Surface Modification of Carbon Nanotubes as a Key Factor on Rheological Characteristics of Water-Based Drilling Muds

Kazemi-Beydokhti, Amin*$^{+}$**; Hajiabadi, Seyed Hasan; Sanati, Ali**
Petroleum and Petrochemical Engineering School, Hakim Sabzevari University, Sabzevar, I.R. IRAN

ABSTRACT: *This study investigates the effect of functionalized Multi-Walled Carbon NanoTube (f-MWCNT) on rheological properties of water-based drilling muds. Functionalization of multi-walled carbon nanotube was performed by introducing a hydrophilic functional group onto the surface of nanotubes via acid treatment. In order to guarantee the results, X-ray fluorescence, transmission electron microscopy, and thermogravimetric analysis were performed on samples. Temperature and mud density variations were also considered along with the effect of f-MWCNT addition. Furthermore, a novel study was performed on the influence of the degree of functionalization on plastic viscosity and yield stress of drilling mud samples. The results obtained from this study revealed that the addition of f-MWCNT greatly affects the rheological characteristics of water-based drilling muds like plastic viscosity, apparent viscosity, yield stress, and thixotropic properties. Moreover, test results indicated that the shear stress versus shear rate diagram fitted well the Herschel-Bulkley rather than the Bingham plastic model.*

KEYWORDS: *Carbon nanotube; Degree of functionalization; Water-based drilling fluid; Plastic viscosity; Yield stress.*

INTRODUCTION

Performing a successful drilling operation is greatly dependent on the proper design of the drilling fluid [1, 2]. Drilling fluid as defined by the American Petroleum Institute (API) is a mixture of natural and synthetic chemical compounds used in rotary drilling for cooling and lubricating the drill bit. In addition, cleaning the bottom-hole, carrying drilled cuttings to the surface, controlling the formation pressure, maintaining wellbore stability, exerting hydrostatic pressure against formation fluids and ultimately improving the performance of the drill strings and equipment used in drilling operation are among critical functions of drilling muds [3-9]. In order to achieve these goals, different kinds of fluids including liquid or gas or a mixture of liquids and solids can be used in drilling operation [10]. Drilling fluids based on the continuous phase inside them are generally divided into two groups, Water Based Muds (WBMs) and Oil Based Muds (OBMs) [4]. Drilling muds are defined as a specific group of drilling fluids having a high viscosity which is used in deep wells [5]. Despite some excellent

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** To whom correspondence should be addressed.*
+ E-mail: a.kazemi@hsu.ac.ir
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features of oil-based drilling muds such as shale inhibition properties, for reasons like high cost of operation in lost circulation conditions, environmental hazards, increasing risk of fire, impairment of well logging data, formation damage, difficulties in kick control due to gas solubility and possible damages to rubber parts in the circulation system, they are not frequently used in the drilling industry. Therefore, water-based muds are preferred in most conditions such that more than 80 percent of drilling muds used nowadays are of this type [11, 12].

Aqueous and non-aqueous drilling fluids exhibit complex non-Newtonian behavior [13]. Suitable drilling muds must have appropriate rheological properties to perform the above-mentioned tasks [3]. On this basis, the suitability of the additives used in drilling muds can be evaluated according to API standards with factors like its ability to create plastic viscosity, yield stress, apparent viscosity and thixotropic properties [12, 14]. Rheology is best described as the study of the deformation (for solid materials) or flow (for liquid materials) behavior under applied stress [7]. Flow models commonly used in the petroleum industry are defined using consistency curves which are pressure versus flow rate or shear stress versus shear rate diagrams. Based on these diagrams, fluids are divided into Newtonian, Bingham plastic, pseudoplastic or dilatant [4].

Additives used to control the drilling mud viscosity are generally divided into two groups: viscosity enhancers and viscosity reducers [15]. Bentonites due to their hydrophilic property are the most important additives for improving the viscosity of water-based muds [14]. The main mineral component of bentonite is montmorillonite having the highest amount of inflation among the other clays, but in addition, it may contain minerals such as illite, kaolinite, chlorite and also non-clay components which may lead to reducing its viscosifying power. For this reason, other additives should be added to obtain suitable rheological properties [15]. Other examples of viscosity enhancers are asbestos, attapulgite, and polymers [14, 16]. Nowadays, nanomaterials due to their specific physical, chemical, mechanical, electrical, hydrodynamic and thermal properties are the most promising additives used in the petroleum industry [17]. Nanoparticles are defined as solid particles or solid dispersions that are in the size range of 1 to 100 nm. Amanullah and Al-tahini defined nanofluids as the fluids that contain at least one additive of nano-scale size [1]. Due to the ultra-small size of nanoparticles and its proximity to the atomic scale, the laws governing the behavior of these particles are quite different from macro and microparticles [18]. The main purpose of using nanoparticles in drilling fluids is to prevent drilling mud from filtration into the shale formations in high-temperature conditions because normal water-based muds cannot block nanopores of shales resulting in an increased filtration volume and clay swelling around the wellbore [12]. The presence of nanoparticles in drilling mud may result in the blocking of micro-cracks in the shales, thus creating a dense, narrow and an impermeable filter cake. Such mud cake decreases the possibility of lost circulation and stuck pipe due to differential pressure and improve wellbore stability [1]. *Halali et al.* reported that the presence of nanoparticles can reduce the filtration volume of drilling muds up to 95% [19]. In addition, studies have shown that the use of nanoparticles, even in very low concentrations, results in improved electrical properties and thermal and rheological stability of drilling mud [1, 8, 11]. The most important reasons for the optimal performance of nanoparticles in drilling muds include improved surface properties due to the large surface area of nanoparticles, good impact in very low concentrations (less than 1%) of nanoparticles, lower erosion and mechanical defect in equipment due to less kinetic energy and enhanced environmental safety with respect to other materials [8, 17, 20, 21].

Abdou et al. investigated the rheological properties, filtration and gel strength of local bentonite and nano-bentonite and compared them with API bentonite. The results obtained were not satisfied with the API standard [15]. *Khalil et al.* studied the viscoplastic behavior of a biopolymer drilling fluid using eight different rheological models to choose a proper model fitted the experimental data. Results showed that the fitting process was able to successfully predict the rheological behavior of these fluids[22]. Temraz and Hassanein found that the addition of carboxymethylcellulose (CMC) to drilling fluid enhanced the rheological and filtration properties of it and made it suitable for drilling medium depth wells [14]. *Vipulanandan* and *Mohammed* studied the effect of temperature on rheological properties and electrical resistivity of water-based drilling muds prepared with bentonites modified with nanoclays. Their results showed that nanoclay decreased the electrical resistivity of the drilling mud and increased the Yield Stress (YP) and Plastic Viscosity (PV). The addition of Nano-clay also increased the Apparent Viscosity (AV) and the gel strength of the drilling muds [8]. Meister et al applied a graft copolymer in bentonite drilling mud resulted in lower yield stress, lower gel strength and lower API filtrate volume for treated drilling fluids[23]. *Li et al.* studied the effectiveness of Cellulose NanoParticles (CNPs) in enhancing the rheological and filtration performance of WBMs. Results indicated the superior rheological properties, higher temperature stability and better fluid loss characteristics for this additive [24]. *Sadeghalvand* and *Sabbaghi* used TiO_2/polyacrylamide nanocomposite to study the drilling mud properties. According to their study, the nanocomposite contribute to an increase in the drilling muds viscosity and a decrease in the fluid loss and filter cake thickness [1]. *Mao et al.* and *Jain et al.* introduced nanocomposites as an alternative to polymers and clays to improve rheological properties of the drilling fluids [25, 26]. *Ismail et al.* used multi-walled carbon nanotube, nano-silica, and glass beads to improve the rheological behavior of Water-Based Muds (WBM). Their results revealed that multi-walled carbon nanotube can be a better choice as a drilling fluid additive for water-based drilling fluids [27]. *Aftab et al.* used nano-silica, multi-walled carbon nanotube, and Graphene NanoPlatelet (GNP) as drilling mud additives to improve rheological properties and shale inhibition of water-based muds. Their results showed that GNP can be a better choice for enhancement of WBM performance [12]. Moreover, *Abduo et al.*, *Fazelabdolabadi* and *khodadadi* and *Ismail et al.* used multi-walled carbon nanotubes to study the drilling mud properties [11, 17, 20]. Despite some similarity in results, there are certain differences in different works because of the different experimental procedure.

This study investigates the simultaneous influence of three parameters including f-MWCNT, drilling mud density, and temperature on rheological properties of WBMs. Plastic viscosity, yield stress, apparent viscosity, 10 seconds gel strength (Gel 10s) and 10 minutes gel strength (Gel 10m) are properties studied using a Brookfield rheometer. This study was also an attempt to choose a proper model to simulate the rheological behavior of these water-based muds. In another part of this study, the effect of the degree of functionalization on rheological properties was investigated. For this, three steps of functionalization were performed on MWCNTs to obtain different surface modification after which rheological tests were conducted.

EXPERIMENTAL SECTION

Materials

MWCNTs, prepared by a Chemical Vapor Deposition (CVD) method, were purchased from the Us Research Nanomaterials (Houston) with 20-30 nm in diameter. Tap density is 0.28 g/cm^3 and true density is 2.1 g/cm^3 as reported by the manufacturer. In order to prepare the drilling mud samples, deionized water, and local bentonite were used. The X-Ray Fluorescence (XRF) using PANalytical XRF spectrometer (The Netherlands) was performed for composition determination of the local bentonite. Sample preparation for XRF test was performed by pressed pellets method. All other chemical materials were purchased from Sigma–Aldrich without further treatment.

Characterization

In order to guarantee the quality of multi-walled carbon nanotubes, a series of Transmission Electron microscopy (TEM) images have been performed on the samples. Leo 912 AB electron microscope (Japan) operated at 120 kV was utilized to obtain these images. The purity of MWCNTs was reported more than 95%, while its surface area was reported more than 200 square meters per grams. In addition, ThermoGravimetric Analysis (TGA) was performed by a Shimadzu model TGA-50 in the air. An Al_2O_3 crucible at a heating rate of 10 °C/min was applied to heat up samples to 800 °C. The ultrasonic cell crusher 950W (SJIA LAB) was also used for better dispersion of f-MWCNTs in base fluids.

Rheological measurements

The rheological properties of the prepared drilling muds such as plastic viscosity, yield stress, apparent viscosity, Gel 10s, and Gel 10m were measured by the Brookfield RST-CC Rheometer. This apparatus consists of a cylindrical sample holder (Sample cup for FTK-RST), a FTK water jacket and a spindle (Measuring bob CC3-40). The rheometer drives the spindle that is immersed in the sample holder. The sample holder contains the test fluid sample and can provide a rotational speed that can be controlled to vary from 0.01 to 1300 rpm to yield the shear rate from 0.013 to 7800 sec^{-1}. This device measures viscosity by measuring the viscous drag of the fluid against the spindle when it rotates.

Aqueous and non-aqueous drilling fluids, as mentioned previously, exhibit complex non-Newtonian behavior [13]. In normal shear rate range, non-Newtonian fluids are placed into two groups:

Bingham plastic:

$$\tau = \tau_0 + \mu_p \dot{\gamma} \qquad (1)$$

Power law:

$$\tau = K \dot{\gamma}^n \qquad (2)$$

Where τ is the shear stress, τ_0 is the yield stress or yield stress, μ_p is the plastic viscosity, $\dot{\gamma}$ is the shear rate and K and n are the consistency and flow behavior indices in the power law model. An alternative model is also developed according to Bingham plastic model which is called the Herschel-Bulkley (HB) model and is defined as below:

$$\tau = K_1 + K_2 \dot{\gamma}^{K_3} \qquad (3)$$

Where K_1, K_2, and K_3 are HB yield stress, HB viscosity and HB index respectively [28]. The apparent viscosity of non-Newtonian fluids is defined as below which is equivalent to the API definition of the effective viscosity [29]:

$$\mu_p = \frac{\tau}{\dot{\gamma}} \qquad (4)$$

Plastic viscosity and yield stress are defined by the following equations:

$$PV = \theta_{600} - \theta_{300} \qquad (5)$$

$$YP = 2\theta_{300} - \theta_{600} \qquad (6)$$

Where θ_{600} is the dial reading at 600 rpm and θ_{300} is the dial reading at 300 rpm [3].

Yield stress, a parameter of the Bingham plastic model, is defined as the initial resistance to flow caused by electrochemical forces between drilling mud's particles [11]. This is the tensile force between the solid particles; this force is the result of negative or positive electrical charges occurring near or on clay surfaces [30].

Plastic viscosity is defined as the mechanical resistance of fluid due to mechanical friction of solid particles inside it. This mechanical friction decreases the amount of filtration and as a result, the ability of the fluid to flow diminishes. Plastic viscosity strongly depends on the surface area of the particles in a fluid. Therefore, nanoparticles, having large surface areas, can greatly affect plastic viscosity [30].

Gel strength is defined as a quantity that indicates the thixotropic property [30]. Thixotropic property of drilling muds is of great importance since cuttings suspension in pump-off condition is basically related to this value. In order to determine the gel strength of drilling muds, the shear stress must be measured at low shear rate after a mud has set at rest for a period of time (Gel 10s and Gel 10m in the standard API procedure). From another point of view, gel strength is defined as the attractive forces inside the drilling muds under static conditions, a parameter that is amplified by the solid concentration although high solid concentration may lead to excessive gelation and flocculation [11].

In this study, the density of drilling muds was varied from 66 to 70 PCF (Pounds per Cubic Feet). In order to investigate the effect of f-MWCNT on rheological properties of these drilling muds, varying concentrations of f-MWCNT from 0 to 0.2 vol. % was added and the rheological parameters were measured in the temperature range of 30 to 40 °C using Brookfield rheometer with the speed range of 0.01 to 1000 rpm.

Preparation of f-MWCNTs

The raw MWCNTs are hydrophobic and are not compatible with aqueous environments. Therefore, surface modification of CNT is necessary to obtain a modified mixture. The reflux system with acid treatment was used to modify the surface of nanotubes with hydroxyl and carboxyl functional groups. This reaction was performed through the dispersion of MWCNTs in the mixture of H_2SO_4-HNO_3 (1:2 v/v) at 60 °C for 2 hours. Due to safety reasons, the reflux system was placed under a ventilating hood. Several short-time sonications were used to disentangle nanotubes from each other during the acid treatment. Different temperatures and different acid treatment times were applied to change the quantity and quality of surface modification of CNTs. The prepared solution included a large amount of metal catalysis, amorphous carbon fragments, and excess acids. Hence, the mixture was ten times diluted with distilled water and passed through Whatman quantitative filter paper, hardened low ash grade 50 (estimated pore size 2.7 µm). A vacuum system was utilized for better filtration of functionalized MWCNTs. In order to check the quality of f-MWCNTs, pH of filtrates was measured repeatedly to reach a neutral filtrate by acid elimination. The oxidized MWCNTs were then dried at mild conditions in the lab dryer.

Preparation of Mud samples

Based on the required mud density and the percentage of nanomaterial presenting in the mud, 0 to 0.4534 grams of f-MWCNTs were dispersed in 100 mL of the deionized water by an ultrasonic device for at least 10 minutes to obtain the nanofluid of the f-MWCNT in an aqueous solution as the base fluid. Then 9.598 to 21.112 g of local bentonite were added while being stirred for 20 minutes at 500 rpm by a WiseCircu stirrer (Korea) to prepare nano-based drilling muds in the density range between 66 to 70 PCF.

RESULTS AND DISCUSSIONS

XRF analysis

Table 1 shows the XRF results for the local bentonite. XRF Values obtained from XRF analysis of local bentonite showed that the SiO_2/Al_2O_3 ratio was 4.7 which is near the range expected for montmorillonite that is the main component of bentonite.

The ratio of $\{(Na_2O+K_2O)/(CaO + MgO)\}$ in local bentonite was found to be 0.78 confirming the sample can be classified as Calcium bentonite.

Table 1: Chemical analysis for local bentonite.

Element	Local bentonite (%)
SiO_2	63
Al_2O_3	13.2
CaO	3.71
Fe_2O_3	2.75
K_2O	2.02
Na_2O	1.95
MgO	1.36
SO_3	0.477
TiO_2	0.372
Cl	0.247
ZrO_2	0.0602
SrO	0.0542
L.O.I	10.8

TEM and TGA Studies

TEM images show the structural change of carbon nanotubes during the chemical reaction. Acid treatment covers the surface of nanotubes by –COOH groups leading to the hydrophilicity of nanotubes and cutting the tubular structure of MWCNTs in different directions. It should be noted that the best distribution of MWCNTs may be obtained by minimum structural changes and the maximum hydrophilicity in the based fluid [31, 32]. Fig. 1 shows the tangible changes during the acidic reaction. The uniform shape of MWCNTs (Fig. 1-a) has been altered to oxidized MWCNTs with irregular tubular shapes. The arrows show the CNT sectional cuttings.

The TEM technique is a qualitative method which is able to show the structural changes in chemical processes. Therefore, if the number of functional groups is needed, the TGA method will be useful. This analysis is extensively used for the characterization of different types of carbon nanostructures such as carbon nanotubes, carbon nanohorns, Graphene, etc.

Fig. 2 shows the TGA results of MWCNTs both before (Fig. 2-a) and after (Fig. 2-b) the functionalization process. TGA technique is a quantitative method in which changes in chemical properties of materials are measured. As observed in Fig. 2-a, the weight loss of pristine nanotubes is negligible below 500°C. At temperatures above 500°C, the weight loss accelerates sharply representing the uniformity of structure and oxidation of carbon nanotube in the low temperature range. Fig. 2-b shows the fact that the thermal stability of MWCNTs decreases after functionalization. The reason why is because of the surface chemical alteration of MWCNTs and the formation of functional groups on the nanotubes. Moreover, the main chemical change is observed around 210°C mainly due to oxidation of functional groups at a lower temperature. This alteration is around 15%, corresponding to the presence of one functional group for about 21 atoms of carbon. It should be mentioned that the carboxyle groups on the surface of MWCNTs can absorb water, which is eliminated at the temperature below

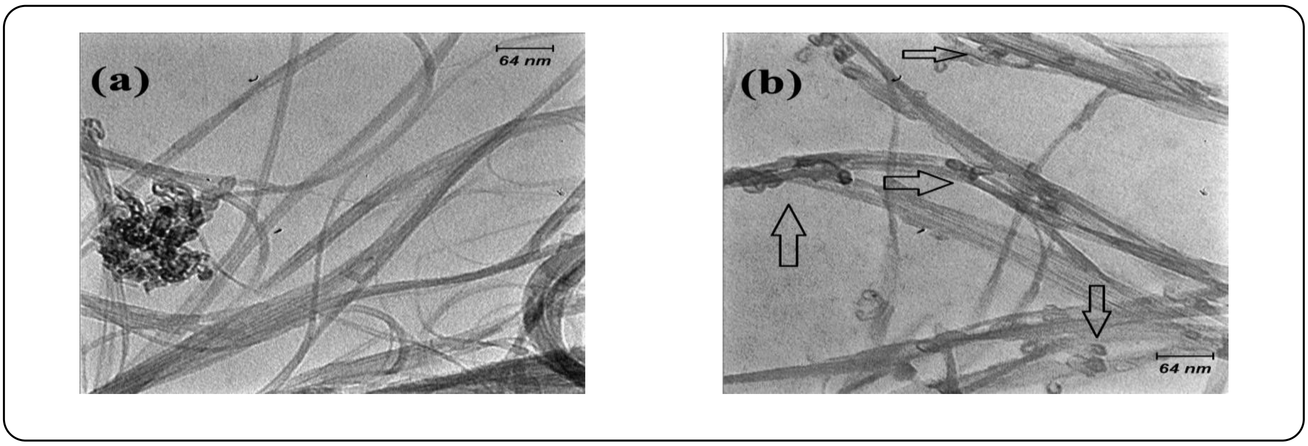

Fig. 1: TEM images of MWCNTs (a) before and (b) after acid treatment.

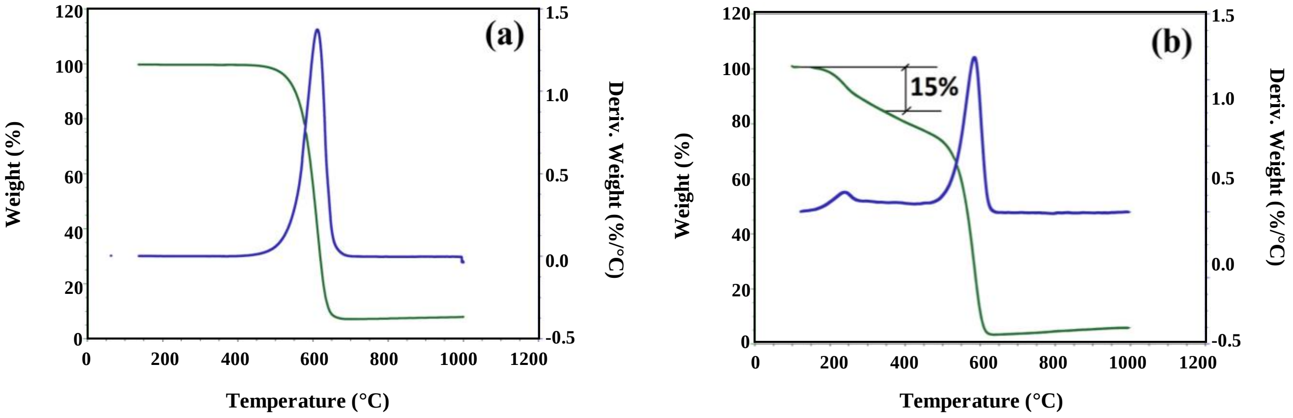

Fig. 2: TGA plots of MWCNTs (a) before and (b) after acid treatment in air.

150°C (not shown). In most cases, It is not more than one percent by weight [32, 33].

Drilling fluid studies

Rheology of the nano-based drilling muds prepared with different densities and varying concentrations of f-MWCNT at different temperatures were studied. Yield stress, plastic viscosity, apparent viscosity, and gel strength were measured according to API specifications. Yield stress and plastic viscosity were determined based on Bingham plastic and Herschel-Bulkley models. In order to guarantee the results, all experiments were repeated twice for certainty.

Table 2 shows the rheological properties of treated water-based muds formulated with 0.1 vol. % of functionalized MWCNT at various temperatures. This table includes the constants of the rheological models obtained from conducted experiments containing the plastic viscosity and yield stress for the Bingham Plastic model, as well as the HB yield stress, HB viscosity, and HB index for the Herschel- Bulkley model. The data obtained from 0 vol.% and 0.2 vol.% of f-MWCNTs show similar trends.

Rheological properties of the prepared drilling muds are investigated and described as follows:

(a) Plastic Viscosity

Fig. 3 shows the effect of temperature and the addition of different concentrations of f-MWCNT on plastic viscosity of drilling fluids prepared with different densities. According to the results obtained from conducted experiments, plastic viscosity was improved for all drilling mud samples by adding f-MWCNT at various temperatures. The reason why is because the carbon nanotubes are needle-shaped. Needle-shaped

Table 2: Rheological properties of treated water-based muds formulated with 0.1 vol. % of functionalized MWCNT at various temperatures.

Conditions		Bingham Model				Herschel- Bulkley Model				Gel Strength	
Mud density (PCF)	T (◦C)	PV (cp)	YP (pa)	AV (cp)	R^2	K_1	K_2	K_3	R^2	Gel 10s (pa)	Gel 10m (pa)
66	30	11.25	6.97815	16.65	0.995	6.2937	0.0348	0.8401	0.9988	6.2683	8.2493
66	35	9.45	7.71775	15.45	0.9967	6.9475	0.0189	0.9119	0.9992	6.6255	9.3849
66	40	7.55	9.01245	14.6	0.9704	8.6722	0.003	1.1471	0.9992	7.0155	10.8269
68	30	11.5	13.8741	22.3	0.9923	14.3233	0.0194	0.9290	0.9993	15.2503	19.2637
68	35	9.9	17.2847	23.3	0.9963	17.7399	0.0105	0.9939	0.999	18.7454	24.9399
68	40	7.05	21.4052	23.65	0.971	20.8841	0.0086	0.9970	0.9986	22.7642	27.7861
70	30	16.5	64.2677	66.3	0.9939	65.8211	0.0221	0.9734	0.9953	42.8013	63.676
70	35	12.7	77.7533	73	0.9561	74.9598	0.703	0.4808	0.9848	42.6354	61.7477
70	40	8.9	95.1	79.65	0.9701	81.138	0.0824	0.671	0.9903	43.2	64.2

particles increase the mechanical frictions inside the drilling muds. Particles inside the drilling muds are constantly being rotated and when the particles are needle-shaped, the ease with which rotation can occur is less predictable, hence, increasing the shear rates and the plastic viscosity. The large surface area of carbon nanotubes is another factor causing the plastic viscosity to be increased. In addition, by comparing the diagrams shown in Fig. 3, one can understand that the plastic viscosity was increased by increasing the mud weight (addition of bentonite). Bentonite concentration increases all rheological properties. When the mixture of bentonite, a water soluble clay, and water is exposed to sufficient shear stress, bentonite particles separate into individual clay platelets having negatively-charged faces and positively-charged edges, thus constructing a house-of-cards colloidal structure [34]. This colloidal structure makes drilling muds thicker and improves the rheological properties of the samples. Temperature, on the other hand, having a direct effect on plastic viscosity of the samples was investigated in this work. As it can be seen in Fig. 3, increasing temperature caused the plastic viscosity to be decreased since the continuous phase's viscosity is decreased by increasing temperature.

(b) Yield stress

As shown in Fig. 4, the addition of f-MWCNT increased the yield stress of the drilling muds. Naturally, bentonite suspensions show resistance against deformation. The existence of yield stress in drilling mud samples is due to this resistance to flow until the applied shear stress exceeds the resistance, i.e., the yield stress of the suspension. In other words, the existence of an interconnected three-dimensional network of flocks is believed to be the main reason for the yield stress of the drilling mud suspensions [35]. Needle-shaped carbon nanotubes, when added to drilling mud samples, increase the resistance inside the drilling muds because of the enhanced mechanical friction inside the suspension. Therefore, the amount of shear stress needed to exceed this resistance will increase and yield stress of the samples increases with increasing the f-MWCNT concentration. In addition, increasing the mud weight, as shown in Fig. 4, increased the yield stress value since bentonite concentration is increased and the resistance to flow is enhanced. Also observed from this figure is the fact that the yield stress of all drilling mud samples increased with increasing temperature. An increase in temperature brings about a consequent change in ionic activities and base-exchange equilibria and alters the balance between attractive and repulsive forces between clay particles. Therefore, the degree of dispersion or flocculation of clays inside drilling muds may be altered, hence influencing the rheological properties particularly yield stress [36]. In this research, increasing temperature caused the electrochemical forces inside the drilling muds to be improved and as a result the resistance to flow is increased causing the yield stress value to be enhanced.

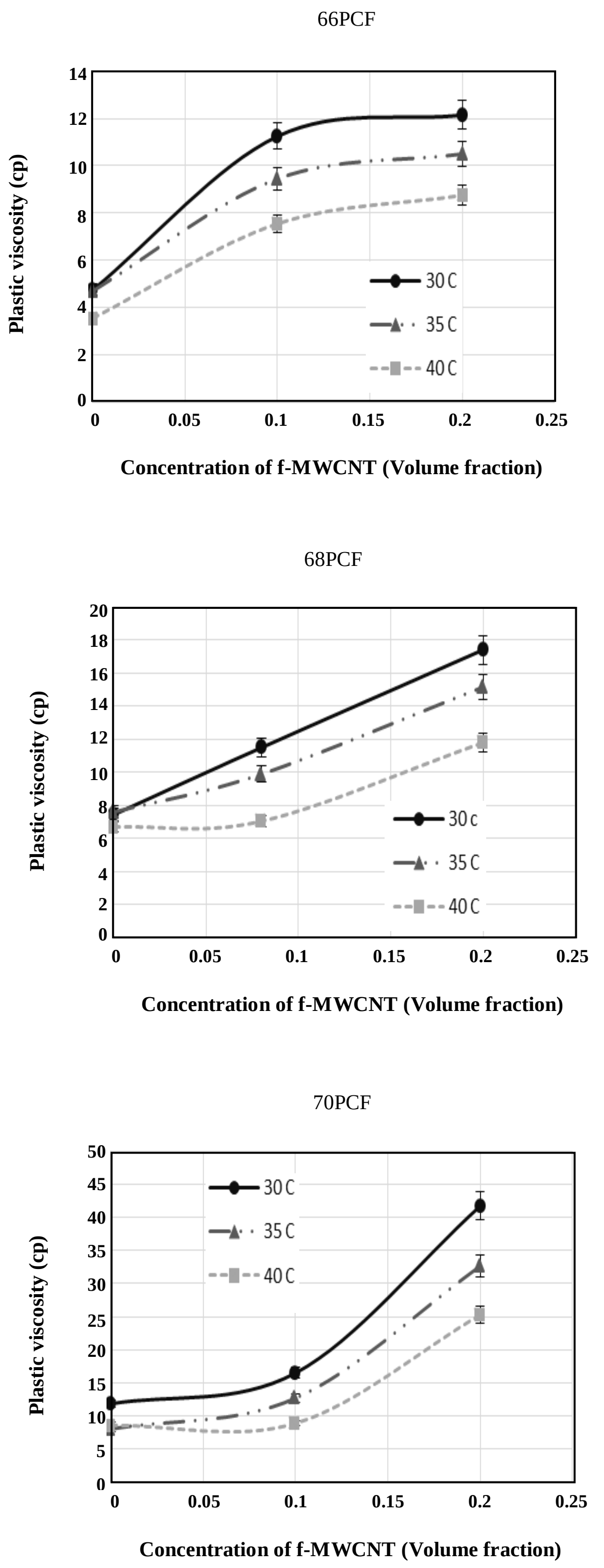

Fig. 3: Effect of f-MWCNT on plastic viscosity of WBMs at various temperatures and densities.

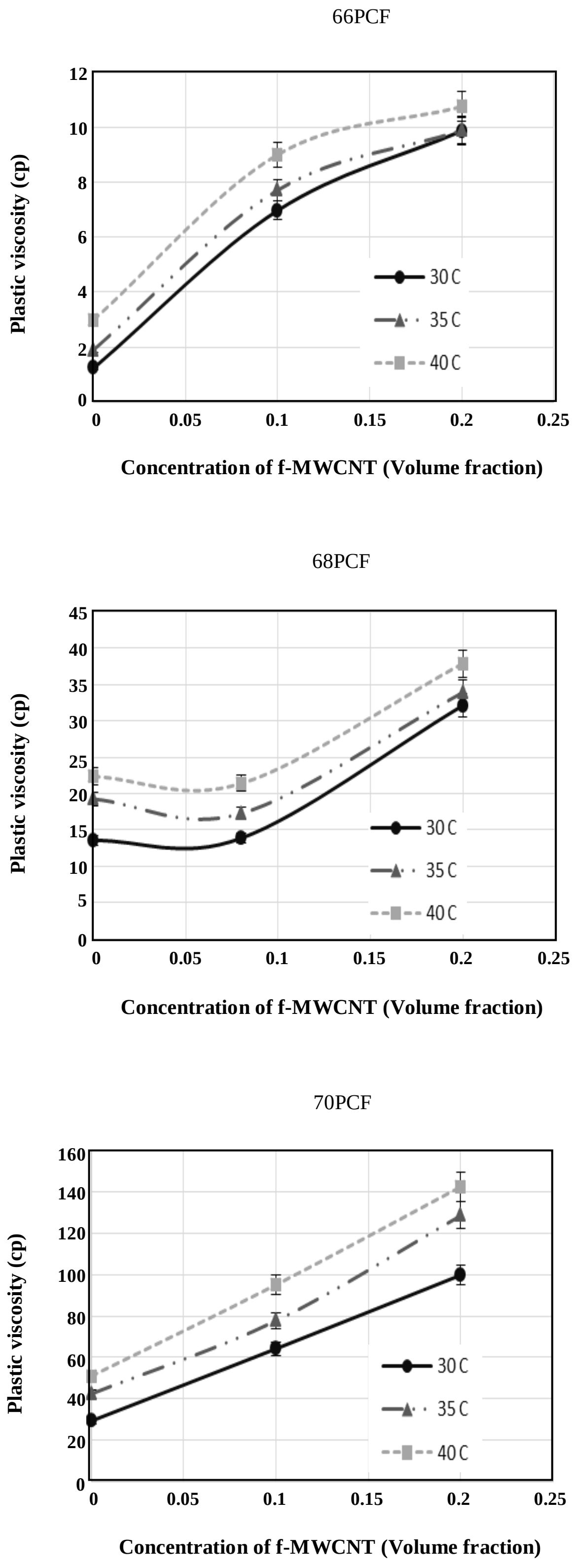

Fig. 4: Effect of f-MWCNT on Yield stress of WBMs at various temperatures and densities.

(c) Apparent Viscosity

Fig. 5 shows the effect of mud density, f-MWCNT, and temperature on apparent viscosity of drilling muds. One can understand easily from this figure that the addition of f-MWCNT to water-based drilling muds increased the amount of apparent viscosity for all samples. Moreover, mud weight directly affected the apparent viscosity. The reason why apparent viscosity increased with increasing mud weight and f-MWCNT concentration is that bentonite and f-MWCNT enhance the friction inside the drilling muds and impose mechanical resistance to flow. Temperature also affected the apparent viscosity of drilling muds. As can be seen in Fig. 5, no direct relationship is observed because the electrochemical balance inside the drilling mud is altered by increasing the temperature.

(d) Gel Strength

Figs. 6 and 7 show the gel strength of drilling mud samples for different concentrations of f-MWCNT at varying temperature. Fig. 6 provides Gel 10s and Fig. 7 presets Gel 10m. These figures show that increasing the concentration of f-MWCNT has a direct impact on both Gel 10s and Gel 10m. Increasing the temperature increased Gel 10s of drilling muds modified with f-MWCNTs based on density. By comparing the diagrams shown in Figs. 6 and 7, it can be inferred that heavier muds exhibit a greater value of gel strength. In addition, increasing the temperature will tend to increase the gel strength of different mud samples. The reason behind these changes is that gel strength is a measure of a thixotropic property of drilling muds which is a time-dependent property. Gel strength is an indication of drilling mud's ability to suspend drilled cutting and prevent them to fall when circulation has stopped. In other words, gel strength and yield stress are naturally the same except that gel strength is measured in static condition whereas yield stress is measured in a dynamic mode. Therefore, they behave the same as it can be seen in Figs. 4, 6 and 7.

(e) An appropriate model for nano-based drilling muds

Drilling muds are non-Newtonian fluids. The behavior of these fluids is shear-rate dependent. These fluids are divided into two main types based on the value (K_3 in Eq. (3)) which is the flow behavior index of muds;

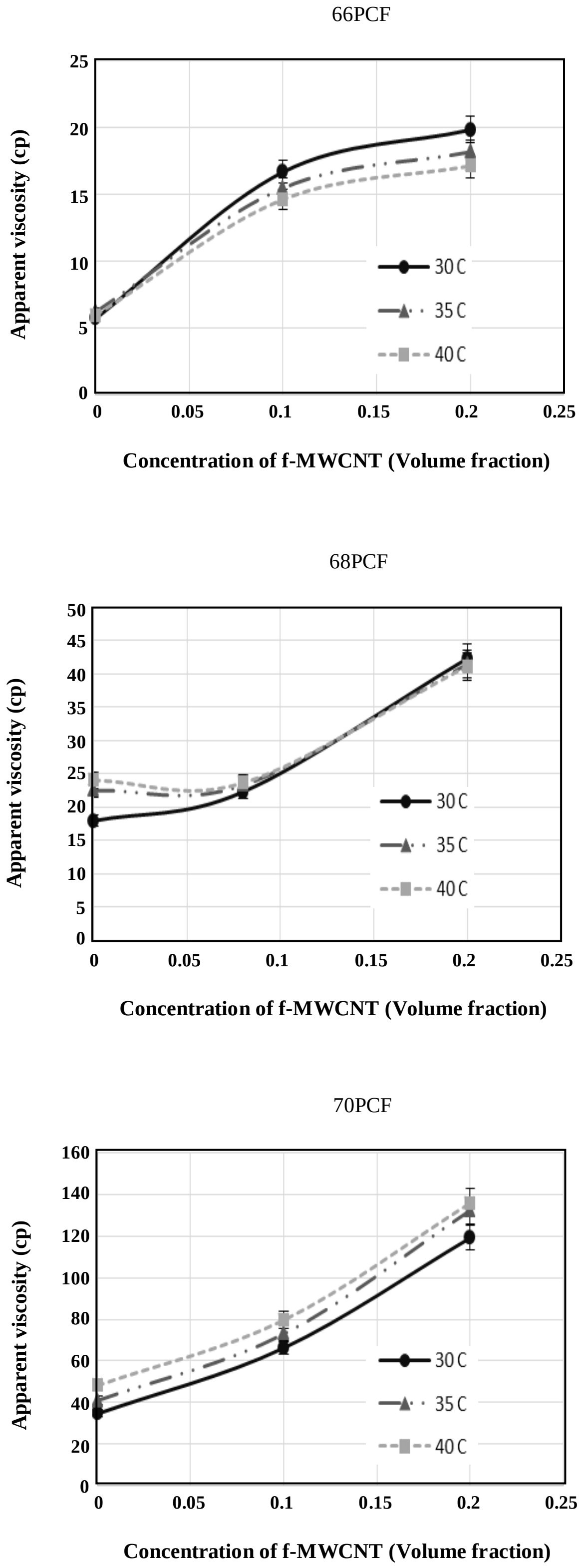

Fig. 5: Effect of f-MWCNT on Apparent viscosity of WBMs at various temperatures and densities.

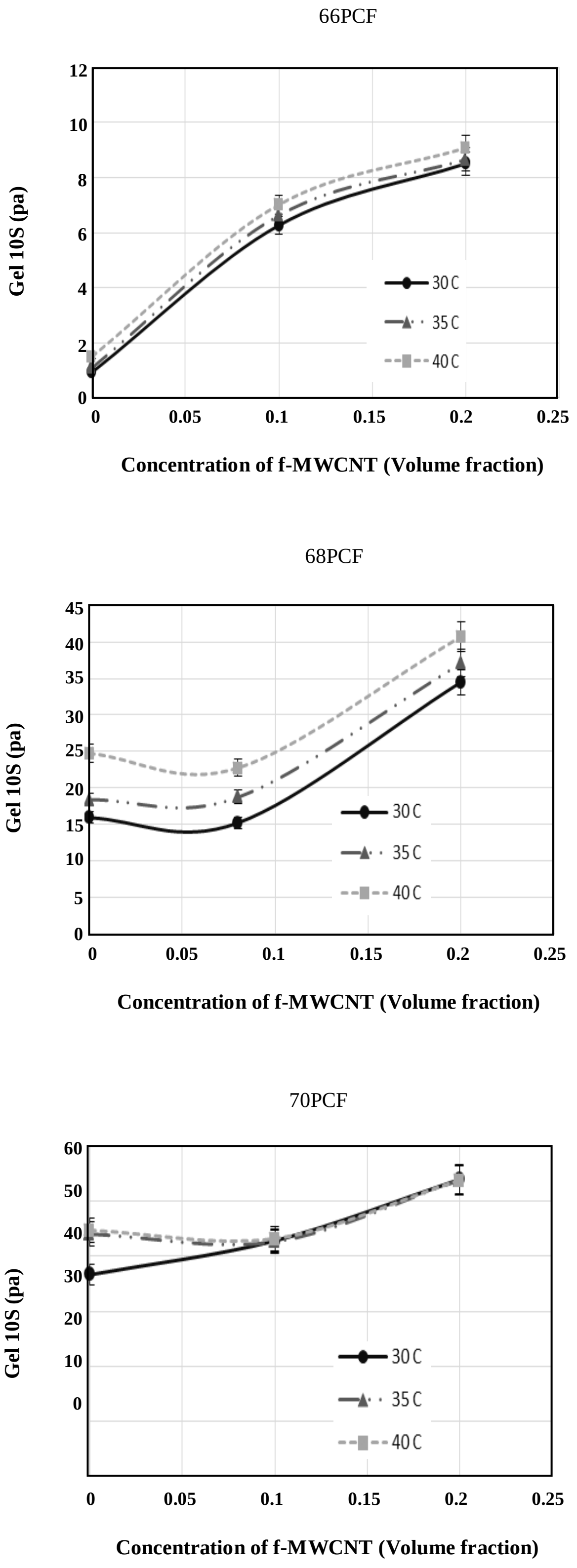

Fig. 6: Effect of f-MWCNT on initial Gel strength (10 seconds) of WBMs at various temperatures and densities.

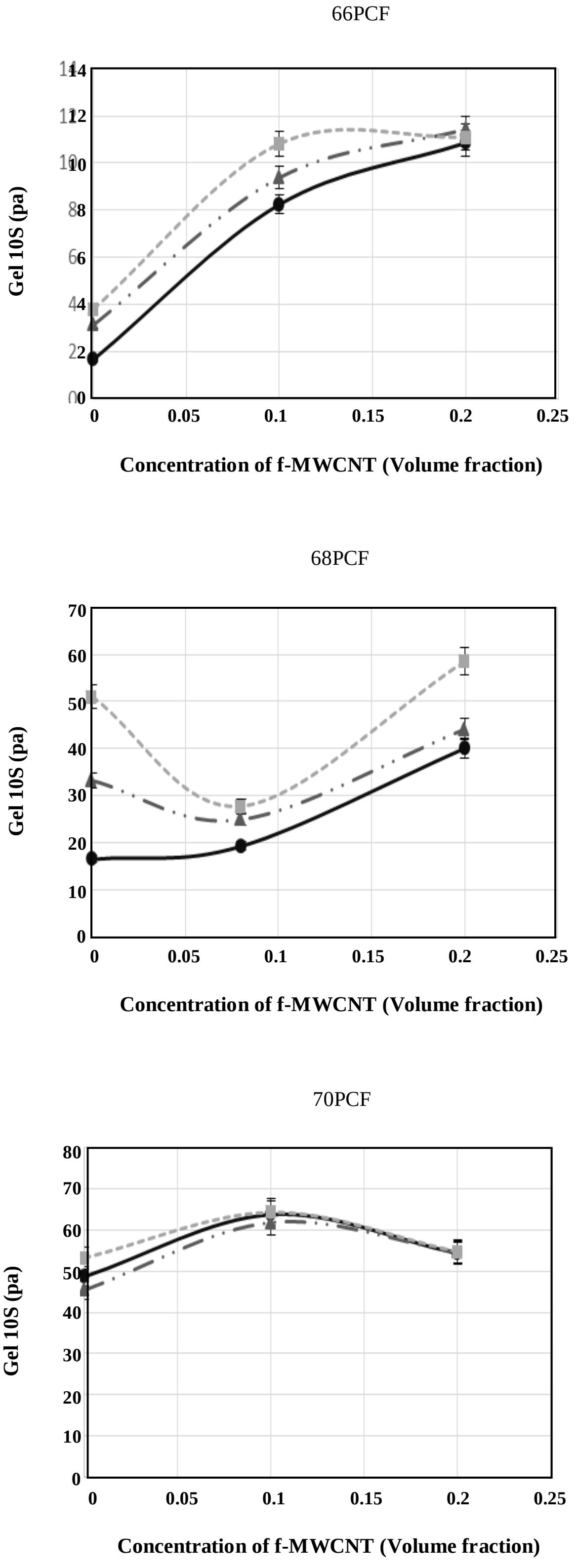

Fig. 7: Effect of f-MWCNT on final Gel strength (10 minutes) of WBMs at various temperatures and densities.

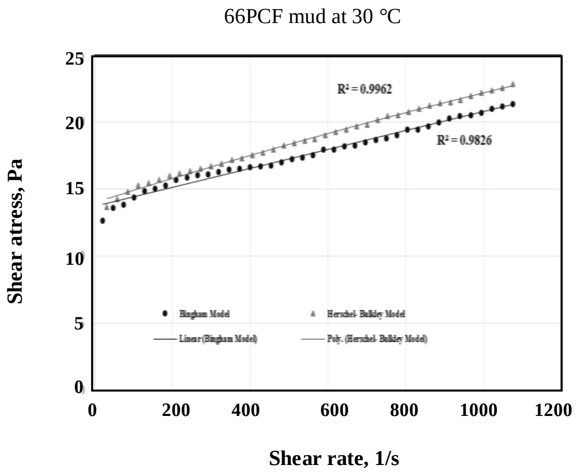

Fig. 8: A comparison between Bingham and Herschel-Bulkley models.

shear thinning fluid for $n < 1$ and shear thickening fluids for $n > 1$. $n=1$ exhibit Newtonian fluids. Most of the nano-based drilling fluids tested in this work behaved like shear thinning materials that are, the viscosity decreases by increasing the shear rate, although some samples showed shear thickening behavior. The shear thickening behavior (dilatancy) is observed mostly at high temperature and high concentration of f-MWCNT. In this case, the apparent viscosity increases reversibly as the shear rate increases although such behavior is not as common as Shear Thinning. Shear thickening behavior depends on four factors in general: concentration, the anisotropy of shape, size, and density. Since f-MWCNT nanoparticles are needle-shaped, applying shear on drilling mud suspensions formulated with f-MWCNT effectively increases the occupied volume hence increasing the apparent viscosity of drilling mud samples and as a result shear thickening behavior is improved. Higher temperatures signify this behavior by increasing the movement of particles inside the samples.

A comparison of models is presented in Fig. 8. This figure gives the best-fit values for the models considered in this study for a sample of mud. Moreover, as it can be seen in Table 2, the Herschel- Bulkley model fits better with the experimental data giving correlation coefficients (R^2) around 0.99.

Effect of functionalization on rheological properties of drilling muds

Another important objective of this study was to investigate the effect of the degree of functionalization on the rheological properties of WBMs. Three steps of functionalization were applied to MWCNTs to obtain a different surface modification. Step 1 refers to 1 hour of acid treatment, step 2 to 2 hours of acid treatment and step 3 to 3 hours of acid treatment. From step 1 to 3, due to increasing the treatment time and higher oxidation, MWCNTs were split into smaller pieces and chopped. Therefore, the negative charges on the surface of the oxidized nanotubes increased thus affecting the rheological properties of drilling muds. It is worth mentioning that the previous experiments in this work were performed using MWCNTs with step 2 functionalization. In order to evaluate the effect of this parameter, drilling mud samples with the same amount of MWCNTs (0.1vol. %) but different degrees of functionalization were prepared. Moreover, to eliminate the effect of other parameters, the density of all drilling mud samples was considered 66 PCF and all tests were conducted at 30 °C. Fig. 9 shows the results obtained from the rheological measurement of these samples as well as the TGA diagram (Fig. 9-a, b, and c) for different functionalization. As can be seen in Fig. 9-d, by increasing the degree of functionalization, plastic viscosity increased due to enhanced mechanical friction between smaller nanotubes and increased surface area of this nanotube. However, because of the nature of the plastic viscosity and its direct dependence on the friction between particles, increasing the negative charges in drilling mud samples did not affect the plastic viscosity. It was also observed in Fig. 9-e that with increasing functionality, the yield stress was first increased and then followed a downward trend. Increasing the amount of yield stress in low levels of functionalization is assumed to be due to crushed particles of carbon nanotubes and the relative difficulty with which drilling mud flows. On the other hand, increasing the negative charges in drilling mud samples at higher levels of functionalization inversely affected the yield stress and led to a decreasing trend mainly due to enhanced repulsive forces within the samples which is prevailing the effect of particle crushing. It should be noted that bentonite platelets due to the replacement of Si^{4+} with Al^{3+} ion, have negative charges on their surface. So, each factor increasing the negative charges will increase the repulsive forces between these platelets and decrease the yield stress value.

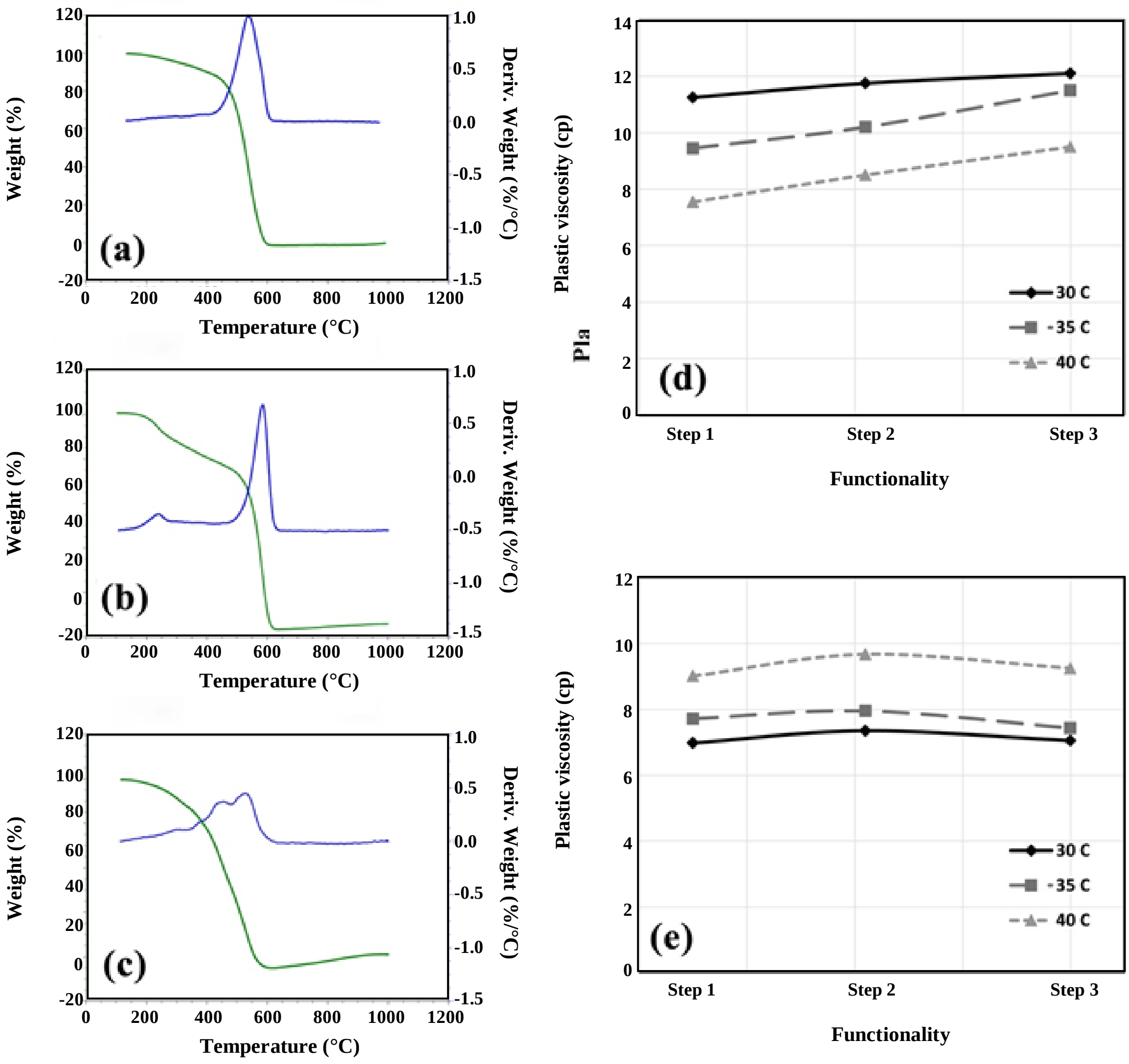

Fig. 9: Effect of functionalization on rheological properties of drilling fluids.

CONCLUSIONS

Nano-based drilling muds were prepared using f-MWCNTs added to WBMs. The simultaneous effect of three parameters including nanotube's functionalization, mud density and temperature were investigated on rheological properties of these samples. Owing to the hydrophobicity of MWCNTs and in order to better disperse the nanotubes, the chemical modification was performed on the surface of CNTs by acid treatment. TEM images clearly show the effect of treatment on surface modification of nanoparticles. These quality images indicate that MWCNTs were split into smaller pieces and chopped, thus the uniform shape of them has been altered to oxidized MWCNTs with irregular tubular shapes. The degree of functionalization was determined by TGA analysis in different times giving the quantitative measuring of the amount of functionality. XRF analysis also confirmed that the clay used to prepare drilling mud samples was calcium based bentonite. It was found that by adding even small concentrations of f-MWCNT, the rheological properties of samples was improved and the appearance of drilling muds was extremely changed. Moreover, test results indicated that the rheological behavior of WBMs was better described by Herschel-

Bulkley model rather than the Bingham plastic model. The last part of our study involved a novel study on the effect of the degree of functionalization on rheological properties of drilling mud samples. It was observed that plastic viscosity and apparent viscosity were increased by increasing the degree of functionalization while yield stress was first increased and then followed a downward trend.

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