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Using Nanomaterials to Optimize Mud Rheology at HPHT Wells throughout Experimental Work

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Abstract:
Significant quantities of hydrocarbon reserves are contained in high pressure high temperature reservoirs (HTHP). Development of these reserves will require drilling fluids with high heat capacities to withstand those conditions. Nano-structured materials exhibit many distinctive properties due to their small grain size and large specific surface. Experimental measurements of heat capacity at constant pressure indicate that the heat capacity values of those materials are frequently higher than those of coarse-grained materials. Therefore, this paper proposes the use of Nanocomposites as an additive in the drilling fluid to optimize its yield point.
In this paper, the authors proposing a solution to one of the most important challenges of the drilling fluids in HPHT wells; carrying the drill cuttings back to the surface for continuous circulation.
Multiwalled carbon nanotubes (MWCNTs) was functionalized and added to polymer (polystyrene-butadiene rubber copolymer matrix). The prepared MWCNTs were modified and characterized transmission electron microscopy (TEM) and X-ray diffraction (XRD). Furthermore, the prepared polymer/MWCNTs nanocomposites were used for HPHT (high pressure high temperature) drilling of oil base mud which also prepared and used in this method. The consequence of polymer and polymer/MWCNTs nanocomposites on the rheological properties of oil base mud which indicates using the polymer and polymer nanocomposites with different percentage from (0.5 to 3 gm.) in all percent the results it is very good, this means that the increase of polymer is reasonable for the increase of apparent viscosity, plastic viscosity and yield point at high temperature. Also, polymer/MWCNTs nanocomposites reveal increase of apparent viscosity, plastic viscosity and yield point at high temperature.

Keywords: *MWCNTs, nanocomposites, TEM, HPHT, oil base mud, plastic viscosity, drilling.*

1. Introduction

Drilling for oil and natural gas involves two major constituents: man power and hardware systems. The man power includes a drilling – engineering group and a rig-operation group. The first group offers engineering maintenance for optimum drilling operations, including rig selection and design of mud program[1], casing and cementing programs, the hydraulic program, the drill bit program, the drill string program and the well control program. After drilling begins, the daily operations are handled by the second group, which consists of a tool pusher and several drilling crews (derrick and motor personnel, etc.). There are two drilling methods used in the petroleum industry, the cable tool method and rotary drilling method, the first oil well was drilled in 1859 to a depth of (65 ft) by cable tool method and was employed by the early Chinese in the drilling of brine wells [2].
Rotary drilling method, started by a French civil engineer in 1863. It's the most important method that performs a rotary grinding action. This method is more effective in drilling shallow and unconsolidated sands than the cable tool method that is still working in some of the European countries as well as USA. Drilling deeper and more challenging wells have been possible by the effect of the improvements in drilling technologies including more efficient as well as active drilling fluids. On the other hand, petroleum industry requires the reduction of drilling costs with environmental concerns.
The cost reduction may be accomplished mainly by three ways, increasing the drilling efficiency by minimizing well bore instabilities, lower the cost of fluids and preventing modification, over engineering of the fluid and reducing the number of platform and wells [3,4].

The composition of drilling mud will depend upon the requirements of the particular drilling operation. Holes must be drilled through different type formation, requiring different type drilling fluid. Economics, contamination, available make up water, pressure and temperature[5].

Water alone is sometimes an ideal drilling fluid and frequently used to drill areas where trouble free low pressure formation exists. In some areas, drilling can be started with water and the drilled solid incorporated into the water resulting in a reasonably good mud. In other areas, it may be necessary to add commercial clays to the water prior for starting drilling operation, the clays serve dual purposes: first, to give viscosity to the drilling fluid and second, to seal the walls of the hole that the fluid circulated will not be lost to permeable formation being drilled.

There are numerous mud additives that are called "polymers and polymer nanocomposites". A strict definition of a polymer is an organic chemical having a molecular weight above200, with greater than eight repeating units. They vary greatly in function and basic properties, i.e., stability, charge, etc. In general, polymers can be classified as natural, modified-natural and synthetic [6].

Numerous types of polymer can be added to clear water to assist in the flocculation and settling of drilled solids at the surface. When used properly, these polymers used with an electrolyte such as lime or calcium chloride can keep drilling water clean and clear at the suction. Polyacrylates are synthetic materials manufactured from petroleum feed stocks [7]. They are not as complex structurally as the natural Polymers and usually have a straight-chain carbon backbone with different side chains, depending on the end product desired. They are usually anionic. Examples of generic and trade names include: polyacrylates, vinyl polymers, copolymers, vinyl acetate, and maleic anhydride. Their uses are: low molecular weight (< 1000)-thinners and deflocculates; medium molecular weight (up to 100,000 MW)--fluid loss control, flocculants and shale stabilizers; high molecular weight (> 100,000 MW)-bentonite extenders and flocculants.

Nanocomposites based on polymeric matrices gained significant interest after the report f nanoclays filled nylon-6 by Toyota in 1993 [8]. but the actual mention of the term was first found in the work on Lan and Pinnavaia[9]. Surprisingly automobile tires in which carbon black acts as a reinforcement is also an example of a nanocomposite. However, the term ''nanocomposite'' is not generally used to describe such composites. A nanocomposite is considered to be a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nm according to Ajayanet al[10], and this nanocomposite used for different applications [11,13].

Meanwhile Iijima's publication on multi-wall carbon nanotubes in Nature [14].and following the discovery of single walled carbon nanotubes two years later [15]. There has been an extraordinary explosion of related research. Because of their unique mechanical, electrical and thermal properties combined with low density, MWCNTs have a wide range of applications in various areas [16]. Furthermore, MCNTs exhibit brilliant mechanical, electrical, and magnetic properties as well as nanometer scale diameter and high aspect ratio, which make them an ideal reinforcing agent for high strength polymer composites. However, since CNTs usually form stabilized bundles due to Van der Waals interactions, are extremely difficult to disperse and align in a polymer matrix. Multiwalled carbon nanotubes (MWNTs) can be considered as a collection of concentric SWNTs with different diameters. MWNTs may consist of one up to ten and hundreds of concentric shells of carbons with adjacent shell separations of about 0.34 nm. The carbon network of shells is closely related to the honeycomb arrangement of the carbon atoms in the graphite sheets. The diameters of CNTs range from 0.2 to 2 nm for SWNTs and from 2 to 100 nm for MWNTs, while the lengths of CNTs range from several hundred nanometers to several micrometers.

The biggest issues in the preparation of MCNT-reinforced composites reside in efficient dispersion of MWCNTs into a polymer matrix, the assessment of the dispersion, and the alignment and control of the MWCNTs in the matrix. There are several methods for the dispersion of nanotubes in the polymer matrix such as solution mixing, melt mixing, in-situ polymerization and chemical functionalization of the multi wall carbon nanotubes, etc. These methods and preparation of high performance polymer/MWCNT nanocomposites are designated in this work. There are several approaches for functionalization of MWCNTs including defect functionalization, covalent functionalization and non-covalent functionalization[17].

The objective of this paper is to study the effectiveness of Nanocomposites on maintaining a high yield point at HPHT conditions. Nanocomposites also function as fluid loss reducers. Therefore, this project proposed a new approach of developing a cheaper, safer, environmentally friendly and more efficient mud system that improves the yield point and cuts down vast amounts of money. In this paper, the author proposing a solution to one of the most important challenges of the drilling fluids in HPHT (high pressure high temperature) wells circulation.; carrying the drill cuttings back to the surface for continuous.

2. Materials and Method

2.1. Materials

- Polymer was obtained from misr petroleum Company, Egypt.
- Multi-walled carbon nanotube (MWCNTs) was obtained from Sigma-Aldrich.
- Ammonium hydroxide was supplied by Synth laboratory.

2.2. Methods

2.2.1. Functionalization of MWCNTs

In the first procedure of functionalization (MWCNTs), MWCNTs were suspended in a mixture of H_2SO_4/HNO_3 (3:1) at room temperature. After that MWCNTs were treated in an ultrasound bath for 2 h and upheld for 15 h. Subsequently, this solution was neutralized with ammonium hydroxide and filtered with a 0.22 mm cellulose acetate membrane. The MWCNTs were washed several times using deionized water until the pH 5, 5. Then 0.5 grams of Polystyrene-butadiene rubber copolymer dissolved in 30ml diesel. And 0.5grams of functionalization MWCNT dispersed in 30ml diesel in Ultra sonication device for 30 minutes were added slowly to the oil base mud with good stirring at 70-80 f^o for 1 hour and The mixture is then thermally aged in hot rolling over for 16 hours at 350 f^0, after 16 hrs, the mixture is out and the rheological parameters are measured again using the HPHT viscometer at120 f^0 and the HPHT fluid loss at 350 f^0 and 500 psi

2.2.2. Preparation of polymer/ MWCNTs nanocomposites

The MWCNTs was added to the functionalized polymer matrix with different concentration from (0.5 to 3 gm.) and then this nanocomposite was used for HPHT drilling of oil base mud.

2.2.3. Preparation of oil base mud sample from EMAC company

2.2.3.1. Composition of Oil Base Mud Sample

This method involve mixing of the row materials in different precentage, after this ,the brine water is added to mixure drop by drop through stirrer in barrel for 1 houre. Then they are put in thermo cup using different temperatures. The next step is to measure the mud rheology by HPHT viscometer.

Deisel	238 ml
Emulsifier	4.2 ml
Wetting agent	1.7 ml
Viscofire	8 g
Lime	3g
Barite	255g
Filter loss Reducer	2.5 g
Brine water	(33ml water + 15 g $CaCl_2$)

Table 1: Composition of oil base mud

Controlling mud wight depends on the precentage of deisal and barite.
- Mud weight of this sample =12 PPg
Oil / water ratio = 88/12
-Measure of mud rheology as the following

Plastic viscosity	$= \Theta_{600} - \Theta_{300}$
Yield point	$= PV - \Theta_{300}$
Apparent viscosity	$= \Theta_{600}/2$
Low shear	$= 2\,\Theta_3 - \Theta_6$

2.3. Characterization

2.3.1. X-ray Diffraction

The XRD patterns of the chitosan nanocomposites were carried out on a Diano X-ray diffractometer using CoKα radiation source energized at 45 kV and a Philips X-ray diffractometer (PW 1930 generator, PW 1820 goniometer) with CuKα radiation source (λ = 0.15418 nm). The basal spacing (d) was calculated from the (001) reflection via the Braggs equation, ($n\lambda = 2d \sin\theta$)
Where n is an integer, λ is the wavelength of incident wave, d is the distance between the planes in the atomic lattice, and θ is the angle between the incident ray and the scattering planes.

2.3.2. Scanning electron microscopy (SEM) and EDX measurement

The morphology of the obtained polymer nanocomposite was assessed by scanning electron microscopy (SEM), (JSM 6360LV, JEOL/Noran). The microscope was attached to a dispersive energy spectrometer (EDS). The images were obtained using an accelerating voltage of 10–15 kV. Before examination the samples were sprayed with a fine layer of gold using a low deposition rate, refrigerated and placed at the maximum distance from the target to prevent their damaging.

2.3.3. Transmission electron microscopy (TEM)

The structure and surface morphology of the prepared nanocomposites were examined using JEOL JEM-1230 transmission electron microscope (TEM) with acceleration voltage of about 80 kV. The microscopy probes of the nanocomposites were prepared by adding a small drop of the emulsion of polymer nanocomposites onto a Lacey carbon film- coated copper grid and allowed to dry initially in air then by applying high vacuum

2.3.4. Infrared (IR) spectral analysis

FT-IR spectra of prepared nanocomposites containing functionalized MWCNTs were recorded in the range of 400–4000 cm^{-1} on (Shimadzu 8400S) FT-IR Spectrophotometer.

3. Result and Discussion

Electrical stability (ES) of an oil-based mud is considered a measure of its emulsion stability. In the laboratory, a mud with a high degree of emulsion stability is generally smooth, shiny and does not adhere to the stirring spindle of a mixer. By contrast, a mud with a low degree of emulsion stability is dull, grainy and shows a marked tendency to adhere to the spindle. The oil wetness or oil wetting tendency of an invert emulsion mud is defined here as the ability of the mud to incorporate foreign materials into the external, or oil phase. A mud with high emulsion stability is phase. A mud with high emulsion stability is oil wet, by definition, but may not necessarily be oil wetting. In his patent application for the first ES meter, Crittend on hypothesized that ES is related to the stability of W/O emulsions and that higher ES voltages correspond to more stable, or "tighter", emulsions

3.1. Functionalization of MWCNTs

As carbon nanotubes have strong aromatic character they incline to aggregate due to van der Waals interactions (- stacking). This leads to the formation of large bundles of MWCNTs that do not easily dissociate. As a result, carbon nanotubes in their unmodified state are completely insoluble in most solvents (with very few exceptions). This feature complicates the use of MWCNTs in most applications (composite materials, molecular electronics etc.), and further prohibits the development of molecular assemblies with nanotubes as building blocks.

For this reason, purification of carbon nanotubes has been an area of extensive research, and numerous methods based on filtration, chromatography, gas-phase oxidations and liquid-phase oxidations have been developed. The most commonly applied methods for purification involves treatment of the MWCNTs with oxidizing acids such as HNO_3 and/or $H2SO_4$. While these methods are capable of removing various types of impurities from the MWCNT material they may also cause serious damage to the MWCNT sidewalls and cut the tubes into shorter pieces. This is accompanied by the introduction of oxygen containing groups such as carboxylic acids to the MWCNTs which, on one hand can be advantageous for solubility and for further failing group chemistry. Conversely, the disadvantage of this can be carbon nanotubes of significantly lower quality.

3.2. TEM Observation of MWCNTs and F-MWCNTs

Fig.1 (a and b) displays the TEM of MWCNTs before and after modifications,

Multi walled nanotubes (MWNTs). A higher amount of F-MWNTs than MWNTs can be observed. Photos also indicate that there was little damage to the surface of CNTs after chemical treatment (CNTsn). Hence, the presence of a different material around nanotubes can be noticed on functionalized nanotubes.

Conducting polymers are attached to CNTs surfaces by in-situ polymerization to improve the process ability, In-situ polymerization method has also been used for the preparation of polystyrene butadiene rubber /CNTs nanocomposites, The MWNTs were relatively well dispersed in the polymer matrix by in-situ polymerization method with the aid of a dispersing agent,

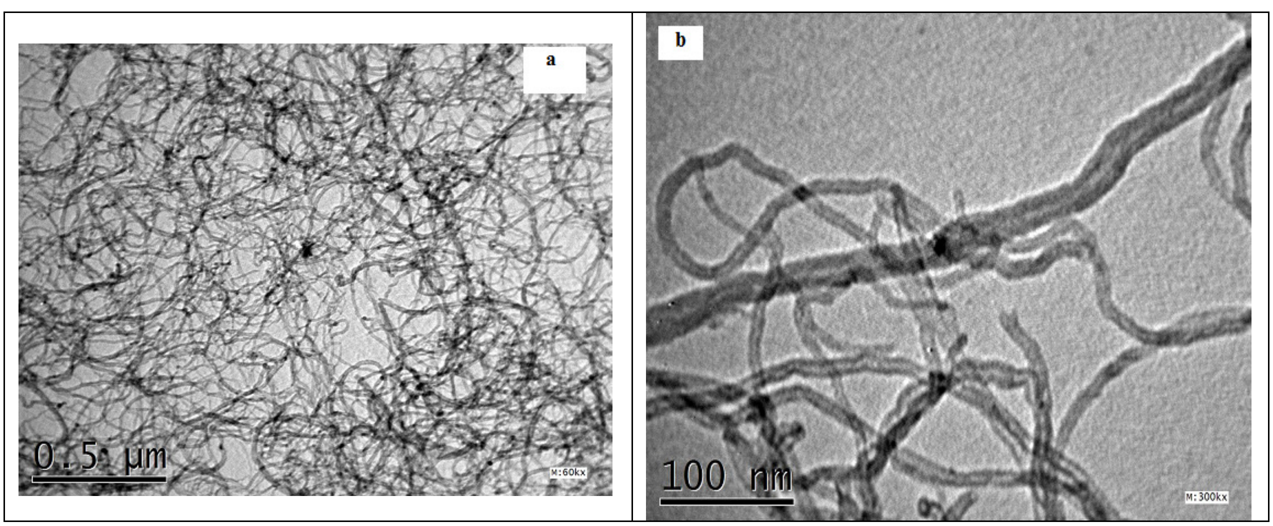

Figure 1: TEM images of a) MWCNTs, b) functionalized MWCNTs,

3.3. SEM of polymer nanocomposites

Fig 2. Exhibited the scanning electron microscope of polymer/MWCNTs nanocomposites which MWCNTs dispersed in polymer matrix that gives maximum interaction between polymer and MWCNTs leading to enhancement of nanocomposites in drilling process of oil base mud.

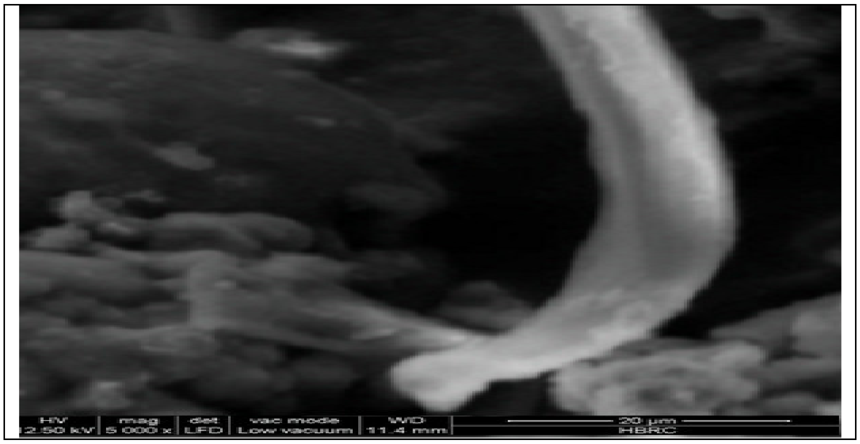

Figure 2: SEM images of polymer nanocomposites

- In this paper, the author proposing a solution to one of the most important challenges of the drilling fluids in HPHT (high pressure high temperature) wells circulation as Table (2); carrying the drill cuttings back to the surface for continuous polymers have been widely used as drilling additives because of their unique structure that makes them able to plug pores, and stand the high temperature and pressure conditions. However, the properties of the mud can be further enhanced by using Nanomaterials that can enable the drilling fluid to function better under extreme conditions.

composition	Before hot rolling				After hot rolling				Fluid loss (ml/30 mins)	Electrical stability (beek volt
	RPM	Results	PV	Yield point	RPM	results	PV	Yield point		
Sample of blank	600 300 200 100 6 3	60 38 29 22 10 8	22	16	600 300 200 100 6 3	58 36 28 22 9 8	22	14	12	850
0.2MWNTs with 0.5 polymers after(16 hrs)	600 300 200 100 6 3	65 41 33 25 11 9	24	17	600 300 200 100 6 3	61 39 30 23 10 8	22	17	8	1000
0.5 MWNTs With 0.5 polymers after (16 hrs)	600 300 200 100 6 3	72 47 35 24 12 11	25	22	600 300 200 100 6 3	67 44 34 26 11 10	23	21	7	1100
0.5 polymer Instead of Filter loss reducer in Oil base mud	600 300 200 100 6 3	65 42 33 25 12 10	23	19	600 300 200 100 6 3	62 40 31 22 11 10	22	18	7	1000

Table 2: Influence of polymer nanocomposites based on MWCNTs on oil base mud

3.4. Influence of PSBR nanocomposites on Properties of Mud Rheology.

The various samples were heated in hot rolling at 350 ºf for 16 hrs and after cooling they were reheated at120 ºf. The results of mud rheology obtained (as shown in the table)

- -The Plastic viscosity = $\Theta_{600} - \Theta_{300}$ and Yield point = PV - Θ_{300}

a. Plastic viscosity for sample of blank at 120 ºf =58-36 = 22
   - → yield point for sample of blank at 120 ºf = 22-36 =14
   - → fluid loss =12 and the electrical stability =850.

b. Plastic viscosity0.2 gm MWNTs With 0.5 gmpolymers at 120 ºf = 61-39 = 22
   - → yield point 0.2 gm MWNTs With 0.5 gm polymers at 120 ºf = 22-39 =17
   - → The fluid loss decreased from 12 to 8 and the electrical stability increased from 850 to 1000.

c. Plastic viscosity0.5 gm MWNTs With 0.5 gm polymers at 120 ºf = 67-44 = 23
   - → Yeiled point 0.5 gm MWNTs With 0.5 gm polymers at 120 ºf = 23-44 =21
   - → The Fluid loss and electrical stability gave the slight change..

d. Plastic viscosity0.5 polymer Instead of Filter loss reducer in Oil base mud at 120 ºf = 62-40 = 22
   - → Yeiled point 0.5 polymer Instead of Filter loss reducer in Oil base mud at 120 ºf = 22-40 =18
   - → The fluid loss became 7 and the electrical stability equal 1000. Thus, we can Conclude that this polymer works efficiently as a filter loss.

3.5. Effect of Viscosity (yield point) on Cutting Recovery, Fluid Losses and Electrical Stability on Mud Rheology.

The viscosity of oil based mud increases as the amount of MWCNTs with polymer nanocomposites increase.

From table (2) the effect of addingMWCNTswith polymer nanocomposide to oil based mud lifting capacity for various flow rates. The percentage of the cutting recovery indicates the mud ability to lift cuttings from the bottom hole to the surface.Fluid losses decreased as MWCNTs nanocomposite added to the oil base mud to solve many hole problems as sloughing in shaly formation.These changes depend on the cutting size and annular velocity. The improvement of cutting recovery is very significant for small cutting size as compared to the bigger cutting size.

The improvement in mud cutting lifting capacity is due to addition of 0.2 and 0.5gm MWCNTs with 0.5 polymers to the mud, since the nanocomposite product will improve the mud rheological properties. The nanoparticles material can enhance the stability against based mud since surface forces can easily balance the gravity force. When the force acts downward have less potential to settle down to the bottom of borehole. Therefore, under these conditions, the cutting scan easily is transported to the surface. But, this is not always true because the high viscosity can be achieved when the dispersion of clays in the mud is high. From this study, adding MWCNTs with polymer nanocomposide to oil based mud will influence mud viscosity, gel strength and fluid losses.

When adding 0.5 gm of nanocomposite product to the mud sample, the electrical stability value increases from 850 to 1000 and 1100, this means that the charge of mud in liquid phase is equal to solid phase, which leads to the stability of mud at high pressure high temperate wells and improves the yield point and fluid losses.

In general, high gel strength of mud increases viscosity. But, this is not always true because the high viscosity can be achieved when the dispersion of clays in the mud is high. Form this study, adding MWCNTs nanocomposites into the oil based mud will influence yield point, gel strengths, fluid losses and electrical stability, these unique nanoparticles can function as fluids viscosity stabilizer to significantly improve the cutting recovery.

4. Conclusion

In this paper multiwalled carbon nanotubes (MWCNTs) was successfully functionalized and used in nanocomposites prepared from polystyrene-butadiene rubber copolymer matrix. The prepared polymer/MWNTs nanocomposites were characterized using transmission electron microscopy (TEM). Additionally, the prepared polymer/MWCNTs nanocomposites were used for HPHT (high pressure high temperature).

Therefore, are going to use Carbon Nanocomposites (Table2) as a drilling fluid additive to:

- Maintain a high viscosity (yield point) at HPHT conditions.
- Provide higher efficiency in pore plugging, and hence effectively reduce fluid loss
  - → Nanofluids improve the fluid performance dramatically
  - → CNT-Polymer Nanocomposites are not effective in WBM compared OBM
  - → The YP was maintained for nearly all the samples after tested at HPHT conditions (compared to reduction in case of no CNT)
  - → Samples of double the concentration show better effect on fluid loss
  - → Samples of double the concentrations, have increase yield points (higher polymer percentage)

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