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Comparison of rheological properties of graphene / carbon nanotube hydrogenated oil based biodegradable drilling fluid

Y H Chai[1], **S Yusup**[1], **V S Chok**[2], **S Irawan**[3], **J D B S Singh**[4], **B L F Chin**[5]

[1] Biomass Processing Laboratory, Center of Biomass and Biofuels Research, MOR Green Technology, Chemical Engineering Department, Universiti Teknologi PETRONAS, Seri Iskandar, 32160 Perak, Malaysia
[2] Chemical Engineering Department, Heriot-Watt University Malaysia, No. 1, Jalan Venna P5/2, Precinct 5, 62200 Putrajaya, Malaysia
[3] Petroleum Engineering Department, Universiti Teknologi PETRONAS, Seri Iskandar, 32160 Perak, Malaysia
[4] Graphene Nanochem Plc, Suite 0.2, Level 9, WORK@Clearwater Changkat Semantan, Off Jalan Semantan, Damansara Heights, 50490, Kuala Lumpur, Malaysia
[5]Department of Chemical Engineering, Curtin University Sarawak Campus, CDT 250, Miri 98009, Sarawak Malaysia

E-mail: drsuzana_yusuf@utp.edu.my

Abstract. An experimental investigation has been carried out to investigate the rheological properties of graphene / carbon nanotube hydrogenated oil based biodegradable drilling fluid at different nanoparticle loadings. The rheological behaviours of interest in this investigation are the viscosity and shear stresses of two different nanofluids respectively. The limiting parameters in this study are 25 ppm, 50 ppm and 100 ppm weight concentration at operating temperature ranging from 30^{o}C to 50^{o}C. Both nanofluids are subjected to shear rate ranging from 0 – 140 s^{-1} for comparison of rheological behaviours. Both samples' viscosity reduces to base fluid's viscosity value at higher shear rate with carbon nanotube-hydrogenated oil yielding higher viscosity compared to graphene-hydrogenated oil for all nanoparticle loadings at lower shear rate. Shear stress analysis also shows similar results with carbon nanotube based samples showing higher stress between the two at all particle loadings. Both samples show Newtonian behaviour that is similar to base fluid even at higher particle loadings. Analysis revealed both nanofluids yields close to zero yield stress even with the presence of graphene or carbon nanotube particles. The significance of this study shows that addition of low nanomaterials for enhancement of drilling fluids can improve its thermophysical properties without compromising the quality of drilling fluids such as viscosity and shear stress properties.

1. Introduction

Drilling fluids are categorized into three general types, namely water based mud (WBM), oil based mud (OBM) and synthetic based mud (SBM). While such drilling fluids are widely available in the market, the need for an environmental friendly drilling fluids which possess low toxicity and biodegradable attributes are highly desired [1].

In the drilling sector, the formulation of a potentially suitable drilling fluid is greatly sought after. Drilling fluids readily deteriorate when subjected to high temperature and high pressure environment

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hinders drilling operations [2]. The variations in conditions of reservoir types and drilling processes requires suitable drilling fluids to be customized accordingly. The incorporation of nanotechnology to develop and improve drilling fluid formulations is regarded as one of the solutions to such problems [3].

Nanofluids are made up of binary systems where solid and liquid phases are present which contains metallic or non-metallic nanoparticles suspensions that have the average size of 100 nm or less [4]. Numerous investigations exhibited nanofluids with enhanced thermophysical properties such as thermal conductivity, electrical conductivity and viscosity. Kole and Dey [5] obtained up to 15% thermal conductivity enhancement with 0.395 vol% functionalized graphene in ethylene glycol. Hadadian et al. [6] observed an anomalous enhancement in electrical conductivity properties in distilled water at 25,678% enhancement at 0.0006 mass fraction of graphene oxide at room temperature. Furthermore, Ding et al. [7] dispersed 0.5 wt% carbon nanotubes into distilled water to achieve over 350% enhancement in heat convection at laminar flow.

Addition of nanoparticles have been proven useful in heat transfer applications especially at higher nanoparticle loadings but the trade-off point resulted in the increase of nanofluid viscosity. Mishra et al. [8] reported that viscosity of nanofluids increases with respect to the volume concentration of nanoparticles. While effect of viscosity could be unfavourable to heat transfer systems [8], benefit of high viscosity properties in drilling fluids enable solid cuttings to be kept at suspension at low shear rate to prevent sagging when channelling drilling muds out from the wellbore [9]. However, Vajjha and Das [10] showed that particle loadings greater than 3 vol% exhibits penalty drop and increment in pumping costs.

Despite numerous publications regarding the thermo-physical properties of nanofluids, there has been little publications on the rheological behaviour of nanofluids [11-13] especially on the rheological behaviours of vegetable oil containing nanoparticles.

The focus of this paper investigates the rheological properties of hydrogenated oil-based drilling fluid which is dispersed with graphene nanosheet and carbon nanotube nanoparticles respectively by using hydrodynamic and acoustic cavitation (HAC) combination as two-steps dispersion method.

2. Materials and Methods

2.1. Materials

All materials in this study, namely hydrogenated oil-based drilling fluid, graphene nanosheet and carbon nanotube powders, were procured from Platinum Green Chemicals Sdn. Bhd., Malaysia. Fourier Transform Infrared (FTIR) spectroscopy analysis of graphene nanosheet and carbon nanotube is as shown in Fig. 1 and Fig. 2 respectively. Both FTIR spectra shows the presence of O-H functional groups which falls within the range of 2800 to 3500 cm^{-1} which shows good agreement with the presence of stretching vibrations of O-H bonds [14].

There are trace presence of halogen atoms exists in both nanoparticles. C-N stretching at 1100 cm^{-1} is found on graphene nanosheet surfaces while CH_2X groups is found on the surface of carbon nanotube to form alkyl halides. The presence of nitrogen as halogen maybe derived during the preparation and exfoliation of graphene nanosheets and carbon nanotubes using nitric acid [15].

Hydrogenated oil is comprised of a mixture of straight chain and branched paraffin of carbon chain length from C15 to C18. The thermophysical properties of hydrogenated oil is highlighted in Tab. 1.

2.2. Nanofluids preparation

The targeted concentration of nanoparticles in this study are fixed at very low nanoparticle loadings, namely 25 ppm,50 ppm and 100 ppm for both graphene nanosheet and carbon nanotube respectively to ensure no alteration on the rheological behaviour of hydrogenated oil-based nanofluids.

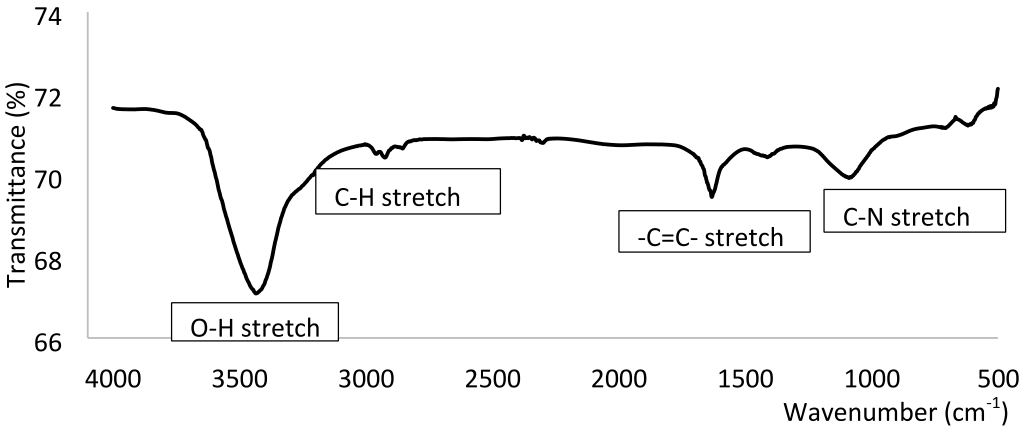

Figure 1. FTIR spectra of graphene nanosheet.

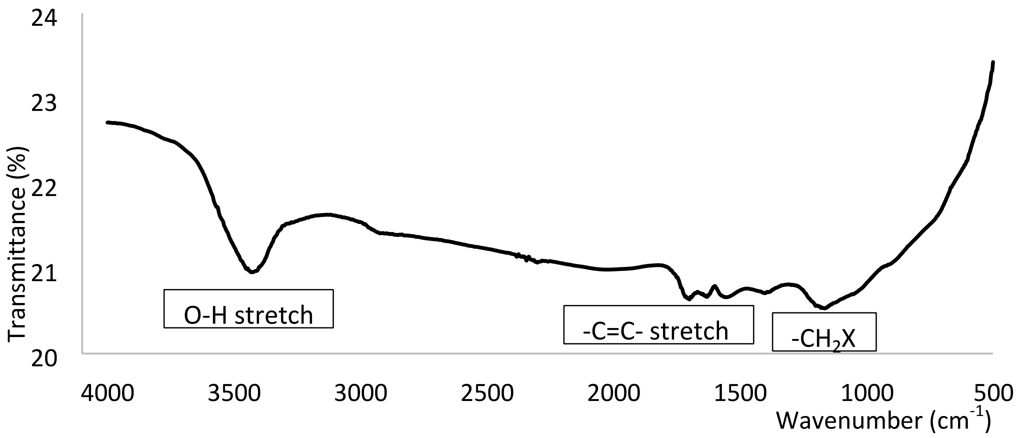

Figure 2. FTIR spectra of carbon nanotube.

Table 1. Thermophysical properties of hydrogenated oil.

Density (kg/m^3)	Viscosity (cP)	Boiling Point (°C)	Oxidizing Properties
780 (at 15°C)	1.5 – 2.0 (at 40°C)	330	None

Two-steps dispersion method was used to physically disperse nanoparticles into hydrogenated oilbased drilling fluids via hydrodynamic and acoustic cavitation (HAC) combination. Before each HAC dispersion at all concentrations, nanoparticles are pre-homogenized via high-speed shearing at 800 rpm constantly for 15 minutes with the schematic set-up as shown in Figure 5.

Pre-homogenized nanofluids were transferred to a single-stage hydrodynamic cavitation (HC) unit for further dispersion. A variable frequency drive (VFD) pump with the range of 0 to 50 Hz frequency was used to control the inlet flow of nanofluid to one-hole orifice with outer diameter of 1 mm. HC dispersion was carried out for 3 hours at 10 bar with flow rate of 1.5 L min^{-1} averagely.

Bath Ultrasonic Branson 8510E-DTH with 320 W power and 40 kHz frequency was used to homogenize nanofluid samples. Samples carried out in HC dispersion were collected and transferred to

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ultrasonic bath for 3 hours of ultrasonication process to further homogenize the suspended nanoparticles in hydrogenated oil-based nanofluid.

2.3. Rheological analysis

Malvern Bohlin Gemini II Rheometer was used to measure the viscosity and shear stress values of hydrogenated oil-based nanofluids. The rheometer is connected to a PC controlled Peltier plate temperature controller to vary the temperature. The pre-set gap for the spindle to the plate is set at 30 µm. The selected spindle in this study is a stainless steel cone-and-plate spindle with 2° angle and 40 mm diameter.

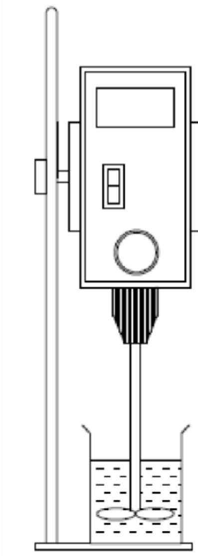


Figure 3. Schematic set-up of high speed stirrer.

All measurements have a delay time and integration time of 10 seconds to record data at steady state conditions. In this study, the data collection of the rheometer is viscosity and shear stress parameters with respect to temperature, shear rate, nanoparticle concentration and types. The shear rate in this study is within the range of 0 to 140 s^{-1} at the temperature range of 30°C to 50°C with 10°C step increase. Each measurement was repeated 3 times with a new sample to ensure the hydrogenated oil-based nanofluids do not deform when subjected to stress. Each samples were subjected to 20 minutes of ultrasonication to ensure homogeneity in each samples before performing rheological analysis.

3. Models

The application of rheological models to determine the shear stress – shear rate relationships are used to predict rheological behaviours due to an array of applications with various rheological characteristics. Non-Newtonian models considered in this study are Bingham Plastic model and Power Law model that are widely used for prediction of rheological behaviours.

3.1. Bingham Plastic model

Bingham Plastic fluids exhibit an “infinite” viscosity until a sufficiently high stress is applied to initiate flow. Eq. 1 shows the Bingham Plastic model.

$$\sigma = \sigma_o + \mu \quad (1)$$

where σ is the shear stress, σ_0 is the limiting shear stress, μ is the viscosity and γ is the shear rate.

The limiting shear stress is often referred to as Bingham yield stress of the material [16]. The Bingham Plastic model is calculated by a simple regression analysis due to its linear equation model.The Bingham Plastic model is suitable for colloidal systems that shows Bingham behaviours.

3.2. Power Law model

The Power Law model is also referred to as Ostwald model. Numerous non-Newtonian materials behaves differently as the shear rates increase. The changes made to viscosity at increasing shear rate can be categorised into two groups, namely shear thinning and shear thickening.

Shear thinning or pseudoplastic effect refers to the decrease in viscosity at higher shear rate while shear thickening has the opposite effect. The Power Law model is shown in Eq. 2.

$$\sigma = \mu . \gamma^{n} \tag{2}$$

where σ is the shear stress, , μ is the fluid viscosity, γ is the shear rate and n is the power law index of the material. When $n < 1$, the material possess shear thinning behaviour while $n > 1$ shows a shear thickening fluid

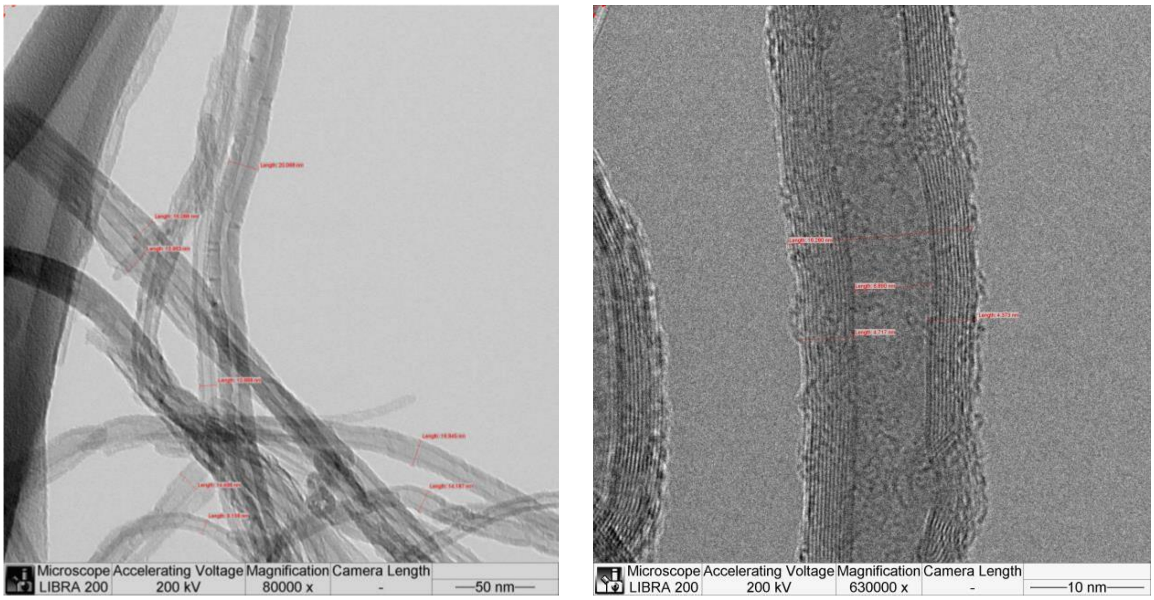
The Power Law model is suitable for material that flows under small shear rate range between 10^1 to 10^4 s^{-1} [16]. At higher shear rate range, the materials will deviate from this relationship.

4. Results and Discussions

4.1. TEM analysis of nanoparticles

Transmission electron microscope (TEM) images of nanoparticles types are taken with Zeiss Libra 200FE Microscope. Fig. 4 shows an image of graphene nanosheet which was taken at 20,000x magnifications. Several dark layers are superimposed on one another which denotes stacking of several graphene nanosheet layers. At Fig. 5(a), image of carbon nanotubes are taken at 80,000x magnification with average outer diameter within the range of 10 to 12 nm.

Figure 4. TEM image of graphene nanosheets at 20,000x magnification.



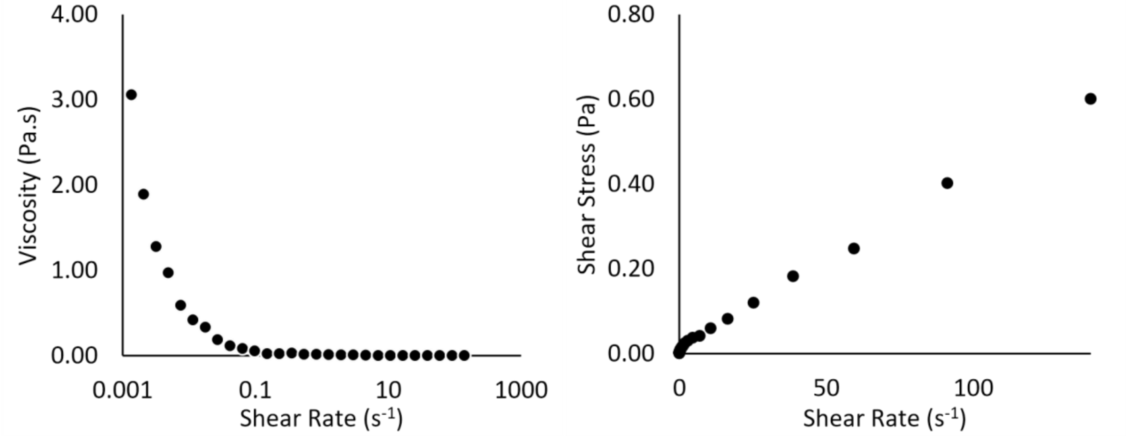
(a) (b)

Figure 5. TEM image of carbon nanotubes at (a) 80,000x and (b) 200,00x magnification.

Furthermore, it can be seen from Fig. 5(a) carbon nanotubes are easily entangled with one another due to its high length-to-diameter (L/D) ratio. The mean diameter outer layer thickness is 4.7nm with inner diameter within the range of 7 nm as shown in Fig. 5(b).

4.2. Rheological properties of hydrogenated oil-based drilling fluid

The rheological behaviour of hydrogenated oil-based drilling fluid can be deduced from the relationship between viscosity, shear stress and shear rate parameters. Fig. 6(a) and Fig. 6(b) shows the viscosity and shear stress with respect to shear rate at 30°C respectively.



(a) (b)

Figure 6. Graphical illustrations of (a) viscosity and (b) shear stress of hydrogenated oil-based fluid at 30°C.

Bingham fluids behave rigidly at very low stresses but flows as viscous fluids when sufficient stress is applied. Although Fig. 6(b) depicts similar rheological profile to a Newtonian fluid, the viscosity shown in Fig. 6(a) decreases exponentially with increasing shear rates. Viscosity of Newtonian fluid remains constant regardless of shear rate applied, while viscosity of Bingham fluid varies with respect to shear rate.

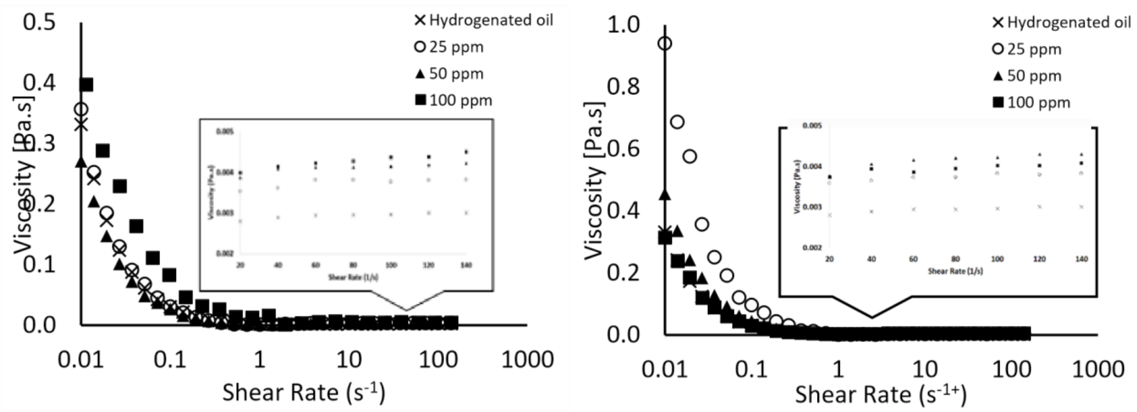
Therefore, hydrogenated oil-based drilling fluid used in this study exhibits Bingham fluid properties with shear thickening behaviour and near zero shear stress.

4.3. Effect of nanoparticle concentration on viscosity of hydrogenated oil-based nanofluids

As observed from Fig. 7(a) and Fig.7(b), the addition of nanoparticles does not influence the viscosity profile of hydrogenated oil-based nanofluid. At very low shear rates, the viscosity of nanofluids are closely similar and overlapped at all concentrations at the higher shear rate range.

The addition of nanoparticles increases the viscosity properties of hydrogenated oil with respect to concentration. Similar findings by other researchers also show viscosity of nanofluids increases with respect to concentrations but decreases at higher shear rates [5; 17-18]. The increase in solid particle concentrations within liquid suspension increases the inter-particle frictions which increases the resistance of fluid to flow and subsequently increases the viscosity of nanofluids [17].

The effect of nanoparticle "jamming" at the bottom of the cone-and-plate spindle should be taken into account contributing in minor fluctuations of viscosity as seen in Fig. 8.



(a) (b)

Figure 7. Effect of (a) graphene nanosheet and (b) carbon nanotube concentration at 50°C on viscosity of hydrogenated oil-based nanofluid.

Furthermore, it can be observed from Fig. 7 (a) and Fig. 7(b) hydrogenated oil-based nanofluids exhibit slight shear thickening behaviour at higher shear rate. Ijam et al**.** [19] and Kinloch et al. [20] both attributed this profile to the percolation structure of nanoparticles suspended in the base fluid. The percolation structure formed is broken down when high level of shearing is achieved to form primary particles and subsequently the stress and viscosity increases with increasing rate.

4.4. Effect of temperature on viscosity of hydrogenated oil-based nanofluids

Viscosity properties is also influenced by temperature. At higher temperature, the viscosity of all fluids yielded lower viscosity values as compared to lower temperature conditions at similar concentrations. Fig. 8 shows a linear declining relationship between viscosity and temperature regardless of the types of nanoparticles dispersed into hydrogenated oil.

The intermolecular attractions between nanoparticles and the particles of base fluids are highly influenced by temperature. The increase in temperature provides higher energy into the system, which subsequently decreases the interparticle and intermolecular adhesive forces of the particles [21] leading to the decrease of fluid's viscosity. Similar results by other researchers [19; 22] exhibit identical behaviour as well.

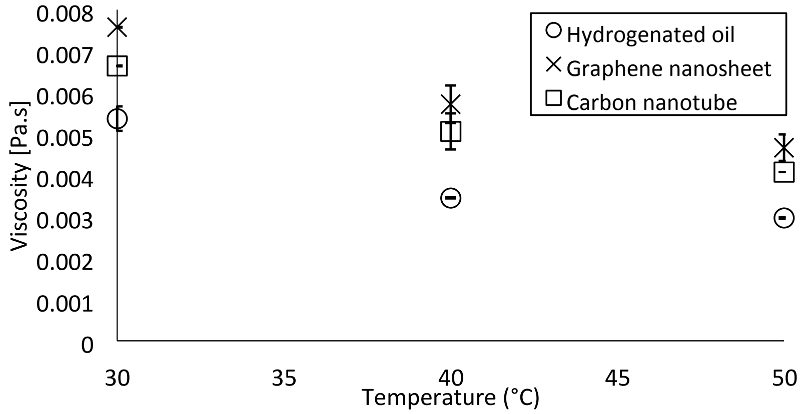


Figure 8. Effect of temperature on viscosity of hydrogenated oil-based nanofluid

4.5. Effect of nanoparticle concentration on rheological behaviour of hydrogenated oil-based nanofluids

Figure 9(a) and Figure 9(b) shows the comparison between experimental data and rheological models of graphene nanosheets and carbon nanotubes nanofluids with respect to different nanoparticle concentration respectively. As observed, Bingham model gave a better fitting compared to Power Law model at all concentrations.At lower shear rate, the experimental data are able to fit closely to the Power Law model. However, the predicted shear stress values deviated further away from the experimental data at higher shear rate. This is attributed to the flow behaviour index, $n > 1$, as there is slight shear thickening at higher shear rates as observed in Figure 7(a) and Figure 7(b).

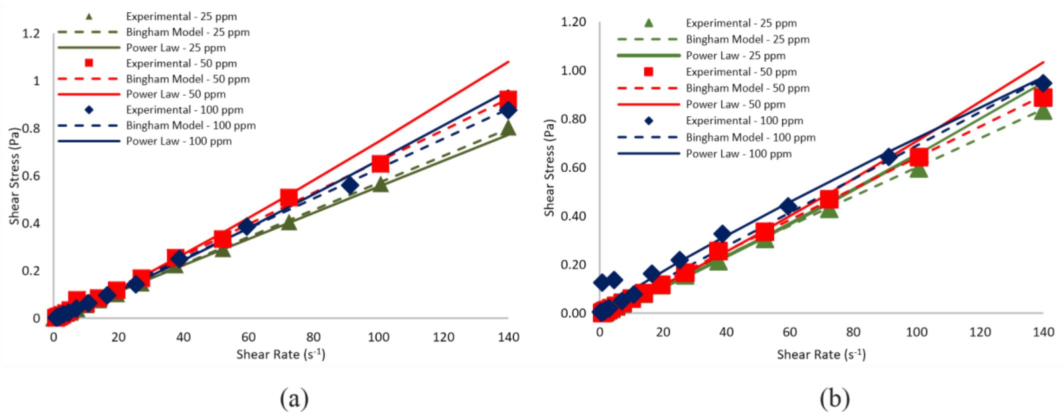


Figure 9. Comparison of experimental data and rheological models of (a) graphene nanosheet and (b) carbon nanotube – hydrogenated oil-based nanofluid at 30°C

5. Conclusion

From this study, hydrogenated oil-based fluid exhibit a non-Newtonian behaviour with shear thinning properties. The presence of very low nanoparticles loadings increases the viscosity of hydrogenated oilbased nanofluids and does not change its rheological behaviour. The slight increase in viscosity and shear stress properties maybe useful in the oil and gas industry in suspending solid cuttings during drilling operations while simultaneously improving the thermophysical properties of drilling fluids.

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