



Study effect of initiators on performance of copolymer used as pour point depressant for Diamond crude oil, Blocks 01&02, offshore Vietnam

Dao Viet Than², Thai Hong Chuong¹, Dao Quoc Tuy², Bui Dac Trung¹,

¹*DMC-Drilling Fluids and Well Services, DMC Coporation, Vietnam*

²*School of Chemical Engineering, Hanoi University of Science and Technology, Vietnam*

*Email: thandv@pvchem.com.vn

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ABSTRACT

Diamond oil field is located in Blocks 01&02 Offshore Vietnam. Crude oil from Diamond Well Head Platform (WHP) is evacuated to FPSO via 20km - 10" subsea flexible pipeline. The lowest seabed temperature in the field is 22°C, while pour point temperature of this crude oil is very high (36°C) due to high parafin content (about 25% by weight). So studying to synthesize a copolymer use to reduce pour point temperature of this oil is very important. The copolymer must have ability to reduce pour point temperature of the crude oil from 36°C to 21°C

The synthesis process occurred via copolymerization of acrylate, methacrylate and vinyl acetate monomers using free radical polymerization method in Solvent 100 as a solvent. There are many factors which affect copolymerization reaction and therefore they will impact on the structure and performance of the said copolymer. One of the most important factor is a ratio of initiator to monomer in the reaction.

Therefore the aim of this research is to choose an appropriated ratio of initiator to produce a copolymer which can reduce pour point temperature of Diamond crude oil from 36°C to 21°C at dosage of 1.750ppmv

Introduction

Paraffin wax crystallization is one of the major challenges during crude oil production.¹ As the crude oil is transported through subsea pipelines, cooling of the oil induces wax crystallization once the wax appearance temperature (WAT) is reached. Issues associated with wax crystallization include increased fluid viscosity, formation of a wax deposition layer, pipeline restart issues due to waxy gelation, blocking pipeline and reduced separation efficiency due to the formation of Pickering emulsion.² Managing wax related issues entails significant costs, but if these

issues are not addressed properly they can lead to production stop and even the loss of equipment.^{3,4}

Various methods to address the deposition and precipitation of waxes are theoretically proposed and applied in practice with the purpose of improving the flowability of waxy crude oils. After all, the prevention methods are undoubtedly more economical compared to what the remediation methods offer. Fundamentally, these prevention methods are broadly categorized as thermal, mechanical, and chemical.

Pour point depressants (PPDs) as well as wax inhibitors, flow improvers are widely applied in

pipeline transportation of waxy crude oils to ensure low fluid viscosity and prevent gelling, blocking.^{5,6}

PPDs are considered to interfere with the wax nucleation and crystallization process. Whereby, part of the molecule must interact or cocrystallize with the wax to modify or interfere with its crystallization. Another part of the molecule can prevent further wax growth by covering sites where new wax molecules would attach. This delays the formation of three-dimensional wax crystals and prevents the formation of structured wax lattices at the pipe wall.^{7,8}

Long-chain alkyl (meth)acrylates, such as octadecylacrylate (ODA), are a class of acrylic monomers that have a good affinity for nonpolar solvents or oil. Due to lipophilic nature of long-chain alkyl groups, polymers based on these monomers find widespread application to produce pour point depressants¹⁰. However, their polymers have a tendency to be in a crystalline state, long alkyl side chains may crystallize in spite of amorphous backbone, which decreases their oil absorbency. To reduce this undesirable effect, the method of copolymerization with other monomers is used so that amorphous copolymers can be obtained.^{11,12}

In this article, acrylates, methacrylates and vinyl acetates have been used as monomers to synthesize PPDs by free-radical solution copolymerizations using initiators.

In the copolymerization, the monomer ratio, reaction temperature, reaction time, and content of initiator are crucial factors from the chemical industrial point of view which contributes to improving the yield of the copolymer, particularly in tailor-made copolymers with desirable physical and chemical properties.⁹

An appropriate initiator should provide a steady supply of radicals during the entire reaction. The needed supply will exist if the initiator has a lifetime comparable to the time required for completion of the reaction being conducted.¹³ The lifetime of an initiator is often described in terms of the amount of time required for 50% of the material to react, that is, its half-life. Continuous formation of radicals is necessary because the time of existence of a typical radical chain is short, usually less than one second; consequently, new chains must be started regularly.¹³

2,2'-Azobis(isobutyronitrile) (AIBN) is easily the most widely used initiator in radical reactions of carbohydrates. There are compelling reasons for this status. AIBN has a half-life of one hour at 85°C (five

hours at 70°C);^{13,14} consequently, it can continuously supply sufficient initiating radicals at moderate temperatures for reactions requiring several hours to reach completion. Other advantages of AIBN are that it is easily handled, generates good yields of radicals (yields of radicals available for chain initiation are not 100% because some radicals combine before they can escape from the solvent cage), and has a rate of decomposition that is almost independent of the solvent.

The aim of this paper is to choose an appropriated ratio of initiator - AIBN for the free-radical solution copolymerization to synthesize PPD from monomers including behenyl acrylate, stearyl methacrylate and vinyl acetate.

Experimental

Materials

Three monomers were used in this study; include behenyl acrylate, stearyl methacrylate and vinyl acetate purchased from Basf, Dow or Sigma Aldrich. Other chemicals such as AIBN was used as the initiator, Solvent 100 as solvent and ethanol for purification.

The crude oil used in the study was taken from Diamond oil field. Its characteristics are listed in Table 1 below.

Table 1: The physicochemical characteristic and composition of Diamond crude oil (extracted gas)

Characteristics	Method	Unit	Value
Density at 15°C	ASTM D1298	g/ml	0.8535
API gravity	ASTM D1298	°API	34.2
Pour point	ASTM D97	°C	36
Dynamic viscosity at 40°C	Viscometer VT550	mPa.s	32.58
n-paraffin content	UOP-46	% wt	24.32
Asphaltene and resin content	GC, LC, IP 143-90	% wt	5.436
Wax Appearance Temperature	DSC	°C	55
Wax disappearance Temperature	DSC	°C	69.76

Experimental set up for synthesis of copolymer

The PPDs were synthesized from monomers including behenyl acrylate, stearyl methacrylate and vinyl

acetate through the free-radical solution copolymerization technique by utilizing a firm mass ratio of 45, 6 and 6 grams respectively. The reaction was conducted in a three-neck round-bottomed flask equipped with a thermometer, paddle, reflux condenser, and nitrogen gas inlet. Figure 1 shows the experimental apparatus. A mixture of monomers was dissolved in 45 grams of Solvent 100 under constant stirring at a temperature of 80°C for 210 minutes of reaction time and a nitrogen atmosphere for 30 min. AIBN used as an initiator at a range of mass from 0.06; 0.12; 0.18; 0.24 grams was added the reaction when its temperature reached to 60°C.



Figure 1: The experimental apparatus

After the reaction had been completed, the copolymer product was diluted into a 40% solution in Solvent 100 forming a PPD. A predetermined part of the PPD was used to evaluate performance on the Diamond crude oil and to measure its dynamic viscosity by Viscometer - VT550. The rest of the PPD was added ethanol to precipitate the copolymer. Thereafter, the copolymer was filtered washed two times with ethanol. The obtained product was dried in an oven at 45°C for at least 12h with the final state of the copolymer being an opaque white powder. The pure copolymer then was used to determine the yield of the copolymerization reaction, average molecular weight (Mw) and the polydispersity index (PDI) by Gel Permeation Chromatography (GPC).

Results and discussion

The influence of content of the initiator on the yield

Relationship between the concentration of the initiator and yield was shown in figure 2. The copolymer yields initially increased with increasing content of the initiator – AIBN from 0.06 g to 0.18 g. The highest yield was 80 % at 0.18 g of AIBN. Afterthat, beyond 0.18 g of AIBN, the copolymer yield started declining

very slowly. This may be explained as a higher content of the initiator beyond 0.18 g leads to earlier termination of more growing chains via molecules collision which produces eventually higher number of short grafted chains. This is clearly illustrated in the synthetic product characterization (Table 2 presented in the next section) when the average molecular weight of the product has decreased significantly.

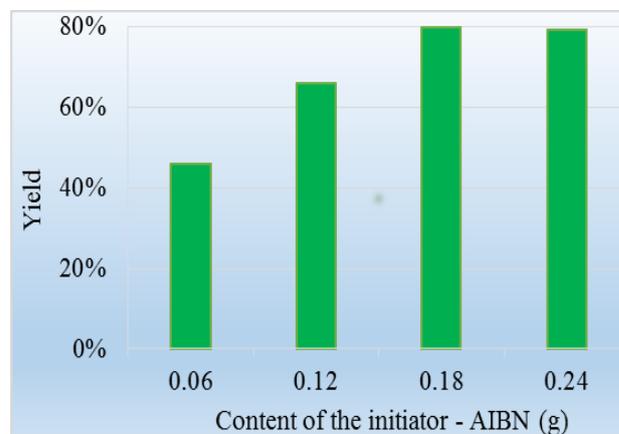


Figure 2: The influence of content of the initiator on the yield

The influence of content of the initiator on the dynamic viscosity, Mw and PDI of the copolymer

The dynamic viscosity, Mw and PDI of the copolymers in the copolymerizations were presented in Table 2 below:

Table 2: The influence of content of the initiator on the dynamic viscosity, Mw and PDI of the copolymer

Content of AIBN (g)	μ (cP at 20°C)	Mw (dalton)	PDI
0.06	111	53,292	1.216
0.12	127	45,074	1.405
0.18	148	40,238	1.597
0.24	147	37,967	1.685

The initiator has a big effect on the average molecular weight (Mw) and the polydispersity index (PDI) of copolymers. When the content of initiator - AIBN increases, the polydispersity index increases from 1.216 to 1.685, but the average molecular weight decreases from 53,292 dalton to 37,967 dalton. Meanwhile the dynamic viscosity of copolymer initially increased with

increasing content of the initiator – AIBN from 0.06 g to 0.18 g; afterthat it started declining very little as shown in Table 2.

The influence of content of the initiator on performance of copolymer used as pour point depressant on Diamond crude oil

The influence of content of the initiator on pour point temperature of the crude oil treated by the PPDs.

The performance of PPDs synthesized at different concentrations of the initiator – AIBN on pour point temperature of Diamond crude oil was presented in Figure 3.

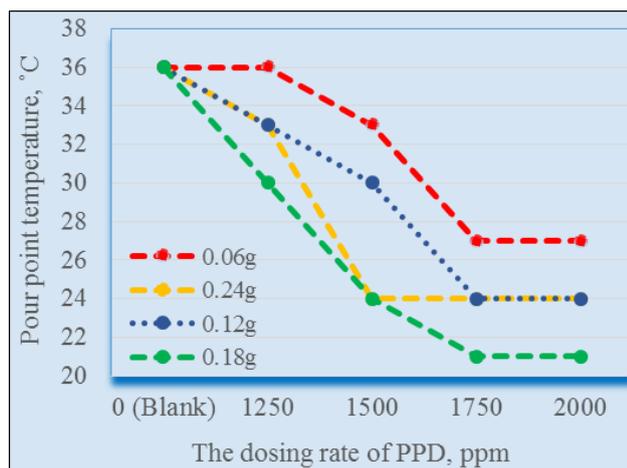


Figure 3: The influence of content of the initiator on pour point temperature of Diamond crude oil treated by PPDs

As showed in Figure 3, when the content of initiator - AIBN increases from 0.06 g to 0.18 g, the performance of the PPDs increase. This may be due to the increase of the yield leading the increase in the number of active copolymers. However, when the content of initiator – AIBN is greater than 0.18 g, the performance of the PPDs diminish. This may be due to the increase of chain transfer reactions and termination reactions causing the average molecular weight decreases and the polydispersity index increases leading the reduction in the number of active copolymers.

So, the performance of the PPDs is the highest when 0.18 g of AIBN was used to synthesize the copolymer. The optimal PPD can reduce the pour point temperature of the Diamond crude oil from 36 °C to 21 °C at 1750 ppm of dosing rate.

Determination of viscosity, gel strength and the paraffin deposition can more illuminate the performance of the optimal PPD as below.

The influence of the optimal PPD on the viscosity of the Diamond crude oil

Viscosity is a crucial factor in transporting crude oil, due to the challenges relating to higher viscosity that limits the installed capacity of pipelines and the pumping infrastructure used.

The viscosity of the Diamond crude oil treated by the optimal PPD was determined by Hakke Viscotester VT-550. The crude oil was add the PPD at concentrations of 1000, 1250, 1500, 1750, 2000 ppm respectively and then it is taken to measure the viscosity at different temperatures. The results were presented in Table 3 and figure 4.

Table 3: The viscosity of the Diamond crude oil treated by the optimal PPD at different dosages

Temperature	Viscosity at different dosages (ppm), mPa.s					
	Blank	1000	1250	1500	1750	2000
21	2952	1123	811.6	619.7	413.2	290.2
23	2258	721.8	543.5	426.7	255.8	185.7
25	1650	336.9	253.3	247.2	123	90.99
27	1171	124.2	121.7	94.68	62.71	45.5
29	787	55.33	54.1	41.81	40.58	24.59
31	452.5	38.12	29.51	24.59	20.9	15.99

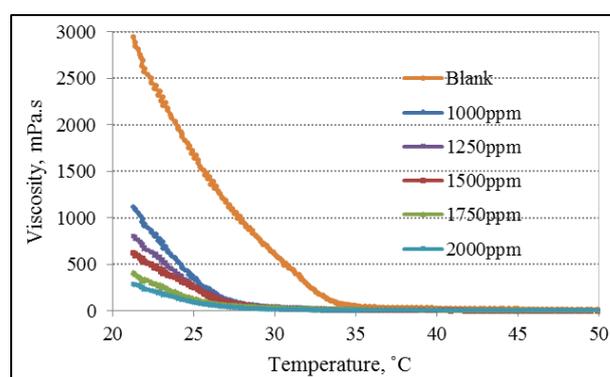


Figure 4: The profile of viscosity vs. temperature of the Diamond crude oil treated by the optimal PPD at different dosages.

The results showed that at high temperatures (above pour point temperature of the crude oil) the viscosities of the crude oil were not much different between the crude oil treated and untreated by PPD.

As the temperature drops, the effectiveness of the optimal PPD was clearly shown. The viscosity of the

crude oil reduce significantly; from 452.5 mPa.s of the blank to 20.9 mPa.s when treated by 1750 ppm of the optimal PPD at 31 °C; and from 2952 mPa.s of the blank to 413.2 mPa.s at the same dosing rate of the PPD at 21 °C. This means that the crude oil can be transported with less energy loss.

The influence of the optimal PPD on the paraffin deposition of the Diamond crude oil

Wax deposition (paraffin deposition) in pipelines results from the precipitation of n-alkanes with carbon number higher than 18 from the waxy crude oil under a cold environment. This deposit grows in thickness forming a wax crystal network, which blocks the flowline, avoiding the flow of the oil inside it.

The wax deposition of the Diamond crude oil treated by the optimal PPD was determined by Cold Finger apparatus of F5 Technologie. The crude oil was add the PPD at concentrations of 1000, 1250, 1500, 1750, 2000 ppm respectively and then it is taken to measure the wax deposition rate. The results were presented in Table 4.

Table 4: Wax deposition of the Diamond crude oil treated by the optimal PPD at different dosages.

Temperature		Wax deposition at different dosages (ppm), g/m ²					
Oil	Cold finger	Blank	1000	1250	1500	1750	2000
60	50	83.7	29.3	23.6	19.5	17.9	15.2
50	40	775.6	76.5	65.9	52.4	49.5	48.9
40	30	1203.2	103.2	90.2	77.6	66.1	60.1
30	21	Freezing	245.6	220.4	202.9	189.6	163.9
Total wax deposition, g/m ²		> 2062.5	454.6	400.1	352.4	323.1	288.1
Efficiency (reduction), times			4.5	5.2	5.9	6.4	7.2

The results from Table 4 showed that the wax deposition has reduced significantly when treated by the optimal PPD at different dosages. The wax deposition rate of the Diamond crude oil treated by the PPD at 1750 ppm of dosing rate was 6.4 times lower than the untreated crude oil. This presented a high efficiency of the synthesized PPD in decreasing wax deposition.

The influence of the optimal PPD on the gel strength of the Diamond crude oil.

Gel strength is an important parameter concerning the restart process of crude oil transportation pipelines. In the case of planned or unexpected shut down situations, where the gel is formed under quiescent conditions, the gel strength can be measured through the yield stress, which is the minimum shear stress needed to break the gel formed and restart the flow inside pipeline. Thus, the restart of crude oil transportation pipelines is associated to the gel strength, and thereby the yield stress.

The gel strength of the Diamond crude oil treated by the optimal PPD was determined by Hakke Viscotester VT-550. The crude oil was add the PPD at concentrations of 1000, 1250, 1500, 1750, 2000 ppm respectively and then it is taken to measure the gel strength at different temperatures. The results were presented in Table 5 and figure 5.

Table 5: The yield stress of the Diamond crude oil treated by the optimal PPD at different dosages

Temperature	Yield stress at different dosages (ppm), Pa					
	Blank	1000	1250	1500	1750	2000
21	75.84	47.31	35.12	30.65	22.6	11.3
23	55.84	32.73	20.18	16.14	10.13	6.06
25	36.38	20.94	7.69	5.69	3.46	2.04
27	24.57	11.93	2.88	2.05	1.14	0.76
29	15.87	6.94	1.07	0.71	0.32	0.25
31	7.44	3.22	0.3	0.22	0.18	0.12

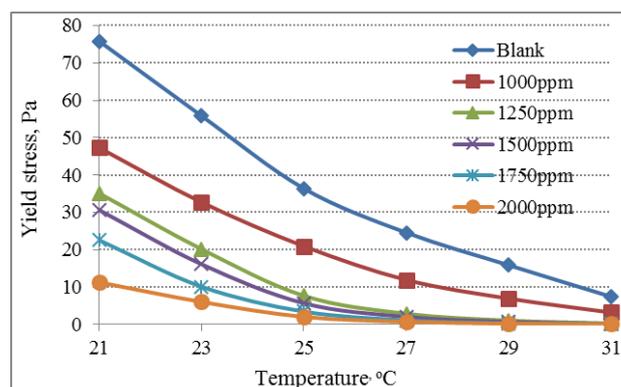


Figure 5: The profile of yield stress vs. temperature of the Diamond crude oil treated by the optimal PPD at different dosages.

The results showed that PPD was significantly effective in reducing the gel strength of Diamond crude oil. The yield stress of the crude oil descended considerably; from 7.44 Pa of the blank to 0.18 Pa when treated by 1750 ppm of the optimal PPD at 31 °C; and from 75.84 Pa of the blank to 22.6 Pa at the same dosing rate of the PPD at 21 °C. In other words, the gel strength of Diamond crude oil treated by the PPD at 1750 ppm of dosing rate was 41.3 and 3.4 times lower than the untreated crude oil at 31 °C and 21 °C respectively.

Conclusion

This study had investigated the effect of the initiator on copolymerization synthesizing copolymer used as pour point depressant and its performance on Diamond crude oil.

The optimal content of the initiator – AIBN for this free-radical solution copolymerization reactions was 0.18 g. At this concentration, the yield of the reaction synthesizing copolymer was highest which reached 80% and the performance of the copolymer used as PPD was the best.

The Diamond Crude Oil, when treated with the optimal PPD, had a significantly improved property compared to its properties without chemical treatment. At 1750 ppm of dosage of the PPD, the pour point temperature reduce from 36 °C to 21 °C; the viscosity reduce from 2952 mPa.s to 413.2 mPa.s at 21 °C; the wax deposition was 6.4 times lower and the yield stress descend from 75.84 Pa of the blank to 22.6 Pa at 21 °C.

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