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# Effect of Diesel Oil, Nanoparticle and Polymeric Nanocomposite PPD on Waxy Crude Oil: From a Flow Assurance Perspective

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**ABSTRACT**: Flow Assurance is of prime importance in the Petroleum Industry as the flow through a conduit should be assured in a well-planned manner so that the properties of the crude are intact throughout. In Indian scenario, it has gained importance as of now so by looking at the cost of treatment required at surface facilities in industry. This paper aims to bridge the gap between Science of nanotechnology with flow assurance visualization in a detailed experimental laboratory analysis. The flow behaviour characterization and fluid properties such as viscosity, storage modulus, loss modulus, loss factor were studied against shearing rate, temperature, angular frequency and a comparative analysis have been done to justify the novelty of using poly(methyl methacrylate)-graphene oxide (PMMA-GO) nanocomposite in crude sample. This paper also additionally focuses of addition of pour point depressant to assure the flow and deliverability at processing facilities.

**KEY WORDS** : Flow Assurance, Nanoparticle, Nanocomposite, Pour Point Depressant, Poly(methyl methacrylate)-Graphene oxide

## I. INTRODUCTION

The present scenario of Oil and Gas production needs intervention and improvement in all around aspect with the use of advanced technologies to boost up recovery considering the time factor and increasing energy demand. The origin of the term 'Flow Assurance' dates back to 1990s coined by Petrobras which refers to "Guarantee of Flow" [1]. In this regard, correlating the concepts of fluid dynamics and nanotechnology, the rheological and fluid property profiles can be modified exclusively. Heavy crude production is generally observed in age old oilfield in India and surprisingly which is a major concern and consequently a viscosity less than 200mPa.s is generally desired at the pumping temperature [2]. Hence it can inferred that this heavy crude needs a viscosity reduction additive basically which will lay down the viscosity profile in such a way that a seamless flow can be assured at all nodal points. The conventional intervention with the produced heavy crude includes heating of crude and consequent heating of pipelines [3], use of pour point depressants [4], emulsification of crude oil in water [5], implementation of core annular flow [6], viscosity reducers[7], dilution or blending of crude oil with lighter alcohols [8,9]. The waxy content of the high viscosity crude clears the fact that there is a need of nanocomposites to enhance recovery from the perspective of flow assurance.

Subsequently, the use of Co-Ni nanocomposite have been suggested by researchers for the purpose of dewaxing of crude for flow through production tubing[10]. While some studies have inferred that the use of suitable oil in water emulsions helps in reduction of pour point and viscosity and thereby facilitating the transportation process [11-15] which were prepared by mechanical homogenization method [16]. The high frequency ultrasonic waves triggered through crude sample surprisingly disintegrated the associated carbon compounds as suggested in a study [13]. Other studies have suggested such as the use of natural cashew nut shell liquid by esterifying with polyethylene glycol as pour point depressant in crude[17]. Studies have also found that the use of silica and alumina nanoparticle in crude sample have drastically reduced its viscosity therein[18].

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This paper aims at synthesis of a novel Poly(methyl methacrylate)-Graphene oxide (PMMA-GO) nanocomposite which will play an important role in affecting fluid properties of the crude oil significantly making it suitable for flow through conduits in Oil and Gas facilities. This study paves a way forward for the effective use of the mentioned nanocomposite synthesized in laboratory which helps in reduction of viscosity, pour point, shearing rate, storage and loss modulus of the crude taken into consideration for the investigation.

## II. MATERIALS AND METHODOLOGY

The crude oil sample was obtained from Oil India Limited, Duliajan, Assam, India. The diesel used with the crude sample has been bought from shop which was further double distilled in the laboratory. The viscosity measurements were done with the assistance of Anton Paar 72 Rheometer. Modified Hummer's method was used to synthesis for graphene oxide from graphite powder by chemical oxidation with $KMnO_4$ in presence of sulfuric acid. Oscillation test for determination of frequency sweep was carried out in the Plate Plate (PP) configuration. The polymerized Graphene Oxide was synthesized in the laboratory and later on grafted to finally synthesize poly(methyl methacrylate)-graphene oxide (PMMA-GO) nanocomposite. The samples are listed in **Table I** which were analysed and thereby a comparative study was drawn.

**Table 1. Composition of the samples for experimental study**

| Sample | Composition |
|---|---|
| I | Crude |
| II | 70/30 (Crude/Diesel) |
| III | 0.5% Graphene 70/30 (C/D) |
| IV | 1% Graphene 70/30 (C/D) |
| V | 1.5% Graphene 70/30 (C/D) |
| VI | Poly(methyl methacrylate)-Graphene oxide (PMMA-GO) nanocomposite |

## III. RESULTS AND DISCUSSION

### *A.* Measurement of Amplitude Sweep

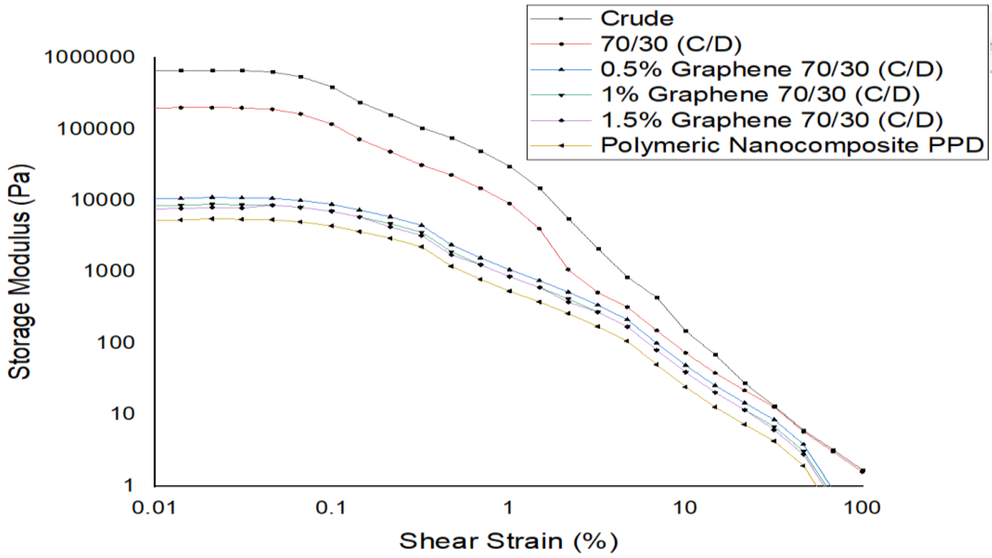


**Figure 1. Amplitude Sweep measure by oscillation test**

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An oscillation test was performed to determine and measure the amplitude sweep. The test conducted was based on the simple concept of oscillation of pendulum wherein the amplitude changes while keeping the frequency parameter to be constant. After the test, a graph has been obtained as illustrated in **Figure 1.**which depicts the trend of variation of storage modulus with respect to shear strain in percentage. It can be observed that at a Shear Strain of 0.021% the corresponding values of storage modulus has been reported as 674980 Pa, 76812 Pa, 11208 Pa, 8966.4 Pa, 8069.76 Pa and 5604 Pa for Crude, Crude in Diesel, 0.5 % , 1% and 1.5% Graphene in 70/30 (C/D) and the Polymeric Nanocomposite PPD respectively. But there is a decreasing trend for the graphical representation and this is significant at 46.5% Shear Strain wherein the values of storage modulus contributes as 6.0821 Pa, 5.788 Pa, 3.858 Pa, 3.0874 Pa, 2.77834 Pa and 1.9294 Pa for the mentioned samples respectively. It is known that a decrease in storage modulus reduces viscosity of the sample and specially with the use of Polymeric Nanocomposite there was a slight decrease in viscosity as compared to Graphene and raw crude samples.

### *B.* Viscosity vs. Shear Rate Plot

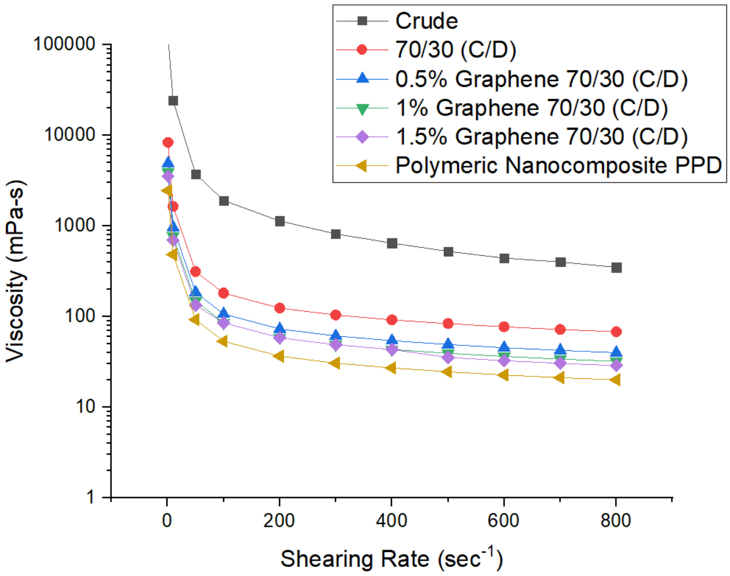


**Figure 2. Viscosity profile with respect to variation in Shearing Rate**

The viscosity of the samples under consideration has been plotted in **Figure 2**. after the experimental work carried out at different shearing rate in sec $^{-1}$. The observations made from the plotted profile is that initially at shearing rate of 1 sec $^{-1}$ , the viscosity of the five samples were noted in the manner of 120252, 8369.27,4923.1, 3938.48, 3544.632, 2461.55 mPa-s but as seen in the plot there is a drastic decreasing trend of viscosity for the 70/30 (C/D) sample. Furthermore, at a high shearing rate of 700 sec $^{-1}$ , the viscosity measures were noted as 401.2, 72.8, 42.4, 33.92, 30.528, 21.2 mPa-s which refers to the fact that viscosity of the samples reduced with the effect of the additives but only Polymeric nanocomposite PPD itself reduces the value drastically ensuring seamless flow through different conduits.

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### *C.* Viscosity vs. Shear Rate at 30°C

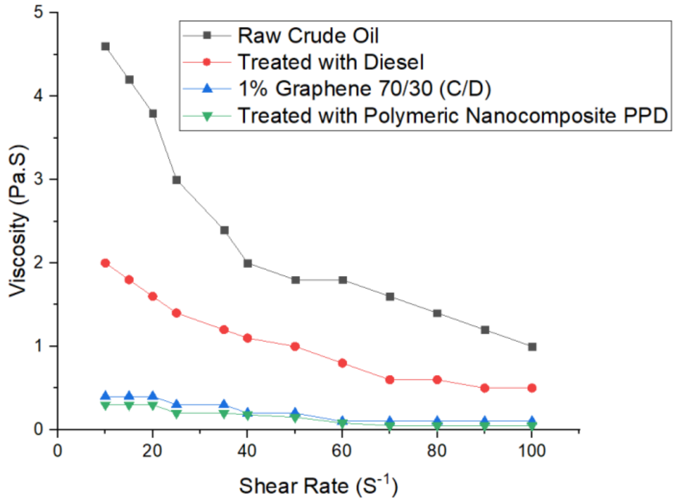


**Figure 3. Viscosity vs. Shear Rate at 30°C**

Additionally, the effect of temperature was studied on the viscosity of the samples of graphene and polymeric nanocomposite with respect to raw crude sample. **Figure 3.**depicts the representation at 30°C and against a shear rate of 40 sec $^{-1}$ viscosity of 2 Pa.s, 1.1 Pa.s, 0.2 Pa.s and 0.18 Pa.s have been observed which shows a clear decreasing rate trend with the use of polymeric nanocomposite.

### *D.* Viscosity vs. Shear Rate at 20°C

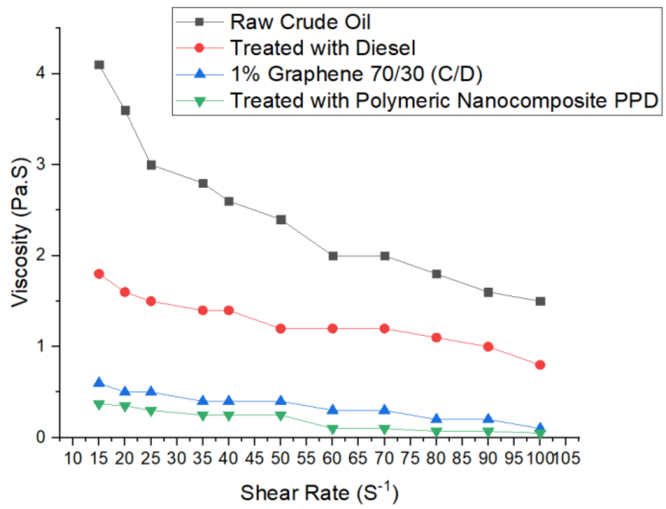


**Figure 4. Viscsosity vs. Shear Rate at 20°C**

Subsequently, viscosity vs. shear rate analysis was done at 20°C and the graph plotted for the values is shown in **Figure 4.** Similarly the values of viscosity were noted at 40 sec $^{-1}$ as 2.6, 1.4, 0.4 and 0.25 Pa.s respectively. This led to the inference that viscosity increases with the increase in temperature but decreases with increasing shear rate where wax is not stable with special reference to polymeric nanocomposite.

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### *E.* Pour Point Estimation

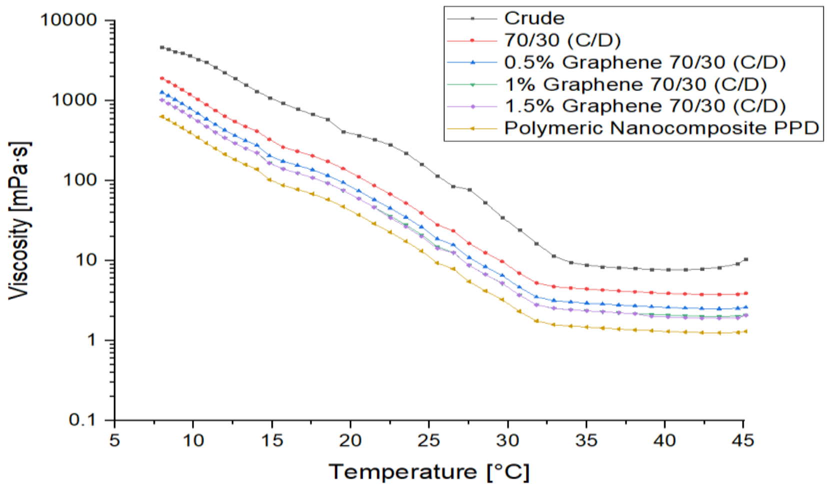


**Figure 5. Viscosity against Temperature Plot for Pour Point Estimation**

The pour point of a fluid sample is an estimation of the point of interest where the fluid ceases to flow. This experimental investigation was carried to estimate the pour point of the samples with the help of a viscosity vs temperature graphical representation of the reported laboratory data. Now, from tangential estimation of the plotted curves in **Figure 5.**it has been observed that for raw crude sample the pour point is around 23.90 °C while in a there is a drastic reduction in the associated value in 1% Graphene sample to be around 20.56 °C. Moreover, the use of polymeric nanocomposite PPD have shown a pour point reduction in and around 15.69 °C which is a preferable value from flow assurance directives as it will serve as a novel pour point depressant in the crude under investigation.

### *F.* Thixotropic Analysis Plot

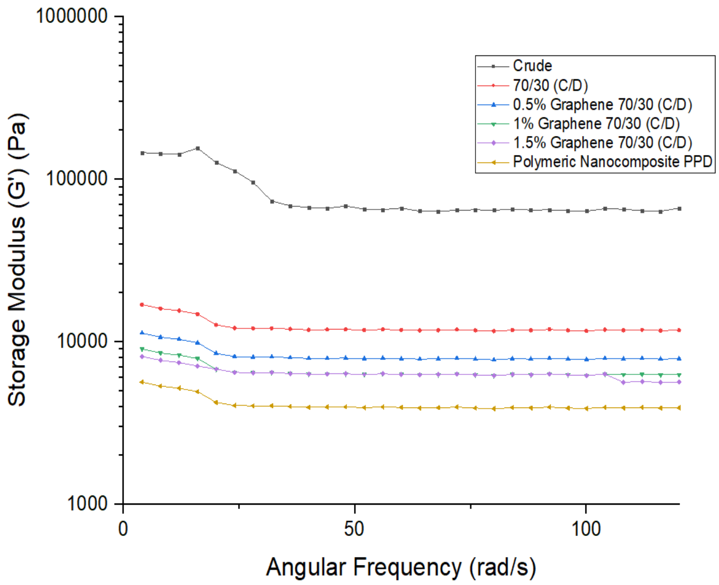


**Figure 6. Thixotropic analysis based on storage modulus vs angular frequency plot**

Thixotropy is the property of a fluid to become less viscous when a shearing force is applied. **Figure 6.**depictsthe plot of storage modulus (Pa) vs angular frequency (rad/s) and upon the analysis of this viscoelastic rheological property it has been observed that at an angular frequency of 12 rad/s, the storage modulus values have been reported as 142920, 15543, 10362, 8289.6, 7460.64, 5181 Pa respectively for the samples listed in the plot. But seemingly, after an angular frequency of around 40 rad/s the there is no change observed in the storage modulus trend and regarding the case of 1% optimized graphene sample the same consistency has been observed after an angular frequency of 24 rad/s approximately. However, looking at the overall trend, the storage modulus has further decreased in case of polymeric nanocomposite which clears the fact that it is an efficient medium to decrease the viscosity of the crude.

## IV. CONCLUSION

The laboratory experiments carried with respect to the flow assurance of crude through pipelines suggested that use of polymeric nanocomposite pour point depressant in crude will provide a seamless and ease of flow. The following observations are made based upon the analysis of the work:

- The novelty of the work lies in the fact that in the present scenario the use of nanoparticles such as Fe, Graphene, Silica in crude is not feasible from the aspect of precipitate formation with alteration of temperature and thereby polymeric nanocomposites proved to be advantageous in this context.
- The viscosity profile analysis with the help of amplitude sweep and with respect to shearing rate have suggested a reduction in viscosity of the crude under investigation which is a way forward to deal with heavy crudes produced from different oilfields.
- The Storage Modulus being an important fluid dynamics property have shown decreasing trend with polymeric nanocomposite which ensures the ease of hydrocarbon flow with subsequent viscosity reduction.
- The effect of temperature and shear rate was also simultaneously studied which showed better results in case of polymeric nanocomposite.
- Thus, the use poly(methyl methacrylate)-graphene oxide (PMMA-GO) nanocomposite seems to be feasible from flow assurance aspect and would thereby ease processing at oil and gas industry.

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