

Synthesis and Characterization of Methacrylate Based Polymeric Additives for Crude Petroleum Oil

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Abstract:

Wax deposition in crude oil especially at low temperature causes serious problem during its storage and transportation since this deposited wax gradually immobilizes the oil. Thus, waxy crude oils have high pour point resulting lots of handling problems. To solve this problem, a number of flow improvers (FI) or pour point depressants (PPD) have been prepared. But still it is a challenging aspect of this research area to find out the perfect chemistry with an improved efficiency and cost-effective additives over the conventional one. In this context and in continuation of our effort for the development of additive systems for lube and crude oils, homo polymer of decyl methacrylate and its copolymers with styrene and vinyl acetate at different percentage composition in the presence of benzoyl peroxide (BPO) as initiator have been prepared. All the prepared polymers are characterised by FT-IR, NMR and Gel Permeation Chromatography (GPC). The prepared additives showed excellent performance as flow improver (FI) or pour point depressant (PPD) in crude oil.

Keywords: Crude oil, additives, flow improver, wax crystal network, homopolymer, copolymer.

Introduction

Crude oil is a complex mixture of hydrocarbons containing non-polar n-paraffins and polar components such as asphaltenes and resins (Huang et al., 2011). When the temperature decreases paraffin precipitates out from the crude oil and forms wax crystals network. Their presence causes many problems (Guo et al., 2006) during storage and transportation mainly because of the crystallization and deposition of paraffin wax crystals in the flow line causing a number of handling problems as well in regions where the service temperatures (Xu et al., 2011; Frohlich et al., 2005; Atta et al., 2011; Al-Shafey et al., 2011) are or become seasonally very low (Song et al., 2005; Huiyang et al., 1991).

Pour point depressants do not in any way affect either the temperature at which wax crystallizes from solution or the amount of wax that precipitates. When wax crystals form, pour point depressants co-crystallize along with the wax species present in the oil and modify the growing pattern of wax crystal structures. Additionally, the wax crystals are kept apart from each other by the PPD backbone, and as a result of this steric hindrance, the wax crystals are no longer able to form three-dimensional structures with each other that inhibited the flow property.

Some commercially available properly designed polymeric flow improvers are poly (ethylene-co-vinyl acetate) (EVA) (Machado et al., 2001), poly(ethylene-butene) (PEB) (Schwahn et al., 2002), polymethacrylates (Soldi et al., 2007; Jung et al., 2011), and modified maleic anhydride copolymers (Wu et al, 2012; Xu et al., 2011; Deshmukh and Baramde, 2011). Basically, these polymeric wax inhibitors consist of a non-polar long hydrocarbon chain of 14 to 25 carbon atoms in addition with a polar segment typically acrylates or acetates. The hydrocarbon part is responsible for the interaction between the additive and paraffin of the oil while the polar part limits the degree of co-crystallization and thus inhibits the aggregation stage. Recently Chen et al. investigated the interaction of crude oil waxes with polyacrylate pour point depressants (PPDs) bearing different structures and reported that polyacrylate polymers with polar building blocks interacted more easily with the paraffin content which would effectively inhibit wax-crystal precipitation and improve crude oil low-temperature fluidity (Chen et al., 2014). Another study supports that an efficient polymeric additive for paraffin oils should be a linear polymer or copolymer having pendant hydrocarbon chain groups (Kumar, 1989). Again,

some investigations indicated that molecular weight (MW) and molecular weight distribution (MWD) should also play an important role in the performance as a flow improver for crude oil (Borthakur et al., 1996; Castro et al., 2011). For example, polybehenyl acrylate with a lower MW exhibited better efficacy as a flow improver for asphaltene-rich crude oil (Chanda et al., 1998) and acrylate/methacrylate polymer additives with a lower range of MWs achieved the optimum effectiveness for waxy crude oils (El-Gamal et al., 1994). According to Kuzmic et al., polymeric additives of alkyl acrylate with styrene, acrylic acid, and 1-vinyl-2-pyrrolidone with MWs below 20000 were not efficient for crude oils from Croatian oil fields (Ercegkuzmic et al., 2008) while in another study by Taraneh et al., it was reported that ethylene vinyl acetate copolymer with a higher MW was the better additive for crude oils with low asphaltene contents (Taraneh et al., 2008). T. J. Behbahani had investigated the influence of different concentrations of polymeric flow improver such as dodecylpolymethacrylate and tetradodecylpolymethacrylate on pour point of waxy oils and found that the higher molecular weight flow improver (tetradodecylpolymethacrylate) had better efficiency on pour point of waxy oils (Behbahani, 2014). Moreover, the performance of a flow improver is also related to the wax and asphaltene composition in the crude oil (Kumar, 1989; Borthakur et al., 1996; Ercegkuzmic et al., 2008; Castro et al., 2011). Hence it can be summarized that the performance of a polymeric flow improver is dependent upon both the structure of the flow improver and the oil composition (El-Gamal et al., 1992).

Vinyl acetate copolymer, acrylate copolymer and their derivatives (Qian et al., 1996; Jordan et al., 1978) are broadly applicable to improve the flow ability of very waxy crude oil, diesel fuel and other base oils at low temperature. Vinyl acetate copolymers satisfy most of the properties which a good additive must possess. On the other hand, methacrylate polymers, the first of the polymeric pour point depressants, continue to be viewed as the best chemistry available today due to the molecular structure of the polymers and the tremendous flexibility in chemical structure. In the present context, we have prepared homopolymer of decyl methacrylate and its copolymers with styrene and vinyl acetate separately at different percentage compositions and evaluated them as flow improver for crude oil collected from Oil India Ltd, Duliagan, Assam (India). The properties of the crude oil are listed in table 1.

Experimental Section

Materials

Methacrylic acid (MA, 99%, LOBA Cheme Pvt. Ltd.), Styrene (99%, Sigma-Aldrich), Vinyl acetate (VA, 99%, S. d Fine Cheme Ltd.), Decyl alcohol (DA, 98%, SRL Pvt. Ltd.) were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), Hexane (99.5%, S. d Fine Cheme Ltd.) and Methanol (98%, Thomas Baker Pvt. Ltd.) were used after distillation. Hydroquinone (99%, Merck Specialties Pvt. Ltd.) and Benzoyl peroxide (BZP, 98% Thomas Baker Pvt. Ltd.) were purified by recrystallization before use. Conc. H_2SO_4 (98%, Merck Specialties Pvt. Ltd.) was used as received. Crude oil was collected from Oil India Ltd, Duliagan, Assam (India). Before experiment the crude oil was tested for pour point and was found 24 ° C.

Preparation of the monomer and its purification

The monomer (decyl methacrylate, DMA) was prepared by reacting 1.1 mol of methacrylic acid with 1 mol of decyl alcohol in the presence of concentrated sulfuric acid as a catalyst, 0.25 % hydroquinone with respect to the total reactants as polymerization inhibitor, and toluene as a solvent. The method of esterification and its purification were carried out by the process as reported in the earlier publication (Ghosh et al., 2011).

Preparation of polymers:

The polymers (homo and copolymers) were prepared by free radical polymerization (scheme1) at different percentage composition of monomers (table 2) in presence of BZP as initiator (0.5% w/w, with respect to the total monomer). The process of polymerization and purification of polymer was carried out by the procedure as reported in our earlier publication (Ghosh et al., 2011). (Please insert scheme 1 here)

Measurements

Molecular weight determination

The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by GPC method (Water 2414, polystyrene calibration) in HPLC grade THF (0.4%, w/v) at 308K temperature at a flow rate of 1mL/min.

Spectroscopic Measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the wave number range (400 to 4000) cm^{-1} . NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl_3 was used as solvent and tetramethylsilane (TMS) as reference material.

Performance evaluation as pour point depressants/flow improvers in crude oil

The effect of additive concentration on pour point of the crude oil was tested by using different doping concentrations ranging from 1% to 6% (w/w) for each of the prepared polymer. According to the ASTM D 97-09 method the pour points of the prepared solutions were measured using cloud and pour point tester model WIL-471 (India).

Results and Discussion

Molecular Weight Analysis:

The experimental values of M_n , M_w and PDI (polydispersity index) of the prepared polymers are tabulated in table 2. From table 2, it can be stated that on increasing the percentage of styrene or vinyl acetate both the number average molecular weight and weight average molecular weight gradually increases. But the copolymers of vinyl acetate are less poly-dispersed than those of styrene-based copolymers. (Please insert table 2 here)

Spectroscopic analysis:

The homopolymer of decyl methacrylate shows IR absorption band at 1735.8 cm^{-1} corresponds to the ester carbonyl group and those at 1064.6, 710 and 690 cm^{-1} are due the bending of C-H bond. Due to the presence of $-\text{CH}_2\text{CH}_3$ group the peak at 2854.5 cm^{-1} and 2924 cm^{-1} appeared and for the CO stretching vibration the peaks at 1465.8, 1404, 1229, 1211 and 1149.5 cm^{-1} appeared. The IR spectrum of copolymers of decyl methacrylate with styrene (P-2 to P-5) are similar and exhibited the following results: The absorption band for ester carbonyl group at 1735.8 cm^{-1} shifted to 1728.1 cm^{-1} in the copolymer and the peaks at 748.3 cm^{-1} and 702 cm^{-1} were due to the C-H bond of the phenyl group of styrene. For the copolymers of decyl methacrylate and vinyl acetate (P-6 to P-9) the IR spectrum are similar and showed the following results: Peaks at 1732.9 cm^{-1} and 1716.5 cm^{-1} indicate the presence of ester carbonyl groups and the peaks at 2853.6 cm^{-1} and 2922.9 cm^{-1} are for the $-\text{CH}_2\text{CH}_3$ group. The peaks at 1456.2 cm^{-1} , 1377.1 cm^{-1} , 1368.4 cm^{-1} , 1321.1 cm^{-1} , 1296.1 cm^{-1} , 1238.2 cm^{-1} , 1163.0 cm^{-1} , 1065.5 cm^{-1} and 1011.6 cm^{-1} were due to CO stretching vibration and absorption bands at 814.9 and 721.3 cm^{-1} were for bending of C-H bond.

In the ^1H NMR data of the homopolymer, the methyl and methylene protons appeared in the range of 0.890 to 1.934 ppm for all alkyl groups and a broad peak at 3.928 ppm for the protons of $-\text{OCH}_2$ group. Absence of any peak in the range of 5-6 ppm corresponds to sp^2 carbon confirms the polymerisation. In the ^1H NMR of the copolymers of styrene, a broad peak at 7.014-7.329 ppm appeared for the protons of phenyl group. The peaks appeared in the range of 3.933-4.15 ppm indicated the presence of $-\text{OCH}_2$ protons. All the sp^3 protons appeared in the range of 0.9-1.942 ppm. Here again the absence of peaks in the range of 5-6 ppm indicated

total polymerisation. In the ^1H NMR of copolymers of vinyl acetate a broad peak at 3.926-4.158 ppm indicated the protons of $-\text{OCH}_2$ and $-\text{OCH}_3$ groups. The hydrogen atoms attached to sp^3 carbons appeared in the range of 0.858 ppm to 2.637 ppm. Absence of any peak in the range of 5-6 ppm confirmed the polymerisation successfully.

In ^{13}C NMR of the homopolymer, the peaks at 177.54 ppm indicated the presence of ester carbon. The peaks at 65.03 ppm and 64.88 ppm confirmed the presence of $-\text{OCH}_2$ carbon and peaks in the range of 14.16–45.12 ppm accounted for all sp^3 carbon atoms of alkyl groups. Absence of sp^2 carbon and hence total polymerization was confirmed by the absence of any peak in the range of 120-150 ppm. In the ^{13}C NMR of the copolymers of styrene, the peaks in the range of 176.8-177.79 ppm indicated the ester carbons. The phenyl carbons appeared in the range of 125.04-128.56 ppm. Peaks appearing at 64.86 ppm and 65.02 ppm indicated the $-\text{OCH}_2$ carbon whereas peaks in the range of 14.12-54.41 ppm corresponded to all the sp^3 carbons.

In ^{13}C NMR of the copolymers of vinyl acetate the peaks at δ 176.60 -176.70 ppm were due to the presence of ester carbonyl group. The peaks at 64.66 - 65.06 ppm corresponded to the $-\text{COCH}_3$ methyl carbon and $-\text{OCH}_2$ carbons, peaks ranging from 14.08–45.09 ppm for all other sp^3 carbons. Again, no peak in the range of 120-150 ppm indicated the absence of sp^2 carbons and confirmed the polymerization.

Analysis of pour point values

The experimental values of pour point are given in table 3. The values suggest that all the prepared polymers (P-1 to P-9) can be used effectively as pour point depressants (PPD) or flow improvers (FI) for Duliajan crude oil. The copolymers (P-2 to P-9) are better than the homopolymer (P-1) as FI. But with varying concentration, the pour point values do not linearly co-relate. In case of the copolymers of decylmethacrylate and styrene (P-2 to P-5), P-2 copolymer with the lowest percentage of styrene (2.5%) acts as the better FI than the others and using 5% (w/w) solution of this polymer we get the lowest pour point of 8.1°C. Increase in the percentage of styrene results in increasing the phenyl content in the additive. Hence it may be the reason behind that P-3 to P-5 copolymers with higher percentage of styrene gradually showed higher pour point and at 6% (w/w) solution P-5 copolymer with highest percentage of styrene (10%, w/w) shows highest pour point of 16.1°C. The vinyl acetate copolymers (P-6 to P-9) showed better results than the copolymers of styrene. These polymers are better FI and may be due to absence of phenyl group which reduces the adsorption of the polymer molecule on the wax crystals (Abdel-Azim et al., 2006) that happened in case of styrene copolymers. The P-7 copolymer having 5% (w/w) vinyl acetate proved to be the best flow improver among all the prepared polymers. At 5% concentration this polymer showed lowest pour point of 4.2 ° C. Polymers with higher molecular weights especially P-5 and P-9 showed comparatively poor results. It may be because of their low solubility in the crude oil. (Please insert table 3 here)

Conclusion

From the above study it is found that homopolymer of decyl methacrylate and its copolymer with styrene and vinyl acetate are effective as flow improver for the crude oil. The vinyl acetate-based copolymers are better as flow improver than styrene based copolymers. Moreover, it was also found that copolymers with lower molecular weight are more effective as flow improver than copolymers with higher molecular weight. Therefore, molecular weight and the chemistry of polymer chain have a significant role in relation to the performance of the additives as flow improvers for crude oil.

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Scheme 1

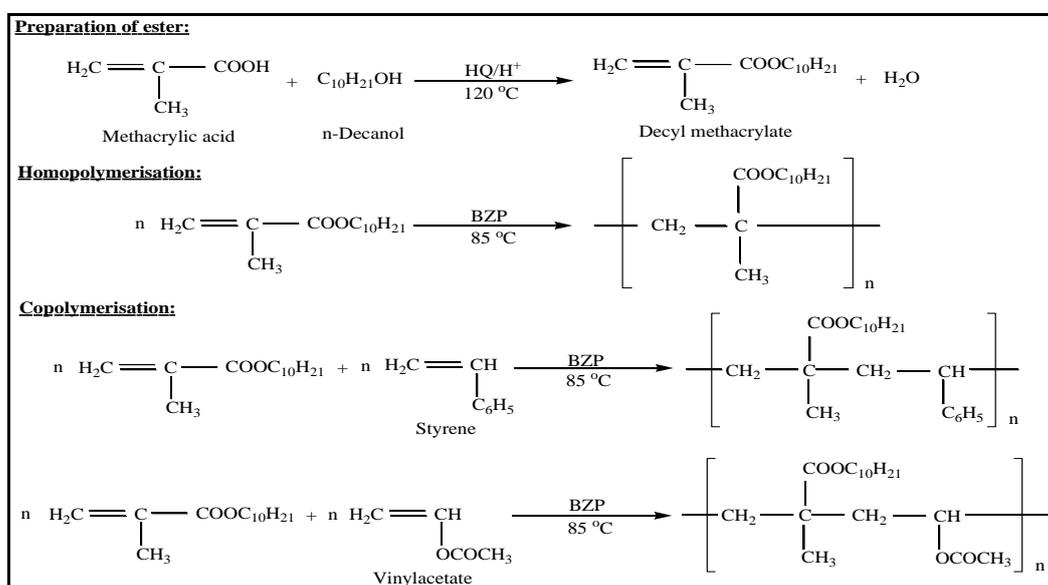


Table 1: Specification of the crude oil

Source	Duliajan, Assam
Pour point	24°C
Density	900 Kg/m ³
Plastic viscosity	5.2 mPa.S at 27°C
Yield value	10 dy/cm ² at 30°C
Wax content	>10%

Table 2: Percentage composition, M_n , M_w and PDI values of polymers (P-1 to P-9)

Polymer code	% of DMA	% of Sty.	% of VA	M_n	M_w	PDI
P-1	100	-	-	20482	49682	2.4256
P-2	97.5	2.5	-	21592	58982	2.7316
P-3	95	5	-	27457	77688	2.8294
P-4	92.5	7.5	-	28946	81556	2.8175
P-5	90	10	-	30345	93842	3.0925
P-6	97.5	-	2.5	21575	33018	1.5300
P-7	95	-	5	24013	35842	1.4920
P-8	92.5	-	7.5	56866	66210	1.1640
P-9	90	-	10	61990	81219	1.3100

DMA = Decyl methacrylate, Sty. = Styrene, VA = Vinyl acetate, M_n = Number average molecular weight, M_w = Weight average molecular weight, PDI = Polydispersity index

Table 3: Pour point data with respect to the different concentrations of the additives in crude oil

Polymer code	Pour point (°C) of additives doped crude oil (% in w/w)						
	0%	1%	2%	3%	4%	5%	6%
P-1	24	13.5	12.9	12.2	11.5	10	10.3
P-2	24	10.5	10.1	9.8	9	8.1	8.5
P-3	24	10.7	10.4	9.5	10.9	11.1	12
P-4	24	10.8	10.1	9.5	11.2	12.5	13
P-5	24	13.8	14.1	14.9	15	15.5	16.1
P-6	24	8	7.8	7.5	8.1	9.2	10
P-7	24	7.9	6.8	6.1	5.9	4.2	4.5
P-8	24	8.5	8	7.5	8.1	8.6	9
P-9	24	10.1	10.8	11.9	12.5	13	13.8