AADE-11-NTCE-3

Flow Behavior of Nanoparticle Stabilized Drilling Fluids and Effect of High Temperature Aging

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Abstract

Nanoclay and nanosilica were used to stabilize invert emulsion model drilling fluids for HTHP application. Though each nanomaterial can stabilize the emulsion by itself, best properties were obtained when both were used. Yield stress and plastic viscosity were found to be dependent on composition and the hydrophobic/hydrophilic nature of the nanoparticles. Adding barite results in loss of yield stress, however, it can be regained by increasing the nanosilica content. Aging at 225°C (437°F) for 96 hrs showed that the nanoparticle stabilized emulsions remain stable with only small changes in rheological properties.

Introduction

Drilling fluids serve many purposes in a drilling operation; these include the removal of cuttings, lubricating the drill bits, maintaining the stability of the hole and preventing the inflow-outflow of fluids between borehole and the shale formation [1]. Many different kinds of drilling fluids can be formulated to serve the drilling needs which require careful balancing of often contradictory requirements. Depending on the characteristics of the base fluid, the drilling fluids are classified as water-based (brines or muds), oil-based (oil-dispersions or invert-emulsions) or gaseous fluids (foams, aerated muds or aphrons). Water-based fluids or muds (WBM) are the most common. However, they are suitable only for relatively low temperature and pressure drilling operations. For high temperature and high pressure (HTHP) drilling operations, the requirements for the drilling fluids are more severe, and usually oil-based fluids or muds (OBM) are employed. According to the US Department of Energy Deep Trek program [2], a HTHP drilling operation is defined as one where the bore hole static temperature (BHST) exceeds 177°C (350°F) and the pressure is in excess of 25,000 psi. However, as the depth of the drilling wells keeps increasing, more severe drilling conditions can be expected which may exceed 315°C (600°F) temperature and 40,000 psi pressure [3]. In such extreme conditions, oil-based drilling fluids are preferred because of their better stability [1, 4, 5]. However, at HTHP conditions, drilling fluids are also likely to experience gelation, degradation of weighting materials and the breakdown of polymeric additives which act as viscosifiers, surfactants and fluid-loss additives [6]. Note that the thermal degradation of polymeric additives leads to loss in rheological properties which can cause serious operational problems such as barite sag. OBMs, in particular, are more susceptible to barite sag [5] at HTHP conditions. Thus, developing OBMs for HTHP operations which maintain their rheological properties remains a desirable task.

In OBMs, the solid phase contains viscosifiers and weight materials in addition to drill solids. Organophilic clays are common viscosifiers, while barite is a common weighting material; the former helps to control the viscosity while the latter allows for adjustment of the density. At HTHP conditions, however, the polymeric components of drilling fluids are likely to experience thermal degradation [6] which results in breakdown of the emulsion and fluid phase separation. This can cause serious operational problems, including the undesirable phenomenon of barite sag [5]. Thus, developing OBMs which maintain their morphology and rheological properties during HTHP operations is a desirable task. This is the objective of the research described here, and it requires the utilization of non-polymeric additives such as nanoparticles.

Nanoparticles can be used to stabilize water-in-oil emulsions in place of polymeric surfactants. Similar to surfactants, nanoparticles and microparticles can also be hydrophobic, hydrophilic or amphiphilic. They can exhibit a large free energy of adsorption and attach themselves to the oil-water interface, especially for particles of intermediate wettability [7]. Also, relatively hydrophilic particles tend to form oil-in-water emulsions, while the use of relatively hydrophobic particles results in water-in-oil emulsions. The degree of hydrophobicity or hydrophilicity can be determined by making a measurement of θ_{ow}, the contact angle that the particle makes with the interface. In quantitative terms, ΔG, the energy required to remove a particle of radius R from an oil-water interface of tension γ_{ow} into oil is given by:

$$-\Delta G = \pi R^2 \gamma_{ow} \left(1 + \cos\theta_{ow}\right)^2 \qquad (1)$$

and this quantity takes on its maximum value when θ_{ow} is 90°. Thus, for angles which have values slightly less than or slightly greater than this value, colloidal particles are essentially irreversibly adsorbed at the interface.

Since microparticles and nanoparticles of various shapes, sizes and surface characteristics are commercially available, these can be employed for imparting stability to invert emulsions used as drilling fluids. Indeed, hydrophobic nanosilica [8-10] and organically-modified bentonite clay [11, 12] have both been used to stabilize water-in-oil emulsions. In the present work, however, we examine the effect of using a combination of hydrophobic nanosilica and organically-modified nanoclay on the rheology of invert emulsions.

Materials

Poly 1-decene, an olefin oil, was used as continuous phase for invert emulsions. It was purchased from Sigma-Aldrich and had a viscosity of 0.8 poise, density of 833 kg/m^3 and boiling point of 316^{o}C. The dispersed phase was deionized water. Organically-modified nanoclays were obtained from Southern Clay Products. These are montmorillonite based clays which have been modified by various organic cations by means of a cation exchange reaction to make them hydrophobic for easy dispersion in non-polar media. Depending on the nature of the organic treatment, these clays can have varying degree of hydrophobicity. The nanoclays used in this work, in increasing order of hydrophobicity, were: Cloisite 30B, Cloisite 25A, Cloisite 20A and Cloisite 15A. Hydrophobic nanosilica particles were Aerosil® R104 (12 nm), Aerosil® R106 (7 nm), Aerosil R974 (12nm) and Aerosil R972 (16 nm) and they were provided by Evonik-Degussa. According to manufacturer, Aerosil R104 and R106 are treated with octamethylcyclotetrasiloxane, whereas R 974 and 972 are treated with dimethyl dichlorosilane to make the particles hydrophobic. For purposes of comparison, Witcomul® 3158, an oil soluble sulfonate emulsifier for invert emulsion drilling fluids, was obtained from Akzo-Nobel. Excalibar brand API-grade Barite supplied by Van Horn, Metz & Co., Inc. of Pittsburgh was used as the weighing agent. It had a specific gravity of 4.2 and a median size of 15 micrometers.

Experimental Methods

Invert emulsions were prepared by emulsifying water in nanoparticle containing oil. For this, a calculated amount of nanoclay was first dispersed in 70 ml of oil and ultrasonicated for 20 seconds using a high intensity 750 watt power ultrasonic horn and then left overnight for dispersion to take place. After this, the required amount of nanosilica was added, and the mixture was ultrasonicated again for 20 seconds. The dispersion was now allowed to rest for at least 24 hours. To prepare the emulsion, 30 ml of deionized water was added slowly to the oil dispersion while homogenizing at 24,000 rpm for 2 minutes by high speed stirring with an IKA Ultra Turrax rotor-stator mixer. Water must be added slowly rather than in bulk as all the water may not emulsify, and a portion of it may form a separate phase. Upon emulsification, a white gel-like emulsion was obtained. This was left to rest for 24 hrs for equilibration and to allow time for water to hydrate the nanoclay before making any measurements. It should be noted that the nanoparticle content reported here is on the basis of oil content and not the total amount of emulsion. For surfactant containing emulsions, the surfactant was added in place of nanosilica particles to the nanoclay-oil dispersion and then water was emulsified as described above.

The morphology of the emulsion, i.e., the dispersed phase size and size distribution was characterized with the use of an optical microscope fitted with a digital camera. ScionImage software was used to capture and analyze the images. A standard grating was used to calibrate the images. As the emulsions were quite concentrated to observe directly, they were diluted with additional oil for the microscopy work. A droplet of the diluted emulsion was placed on a slide and then covered with a cover slip before observing in the microscope.

To make the weighted fluids of specific gravity 1.3 or 1.5, required amounts of washed and dried barite were added to the invert emulsions while stirring with the high speed homogenizer for two minutes.

Rheology measurements were carried out to determine yield stress and the plastic viscosity of these model drilling fluids with the help of a Carri-Med CSL100 stress controlled rheometer fitted with parallel plate fixtures. The diameter of each plate was 4 cm, while the gap was set at 1 mm for all the experiments. Before making measurements, all the samples were pre-sheared for 1 hour at 850 s^{-1} to impart a common shear history. This was followed by 10 minutes of rest. Then stress ramp up and ramp down experiments were performed to obtain flow curves from which the yield stress and plastic viscosity could be calculated. All rheology measurements were carried out at 25^{o}C.

High temperature aging of the model drilling fluids was carried out at 225^{o}C using a 500 ml Fann aging cell. The cell was pressurized to 500 psi by nitrogen gas to prevent the evaporation of water contained in the drilling fluid. The pressurized cell was placed in a pre-heated oven for static aging for 96 hrs. The aged drilling fluids were depressurized once the contents of the cell had cooled to room temperature. The aged emulsion was degassed in a vacuum chamber before being examined for rheology and morphology properties as described earlier.

Results and Discussion

Drilling fluids should exhibit a gel structure with apparent yield stress so as to prevent the settling of suspended solids, such as hole-cuttings and barite particles, should the flow be stopped for any reason. However, the gel structure should disintegrate quickly once the flow is restarted. In other words, a drilling should have a high viscosity at low shear rates to keep solids in suspension but a low viscosity at high shear rates in order that pumping costs not become excessive during an actual drilling operation. Such behavior is obtained by adding polymeric additives and clay particles that form a long range three dimensional network that breaks down on applying a shear stress but quickly re-builds on the cessation of flow.

Several simple models are available (see, for example, Gupta, 2000 [13]) to represent yield stress fluids which include the Bingham plastic, Casson and Herschel-Bulkley models. Although none of these models fits the experimental data perfectly, the Casson equation was found to be the best amongst the available equations for the drilling fluids described in this work. This is a two-constant equation that gives the shear stress τ in terms of the shear rate $\dot{\gamma}$ as:

$$(\tau)^{1/2} = (\tau_0)^{1/2} + (\eta_\infty \dot{\gamma})^{1/2} \qquad (2)$$

in which τ_0 and η_∞ are the Casson model yield stress and plastic viscosity respectively.

Invert emulsions were prepared with nanoclay and nanosilica as emulsion stabilizers. It was found that though both nanoclay and nanosilica can stabilize the emulsions, the nanosilica was more effective in this regards, and it had large effect on the droplet size. In addition, it was found that the most stable emulsion was obtained when both nanoclay and nanosilica were used in combination. Figure 1 shows flow curves for invert emulsions prepared with nanoclay and nanosilica. It can be seen that the largest increase in the yield stress and viscosity is obtained when both nanoclay and nanosilica are used together. This kind of effect is also observed in the morphology of the emulsions.

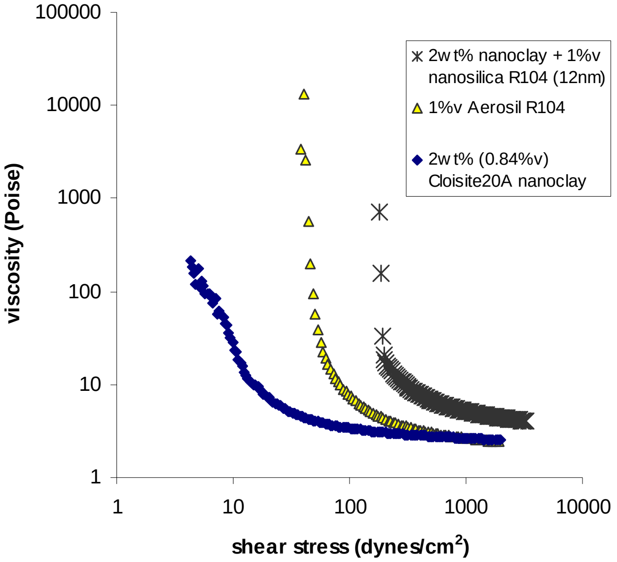

Figure 1. Effect of nanoclay and nanosilica on flow behavior of invert emulsions containing 30%v water.

Figure 2 shows the morphology of these emulsions which reveals that large droplets are obtained for the emulsions that only contain nanoclay, but the droplet size is much smaller for emulsions containing hydrophobic nanosilica, and it is also comparable to emulsion prepared with a polymeric surfactant. Table 1 shows yield stress and plastic viscosity values for these emulsions. It is clear that there is a synergistic effect of nanoclay and nanosilica on the yield stress. It should also be noted that the nano-stabilized fluid has comparable properties to the surfactant stabilized emulsion.

Table 1. Yield stress and plastic viscosity for nano-stabilized and surfactant stabilized emulsions (30%v water)

Composition	Yield stress (dynes/cm^2)	Plastic viscosity (poise)
2wt% nanoclay	3.6	2.33
1%v R104 nanosilica	27.6	1.8
2wt% nanoclay + 1%v nanosilica	54.2	2.26
2wt% nanoclay + polymeric surfactant	44.7	1.82

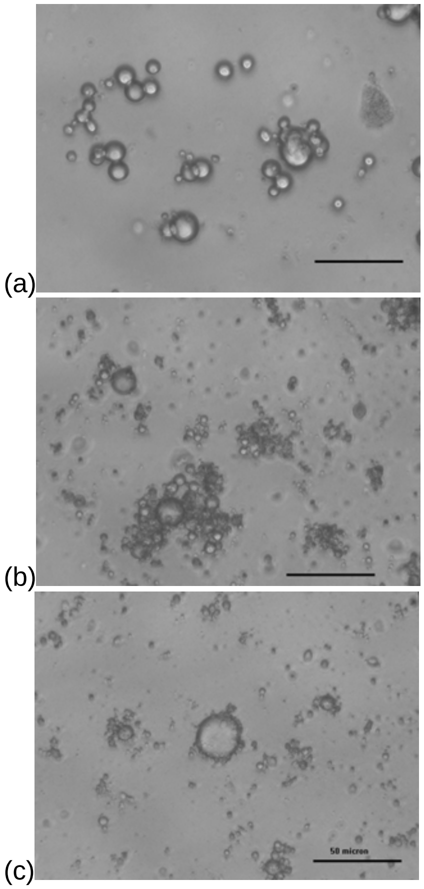

Figure 2. Water droplet distribution in oil stabilized with (a) 2wt% Cloisite 20A nanoclay, (b) 2wt% nanoclay and 1%v Aerosil R104 nanosilica and (c) 2wt% nanoclay and 0.77gm/100ml polymeric surfactant (10xdiluted, Scale bar = 50 μm).

Next we investigated the effect of the relative hydrophobic/hydrophilic nature of the nanoclay on the rheological properties of the invert emulsions. To see the effect of nanoclay hydrophobicity, invert emulsions containing 4%v nanoclay and 0.5%v nanosilica were prepared. The nanosilica was Aerosil R104 in all emulsions and nanoclays used were Cloisite 30B, 25A and 15A. These clays have been organically modified in such a way that their ease of dispersion in a non-polar medium is as follows 15A > 25A > 30B. Figure 3 shows flow curves for these fluids while the corresponding flow parameters are given in Table 2.

Table 2. Effect of nanoclay type on yield stress and plastic viscosity of emulsions (4%v nanoclay + 0.5%v nanosilica)

Nanoclay type	Yield stress (dynes/cm^2)	Plastic viscosity (poise)
Cloisite 30B	8.1	2.58
Cloisite 25A	12.1	3.05
Cloisite 15A	100.9	3.10

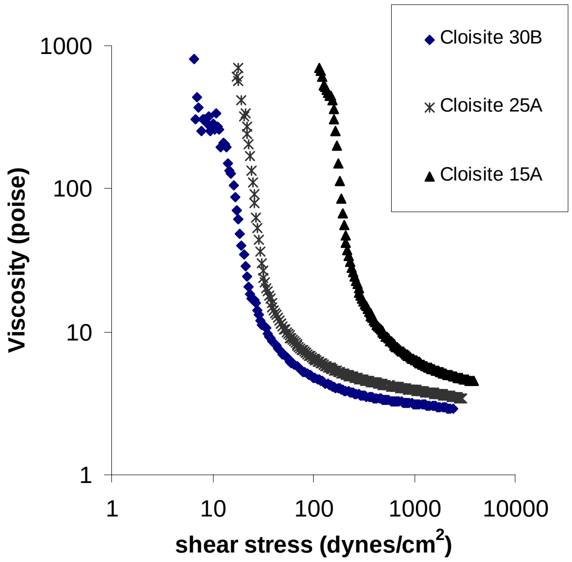

Figure 3. Flow curves showing the effect of nanoclay type on emulsion flow behavior.

Figure 3 and Table 2 show that the ease of dispersion of nanoclay has a very significant effect on the yield stress and the viscosity of these emulsions. This can be expected as the better exfoliation of the nanoclays results in better dispersion of nanoplatelets in the oil which helps in forming a gel network. It also helps in stabilizing emulsion droplets as it is easier for the nanoplatelets to approach the water-oil interface than in the form of large aggregates.

To investigate the effect of nanosilica hydrophilic/hydrophobic characteristics, invert emulsions stabilized by only 1%v nanosilica were prepared. Figure 4 shows flow curves for Aerosil R104 and R974, and Table 3 shows corresponding yield stress and plastic viscosity values.

Table 3. Effect of nanosilica type on yield stress and plastic viscosity of emulsions (1%v nanosilica)

Nanosilica type	Yield stress (dynes/cm^2)	Plastic viscosity (poise)
Aerosil R974 (12nm)	43.2	1.7
Aerosil R104 (12nm)	27.6	1.8

Both, Aerosil R104 and R974, have the same nanoparticle size of 12 nm but R974 is less hydrophobic than R104 which means that R974 has more number of hydroxyl sites on the particle surface to form hydrogen bonds to build a long-range gel structure. Therefore, R974 is more effective in developing a yield stress.

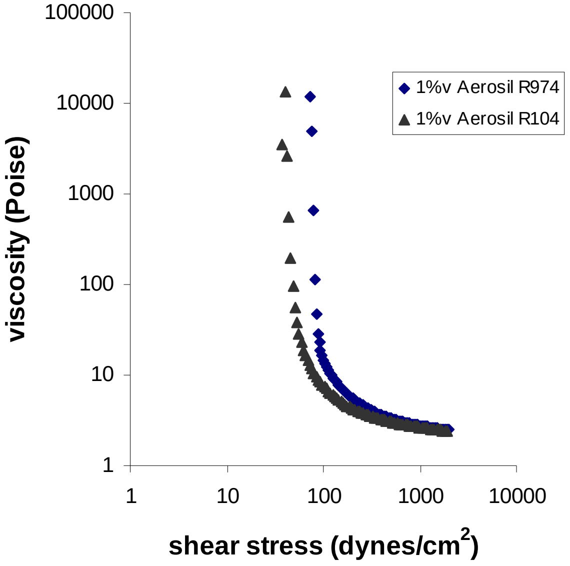

Figure 4. Effect of nanosilica type on emulsion properties.

Effect of Adding Barite

Barite is added to the drilling fluids to increase their specific gravity so that the required amount of hydrostatic pressure can be maintained in the drilling hole to prevent the blow up. API grade barite was added to these nano-stabilized emulsions to obtain fluids of specific gravity 1.3 and 1.5. The unweighted emulsion contained 30%v water which was stabilized by 2wt% Cloisite 20A nanoclay and 1%v Aerosil R104. The specific gravity of this emulsion was 0.9. Figure 5 shows flow curves for barite containing drilling fluids, and Table 4 gives yield stress and plastic viscosity values. It is seen that when barite is added to the emulsion, its yield stress decreases significantly while the plastic viscosity is remains essentially the same. This could due to the fact that the gel structure formed by nanoclay and nanosilica is disrupted by large-sized microparticles of barite. To see if the gel structure can be attained again, the nanosilica content was increased to 2%v. As can be seen from Figure 5 and Table 4, yield stress increases as a result, indicating that the gel structure has formed again. Thus, even for weighted drilling fluids, properties can be changed by adjusting nanoparticle concentration.

Table 4. Yield stress and plastic viscosity for barite containing emulsions (30%v water).

Composition	Yield stress (dynes/cm^2)	Plastic viscosity (poise)
2wt% Nanoclay + 1%v nanosilica	54.1	2.3
2%v nanoslica	346.0	2.3
Barite 1.3 + 2wt% Nanoclay + 1%v nanosilica	29.0	2.2
Barite 1.5 + 2wt% Nanoclay + 1%v nanosilica	44.0	2.1
Barite 1.3 + 2wt% Nanoclay + 2%v nanosilica	332.0	1.8

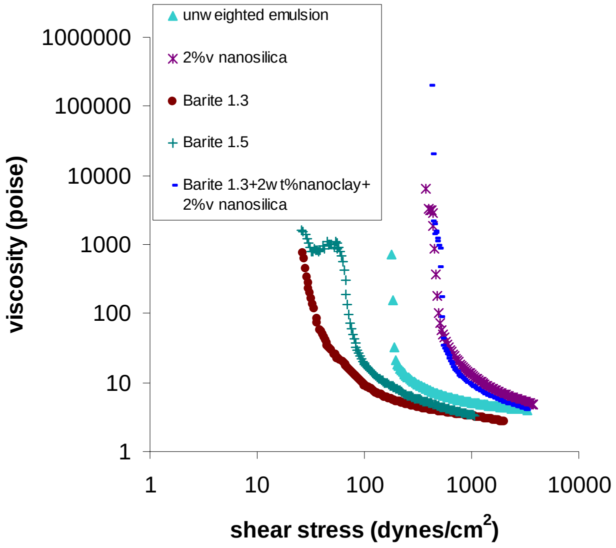

Figure 5. Effect of adding barite on the fluid properties.

Effect of Aging

The main objective of this work is to replace polymeric surfactants with nanoparticles which are more stable at high temperatures. Thus, to see if nanoparticles can maintain effectiveness in preserving rheological properties of invert emulsions, static aging of these model drilling fluid emulsions was carried out using a Fann aging cell. Fresh emulsion (30%v water, 2wt% Cloisite 20A and 1%v Aerosil R104) was loaded in the aging cell and the cell was pressurized to 500 psi by N_2 at room temperature. Then the cell was placed in the oven at 225°C (437°F) for 96 hrs. After which the cell was cooled down and the aged drilling fluid was analyzed. Figure 6 shows the rheology curve for aged drilling fluid compared with the fresh drilling fluid and Table 5 shows yield stress and plastic viscosity values. One can see that after aging there is a decrease in yield stress value which indicates a loss of gel structure. To see if any changes in the morphology also occur due to aging, emulsions were characterized by microscopy. Figure 7a and 7b show that on aging the water droplet size has increased possibly due to coalescence. However, if the aged drilling fluid is again homogenized by high speed stirring, an emulsion with fine droplets is obtained again as seen in Figure 7c. This also results in an increase in yield stress values as shown in Figure 6 and Table 5. It should be noted that when emulsion stabilized by a polymer surfactant was aged, it degraded severely with oil and water phases separating which could not be emulsified again. Thus, we can conclude that nanoparticles are quite effective in maintaining emulsion stability when exposed to high temperatures.

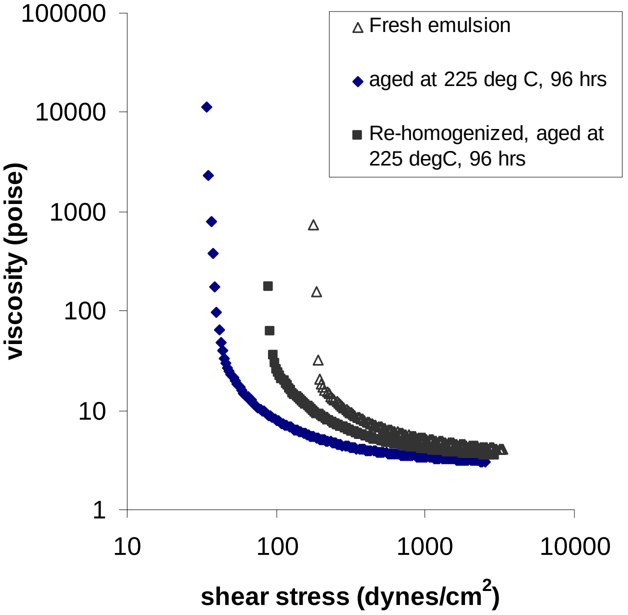

Figure 6. Flow curves for aged drilling fluids.

Table 5. Flow properties of aged emulsions.

emulsions	Yield stress (dynes/cm^2)	Plastic viscosity (poise)
Fresh emulsion	54.2	2.26
After aging, 225°C, 96 hrs	20.4	2.49
After aging and homogenization	41.8	2.64

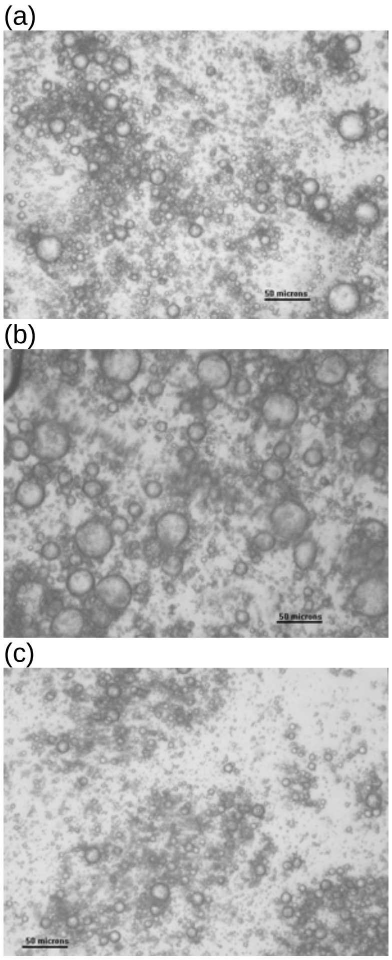

Figure 7. Effect of aging on water droplet distribution in oil stabilized with 2wt% nanoclay and 1%v Aerosil R104 nanosilica (a) fresh, (b) aged at 225^{o}C, 96 hrs and (c) aged and re-homogenized. (5x dilution, Scale bar = 50 μm)

Conclusions

Model oil-based invert emulsions were prepared using nanosilica and nanoclays as emulsion stabilizers in place of polymeric surfactants. Rheological properties were measured to see the effect of nanoparticles, added barite and aging at 225^{o}C for 96 hrs. The results showed the following:

- Stable invert emulsions can be obtained by using organically modified nanoclay and hydrophobic nanosilica.
- Best stability and flow properties are obtained when both nanoclay and nanosilica are used together.
- Nanoclay that disperses easily in oil phase shows better gel formation capacity.
- Relative hydrophilic and hydrophobic nature of nanosilica also has significant effect on gel forming behavior.
- On adding barite, there is a decrease in yield stress value, however it can be regained by increasing nanosilica content.
- On aging at 225^{o}C for 96 hrs, there is some loss in yield stress but emulsion remains stable. Re-homogenizing the emulsion results in recovery of yield stress.

Acknowledgments

This technical effort was performed in support of the National Energy Technology Laboratory's on-going research in "Nanofluids for oil and gas deep hole drilling" under the URS activity number 4.640.920.002.

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