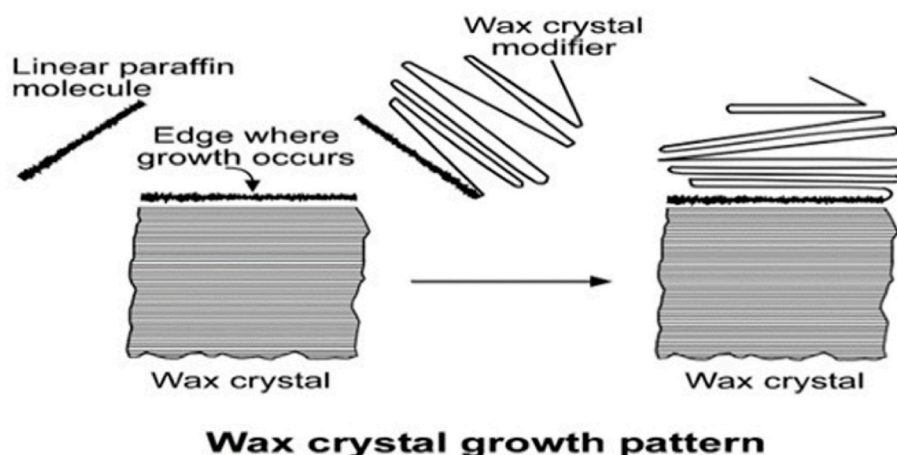


Fig. 1. Typical mechanism of wax crystal modifiers.

removal period for some wells is 2–10 days (Zhang et al., 2014). Thus, transportation of oils and oil blends in the cold season without additives is economically inexpedient.

Typically, commercial PPDs are used to control pour point and wax deposition (Chen et al., 2010; Yang et al., 2015). Their main components are polymeric compounds that usually belong to one of the following three general chemical families: ethylene-vinyl acetate (EVA) copolymers, maleic anhydride copolymers, and polyacrylate copolymers, which are used to modify wax crystals and prevent the formation of crystalline mesh leading to solidification of the entire oil (Chi et al., 2019; Gholami et al., 2019; Ghosh and Das, 2014; Moriceau et al., 2019; Oliveira et al., 2016; Wei, 2015; Yang et al., 2015).

Even so the general mechanism of action of pour point depressors depends on many factors (wax content, wax carbon number distribution, polymer composition, resins, asphaltenes, etc.), it is generally accepted that pour point depressors are wax crystal modifiers (Bilderback and McDougall, 1969; Chi et al., 2019; Yang et al., 2015). Many polymeric EVA-based PPDs are co-crystallized with wax molecules, form a thin layer on the surface of the wax crystals (Fig. 1) and prevent the formation of large agglomerates, which in turn improves the flowability of the waxy crude oil at low temperatures.

Again, EVA copolymers are currently the most commonly used polymeric wax and PPD inhibitors in the petroleum industry (Ashbaugh et al., 2005; Jafari Ansaroudi et al., 2013; Machado and Lucas, 1999; Taraneh et al., 2008; Yao et al., 2020). Moreover, in terms of operational applications, the effectiveness of the PPDs depends on the crude oil composition and the activity of the additive (Jennings and Breitigam, 2010). Historically commercial EVA-based PPDs have shown good depression properties on oil from the Kumkol oilfield of Central Kazakhstan (Kozhabekov et al., 2019; Marenov et al., 2020; Zhapbasbayev et al., 2021). However, due to the presence of polar groups in EVA that increase the likelihood of migration into the aqueous phase, these PPDs have limitations in use due to reduced co-crystallization of PPDs with wax in oils with high water content (Phan et al., 2019). Hydrophobic groups are thought to tend to eliminate the problem of solubilization of depressants in water. For example, it was previously shown that EVA copolymers modified with long side hydrocarbon chains showed significantly better results compared to the original EVA due to the improved solubility of PPD in the organic phase and, accordingly, due to less solubility in aqueous medium (da Silva et al., 2004; Kurniawan et al., 2021; Mansur et al., 2006). In addition, hydrophobically modified synthetic copolymers of (meth)acrylates with long hydrocarbon chains and long branched side groups (Alvares and Lucas, 2000; Alvares et al., 2004; Deshmukh and Bharambe, 2008; Ding et al., 1999) and linear or branched acid polyamides (Kudaibergenov et al., 2019; Song et al., 2005; Soni et al., 2010) showed excellent results when used

as PPDs due to their excellent miscibility with the organic phase. Previously, a number of hydrophobically modified polymer betaines have been used as PPDs for highly paraffinic crude oils from Western Kazakhstan (Didukh et al., 2004; Kudaibergenov et al., 2005, 2019), and it was shown that, depending on the oil used, it was necessary to add from 100 to 500 or even 1000 ppm of polymer depressant to the crude oil. The addition of a polymer depressant to Kazakhstani crude oil lowered the PPT from +15 to -3 °C, while the wax crystals were modified due to the co-crystallization (or absorption) of the paraffin molecule on macromolecular micelles. High molecular weight polymer “SMATWEEN” based on a copolymer of styrene and maleic anhydride with polyoxyethylene sorbitan trioleate, was used as a demulsifier and depressant for many high-paraffinic oils from Kazakhstan oilfields (Orazbekuly et al., 2014). 200 ppm of SMATWEEN reagent was sufficient for the commercial oil from the Kumkol oilfield and the Kumkol-Akshabulak oil blend with a depression of 15 °C and 21 °C, respectively. At the same time, the usual heat treatment, as well as the use of a depressant with low concentrations for highly paraffinic oil from the Zhetybai field, practically did not affect the pour point. This oil requires increasing the depressant concentration to 1000 ppm (the pour point decreased from 33 °C to 21 °C), or even to 5000 ppm (pour point dropped to 18 °C, while kinematic viscosity decreased from 28.2 mm²/s to 24.901 mm²/s). Nadirov et al. (Marenov et al., 2020) prepared compositions of EVA with crude gossypol (CG) isolated from refined cottonseed oil soapstock and studied their effect on the pour point and viscosity of crude oil from the Akshabulak oil field (Kazakhstan). The resulting compositions performed better PPD for crude oil than commercial EVA due to the appearance of additional non-polar and polar groups, as well as the formation of additional hydrogen bonds in the composite, which inhibit and destroy the growth of wax crystals. Despite the huge variety of polymers and polymer composites available for application as PPDs, efforts continue to design new as well as modify existing materials, not only to find cheaper additives but also because PPDs usually do not work in the same way with distinct crude oils, even those mined from the same region (Garcia et al., 1998).

In this work, our main goal was to study the possibility of improving the physical, chemical and operational properties of EVA copolymers, which are widely used as additives in Kazakhstan. To do this, we used the method of radiation grafting of monomers onto EVA macromolecules due to its high efficiency, simple process with low cost, and lack of chemicals other than reagents, so the products can be processed immediately after irradiation without polymer purification (Dergunov and Mun, 2009; Dergunov et al., 2008; Matsumoto et al., 2020; Mun et al., 1999; Nurkeeva et al., 2004; Starke et al., 2013). To better understand the effect of gEVA copolymers on oil behavior at low temperatures, we examined ethylene-vinyl acetate modified with various

Table 1
Physical properties of oil samples that compose Kumkol oil blend (Nadirov et al., 2021).

Oil characteristics	Kazgermunai	PetroKazakhstan Kumkol Resources	Turgai-Petroleum	CNPC - Ai Dan Munai	KOR	Kuat Amlon Munai	Kumkol oil blend
Pour point, °C (ASTM D5853)	12	9	9	6	21	18	12
Density at 20 °C (kg/m ³)(GOST 3900-85)	813.3	810.4	810,4	813.0	878.2	824.8	818,0
Wax content (wt. %)(GOST 11851-85)	14.3	14.4	14.4	11.6	20.1	19.5	12,6
Resins (wt. %)(GOST 11851-85)	8.6	7.6	7.6	16.3	9.2	8.0	6,02
Kinematic Viscosity at 20 °C, mm ² /s (ASTM D445)	11.6	8.0	8.0	11.2	13.9 (@40°C)	6.9 (@40°C)	8.7
Asphaltenes (wt. %)(GOST 11851-85)	0.6	0.1	0.1	0.4	1.3	0.15	0,67
Water cut (vol %)(GOST 2477-65)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Content of oil in Kumkol oil blend, %	35.5	37.5	11.1	4.9	5.3	5.8	–

hydrophobic monomers with varying vinyl acetate co-monomer contents and tested it against a commercial pour point depressant widely used in Central Kazakhstan.

2. Materials and methods

2.1. Reagents and materials

2.1.1. Crude oil

In this study, we used Kumkol oil blend produced in the Kumkol oilfield of Kazakhstan. The basic physical properties of the oil samples and the corresponding test methods are shown in Table 1. In this blend, KOR and Kuat Amlon Munai oils have the highest pour points with a large amount of heavy hydrocarbon fractions (wax content ~20%). However, their contribution to the overall oil blend is low. The water cut of marketable oil is usually <0.5%, however, due to weather and storage conditions in all cases shown, it can increase to 1–2%.

2.1.2. Materials

EVA copolymer with vinyl acetate co-monomer content from 25% to 40%, butyl acrylate (BA), butyl methacrylate (BMA), styrene (St), 2-methyl-2-nitrosopropane (MNP), Fremy's salt K₂NO(SO₃)₂, di-tert-butyl peroxalate (DTBP) as initiator at 5*10⁻³ mol/l obtained from Sigma Aldrich. Monomers were purified by passing through a column packed with aluminum oxide shortly before the synthesis. Industrial solvent (the mixture of aliphatic hydrocarbons with aromatic fraction mixed in proportions of 65% and 35% accordingly) and o-xylene were purchased from Sigma Aldrich. All materials obtained from Sigma Aldrich, all chemicals used without further purification. Commercial EVA-based PPD: Randep - 5102 («RauanNalco » LLP, Atyrau, Kazakhstan) consists of a polymer reaction product of formaldehyde with dinonylphenol and nonylphenol for dispersing asphaltenes. Commercial EVA-based PPD: DMN – 2005 (NPF Depran OOO, Russia) is the mixture of EVA with different molecular mass.

2.2. Graft co-polymers synthesis

Solutions of EVA (5% w/v) in o-xylene or an industrial solvent were mixed with monomers: BMA, BA, and St in various ratios (EVA: monomer = 1: 1; 1: 5; 2: 1, g:g). The samples were mixed with constant stirring until complete dissolution at room temperature. The prepared EVA solutions were packaged in ampoules (7 mL) for each ratio and irradiated at a radiation dose from 110 kGy to 160 kGy. The electron accelerator ELV-4 (Institute of Nuclear Physics in Almaty) with an energy range from 0.8 to 1.5 MeV, with a beam current of accelerated electrons up to 40 mA and a maximum power of up to 50 kW was used as a radiation source. During irradiation of the initial reaction mixture, along with the graft copolymerization of monomers (BMA, BA, or St) on EVA, homopolymerization also proceeds with the formation of the corresponding homopolymer. In order to separate the grafted copolymer from the homopolymer and the unreacted monomer, the reaction

Table 2
Synthesized EVA-based graft copolymers.

Name of solution	Name of ratio				
	Ratio	EVA: BMA	EVA: BA	EVA: St	EVA(blank solution)
EVA1 ^a in o-xylene	1:1	1 (A-E) ^d	10(A-E)	19(A-E)	28(A-E)
	1:5	2(A-E)	11(A-E)	20(A-E)	29(A-E)
	2:1	3(A-E)	12(A-E)	21(A-E)	30(A-E)
EVA2 ^b in o-xylene	1:1	4(A-E)	13(A-E)	22(A-E)	28(A-E)
	1:5	5(A-E)	14(A-E)	23(A-E)	29(A-E)
	2:1	6(A-E)	15(A-E)	24(A-E)	30(A-E)
EVA1 in an industrial solvent ^c	1:1	7(A-E)	16(A-E)	25(A-E)	31(A-E)
	1:5	8(A-E)	17(A-E)	26(A-E)	32(A-E)
	2:1	9(A-E)	18(A-E)	27(A-E)	33(A-E)

^a EVA1 is a polymer with a vinyl acetate co-monomer content of about 35–40%.

^b EVA2 is a polymer with a vinyl acetate comonomer content of about 25–30%.

^c Industrial solvent is a mixture of aliphatic hydrocarbons with aromatic fraction mixed in proportions of 65% and 35%, respectively.

^d The dose of radiation for EVA solutions: A = 110 kGy, B = 120 kGy, C = 130 kGy, D = 140 kGy, E = 160 kGy.

mixture was poured into acetone after completion of the irradiation, in which the homopolymers BMA, BA, and St dissolve well and the grafted copolymer precipitates. The grafted copolymer was purified by threefold resuspension from o-xylene to acetone, then dried in a vacuum desiccator at 70 °C to constant weight. The yield of EVA grafted co-polymers (gEVAp) containing BMA, BA and St abbreviated, respectively, as gEVABMA, gEVABA and gEVAST exceeded 95%. The parameters of graft polymerization, degree of grafting (%G), efficiency of grafting (%E) and degree of homopolymer formation (%H), were determined gravimetrically (Tables 1S–3S). All mixtures are described in Table 2.

2.3. Determination of the mechanism of graft copolymerization on EVA

We investigated the mechanism of graft copolymerization by EPR spectroscopy (Bruker ESP 300 EPR spectrometer) using 2-methyl-2-nitrosopropane (MNP) as a spin trap in sealed glass ampoules. In this study, all reactions were performed using green light (ZS-2 filter with transmittance maximum in the 540 nm region, where MNP solution is practically not absorbed), since MNP in solution under visible light irradiation exhibits photolysis with formation of tert-butyl radical and nitric oxide (two absorption maxima in the optical spectrum of MNP - in

near ultraviolet and in the red region) (Doba et al., 1977). The ampoules with the reaction mixture were evacuated to 0.1 Pa by repeated the freezing process with liquid nitrogen followed by thawing. The concentration of radicals contained in the sample was calculated using double graphical integration of EPR spectra. In spectra complicated by the superposition of lines of several adducts, we used the shape factor (the ratio of the integral spectrum intensity to the amplitude). The shape factor was determined using a model system that was not complicated by the imposition of other lines. To determine the g-factor and hyperfine splitting constants (α), the spectrum of a dilute aqueous solution of Fremy's salt $K_2NO(SO_3)_2$ was recorded simultaneously with the EPR spectrum of the system (Yordanov, 1994).

2.4. Grafted copolymers characterization

The polymer solutions after irradiation were kept in a vacuum oven at 140 °C for 24 h to completely remove the solvent. The structure of the synthesized graft copolymers was confirmed by Fourier-transform infrared spectroscopy (FT-IR) (Figs. 1S–6S, Thermo Nicolet 380, KBr, cm^{-1}): changes were detected in the fingerprint region of 1200–700 cm^{-1} on the product spectra compared to the original spectra of the commercial (unmodified) polymers. Peaks above 3000 cm^{-1} also indicate the presence of aromatic C–H bonds in gEVAS samples.

Molecular weights and molecular weight distributions were determined by size-exclusion chromatography (SEC) in tetrahydrofuran (THF) at 50 °C using a flow rate of 1 mL min^{-1} (Waters 515 HPLC pump & Waters 717 Autoinjector), using a Waters 2414 Refractive Index Detector operating at $\lambda = 660$ nm and Varian 380-LC Evaporative Light Scattering Detector (ELSD) (operating at 3 mW, $\lambda = 670$ nm with detection angles of 7° and 90°) and a four-capillary viscometer. The system was calibrated using PMMA standards with narrow molecular weight distribution (20 standards used for analyses from 7800 g/mol to 1,000,000 g/mol). Size-exclusion chromatography (SEC) was performed on a system equipped with size exclusion columns (Two mixed bed Jordi Gel DVB Medium MB columns, 300 × 7.8 mm, and separation over the molecular weight range from 200 to 3,000,000 g/mol) which were maintained at a temperature of 50 °C. Samples were filtered through a 0.45 μm PTFE filter before analysis. 100 μl sample loops were used for the majority of SEC analysis. The results show a slight increase in MW of grafted polymers according to the degree of grafting, with MW of EVA ~87 kDa and MWs of grafted copolymers ~99–120 kDa.

Differential Scanning Calorimetry (DSC) of polymer samples was performed on a NETZSCH 214 Polyma Differential Scanning Calorimeter (Figs. 7S–8S). All samples were tested by lowering the temperature from 150 to –20 °C with a step of 10 °C/min. The product profiles differ from the starting polymers. One composition: gEVAS24C is an amorphous polymer. The rest have pronounced points of the transition of the aggregate state that is moved to a high temperature which is different from the initial polymers.

2.5. Wax appearance temperature

The Wax Appearance Temperature (WAT) of the oil samples with and without PPD was measured on the standard of SY/T 0545–2012 using a NETZSCH 214 Polyma Differential Scanning Calorimeter (DSC) equipped with the Proteus software. The oil sample was preheated to 60 °C prior to analysis, then transferred to a pre-weighed aluminum crucible and sealed. Each DSC test was performed in an air atmosphere with a flow rate of 24 mL/min in the temperature range of 60–0 °C at a rate of 1 °C/min. It was determined that the WAT for commercial Kumkol oil blend lies in the region of ~38–40 °C (Fig. 9S).

2.6. Microscopy

To visualize the wax crystals, a Euromex polarizing microscope with a VC301 module was used. Pictures were taken at –3 °C. An oil sample

was examined on an LTS 350 temperature-controlled table.

2.7. Pour point measurements

Pour point measurements were conducted according to the modified ASTM D5853 procedure using a Kohler chilling bath (ASTM, 2017). The oil sample was preheated to 60 °C for 1 h. All oil samples were kept in tightly sealed vessels during heating and a 1-h waiting time to ensure that no light fractions were lost. PPD injection was carried out at 60 °C and kept for 30 min at this temperature. During measurements, samples were checked for flow every 3 °C.

2.8. Rheology measurements

The apparent dynamic viscosity of the condensate was measured using a Brookfield Rheometer DV-III+. A small sample adapter and spindle #21 were used for all measurements at a shear rate of 28.16 sec^{-1} . Oil samples were first preheated to 60 °C, then cooled at room temperature overnight, and then preheated to various pre-defined temperatures prior to rheology measurements. In typical experiments, an oil sample was preheated to 60 °C for 1 h. Then PPD was injected at 60 °C and kept for 30 min.

2.9. Evaluation of the efficiency of PPD under static conditions

The amount of wax deposit at different temperatures was measured by the cold finger technique (low shear wax deposition test) (Paso and Fogler, 2004; Singh et al., 2000). The stainless steel cold finger with a hermetically screw-on lid was directly connected to the cryostat system, which regulates the temperature in the range from –30 to +80 °C, and has dimensions: diameter 36 mm and working length 90 mm (Fig. 10S). In this Cold Finger test, the following test conditions were used: Sample size: 70 mL; Oil preheat temperature: 60 °C; Bulk oil temperature: 35 °C; Test duration: 3 h. The oil temperature in the cell was 5–10 °C above the expected WAT. At the end of the test period, the Cold Finger was removed from the oil sample, the free oil was drained from the cold finger (usually 10–15 min), and then the deposit plus residual oil was weighed. To correct the mass of residual oil film remaining on the Cold Finger, a clutch test was performed with the cleaned Cold Finger immersed in oil for 10 s, removed from the solution, and allowed to drain. The mass of oil adhered to the Cold Finger surface was then determined. The deposit accrued based on the cold finger was included in the total weight of the deposit. To improve the accuracy and reproducibility of experiments, several (from 3 to 6) cells are usually used simultaneously in one experiment. One of the cells is always a reference (without reagent), and the rest were filled with oil, to which, after heating, PPD or a wax inhibitor with different concentrations was preliminarily added.

2.10. Evaluation of the efficiency of PPD in dynamic real field conditions

To test wax deposition in dynamics in real field conditions, we used pigs (250 and 255 mm), which were launched into a pipeline (pipeline L = 80 km, d = 255 mm).

3. Results and discussion

We examined the polymeric PPDs in the field and laboratory conditions on the Kumkol oil blend since the Kumkol-Dzhumagaliyeva-Shymkent route is the only major route that is processed with the help of PPD in Kazakhstan. Other major routes, such as CPC and Atyrau-Samara, are not handled by PPDs, instead, they are transported by heaters along the pipeline. After initial screening tests, the 5 most effective PPDs were selected for further testing: gEVABMA7C (MW, 95 kDa), gEVABMA6C (MW, 101 kDa), gEVABA15C (MW, 93 kDa), gEVABA13C (MW, 99 kDa), gEVAS24C (MW, 111 kDa). Here we chose

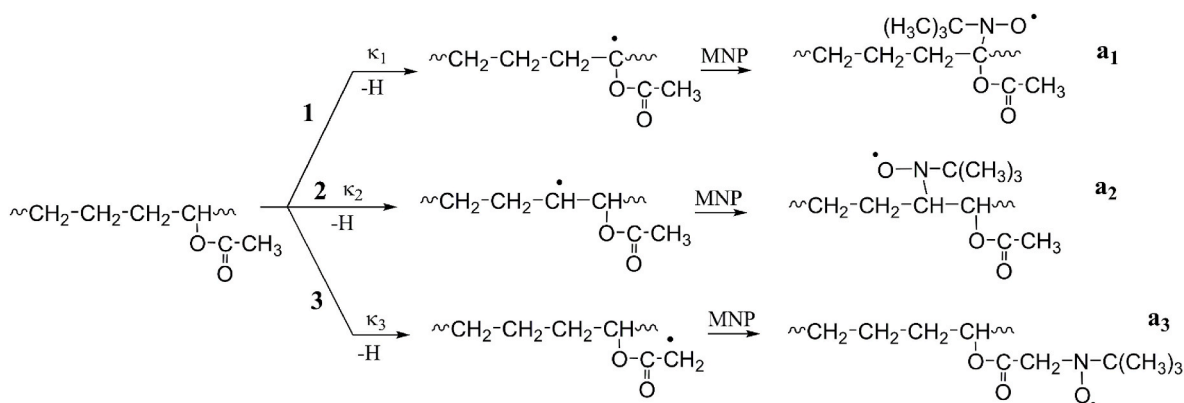


Fig. 2. Scheme of the abstraction of a hydrogen atom from macromolecules of the EVA copolymer and the capture of the resulting macroradicals by a spin trap (MNP).

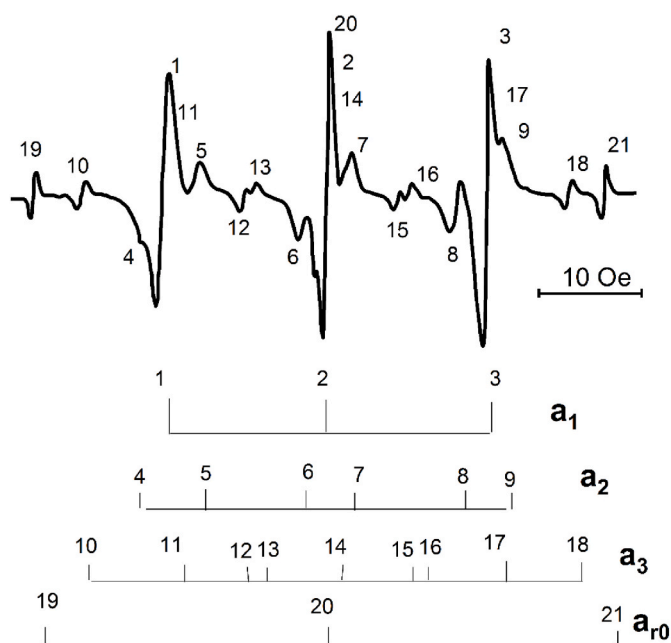


Fig. 3. EPR spectrum of MNP adducts with macroradicals formed during the thermal decomposition of the DTBP initiator in a benzene solution of EVA copolymer (20 °C) in the presence of a spin trap. [DTBP] = 5×10^{-3} mol/l; [MNP] = 3×10^{-2} mol/l; [EVA] = 1.5 wt%.

grafted polymers obtained at irradiation doses of 130 kGy. At lower irradiation doses, monomers did not completely polymerize and a large amount of monomers remained in the initial state, while the parameters of the polymers as PPDs did not differ much from the initial commercial EVA. At higher radiation doses, the polymers crosslinked, which leads to their insolubility and does not allow their use as PPDs. All grafted polymers (except crosslinked ones) were insoluble in water or aqueous bases and completely soluble in *o*-xylene and the industrial solvent most commonly used in pipelines. Thereafter, the reaction products were diluted with *o*-xylene in a 1:1 ratio without additional purification.

3.1. Determination of the mechanism of graft polymerization on EVA

To study the mechanism of graft copolymerization of hydrophobic monomers onto commercial EVA copolymer we used model trapping studies with 2-methyl-2-nitrosopropane (MNP) (Sato and Otsu, 1975) using a method developed by Mun et al. (Nurkeeva et al., 1992). The mechanism of graft radical copolymerization is realized by the

formation of a radical active center on the macromolecule backbone, which initiates the polymerization of the grafted monomer with the formation of side branches. In this work, to determine the nature of the active centers formed on the macromolecule backbones during irradiation with fast electrons, we used model reactions of the interaction of a tert-butoxy radical with an EVA copolymer in a benzene solution. The tert-butoxy radical was obtained by thermolysis of the initiator di-tert-butyl peroxalate (DTBP). These studies show that the formation of radical centers in macromolecules of the EVA copolymer can occur as a result of the abstraction of a hydrogen atom by a tert-butoxy radical from methine (CH), methylene (CH₂), and methyl (CH₃) groups of vinyl acetate units (reactions 1, 2, and 3, Fig. 2). In the presence of a spin trap (MNP), all macromolecules formed as a result of reactions 1–3 are captured by MNP with their attachment to the nitroso group of MNP and the formation of the corresponding stable nitroxyl radicals — adducts a1, a2, a3.

EPR spectrum of MNP adducts with macroradicals formed during the thermal decomposition of the DTBP initiator in a benzene solution of EVA copolymer in the presence of a spin trap is shown in Fig. 3. In EPR spectrum, an intense triplet (1–3, $\alpha_N = 15.2$ Oe (Oersted) and $g = 2.0063$) refers to the MNP (a1) adduct with a radical having an unpaired electron on the tertiary carbon atom. Such a radical can be formed only upon the abstraction of a hydrogen atom from the methine group of

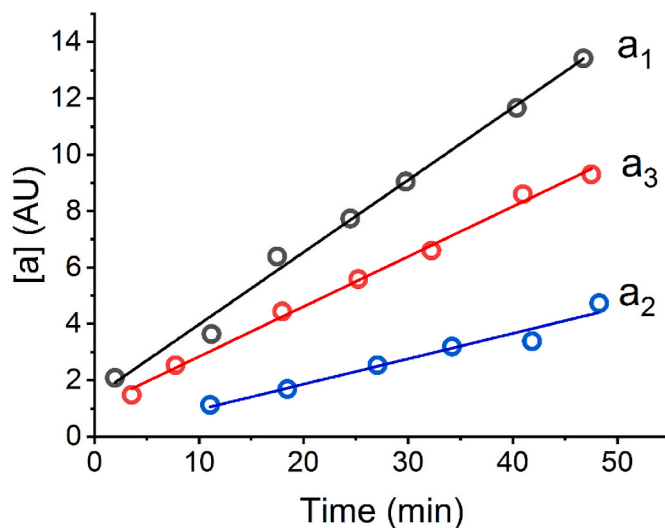


Fig. 4. Kinetic curves of the accumulation of MNP adducts with macroradicals formed during thermolysis of the DTBP initiator in a benzene solution of EVA copolymer (20 °C) in the presence of an MNP spin trap. [DTBP] = 5×10^{-3} mol/l; [MNP] = 3×10^{-2} mol/l; [EVA] = 1.5 wt%.

Table 3

Pour point values of Kumkol oil blend at different preheat values.

Preheat value, °C	unheated	40	50	60	70	80
Pour point, °C	15	12	9	6	3	0

vinyl acetate groups (reaction 1, Fig. 2). A triplet of doublets (4–9, $\alpha_N = 13.8$ Oe, $\alpha_H = 3.7$ Oe, and $g = 2.0061$) belongs to the MNP (a2) adduct with macroradicals having an unpaired electron on the secondary carbon atom (carbon atom CH-groups). Such a polymer radical can be formed with equal probability upon the abstraction of a hydrogen atom from the methylene groups of vinyl acetate and ethylene units of EVA macromolecules (reaction 2 in Fig. 2). The triplet of triplets (10–18, $\alpha_N = 14.9$ Oe, $\alpha_H = 7.9$ Oe, and $g = 2.0064$) in EPR spectrum shown in Fig. 3 refers to MNP (a3) adducts with polymer radicals, having an unpaired electron on the primary carbon atom (on the carbon atom of the CH₂ group). Such a macroradical can be formed only as a result of reaction 3 (Fig. 2) of the abstraction of a hydrogen atom from the methyl group of the vinyl acetate units of the EVA copolymer. Along with the spectrum components belonging to MNP adducts with macroradicals of various natures formed upon the abstraction of a hydrogen atom from macromolecules of the EVA copolymer, another triplet is clearly distinguished in EPR spectrum shown in Fig. 3 (19–21, $\alpha_N = 19.3$ Oe, and $g = 2.0061$). This triplet refers to the adduct formed during the direct capture of tert-butoxyl radicals by the MNP spin trap.

The high stability of MNP adducts with macroradicals of various natures formed upon the abstraction of a hydrogen atom from the macromolecules of the EVA copolymer makes it possible to study not only the mechanism of these reactions but also their kinetics. Fig. 4 shows the initial linear sections of the kinetic curves of the accumulation of adducts a1, a2 a3. Kinetic analysis of such initial linear sections of the accumulation curves is used for estimation of the values of the corresponding kinetic constants (Nurkeeva et al., 1992).

It was found that $\kappa_1/\kappa_2 = 11.7$, $\kappa_1/\kappa_3 = 3.7$ (the values of the kinetic constants increase in the series: $\kappa_3 < \kappa_2 < \kappa_1$). Consequently, the methine groups (CH) of vinyl acetate units are most active in hydrogen abstraction reactions; methyl groups of vinyl acetate units are 3.7 times less active in hydrogen abstraction reactions than CH groups. The methylene groups of the vinyl acetate and ethylene units of the EVA copolymer exhibit the least activity in the reactions of abstraction of the H-atom. Radical centers on macroradicals formed as a result of hydrogen atom detachment from EVA initiate graft copolymerization of the corresponding BMA, BA, or ST monomer onto EVA macromolecules.

Thus, the data obtained by the spin trap method show that the main contribution to the initiation of the process of graft polymerization of hydrophobic monomers ST, BMA, and BA onto the EVA copolymer is made by the reactions of hydrogen abstraction from the methine (CH) groups of vinyl acetate units of EVA polymer.

3.2. Preheat effect on the pour point and rheological parameters study

The different preheating values can significantly affect the pour point and rheological parameters. We performed a number of analyzes with different preheating values for the Kumkol oil blend. The oil sample was preheated to 40, 50, 60, 70, 80 °C for 30 min before analysis (Table 3), after which the pour point and rheological parameters were studied. It appeared that increasing preheat improves the rheological parameters of the oil at lower temperatures and lowers the pour point. However, it is not always economically and energetically justified to use such high preheat, so chemical treatment is looking like the better option here.

3.3. Pour point analysis

The typical concentration of PPDs in the industry ranges from 50 to 5000 ppm with some exceptions (Fang et al., 2012; Taraneh et al., 2008;

Table 4

Pour Points and Depression of Kumkol region oil blend neat and treated with PPDs.

Sample	Dosage, ppm ^e	Pour point, °C	Depression, °C ^b	Dry residue, % mass ^c
Untreated crude oil	–	12	–	
EVA (Randep-5102 ^a)	200	0	12	7
EVA(DMN-2005 ^d)	500	+3	9	15
gEVABMA7C	200/400	–3/–6	15/18	3
gEVABMA6C	200/400	–3/–12	15/24	4
gEVABA15C	200/400	3/–9	9/21	3
gEVABA13C	200/400	3/–3	9/15	3
gEVAST24C	200/400	–3/–12	15/24	4

^a In addition to EVA copolymers, Randep - 5102 consists of a polymer reaction product of formaldehyde with dinonylphenol and nonylphenol for dispersing asphaltenes.

^b Depression value is determined as the delta of the Pour Point values of treated and untreated samples of oil.

^c Dry residue was calculated based on 200 ppm of PPDs.

^d DMN – 2005 is the mixture of EVA with different molecular mass. DMN – 2005 should be heated up to 60 °C and mixed with diesel fuel at ratio 1:4 respectively.

^e All commercial products have been used in their commercial dosages for this petroleum mixture.

Wu et al., 2012). It is well noted that the concentration of PPD is a crucial parameter, additives work best when they match the distribution of paraffins in crude oil (Ruwooldt et al., 2020). In this study we tested all PPDs at a base concentration of 200 ppm as it was compared to an existing commercial product used in Kazakhstan's oil transportation facilities (commercial EVA polymers with a concentration of 200 ppm are used in all tested oils of different sources). Table 4 shows the pour point values when PPD was added at the recommended dosage, compared to an untreated oil blend sample.

As shown in Table 4, the depression temperature and Pour Point of Kumkol oil blend invariably decreased when treated with PPDs. It should be noted that according to Table 1, Kumkol oil blend was a composition of 6 oilfields with different wax content. In alignment with the treatment scheme in the oilfield, PPD was applied at each oilfield separately before blending them all together. Thus, each oil was treated individually before being blended into the Kumkol oil blend (Table 4S). Since the most important flow here is the Kumkol blend, which is transported over 250 km, this oil blend was the subject of interest. As can be seen from Table 3, the addition of PPDs to Kumkol oil blend lowers the pour point to –3 °C. Moreover, the Pour Point and gel point drop achieved with the gEVAp treatment are greater than with commercial EVA, currently in use (Randep-5102) and previously used (DMN-2005). In addition, when recalculating the actual effectiveness of the active part of the PPDs (dry residue), we see that to achieve results similar to the currently used commercial pour point depressant based on EVA (Randep-5102), a lower dosage of the resulting modified polymers is required. Indeed, doubled dosage of gEVAp showed better performance than commercial EVA, with a pure active part corresponding to the amount in the mentioned depressant.

3.4. Rheological data and the WAT determination

The effect of the preheating temperature on the parameters of the rheology of oil samples was preliminary studied. Fig. 5A shows the rheological parameters of the oil blend at different preheats. As can be seen from Fig. 5A, as well as Table 3, at a preheating temperature of 60 °C, all the parameters of interest were optimal, and a further increase in the preheating temperature did not significantly improve them, and it was inexpedient from an economic point of view. It also shows that preheating the oil to 60 °C leads to the melting of all heavy fractions that

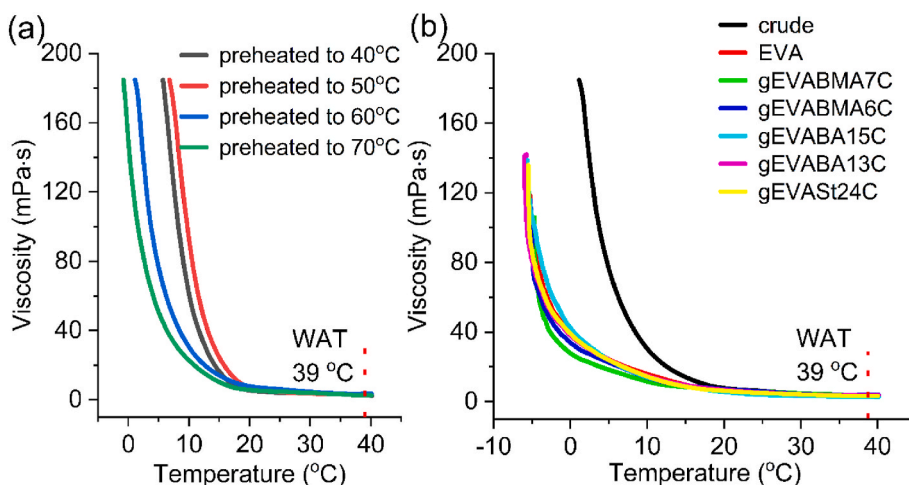


Fig. 5. (a) Viscosity of neat crude oil (Kumkol region oil blend) preheated to various pre-defined temperatures prior to rheology measurements. (b) Apparent viscosity of oil neat and treated with PPDs. Viscosity-temperature changes were measured at a shear rate of 28.16 s^{-1} . In all tests oil was preheated to 60 °C and treated with 200 ppm of PPD.

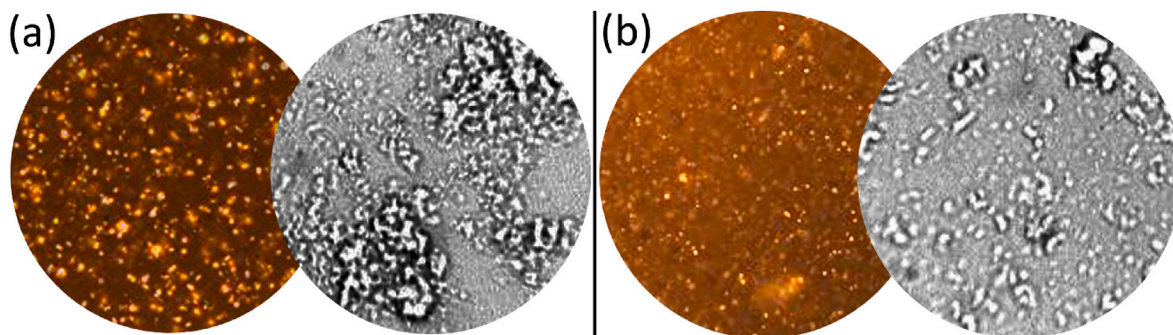


Fig. 6. Effect of gEVAp addition on wax crystal morphology in waxy crude oil. (a) Micrographs of wax crystals of Kumkol waxy crude oil blend, undoped and (b) doped with 200 ppm of gEVASt24C.

may be present in the oil mixture in the form of crystals. At lower pre-heating temperatures, crystallization centers present in the oil that have not been completely melted form a wax matrix, which then accelerates the crystallization of the oil.

Figs. 5B and 11S show the viscosity versus temperature of neat and treated oils. After treatment with PPDs, all curves shifted to a lower

temperature region and remained “pumpable” at a much lower temperature compared to the untreated oil sample. As can be seen from Fig. 5B, in all cases for all PPDs, the viscosity decreases by about 10 times at low temperatures. In this case, the oil has the best aggregate stability and at low temperatures, it turns into a non-Newtonian liquid. The obtained rheological measurements of the dynamic viscosity

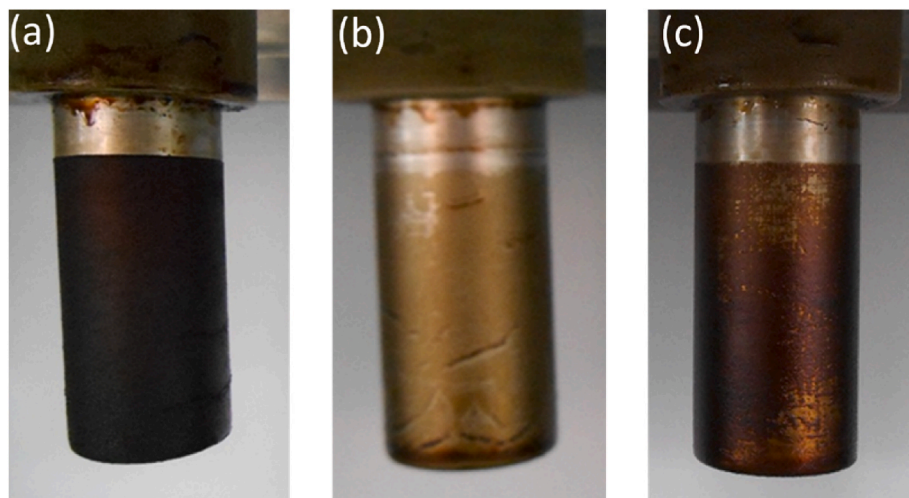


Fig. 7. The appearance of a cold finger from untreated oil (a) and treated with gEVASt24C (b) and gEVABMA6C (c) at 200 ppm rate.

Table 5

Results of cold finger test for untreated oil and treated with EVA and gEVAp at 200 ppm and DMN-2005 at 500 ppm dosage level.

Sample	Deposit, g ^a	Inhibition, % ^b
Untreated crude oil	0.360	0
EVA (Randep – 5102)	0.126	65
EVA (DMN-2005)	0.172	52
gEVABMA7C	0.061	83
gEVABMA6C	0.101	72
gEVABA15C	0.076	79
gEVABA13C	0.104	71
gEVAS24C	0.043	88

^a The duration of all experiments was 4 h. $T_{\text{hot}} = 50\text{ }^{\circ}\text{C}$, $T_{\text{cold}} = 15\text{ }^{\circ}\text{C}$.

^b Inhibition was calculated using the formula: $z = ((m_{\text{oil}} - m_{\text{treated}})/m_{\text{oil}}) \times 100$.

showed that all tested gEVAp are well compatible with crude oil, and the data completely coincide with the observed pour point values and can be used to describe the load on pumps on the main pipeline. During the cold season, the engineer can predict the load on these pumps depending on the temperature of the oil, soil and pipelines.

3.5. Microscopic study

Samples of untreated Kumkol oil blend and treated were studied with a polarization microscope. Micrographs of wax crystals were examined at $-3\text{ }^{\circ}\text{C}$. Micrographs of Kumkol crude oil blend (untreated) and oil treated with gEVAS24C are shown in Fig. 6a and b, respectively. As can be seen regular, compact, platelet shape wax crystals are formed in the treated oil, and the wax crystals become smaller and more dispersed compared to crystals in the untreated oil, and the results are consistent with previous studies of EVA-based polymers (Ashbaugh et al., 2005; Huang et al., 2018, 2019; Jing et al., 2017; Kozhabekov et al., 2019; Li et al., 2018; Marie et al., 2005).

3.6. Cold finger testing

We used cold finger method (Wu et al., 2012) (low shear wax deposition test) to determine the tendency of oil to deposit and the effectiveness of wax inhibitors on waxy oils. The cold finger deposition tests were performed on neat and treated oil samples. The oil sample was pre-treated first. The bulk oil temperature was chosen to be $50\text{ }^{\circ}\text{C}$, about $10\text{ }^{\circ}\text{C}$ above the measured WAT temperature. Cold Finger temperature was set at $15\text{ }^{\circ}\text{C}$, which is about $25\text{ }^{\circ}\text{C}$ below the measured WAT. These conditions allowed us to get 0.360 g on average in all untreated oil cycles. To investigate the effectiveness of this method for Kumkol oil blend, we tested other cold finger temperatures, so at 25 and 20 ° , we obtained 0.12 and 0.21 g of oil deposits on the cold finger surface, respectively. A further decrease in temperature is dangerous due to the approach to the pour point of the oil. In this case, the Cold Finger results may be affected by gelation of the oil along with wax on the Cold Finger, resulting in incorrect results (Figs. 12S and 13S). In these tests, the cold finger simulates the cold walls of the pipeline, and the vessel with heated oil simulates the flow of oil that moves through the pipeline. So, generally speaking, the cold finger test is a pipeline inside out. Fig. 7 shows the appearance of the fingers after testing.

The test results are presented in Table 5. Thus, in the presence of 200 ppm of gEVAp, the wax inhibition efficiency for the Kumkol oil blend reached 70–90%.

3.7. Studies of stability over time

Finally, one of the important parameters of any PPD for oil transporters is the stability of the effect over time due to the long transportation distance. On the route Kumkol - Karakoin - Shymkent, as a rule, the transportation of oil from the Kumkol field to the Shymkent

Table 6

Stability of the pour point of the Kumkol oil blend treated with gEVAS24C and commercial EVA (Randep-5102) at 200 ppm and DMN-2005 at 500 ppm. Test duration 28 days.

Sample	1st day	3rd day	7th day	14th day	21st day	28th day
gEVAS24C	-3	-3	0	0	+3	+6
EVA (Randep-5102)	0	0	+3	+3	+6	+6
EVA(DMN-2005)	+3	+3	+6	+6	+9	+9



Fig. 8. Example of wax formation on a production line without PPD (a) and free-flowing oil treated with 200 ppm gEVAS24C (b).

refinery takes 2–3 weeks. Thus, PPD's ability to reduce viscosity and pour point throughout the entire period is critical. The results of the stability effect for best-performed gEVAS24C and commercial EVA (Randep-5102 and DMN-2005) are shown in Table 6. The main parameter of the study was the pour point. The oil treated with PPD was cooled in the air to room temperature. Then the cooled samples were placed in a cooling unit with a temperature of $6\text{--}7\text{ }^{\circ}\text{C}$, where all subsequent time was kept in the conditions of regular stirring. On the 1st, 3rd, 7th, 14th, 21st, and 28th days after the initial treatment, pour point tests were carried out. gEVAp demonstrated a sufficient depression effect, maintaining $+6\text{ }^{\circ}\text{C}$ even on the 28th day, when the typical travel time from Kumkol to Shymkent is about 21 days. This ensures a good flow throughout the cold season without additional oil processing.

3.8. Field wax inhibition tests: deposition in the pipeline

In addition to the cold flow, transporters face the problem of deposition during the cold season due to the decrease in the temperature of the soil, oil, and pipeline walls. These conditions will favor the deposition of wax (Alnaimat and Ziauddin, 2020). Continuous injection of PPD into the production oil pipeline effectively reduces the pour point temperature and wax appearance temperature (WAT) (Castro and Vazquez, 2008; Elbanna et al., 2017; Ridzuan et al., 2016; Taraneh et al., 2008). Fig. 5 shows oil pipelines before and after PPD treatment. As seen in Fig. 8a, the crude (untreated) oil produced a large amount of thick deposits that clogged the pipes and made transportation difficult. At the same time, after processing the oil with 200 ppm gEVAS24C (Fig. 8b), the oil remained sufficiently fluid, which required lower transportation costs. gEVAS24C was dosed into the commercial oil of the Turgai oil during transportation to the main pumping station Kumkol.



Fig. 9. The resulting pigs from untreated pipelines: (a) taken from the pipeline without PPD treatment, (b) received pig from the pipeline treated with 200 ppm EVA (Randep-5102), (c) received pig from the pipeline treated with 200 ppm gEVAST24C. The oil pipeline is 14.5 km long and 377 mm in diameter. Temperature gradient 60–25 °C.

The mechanical way of dealing with deposition is pigging. Pigging involves sending a semi-hard projectile, usually foam or metal with plastic scraping surfaces, down a pipeline to clean the pipeline. The pig is propelled by gas or production fluids and is introduced at one end of the pipeline and recovered at the other (Gao et al., 2020; Li et al., 2017; Sams and Zaouk, 2000; Wang et al., 2005, 2008). Transporting pipeline was pigged before treating the oil and after (Fig. 9). Nearly complete inhibition (less than 1 kg of wax) was found during field trials with gEVAST24C (Fig. 9c), and the results were superior to those of the commercial EVA product (Fig. 9b).

4. Conclusion

In this work, PPD based on graft copolymers of EVA with different VA and co-monomer contents were successfully obtained by graft copolymerization using a low-energy electron beam irradiation. It was shown by the spin trap method that the main contribution to the initiation of graft copolymerization is made by the abstraction of a hydrogen atom from the methine CH groups of vinyl acetate units of the main EVA polymer. When treated with 200 ppm of gEVAp, the pour point of Kumkol oil blends was reduced from 12 to −3 °C. The inhibition of wax deposition was evaluated under static and dynamic field conditions, and the stability of the depressant effect over time was determined. gEVAp showed sufficient depression effect maintaining +6 °C even at 28th day when typical travel time from Kumkol to Shymkent is near to 21 days. That assures good flow for all cold seasons. The efficiency of wax inhibition by gEVAp for Kumkol oil blend reached 90%. In the absence of polymeric depressants, crude oil produced a large amount of thick deposits, resulting in oil gelling, pipe plugging, and loss of flow. It has been experimentally proven that preheating the oil 20–30 °C higher than WAT can improve the rheological parameters of the oil and lower the pour point. But that is not effective and economically justified energy expenses, thus chemical treatment is the better option here. Application of PPDs on the route Kumkol – Karakoin – Shymkent is justified and effective due to the absence of heating facilities alongside the pipeline. All synthesized gEVAp performed better in all laboratory and field tests than currently used commercial EVA PPD.

Credit author statement

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review & editing, Supervision. The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.petrol.2022.110298>.

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