

Waste Plastic Nanomagnetite Pour Point Depressants for Heavy and Light Egyptian Crude Oil

Rasha S. Kamal, George Michel,* Amr Ageez, and Reem K. Farag



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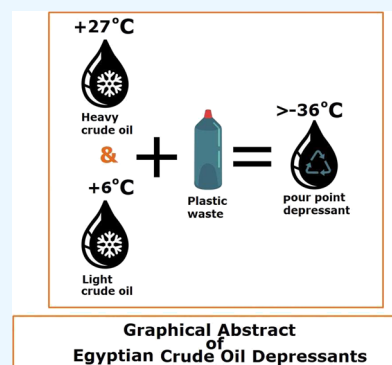
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ABSTRACT: One of the most widely used plastics in the world's rapidly urbanizing population is polyethylene (PE). Globally, there is a growing demand for plastics. Polyethylene plastics do pollute and harm the environment. Although polyethylene is said to be nonbiodegradable, any chemical deterioration can take hundreds of years. This study intends to improve the crude oil property, precisely its pour point, by using polyethylene derived from waste products with magnetic nanoparticles (MNPs) and applying it to heavy and light crude oils. Forty crude oil samples were prepared by changing the PE additive concentration from 0.25 to 2% with 0–2.0% MNP concentration. Dynamic light scattering (DLS), gas chromatography, and photomicrographic techniques were employed during the study. DLS results revealed that nanoparticles of heavy (B) crude oil have bigger particle sizes than light (A) crude oil samples, and the overall distribution of the added nanoparticles was much better in light crude oil than in heavy crude oil. The photomicrographic results revealed that the treated samples using additives provided a significant wax crystal reduction compatible with the provided pour point results. The prepared sample of the treated light (A) crude oil provided a more extraordinary rheology performance than the heavy (B) crude oil. Moreover, prepared crude oil samples with PE additives and MNPs are effective as pour point depressants.



1. INTRODUCTION

Polyethylene (PE) or polythene is one of the most popular plastics in the rapidly urbanizing world. The need for plastics is growing on a global scale.¹ By 2030, it is anticipated that there will be 417 million tons of plastics in circulation, up from 236 million tons currently.² Mainly, polyethylene (PE) is used by industries in manufacturing packaging products such as plastic films and plastic bags, as well as containers in all their forms, including shampoo, water, and milk bottles. Along with many other products and uses, in 2017 alone, there was a production for polyethylene resins that exceeded 100 million tons, accounting for about 34% of the total plastics across the market.^{3,4} The problem with PE is that it has been commercially marketed as the most stabilized and healthy-to-use type of plastic.² Today, most plastics come from petrochemicals made from fossil fuels like oil and gas. From the petrochemical feedstock, about 4% of yearly petroleum production is turned directly into plastics.⁵ Yet, polyethylene plastics cause environmental pollution and harm, albeit indirectly. Polyethylene is characterized as being nonbiodegradable, but it can take hundreds of years for any chemical degradation to begin, which slows down recycling efforts globally, particularly in developing nations with limited recycling knowledge.⁶ Recycling is vital in reducing waste products in the modern world.⁷ Additionally, it is crucial to ensure environmental sustainability by minimizing raw material

extraction and concentrating on reusing waste materials, which help to reroute the economy's waste output.⁵

Magnetic nanoparticles (MNPs) are a type of nanoparticles that can be manipulated through magnetic wave fields.⁸ Iron, nickel, cobalt, or one of their oxide-based magnetic cores and an active group shell layer make up most of a magnetic nanoparticle.^{8,9} MNPs are widely utilized in medical and biomedical fields. There are also several uses for magnetic nanoparticles outside of engineering, notably in petroleum engineering applications. To follow the fluids that flow in the reservoir and identify the production well from which the crude oil in the produced fluids is produced, MNPs can be developed as crude oil tracers.⁹ When used in the petroleum industry, MNPs typically have a coating of sodium oleate and polyvinyl pyrrolidone styrene. This coating allows the particles to selectively absorb the crude oil surface in oil-contaminated water by making oil spills, which can then be filtered using magnetic separation.⁹

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Despite using the preheating system, freezing oil at very low temperatures damages machine parts (oil cannot pour or flow), wasting time and energy. As mineral oils are made up of a complex mixture, they do not freeze as quickly as water. It relies on the temperature at which the oil starts to flow under specific circumstances. This can be decreased by removing the oil's waxy components.^{9,10} The government is burdened with a significant economic issue because the additives used to enhance the flow of lubricating oils are either imported from overseas or made in a laboratory using foreign chemicals.¹¹

Pour point depressants can enable the flow of oil or lubricants at extremely low wintertime temperatures without forming wax while maintaining the oil's pumpability. On the other hand, recycling plastic trash as an additive is thought to safeguard the environment from its buildup or its reuse through various chemical processes, which alters the chemistry of the environment and places a financial burden on the state.¹¹

A recent study demonstrated that using PE can improve the characteristics of oils as their pour point depressants, which is a significant issue for crude oil refineries.¹² Particularly, during the extraction process of crude oils from wells and the process of transportation through pipelines during the winter or at extremely low temperatures, there is a possibility for crude oil to freeze or lose liquidity during the process.¹⁰ It was proven in previous studies that adding polyethylene to lube oils such as mineral oil enhances its efficiency and performance to a level similar to that of synthetic oil.¹¹

Even when it was only prepared from waste PE products, it offers good sustainability for both the economy and the environment.^{12,13} The main aim of this research is to use polyethylene (PE) from waste products, with magnetic nanoparticles as additives, in both heavy and light crude oils to enhance the crude oil characterization, precisely its pour point.

2. EXPERIMENTAL SECTION

2.1. Materials Used and Sample Preparation. The materials used in this study include PE plastic waste, toluene (C₇H₈), magnetic nanoparticles (MN), and heavy and light crude oil samples, which were received from the Egyptian Petroleum Research Institute (EPRI). The heavy and light crude oil sources are Petroshahd Petroleum Co., at Shark Ras El Katara in Egypt, and Borg El Arab at Oyun Musa in Egypt, respectively. Toluene is a colorless, insoluble water liquid with a paint thinner-like odor. It is a substituted aromatic hydrocarbon of phenyl and methyl groups (CH₃). Typically, toluene is utilized as a solvent and a feedstock for industry.

Two sets of samples (40 numbers) were prepared. The first set comprised only 10 samples with liquefied PE and natural crude oil with no MNP additives. The second set contained 30 samples with natural crude oil, MNPs, and liquefied PE plastic.

2.1.1. Preparation of Liquefied PE Plastic Solution. When preparing a liquid PE plastic, PE plastic was cut into small pieces to be correctly weighed to achieve each targeted concentration. The concentrations of PE plastics were maintained at 0.25, 0.5, 1, and 2%. Then, the tiny pieces were thoroughly mixed with toluene and heated on a heat plate at a temperature not exceeding 50 °C, as toluene could be easily vaporized at high temperatures. The reaction of converting PE to a liquid was made using a four-neck reaction flask. The primary rationale behind using toluene to liquefy PE plastics is that once the polymer reaches its melting point,

toluene will act as an antisolvent agent to keep the polymer from returning to its initially solidified state and from losing its liquid state more quickly after cooling.¹⁴ Then, the toluene mixtures prepared with different polythene additive concentrations were added to both light (A) and heavy (B) crude oil solutions and thoroughly mixed.

2.1.2. Preparation of Liquefied PE Plastics with MNP Additive Solution. During the preparation of liquid PE plastics with MNPs, similar concentrations of polythene plastics (0.5, 1, 1.5, and 2%) were maintained. The same steps were followed as described above to prepare liquefied polythene solutions. Afterward, magnetic nanoparticles were added to liquefied polythene solutions in three distinct concentrations (0.5, 1, and 2%). The description of the prepared samples is tabulated in Table 1.

2.2. Instruments and Techniques. The properties of light (A) and heavy (B) natural crude oil specimens were tested following ASTM methods. Table 2 shows the properties

Table 1. Description of Prepared Samples

| sample no. | sample components |
|------------|--|
| 1 | 0.25% PE + light crude oil (A) |
| 2 | 0.25% PE + heavy crude oil (B) |
| 3 | 0.5% PE + light crude oil (A) |
| 4 | 0.5% PE + heavy crude oil (B) |
| 5 | 1.0% PE + light crude oil (A) |
| 6 | 1.0% PE + heavy crude oil (B) |
| 7 | 1.5% PE + light crude oil (A) |
| 8 | 1.5% PE + heavy crude oil (B) |
| 9 | 2.0% PE + light crude oil (A) |
| 10 | 2.0% PE + heavy crude oil (B) |
| 11 | 0.25% PE + 0.5% MNPs + light crude oil (A) |
| 12 | 0.25% PE + 0.5% MNPs + heavy crude oil (B) |
| 13 | 0.5% PE + 0.5% MNPs + light crude oil (A) |
| 14 | 0.5% PE + 0.5% MNPs + heavy crude oil (B) |
| 15 | 1.0% PE + 0.5% MNPs + light crude oil (A) |
| 16 | 1.0% PE + 0.5% MNPs + heavy crude oil (B) |
| 17 | 1.5% PE + 0.5% MNPs + light crude oil (A) |
| 18 | 1.5% PE + 0.5% MNPs + heavy crude oil (B) |
| 19 | 2.0% PE + 0.5% MNPs + light crude oil (A) |
| 20 | 2.0% PE + 0.5% MNPs + heavy crude oil (B) |
| 21 | 0.25% PE + 1.0% MNPs + light crude oil (A) |
| 22 | 0.25% PE + 1.0% MNPs + heavy crude oil (B) |
| 23 | 0.5% PE + 1.0% MNPs + light crude oil (A) |
| 24 | 0.5% PE + 1.0% MNPs + heavy crude oil (B) |
| 25 | 1.0% PE + 1.0% MNPs + light crude oil (A) |
| 26 | 1.0% PE + 1.0% MNPs + heavy crude oil (B) |
| 27 | 1.5% PE + 1.0% MNPs + light crude oil (A) |
| 28 | 1.5% PE + 1.0% MNPs + heavy crude oil (B) |
| 29 | 2.0% PE + 1.0% MNPs + light crude oil (A) |
| 30 | 2.0% PE + 1.0% MNPs + heavy crude oil (B) |
| 31 | 0.25% PE + 2.0% MNPs + light crude oil (A) |
| 32 | 0.25% PE + 2.0% MNPs + heavy crude oil (B) |
| 33 | 0.5% PE + 2.0% MNPs + light crude oil (A) |
| 34 | 0.5% PE + 2.0% MNPs + heavy crude oil (B) |
| 35 | 1.0% PE + 2.0% MNPs + light crude oil (A) |
| 36 | 1.0% PE + 2.0% MNPs + heavy crude oil (B) |
| 37 | 1.5% PE + 2.0% MNPs + light crude oil (A) |
| 38 | 1.5% PE + 2.0% MNPs + heavy crude oil (B) |
| 39 | 2.0% PE + 2.0% MNPs + light crude oil (A) |
| 40 | 2.0% PE + 2.0% MNPs + heavy crude oil (B) |

of A and B crude oil samples. All prepared samples were subjected to further tests.

Table 2. Properties of Light (A) and Heavy (B) Crude Oil Specimens

| experiment | method | light crude oil specimen (A) | heavy crude oil specimen (B) |
|-----------------------------------|-------------|------------------------------|------------------------------|
| density @ 15.56 °C | ASTM D-4052 | 0.8629 | 0.8566 |
| specific gravity | | 0.8637 | 0.8574 |
| API gravity @ 60 °F | | 32.3 | 33.5 |
| kinematic viscosity, cSt, @ 40 °C | ASTM D-445 | 6.036 | 5.38 |
| dynamic viscosity, CP@ 40 °C | | 5.09 | 4.51 |
| total sulfur, wt % | ASTM D-4294 | 1.55 | 0.34 |
| pour point, °C | ASTM D-97 | 6 | 27 |
| asphaltene content, wt % | IP-143 | 3.7 | 0.68 |
| wax content, wt % | UOP-64 | 2.29 | 4.86 |
| flashpoint, °C | ASTM D-93 | <−21 | <−21 |
| water content, vol % | ASTM D-4006 | 0.4 | 12 |
| free water, vol % | ASTM D-4007 | nil | nil |
| ash content, wt % | ASTM D-482 | 0.006 | 0.04 |
| salt content, Ptb | ASTM D-3230 | 10.7 | 2.7 |
| molecular weight | | 107.4 | 111.01 |

2.2.1. Dynamic Light Scattering Testing. Nonetheless, 30 samples with magnetic nanoparticles were tested using the dynamic light scattering (DLS) method. The DLS method utilizes temporal variations in the intensity of scattered light that reflects the diffusion of the particles to determine the size of particles suspended in a liquid. WYATT-DynaPro Plate Reader 1 apparatus was employed during this study to determine the particle size.

2.2.2. Gas Chromatography. Two blank samples of both light (A) and heavy (B) crude oil specimens were tested using gas chromatography (GC). The components of a mixture are distributed between the stationary and mobile phases along the chromatographic column, which leads to the formation of gas chromatographic separation.¹³ GC is used in the petroleum industry for helping in monitoring the compounds in crude oil by injecting the crude into the chromatography column of the system to allow the crude to separate all the components present in the sample slowly. A THERMOQUEST- Trace GC 2000 series apparatus was employed during this study. For this research, the main goal of using GC is to provide evidence for the chemical components present inside each crude oil blank sample, as tabulated in Tables 5 and 6.

2.2.3. Pour Point Measurement. The generation of wax during the transportation and production of crude oil is one of the primary issues with flow assurance in the petroleum industry. Crude oil gets increasingly viscous as temperature drops, and once it drops below the pour point temperature, it cannot flow or be pumped.¹⁶ The lowest temperature at which lubricating oil flows or pours when chilled under controlled conditions is known as the pour point.¹¹ Hence, the pour point is crucial in the petroleum industry. All the prepared 40 samples and 8 more samples (blank samples) prepared by adding only magnetic nanoparticles to natural crude oil without liquefied polythene additives were tested for their pour points using a pour point depressant. A TANAKA-MPC-102s apparatus was deployed to measure the pour point in this

study. The performance of PE and nanoparticles in crude oil was evaluated as pour point depressants by standard ASTM methods.

2.2.4. Photomicrographic Analysis. Photomicrographic examination was used to examine accumulations and changes in the wax crystal shape in lubricating oil. Photomicrographic analysis was conducted using a Shambhavi Impex-SIEBPE-01 apparatus.

2.2.5. Study of Rheological Properties. The prepared samples were tested for their rheological properties using a modular compact rheometer (MCR) 502' (Anton Paar). Shear rate (s^{-1}), shear stress (N/m^2), and viscosity (mPa.s) were measured at different temperatures. The flow and deformation characteristics of diverse materials are measured with the MCR 502 rheometer. It is possible to analyze the dynamic behavior of liquids and liquid solutions in rotating mode. The relative and absolute viscosities of a sample are determined depending on the measurement system. In the oscillatory mode, viscoelastic sample deformation and flow behavior are simultaneously measured. As a result, the sample's loss and storage moduli and complex viscosity are determined.

3. RESULTS AND DISCUSSION

The properties of the light (A) and heavy (B) crude oil samples were tested following ASTM standard methods. The properties of both natural crude oil specimens and the obtained values are tabulated in Table 2.

3.1. Effectiveness as Pour Point Depressants. The temperature at which oil stops flowing while gravity is present is known as the oil pour point. Oil having a high pour point makes starting machinery in cold conditions challenging or impossible. Paraffin wax in cold oil, which has the propensity to crystallize, gives it its hardness. Pour point depressants lessen crystal formations' size and cohesiveness, lowering the pour point and increasing the flux. It might be challenging to store and operate lubricating oils, with waxes present.^{11,17,18}

The pour point temperature ranged up to 6 °C from below −36 °C for light (A) crude oil samples. The highest pour points were observed for blank samples, whereas the lowest was observed for samples with a 2% concentration of magnetic nanoparticles with 0.25–0.5% liquefied polyethylene additive concentration. In contrast, the pour point of blank samples of heavy (B) crude oil showed a maximum of 27 °C temperature, while the minimum value was lower than −36 °C. Similar to light crude oil samples, minimum pour point values were observed from samples that had a 2% concentration of magnetic nanoparticles with 0.25–0.5% liquefied polyethylene additive concentration. Tables 3 and 4 depict the observed pour point values for light (A) and heavy (B) crude oil samples, respectively.

It was observed that the pour point values of both A and B crude oil samples were increased with the increment of liquefied PE additive concentration. In addition, the pour point values drop continuously with the increment of concentration of MNPs for all the liquefied PE additive concentrations for both crude oil types. Nevertheless, the pour point of blank oil samples was not affected by adding magnetic nanoparticles in both A and B oil specimens. The variations of pour point values of light (A) and heavy (B) crude oil samples are depicted in Figures 1 and 2, respectively.

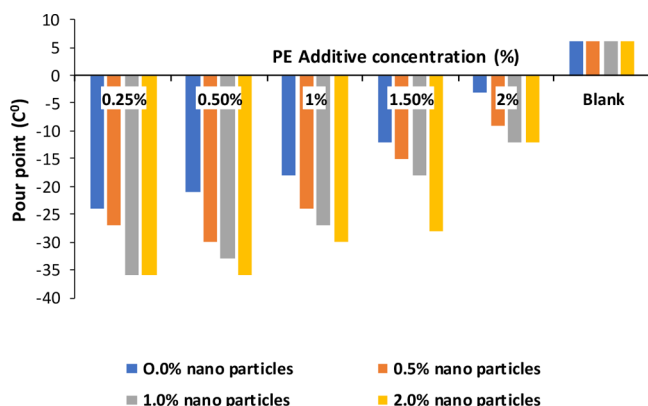
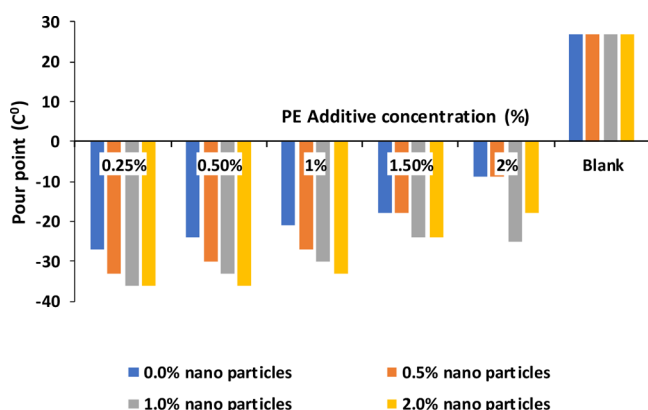
It is evident from Figures 1 and 2 that the prepared PE and MNPs are effective as pour point depressants for both light (A) and heavy (B) crude oils. Further, it was observed that the

Table 3. Observed Pour Point Values for Light (A) Crude Oil Samples

| liquefied PE additive concentration | pour point (°C) | | | |
|-------------------------------------|-------------------|------|------|------|
| | MNP concentration | | | |
| | 0.0% | 0.5% | 1.0% | 2.0% |
| 0.25% | -24 | -27 | -36 | >-36 |
| 0.5% | -21 | -30 | -33 | >-36 |
| 1% | -18 | -24 | -27 | -30 |
| 1.5% | -12 | -15 | -18 | -28 |
| 2% | -3 | -9 | -12 | -12 |
| Blank | +6 | +6 | +6 | +6 |

Table 4. Observed Pour Point Values for Heavy (B) Crude Oil Samples

| liquefied PE additive concentration | pour point (°C) | | | |
|-------------------------------------|-------------------|------|------|------|
| | MNP concentration | | | |
| | 0.0% | 0.5% | 1.0% | 2.0% |
| 0.25% | -27 | -33 | >-36 | >-36 |
| 0.5% | -24 | -30 | -33 | >-36 |
| 1% | -21 | -27 | -30 | -33 |
| 1.5% | -18 | -18 | -24 | -24 |
| 2% | -9 | -9 | -25 | -18 |
| blank | +27 | +27 | +27 | +27 |

**Figure 1.** Variation of pour point with MNP concentration for light (A) crude oil.**Figure 2.** Variation of pour point with MNP concentration for heavy (B) crude oil.

efficiency is decreased by increasing the PE additive concentration. The PE additive shows the best performance

as a pour point depressant at a concentration of 0.25%. This result is parallel to the findings of the study, which was conducted to evaluate the effectiveness of high-density polyethylene waste (HDPE)–waste-modified lube oil nanocomposites as pour point depressants.¹¹ In addition, PE additives showed a higher efficiency as pour point depressants in heavy (B) crude oil than in light (A) crude oil.

Nevertheless, except in blank samples, 1.0 and 2.0% nanoparticle concentrations showed comparatively lower pour point temperatures in all PE additive concentrations for both A and B crude oils. As the pour points of 0.25–0.5% PE additive samples with 1.0–2.0% nanoparticles showed a pour point less than -30 °C, the performance as pour point depressants is similar to that of synthetic oils. Moreover, as the modified samples are prepared using recycled PE material, our work provides an economically and environmentally viable and sustainable approach.

DLS testing was conducted for the second set of light (A) and heavy (B) crude oil samples (30 numbers), which would measure the particle size and provide an estimate for the distribution of the submicron particulate,¹⁴ which was prepared by adding magnetic nanoparticles. The obtained results for light (A) crude oil and heavy (B) crude oil are depicted in Figures 3 and 4, respectively.

A light crude oil sample with 0.5% PE and 2% MNPs reached a peak at 2861 nm of particle size and 363.7 nm width, while the sample with 2% PE and 1% MNPs reached the maximum at 100.5 nm of particle size and 14 nm width. According to Figure 3C, the light crude oil sample with 1% PE and 1% MNPs reached the maximum at 102.2 nm of particle size and 13.18 nm width.

Similar to light crude oil, the heavy crude oil sample with 0.5% PE and 2% MNPs showed a peak at 2877 nm of particle size and 210.9 nm width, whereas the sample with 1% PE and 2% MNPs reached a peak at 104.4 nm of particle size and 10.09 nm width. Nonetheless, the sample with 1% PE and 1% MNPs showed a maximum at 104.4 nm of particle size and 13.18 nm width parallel to a light crude oil sample with similar additive concentrations.

It can be concluded from these results that the MNPs of the heavy (B) crude oil were much larger in size, while the light (A) crude oil sample had a much smaller particle size. This shows that the overall distribution of the added nanoparticles was significantly better in light (A) crude oil than it is in heavy (B) crude oil as the wax crystal particles of the heavy (B) crude oil are much bigger and closer in contact with each other, which makes the nanoparticle distribution across the crude in a much lower rate versus the light (A) crude oil which would have a small-size wax crystal particle in it. As a result, it would allow for a much better nanoparticle distribution.

3.2. Presence of Chemical Components in Crude Oil.

The chemical components present in the crude oil blanks were tested using the GC technique with mass spectrometry GC–MS). The chemical components of light (A) and heavy (B) crude oil blanks observed during the analysis are tabulated in Tables 5 and 6, respectively.

Even with small sample sizes, GC–MS is widely renowned for being an extremely sensitive and powerful analytical tool.¹⁵ GC results for both A and B crude oils are depicted in Figures 5 and 6, respectively. In Figure 5, the hydrocarbon compounds of the light (A) crude oil constituents (from C8 to C28) represent that the more percentages of hydrocarbon

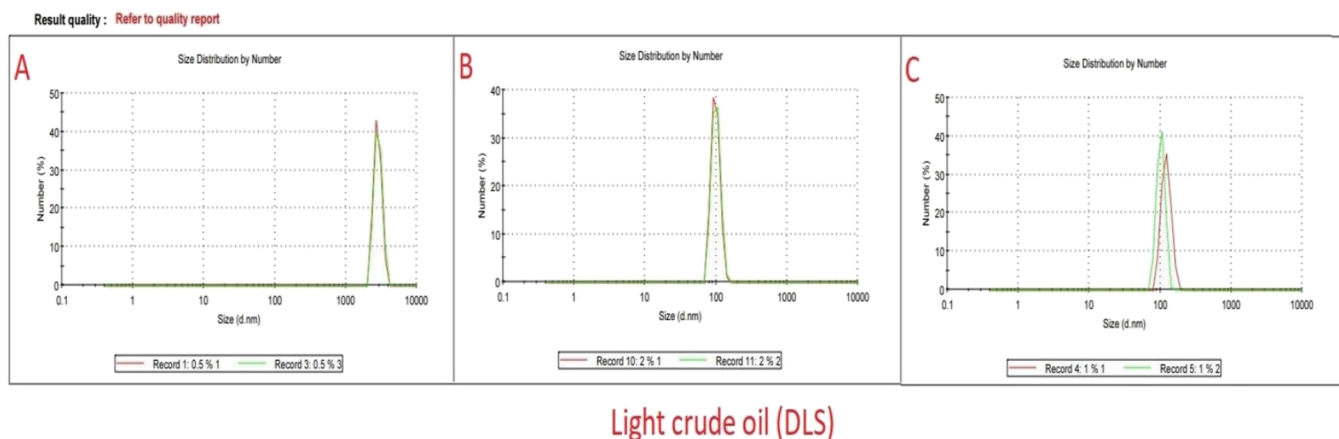


Figure 3. DLS test results for light crude oil with MNPs at (A) 0.5% PE + 2% MNPs, (B) 2% PE + 1% MNPs, and (C) 1% PE + 1% MNPs.

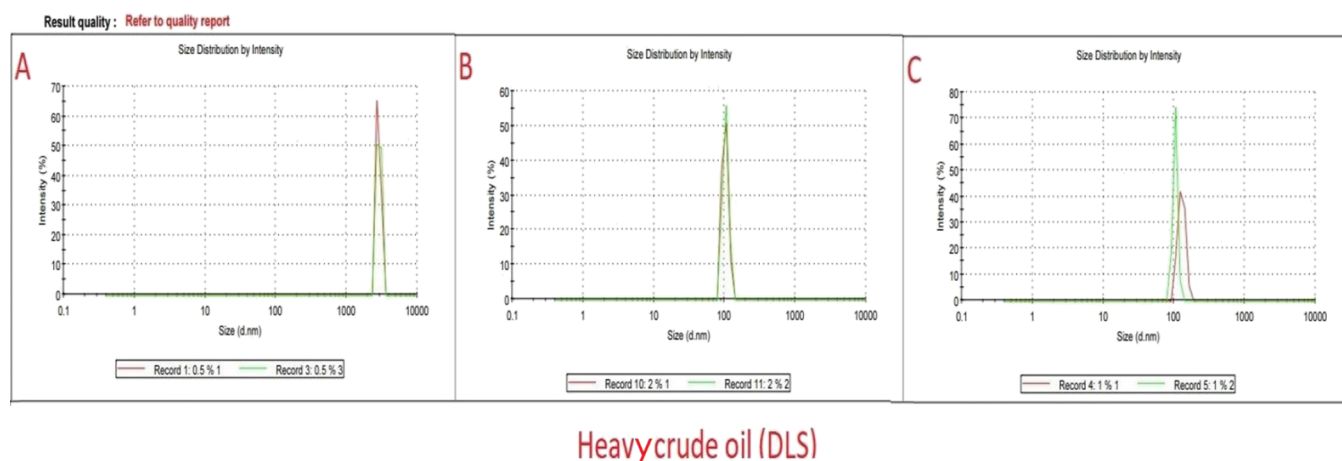


Figure 4. DLS test results for heavy crude oil with MNPs at (A) 0.5% PE + 2% MNPs, (B) 1% PE + 2% MNPs, and (C) 1% PE + 1% MNPs.

Table 5. Obtained results for light crude oil from GC testing

| no | retention time (°) | area percent | library ID | no | retention time (°) | area percent | library ID |
|----|--------------------|--------------|------------------------------------|----|--------------------|--------------|---|
| 1 | 8.5214 | 0.9129 | 1-octanol, 2-butyl- | 21 | 17.8941 | 3.437 | heptadecane |
| 2 | 9.7803 | 2.1983 | methoxyacetic acid, tridecyl ester | 22 | 18.4262 | 3.0931 | tetracosane |
| 3 | 10.5585 | 1.6969 | undecane | 23 | 18.7523 | 1.4345 | tricosane |
| 4 | 10.8446 | 2.8923 | 1-octadecanesulfonyl chloride | 24 | 18.9412 | 2.8836 | pentacosane |
| 5 | 11.5655 | 2.2323 | cyclotetradecane | 25 | 19.1128 | 1.3113 | 3,3'-dimethyl-1,5',8'-trihydroxy-2,2'-binaphthalene-1',4',5,8-tetrone |
| 6 | 11.7773 | 3.4233 | dodecane, 2,6,11-trimethyl- | 26 | 19.2444 | 0.783 | tricosane |
| 7 | 12.3266 | 2.9682 | 1-octadecanesulfonyl chloride | 27 | 19.4333 | 2.7101 | hexacosane |
| 8 | 12.6298 | 4.5992 | 1-octadecanesulfonyl chloride | 28 | 19.7251 | 0.9263 | heptacosane |
| 9 | 13.1505 | 2.7095 | carbonic acid, eicosyl vinyl ester | 29 | 19.9082 | 2.5499 | heptacosane |
| 10 | 13.4195 | 5.0187 | hexadecane | 30 | 20.0684 | 0.7233 | tricosane |
| 11 | 13.7857 | 1.2266 | hexadecane, 2,6,10,14-tetramethyl- | 31 | 20.1885 | 0.9031 | octacosane |
| 12 | 13.9116 | 2.5593 | undecane | 32 | 20.3659 | 2.5464 | octacosane |
| 13 | 14.1633 | 6.0347 | heptadecane | 33 | 20.6463 | 1.855 | octacosane |
| 14 | 14.6726 | 3.8938 | 1-octadecene | 34 | 20.8065 | 3.16 | nonacosane |
| 15 | 14.8614 | 4.9604 | octadecane | 35 | 21.0755 | 1.3141 | octacosane |
| 16 | 15.5252 | 4.8061 | nonadecane | 36 | 21.2357 | 2.4255 | triacontane |
| 17 | 16.1546 | 4.3617 | eicosane | 37 | 21.6934 | 1.2692 | hexacosane |
| 18 | 16.4292 | 1.3116 | 7-methyl-Z-tetradecen-1-ol acetate | 38 | 22.1855 | 0.863 | triacontane |
| 19 | 16.7611 | 4.0571 | heneicosane | 39 | 22.7463 | 0.466 | Tetratriacontane |
| 20 | 17.339 | 3.4826 | docosane | 40 | | | |

compound are from C14 to C22, which matches the hydrocarbons of the prepared samples.

Figure 6 represents the hydrocarbon compounds of the heavy crude oil constituents (from C9 to C22); the more

Table 6. Obtained Results for Heavy Crude Oil from GC Testing

| no | retention time () | area percent | library ID | no | retention time () | area percent | library ID |
|----|--------------------|--------------|---|----|--------------------|--------------|--|
| 1 | 9.031 | 1.2351 | 2(1H)-naphthalenone, octahydro-, trans- | 24 | 17.3507 | 2.3639 | 1-octadecene |
| 2 | 10.7075 | 1.1887 | pentadecafluoro-octanoic acid, octadecyl ester | 25 | 17.694 | 3.0252 | triacontyl pentafluoropropionat e |
| 3 | 11.068 | 0.6515 | pentadecafluoro-octanoic acid, octadecyl ester | 26 | 17.9057 | 3.1013 | tricosane |
| 4 | 11.6287 | 1.3827 | 1-dodecanol, 2-hexyl- | 27 | 18.4264 | 1.2404 | tricosane |
| 5 | 11.9377 | 1.1783 | oxalic acid, cyclobutyl hexadecyl ester | 28 | 18.7411 | 0.8889 | tetratriacontyl heptafluorobutyrate |
| 6 | 12.0979 | 1.1716 | decahydro-1,1,4a,5,6-pentamethylnaphthalen e | 29 | 18.9414 | 0.7975 | pentacosane |
| 7 | 12.4241 | 2.9422 | oxalic acid, isobutyl octadecyl ester | 30 | 19.1074 | 1.2849 | octacosanal |
| 8 | 12.6987 | 2.5162 | 1-decanol, 2-hexyl- | 31 | 19.2332 | 0.9145 | tricosane |
| 9 | 13.1966 | 2.2322 | octacosyl trifluoroacetate | 32 | 19.4392 | 0.9166 | hexacosane |
| 10 | 13.62 | 3.392 | octatriacontyl trifluoroacetate | 33 | 19.5937 | 0.8101 | tricosane |
| 11 | 13.7802 | 1.3296 | hexadecane, 1,1'-oxybis- | 34 | 19.7425 | 1.2391 | dotriacontyl trifluoroacetate |
| 12 | 14.1693 | 5.478 | pentadecane, 2,6,10,14-tetramethyl- | 35 | 19.9141 | 1.1631 | hexacosane |
| 13 | 14.3581 | 2.8616 | octatriacontyl trifluoroacetate | 36 | 20.0458 | 1.3129 | 2,6,10,14- tetramethyl-7-(3- methylpent-4-enylidene) pentadecane |
| 14 | 14.7072 | 2.2072 | dotriacontyl pentafluoropropionate | 37 | 20.2117 | 1.673 | octacosyl trifluoroacetate |
| 15 | 14.9017 | 5.7925 | hexadecane, 2,6,10,14-tetramethyl- | 38 | 20.3662 | 3.121 | octacosane |
| 16 | 15.451 | 5.6618 | octatriacontyl pentafluoropropionate | 39 | 20.658 | 2.8693 | octacosane |
| 17 | 15.7772 | 1.152 | dotriacontyl pentafluoropropionate | 40 | 20.8125 | 4.9849 | octacosane |
| 18 | 16.0232 | 2.3226 | 1-octadecene | 41 | 21.1272 | 2.0376 | hexacosane |
| 19 | 16.1663 | 2.6564 | dotriacontyl pentafluoropropionate | 42 | 21.2359 | 3.2664 | octacosane |
| 20 | 16.4237 | 1.2332 | disparlure | 43 | 21.4762 | 3.1322 | 2,6,10,14-tetramethyl-7-(3-methylpent-4-enylidene) pentadecane |
| 21 | 16.5897 | 2.3744 | dotriacontyl pentafluoropropionate | 44 | 21.6994 | 2.6085 | octacosane |
| 22 | 16.7785 | 1.8704 | cyclotetradecane, 1,7,11-trimethyl-4-(1-methylethyl)- | 45 | 22.2086 | 0.969 | octacosane |
| 23 | 17.139 | 3.1929 | octatriacontyl pentafluoropropionate | 46 | 22.6435 | 0.2568 | octacosane |

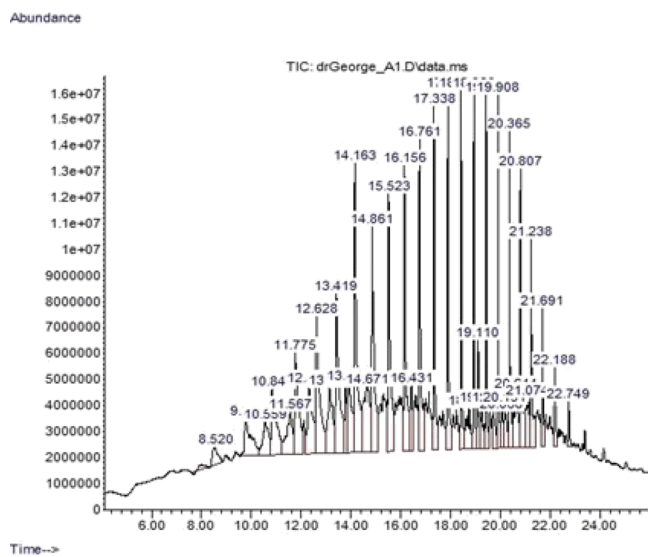


Figure 5. GC results of the blank sample of the light (A) crude oil from Borg El Aran at Oyun Musa.

percentages of hydrocarbon compound are from C17 to C22, which match the constituents of prepared samples.

The conclusions from these GC results are evidence for the compatibility between the chemical components present inside each crude oil blank and the chemical components present inside both additives, whether for polyethylene or magnetic nanoparticles.

3.3. Impact of the Additive Type on Wax Crystal Formation in Crude Oil.

Pour point depressants function by

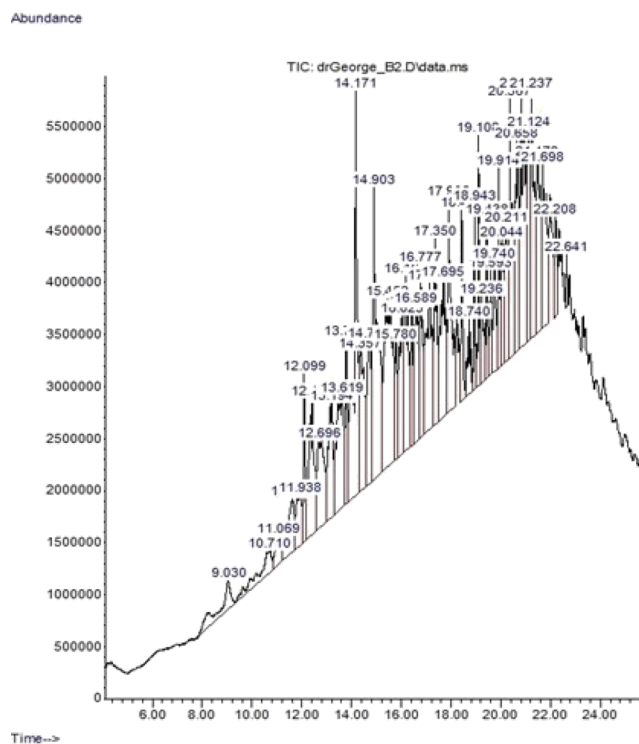


Figure 6. GC results of the blank sample of the heavy (B) crude oil from Petroshahd petroleum Co. at Shark Ras El Katara.

adhering to the wax crystals' surface. The consequent surface layer of the pour point depressants stops wax crystals from

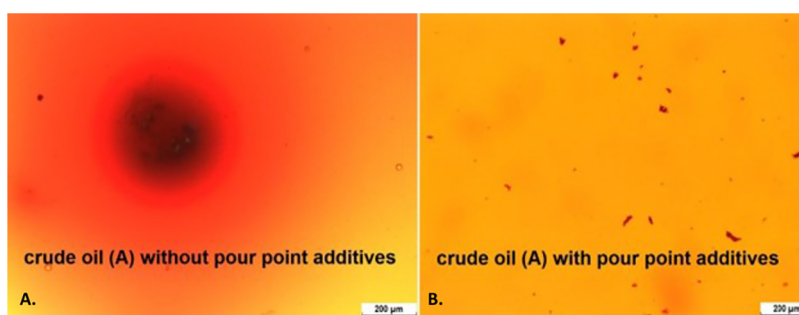


Figure 7. Wax morphology of (A) untreated and (B) treated light (A) crude oil with pour point additives of 0.25% PE + 2% MNPs.

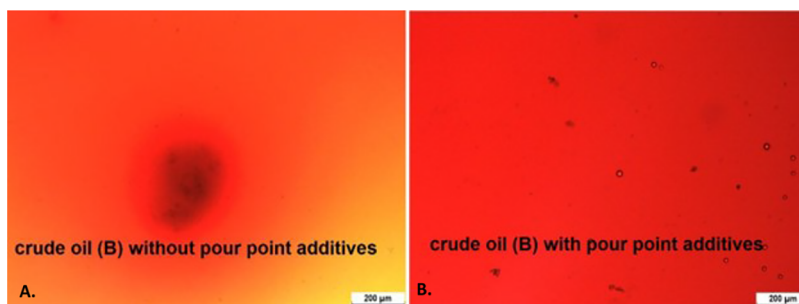


Figure 8. Wax morphology of (A) untreated and (B) treated heavy (B) crude oil with pour point additives of 0.25% PE + 2% nanoparticles.

growing, preventing them from absorbing oil and gelling.^{11,19–22} The observed pour point temperatures of 0.25% PE + 1% MNPs, 0.25% PE + 2% MNPs, and 0.5% PE + 2% MNPs of heavy (B) crude oil and 0.25% PE + 2% MNPs, and 0.5% PE + 2% MNPs of light (A) crude oil samples were less than -36 °C. In contrast, the pour points of blank samples are $+6$ °C and $+27$ °C for light and heavy crude oils, respectively. Thus, the crude oil modified with PE additives and MNPs emphasized a comparatively significant drop in pour points.

By examining the various behaviors of the wax crystallization process, photoanalysis supports other standardized tests that compare the cold properties of treated and untreated crude oils.^{11,23} It is applied here to measure the previously prepared sample's action and its additives as a wax inhibitor or as a pour point depressant by wax modifications based on their concentration and type. Figures 7 and 8 illustrate the photomicrographs of wax morphology of an untreated and modified crude oil with PE additives for both light (A) and heavy (B) crude oil types, respectively.

The untreated oil samples contain large dark circular structured droplets accumulated from wax-like crystals, as shown in Figures 7A and 8A. The modified oil samples treated with additives show a significant wax crystal reduction in the formation and size of a large number of dispersed delicate crystals, as shown in Figures 7B and 8B. Further, with the use of additives, the photomicrographs became much more apparent because of the nonappearance of the accumulated fine crystals and the morphological change in the crystal network structure. The obtained results are parallel with the previous findings.^{11,24}

3.4. Rheological Properties of the Prepared Additives on Crude Oil. When the shear rate increases, viscosity falls for both light (A) and heavy (B) crude oils, as shown in Figures 9 and 10, respectively. The crude oil behaviors and their products are based on rheological measurements and a simple form of a Newtonian fluid (where it has a viscosity with a

shear-independent rate). Newtonian fluid is a liquid that immediately flows upon the application of a minor source of force and where the flow rate is proportional to the applied force's rate. The prepared sample of the treated light (A) crude oil provided a more excellent rheology performance than the heavy (B) crude oil. The results are parallel with the previous findings.^{24,25}

4. CONCLUSIONS

The significant findings of the study can be concluded as follows:

DLS results revealed that nanoparticles of heavy (B) crude oil have a bigger particle size (average between 204.4 and 2877 nm), while light (A) crude oil samples have smaller size particles (average between 100.5 and 2861 nm). Thus, the overall distribution of the added nanoparticles was much better in light crude oil than in heavy crude oil.

The prepared crude oil samples with PE additives and MNPs are effective as pour point depressants.

The GC results provided evidence for the compatibility between the chemical components present inside each crude oil blank and the chemical components present inside both additives, whether for polyethylene or for magnetic nanoparticles.

The photomicrographic results revealed that the samples treated using additives provided a significant wax crystal reduction compatible with the provided pour point results.

The prepared sample of the treated light (A) crude oil provided a more extraordinary rheology performance than the heavy (B) crude oil.

Finally, this research provided a very affordable product that can be used for enhancing the production of crude oil better by reducing the accumulation of the wax crystal structure, solving its transportation problems during winter, and reducing pollution generated from the waste plastics of polyethylene.

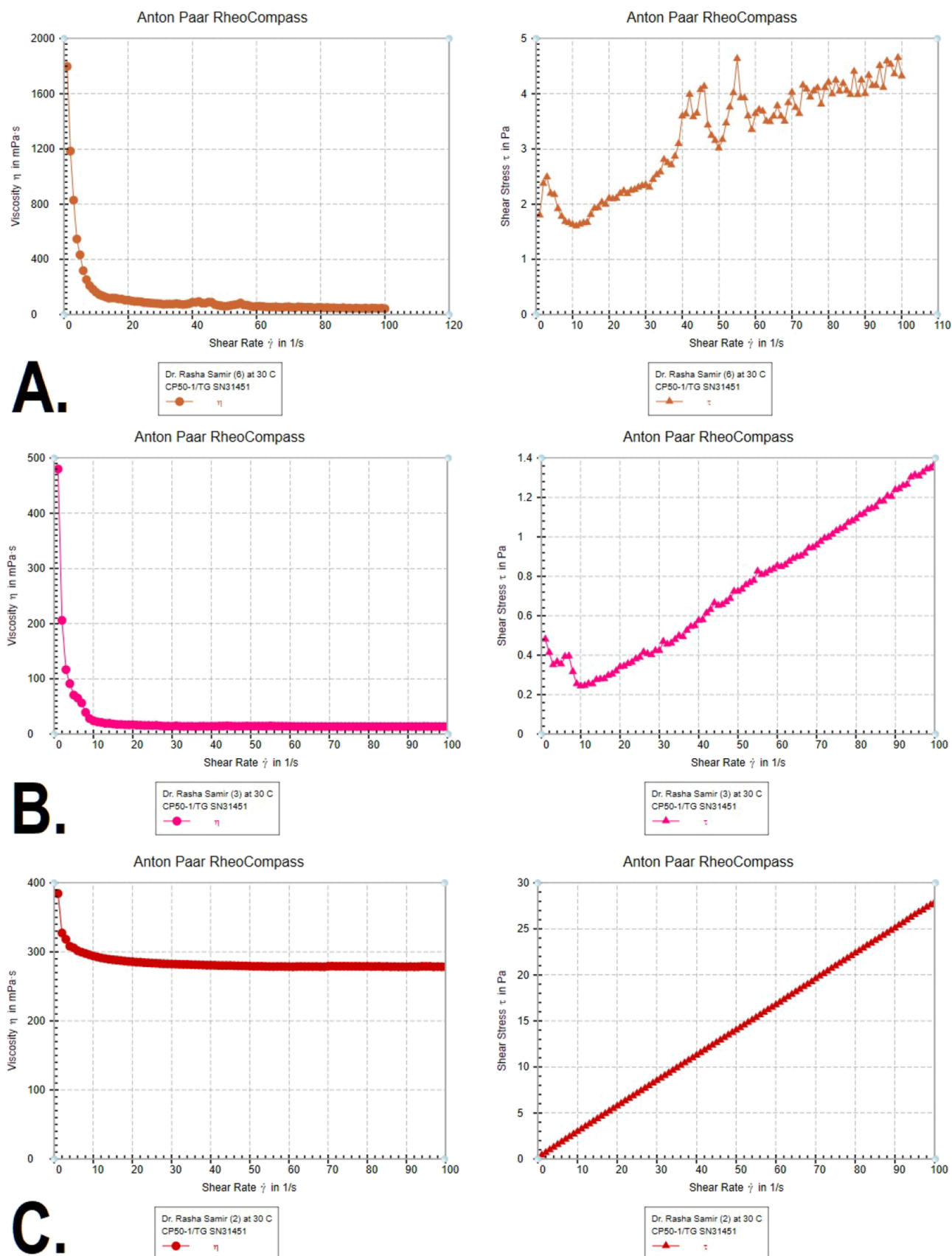


Figure 9. Rheological behavior of the 0.25% PE with (A) 0.5% nanoparticles, (B) 1% nanoparticles, and (C) 2% nanoparticles for light (A) crude oil.

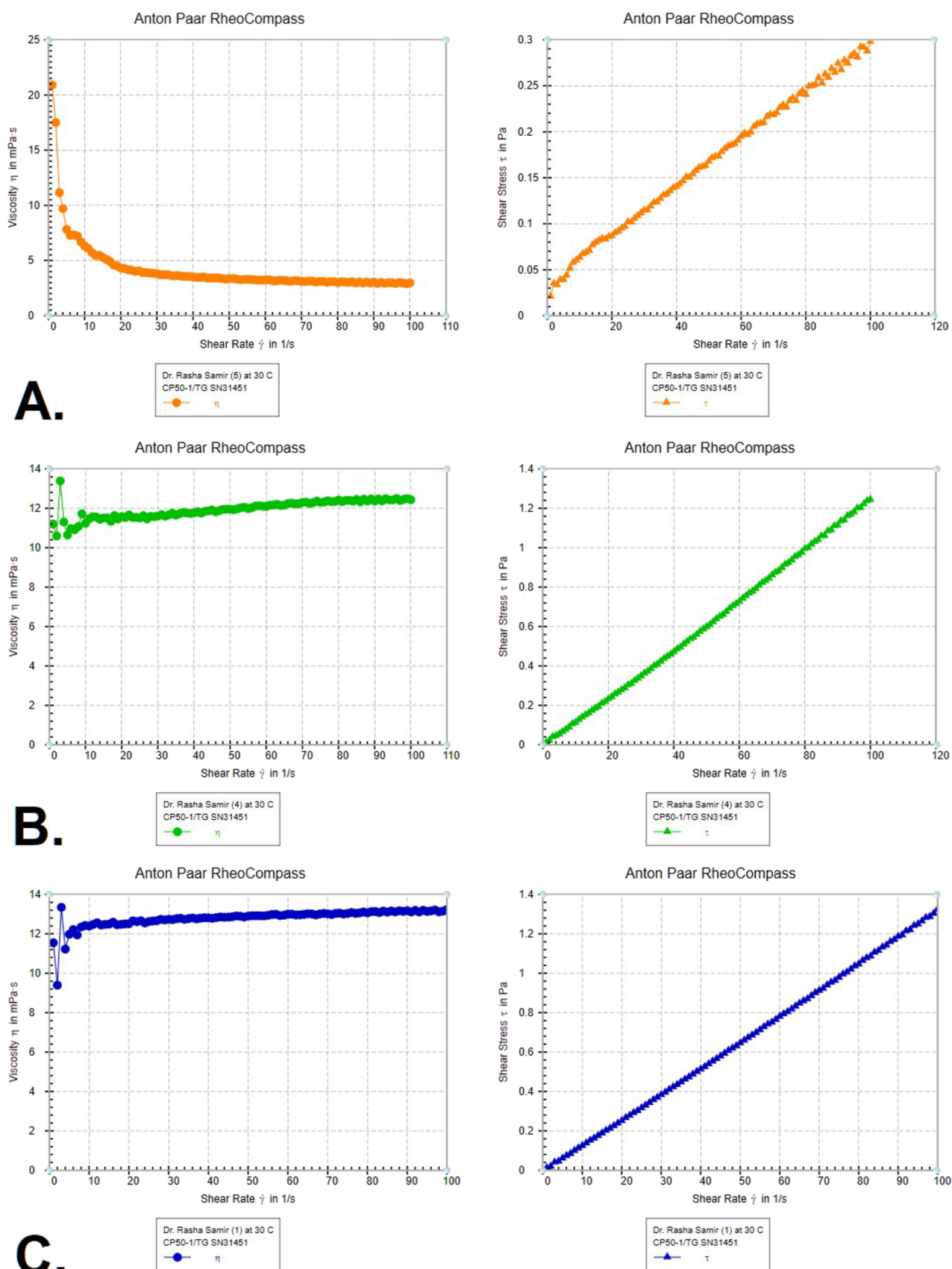


Figure 10. Rheological behavior of the 0.25% PE with (A) 0.5% nanoparticles, (B) 1% nanoparticles, and (C) 2% nanoparticles for heavy (B) crude oil.

AUTHOR INFORMATION

Corresponding Author

George Michel – Faculty of Biotechnology, October University for Modern Sciences and Arts, Giza 3210001, Egypt;

orcid.org/0000-0002-4168-7449; Email: for.all123@outlook.com

Authors

Rasha S. Kamal – Department of Petroleum Applications, Egyptian Petroleum Research Institute, Cairo 11727, Egypt

Amr Ageez – Faculty of Biotechnology, October University for Modern Sciences and Arts, Giza 3210001, Egypt

Reem K. Farag – Department of Petroleum Applications, Egyptian Petroleum Research Institute, Cairo 11727, Egypt

Complete contact information is available at:

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Notes

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