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THE EFFECT OF SILICA BASED NANOCOMPOSITE POUR POINT DEPRESSANT ON THE WAXY CRUDE OIL OF NORTH-EAST INDIA

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Abstract— In the aura of this research we developed the grafted nanocomposite pour point depressant by culmination of a set of monomers namely acrylamide, maleic anhydride, styrene, and octadecyl methacrylate and further grafted to nano silica for improving the flow properties and thereby decrease the temperature of pour point value of the North-East Indian waxy based crude oil. Moreover, to emphasize and understand the central effects of different concentrations of synthesized nanocomposite pour point depressants on the pour point of waxy crude oil, several important experiments were undergone and later its results were compared with the commercial pour point depressant. In addition, the rheological props of the sample crude were also analyzed with and without additives. The results shows that the synthesized nanocomposite has more effectively reduced the viscosity as well as pour point of the sample to desired value when compared to that of the commercially used pour point depressant.

Keywords: **Grafted Nanocomposite, Pour Point Depressant, Wax, Crude Oil, Rheology, Nano silica, Viscosity**

I. INTRODUCTION

The crude of the North-East Indian states like Assam has high percentage of paraffins mix and is saturated with wax. This property of the crude causes development of high pour point and viscosity which create severe flow related problems during the pipeline transportation from upstream to downstream. As soon as the temperature falls below the specific Wax Appearance Temperature (WAT) of the crude oil, paraffin present in it starts depositing on the inner walls of pipelines and creates obstruction to the crude flow. This deposition has non-repairable effects causing blockage to the fluid flow which may be fatal and cause pipe rupture. It has impacts on both economy of the transporting company as well as the environment. [1, 2].

Various attempts have been sighted before to cope with this prevailing issue such as the use of chemical inhibitors like addition of polymers to transporting crude oil. Polymers have been widely in use in perspective of the modern world due to their cost effectiveness and simple manufacturing process. A common use of polymers is the development of Polymeric Pour Point Depressants (PPDs) to improve the rheological properties of waxy crude oil. Out of all these, the comb-like copolymers type and the EVA type PPDs has excellent adaptation and pour point depressing properties and therefore commonly recommended for use in the crude oil transportation. These two forms of polymeric PPDs often develop polar groups and nonpolar carbon chains. The non-polar constituent will help in paraffin precipitation through nucleation and co-crystallization, while the polar groups will create a repulsive effect towards wax crystal deposition and slowdown their growth. Thereby altering the structural framework and wax crystal growth [3, 4].

In recent years researchers have developed interest in developing organic-inorganic Nano composites as they have improved properties such as improvement of flow performance of traditional polymeric PPDs, improvement in mechanical and thermal properties. These Nano composites are formed by little dispersion of non-organic particles into a polymeric matrix. One of the widely used additive is Smectite clay [5, 6].

The dispersed polymeric clay is divide into two forms, intercalated (the registry of clay layer is maintained) and exfoliated (the registry of clay layer is lost). The effect of the exfoliated clay when held in polymers produces high performance Nano composite owing to the abundance of a large number of clay that offers a large area layer for interaction with the polymeric matrix [7]. Various researchers developed PMMA-montmorillonite (MMT) Nanohybrid to improve flow properties and further investigated that exfoliated has effectively improved rheological characteristics of crude oil. Yao et al. compared polyoctadecrylate and polyoctadecylacrylate-clay Nano composite as PPD. It was seen that the addition of modifies clay to polyoctadecrylate improved the rheology properties of crude oil, while the wax crystals develop at elevated temperature [8, 9].

In this research, of a set of monomers namely acrylamide, maleic anhydride, styrene, and octadecyl methacrylate and further grafted to nano silica and characterized by FESEM as well as FTIR analysis. Then, the effect of different concentrations of PPD on pour point were studied. Finally, a thorough investigation of the waxy crude oil's rheology was accomplished using the commercial and synthesized nanocomposite PPD for its suitability in pipeline transportation of waxy crude oil.

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II. EXPERIMENTAL STUDIES

2.1 Materials

The crude oil sample used for the present study was taken from the North-Eastern oil fields, Oil India Limited (OIL), India. Nano-silica oxide powder was bought from SRL Pvt. Ltd. (Mumbai, India). Methacrylate, acrylamide monomers were bought from Sigma-Aldrich (Kolkata, India). Maleic anhydride, ethanol, azobisisobutyronitrile, xylene and styrene were from the Central Drug House (P) Ltd. (New Delhi, India).

2.2 Characterization Methods of Crude Oil

2.2.1 Pour point, Water content and API gravity

The pour point of a crude oil is the temperature below which the crude loses its flow properties due to wax development. ASTM D97-06.11 is used for measuring the temperature of pour point of the samples of crude oils. For this method, standard ASTM apparatus for pour point which includes test jar, thermometer, bath, and jacket was used for the determination of pour-point. The sample was heated and the pour point was obtained at 45 to 48^0 C and then cooled down and

Finally checked at an interval of every 3^0 C. When oil flow ceases on tipping the jar used for test horizontally, the particular temperature is recorded as pour point. It is used for quality estimation of the crude [10, 11, 12].

Values of API gravity of every crude were estimated using specific gravity values at 40^0C. Water content determination was done by centrifuge method (ASTM D 96-58 T). For this method, 25 ml sample and 25 ml of toluene were mixed thoroughly in centrifuge tube and this centrifuge tube is whirled inside the centrifuge set up at desired speed for 10 minutes. After whirling, two layers develop and the amount of water is estimated using the calibration at the bottom of the centrifuge tube [2].

2.2.2. Wax Content and SARA distribution

Wax content determination: take oil sample in a beaker followed by stirring with n-pentane in a mixture ratio of 1:20 (w/v) (weight per unit volume) for an interval of 30 min. Add acetone over the mixture & freeze overnight. Then, solid organic wax was filtered under vacuum in a Buchner funnel using Whatman filter paper 934. Using hot hexane, the wax is then filtered out [2].

For SARA distribution, crude oil and n-heptane are mixed in the ratio 1:30 (w/v), and heated to 40 °C and then cooled to ambient conditions. It was followed by vacuum filtration followed by hot toluene extraction. Maltene (residual filtrate solution) is analyzed to be rich in non-asphaltene constituents like saturates, resins etc. with partially wetting the silica gel by heptane a gel column is generated. For complete extraction of saturates, the Maltene is now allowed to pass through the gel with an extra dose of heptane.

For extraction of aromatics, toluene is allowed to pass over the bed. Resin elution is a stepwise process: First 50:50 (v/v) toluene-methanol mixture flowed, followed by 50:50 (v/v) methanol-chloroform solution, next chloroform and at the last acetonitrile was poured over the bed. Elutes from separate container were collected and the solvent was evaporated to extract solid resins [2, 12].

2.3 Synthesis of the grafted silica-based nanocomposite PPD

Firstly, the surface of nano-silicon oxide was modified by using KH570 [13]. Then, acrylamide, maleic anhydride, styrene, and octadecyl methacrylate in xylene taken in a molar ratio of 1:2:1:5 and mixed together to get homogeneous solution. Afterwards, this solution was taken in a graduated 500 ml three necked round bottom flask. The flask was furnished with an electrically operated sensitive magnetic stirrer (Tarsons, Model: Spinot Digital) and kept in an oil bath maintained at a temperature of 60 ºC, with constant stirring. Later, 2.5 g of modified nano silicon oxide was added to the homogeneous solution and continued to heat at the same temperature (60 ºC) with constant stirring (400 rpm) for 30 min. Afterwards, the solution temperature was increased slowly to 80 ºC with the continuation of the reaction for another 5 hours holding the stirring speed and temperature constant. Throughout the reaction, a stream of nitrogen gas is passed. After the completion of reaction, the reaction mixture was cooled to room temperature and centrifuged at 2000 rpm for 20 minutes to obtain the precipitate. The product (grafted nanocomposite) was finally washed with acetone and dried in vacuum oven at 40 ºC for 6 hours [6, 7, 13].

2.4 Characterization of grafted nanocomposite PPD

Fourier transform infrared (FTIR) spectra of various samples were recorded on PerkinElmer FTIR spectrometer (model Spectrum Two; PerkinElmer, Inc., Waltham, MA, USA) and range for the above measurements is 450 – 4000cm^{-1}. The surface morphology of modified and unmodified nano silica and synthesized nanocomposite were analyzed in Field-emission scanning electron microscopy (FESEM) Supra 55 model (Carl Zeiss, Germany) with Air Lock chamber in powdered form.

III. RESULTS AND DISCUSSION

3.1 Characterization of waxy Crude Oil

As per the specifications laid by API, the crude's API gravity simply indicates it is a heavy crude. The sample crude has been investigated to be highly waxy and can be correlated to its high pour point. The high pour point of this crude has negatively impacted its transportation due to the formation of wax layer on pipelines and hindrance in flow.

Table 2 shows SARA analysis results of the crude oil which reflects very high saturate content. High crude viscosity is simply due to this high saturate fraction. Asphaltene content is low whereas the resin content is high so the resin to asphaltene ratio is high. Greater this ratio, maximum is the asphaltene stability and thus minimum are the chances of asphaltene deposition [12].

3.2 Characterization of synthesized nanocomposite PPD

The nanocomposite structure was confirmed by FTIR spectroscopy. The FTIR spectra of modified and unmodified nano SiO_2 and nanocomposite are shown in Figure 1. These spectra are quite consistent with those presented in the literature [6, 7, 13].

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Table 1: Characteristic properties of crude oil

Parameter	Observed Value
API Gravity	26.8
Pour Point	36^0 C
Wax Content(%(w/w))	15.5
Water Content(%(v/v))	2

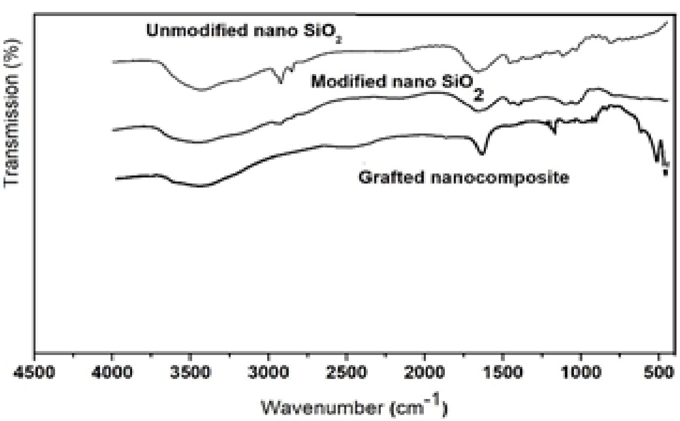
The IR spectra of unmodified nano SiO_2 display a broad adsorption band at 3442 cm^{-1}, due to the stretching frequency of the OH group and a bending peak at 1650 cm^{-1} attributable to H-O-H stretching vibration. The absorption band sought at 1120 cm^{-1} represents stretching of Si-O-Si and symmetric vibration at 470 cm^{-1} for Si-O-Si group. In the case of modified nano-SiO_2 the bands at 2860 cm^{-1} and 2924 cm^{-1} are for the asymmetric and symmetric stretching vibration peaks of the C-H bond. The bands at 3450 cm^{-1} attributes to Si-OH group which indicates the surface of SiO_2 was successfully modified [14].

Table 2. SARA analysis of crude oil sample

Components	Amount (%(w/w))
Saturate	52%
Aromatic	14%
Resin	8%
Asphaltenes	0.5%
Resin: Asphaltenes	11.5%

Figure 1: FTIR of umodified nano SiO_2, modified nano SiO_2 and Grafted nanocomposite

Field-emission scanning electron microscopy (FESEM) (Figure 2) was used for the investigation of morphological characteristics of unmodified nano SiO_2, modified nano SiO_2 and synthesized Grafted nanocomposite. It has been observed that before modification nano SiO_2 is having irregular morphology. After modification, the



irregular appearance of SiO_2 nanoparticle was reduced. This observation suggests that hydroxyl groups present on the surface of nano-SiO_2 particles being replaced by organic groups. The morphology of modified nano-SiO_2 was changed after grafting and exhibited better dispersibility and uniform particle size. This observation suggests that grafting of monomers affect the morphological arrangement of nano-SiO_2. This suggest that the nanocomposite may be formed.

Table 3. Effect of PPDs on pour point of waxy crude oil

Concentration of PPD (ppm)	Pour point in °C treated with	
	Commercial PPD (C1)	Synthesized PPD (S1)
0	36	36
250	33	30
500	29	25
750	27	22
1000	31	24

3.3 Effect of the synthesized (S1) and Commercial (C1) additives on pour point of the crude oil

The effect on pour point of the waxy crude oil treated with and without PPD are presented in Table 3. The results are indicating that the initially pour point of crude oil was high which results the wax accumulation in the pipelines and crude movement hindrance. After treated with PPD the pour point decreased but the performance of synthesised nanocomposite PPD (S1) is highly effective than the commercial PPD (C1). The effect of PPDs with change of concentration were also measured which provide the optimum concentration of synthesized PPD at which the lowest pour point value was observed. As the concentration of PPDs increased the PPDs crystals are started the linkage with wax which results the decrease the pour point of crude oil [2].

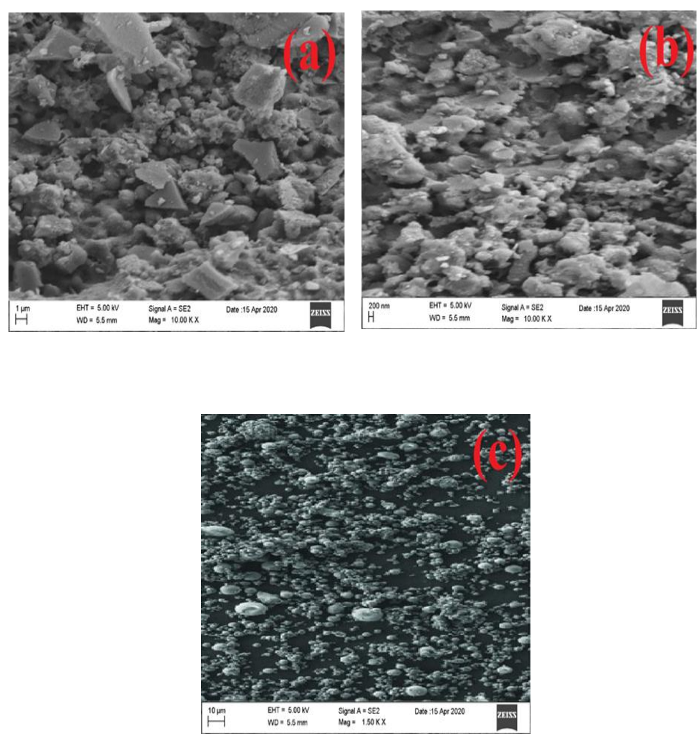


Figure 2: FESEM of unmodified nano SiO_2, modified nano SiO_2 and Grafted nanocomposite

3.4 Effect of the synthesized (S1) and Commercial (C1) additives on Rheology of the crude oil

The effect of PPD on rheology of crude oil are shown in Figure 3 and Figure 4 at 30^0C and 20^0C respectively. Rheological studies were study at 750 ppm of conventional and synthesized PPD. 7500 ppm is the optimum concentration obtained for the lowest pour point of the crude oil. The rheological studies showed that the viscosity is increased with lowering the temperature because of crystallisation of wax molecules and viscosity is decreased with increase of shear rate because of wax molecules were not stabilized at higher shear rate. The results were also indicating that the viscosity was much more reduced when treated with synthesized nanocomposite PPD comparatively than the commercial PPD. So, the synthesized nanocomposite PPD is more effective than commercial PPD.

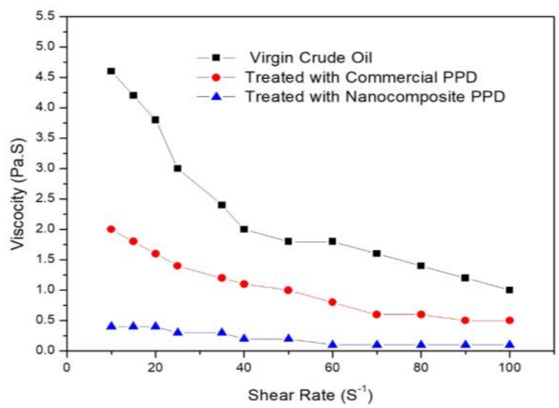


Figure 3: Rheology of virgin and PPDs treated Crude Oil at 30^0 C

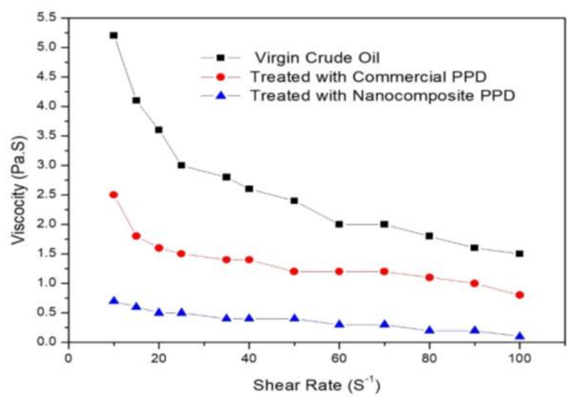


Figure 4: Rheology of virgin and PPDs treated Crude Oil at 20^0 C

IV. CONCLUSION

A novel nanocomposite PPD was synthesized for improve the flow properties and the following conclusions were obtained:

1. The nanocomposite PPD was prepared finally, well characterized and its features on application for improving the pour point and flow of the waxy crude.
2. FESEM and FTIR revealed that the formation of nanocomposite PPD may be due to strong polymer–clay interaction.
3. After treated with PPD the crude's pour point decreased but the performance of synthesised nanocomposite PPD (S1) is highly effective than the commercial PPD (C1).
4. The viscosity of waxy crude oil was much more reduced when treated with synthesized nanocomposite PPD comparatively than the commercial PPD.

V. ACKNOWLEDGMENT

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