About Rheology of Nanofluids

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Abstract. The rheological properties of several tens of nanofluids based on water, ethylene glycol, and engine oil with nanoparticles of various oxides and diamond is studied experimentally. Particle concentrations and their sizes were varied within quite wide range. Tested nanofluids did not contain any dispersants, while the base fluid was Newtonian liquid. It is revealed that in some cases, nanofluids are characterized by non-Newtonian rheological behavior. In the last part of the paper the effect of the nanoparticles on the properties of drilling fluids is discussed.

INTRODUCTION

Nanofluids, that is, suspensions with nanoparticles, are actively studied for the last twenty years in the context of already existing or planned numerous applications (see, e.g., [1] and references therein). Since nanofluids are used in all practical cases in flow conditions, flow nature is determined by their corresponding thermophysical properties. A huge number of publications are devoted to the study of these properties and primarily the thermal conductivity and viscosity. Currently, through experiments as well as by molecular dynamics method it is securely substantiated that these properties cannot be described by the classical theories. Both viscosity and thermal conductivity of nanofluids depend not only on concentration of particles (as in the case of conventional coarse dispersed fluids), but also on their size and material. Moreover, the viscosity of nanofluids decreases with increasing particle size, while the thermal conductivity, in contrast, increases [1-2]. An important property of nanofluids is that their rheological behavior can differ from behavior of the base fluid [3-7].

This work presents the rheological properties of nanofluids based on water, ethylene glycol, and engine oil with nanoparticles of various oxides and diamond. Particle concentrations and their sizes were varied within quite wide range. Tested nanofluids did not contain any dispersants, while the base fluid was Newtonian liquid.

METHODS

All nanofluids used in the described experiments were prepared by the so-called two-step method. To prepare nanofluid, nanopowder, containing particles of predetermined average size, was added in certain proportions to the base fluid. Then, the dispersed system was mechanically stirred and subjected to ultrasonic treatment to destroy the conglomerates of nanoparticles. There is no universal prescription concerning the time necessary for ultrasonic treatment of nanofluid. In our experiments, the processing time was determined so that the measured viscosity did not change with increasing treatment time. Usually, when using the “Sapphire SC-10338” ultrasonic bath, this time was 45 minutes.

Measurement of viscosity coefficient of the nanofluid was carried out with the help of "Brookfield DV2T" rotational viscometer with interchangeable spindles. The viscosity of water-based nanofluids was measured using LV-1 spindle and ULA(0) adapter to measure low viscosities. We used also a rotational viscometer OFITE-900. In all cases the accuracy of the measurements was 1–2%. In the course of measuring, shear rates $\dot{\gamma}$ were increased sequentially up to values of 10^3 s^{-1}.

This allowed studying the dependence of the shear stress tensors of the test fluid on shear rate and thereby determining its rheological properties. The measurements were carried out at a constant temperature. All measurements presented below are performed at 25°C.

When preparing nanofluids, we have used nanopowders obtained from different manufacturers. Nanopowders of SiO_2, TiO_2, Al_2O_3, ZrO_2, Fe_2O_3, and Fe_3O_4 were purchased from JSC "Plasmoterm" (Moscow). Nanopowders of SiO_2 had an average particle size of 10, 16, 25, 50, and 100 nm, TiO_2 – 71, 100, and 150 nm; Al_2O_3 – 50, 75, 100 and 150 nm; ZrO_2 – 44 and 150 nm, Fe_2O_3 – 18 and 50 nm; and Fe_3O_4 – 50 and 100 nm.

The copper oxide CuO nanopowder was produced by LLC "Advanced powder technology" (Tomsk). Its average particle size was 100 nm. A powder of nanodiamonds was produced by FRPC "Altai". The average particle size was determined using x-ray diffraction method and was 5 nm.

RESULTS AND DISCUSSION

Effect of nanoparticle concentration

The emergence of non-Newtonian properties is caused by several factors, such as the concentration of nanoparticles, their size and material, as well as properties of the base fluid. The change in rheological behavior from Newtonian to non-Newtonian pattern occurs with increasing nanoparticle concentration. All investigated non-Newtonian nanofluids turned out to be either pseudoplastic or viscoplastic. In the first case, the rheological behavior of nanofluids is well described by the power-law fluid model

$$\mu = k_v \dot{\gamma}^{n-1} \tag{1}$$

Viscoplastic fluids are characterized by existence of limiting shear stress, and their rheological behavior is described by Herschel–Bulkley fluid model

$$\mu = \left(\tau_0 + k_v \dot{\gamma}^n\right)\dot{\gamma}^{-1} \tag{2}$$

Here, τ_0 – is the yield stress of viscoplastic fluid, n – is the fluid index, while k_v – is the consistency factor. In all cases (for models (1) and (2)) the increase of particle concentration leads to decrease of fluid index, while consistency factor increases.

Non-Newtonian behavior was demonstrated by ethylene glycol-based nanofluids with particles of aluminum and titanium oxides. In both cases the nanoparticles sizes were very close and equal to 150±5 nm. We have studied four volume concentrations ϕ of nanoparticles, namely 0.25, 2, 4, and 6%. The shear rate was varied from 0.4 to 80 s^{-1}. Here again, as the concentration of particles increases, the fluid index decreases, while the consistency factor increases (see Table 1).

TABLE 1. Yield stress and rheological parameters of ethylene glycol based nanofluids with nanoparticles of Al_2O_3 and TiO_2 (Herschel–Bulkley fluid model)

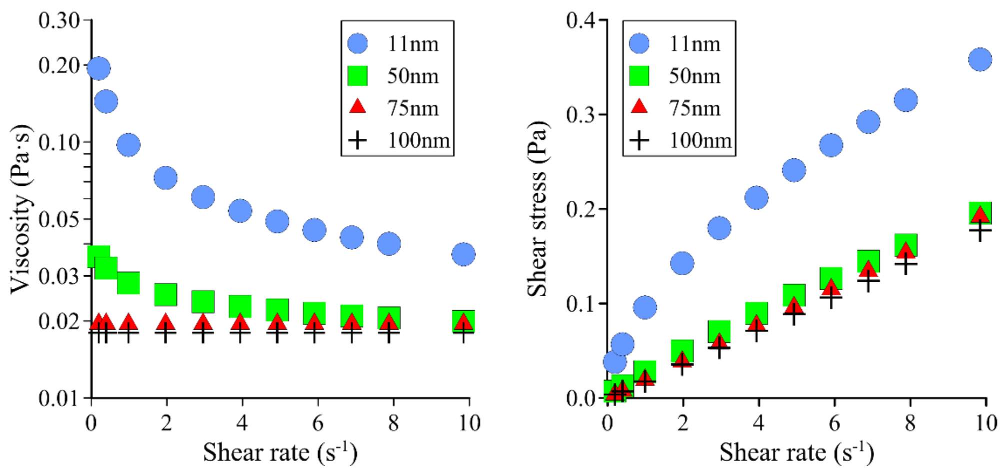
Volume concentration (%)	Al_2O_3			TiO_2		
	Yield stress (mPa)	**Consistency (mPa·s^n)**	**Flow behavior index**	**Yield stress (mPa)**	**Consistency (mPa·s^n)**	**Flow behavior index**
2	17.03	35.00	0.953	153.5	37.41	0.948
4	121.8	57.67	0.835	615.5	212.4	0.696
6	382.3	140.0	0.746	2044	695.0	0.582

In both cases there is a pronounced non-Newtonian rheological behavior of nanofluid, which strengthens with increasing concentration of nanoparticles. At that, pure ethylene glycol is a Newtonian fluid. At low concentrations of nanoparticles, all tested nanofluids were characterized by Newtonian rheological behavior $(\phi \le 0.25\%)$. It is important to emphasize that increasing the concentration of particles in non-Newtonian nanofluid may change its rheological model. Thus, the pseudoplastic fluid acquires a limiting shear stress and becomes viscoplastic.

Effect of nanoparticle size

It was indicated above that the viscosity of nanofluids depend not only on the concentration of nanoparticles, but also their size. If we recall that nanoparticles are particles with characteristic sizes ranged from 1 to 100 nm, this becomes quite clear. Even at low particles concentrations the numerical density of nanoparticles in the disperse fluid is very large. Particles actively interact with each other. In addition to this, the fluid near the nanoparticles is structured [9]. Therefore, if nanoparticles are sufficiently small, the whole dispersion fluid is structured. For this reason, we should expect that a possible change of rheological behavior of nanofluids should depend also on the size of nanoparticles. The experiments confirms this point of view.

Particle size is important parameter determining the rheological behavior of nanofluids. It is revealed that the transition from Newtonian behavior to non-Newtonian one in some cases occurs at a given volume concentration with decreasing size of nanoparticles. Apparently, we can argue that nanofluids with fairly small particles will always obey non-Newtonian rheological behavior, if only their concentrations are not too small (see Fig. 1a). Finally, the rheology of nanofluids with particles of the same size produced from different materials, in general case, will also be different



(a) (b)

FIGURE 1. Viscosity (a) and shear stress (b) of ethylene glycol-based nanofluid containing particles of Al_2O_3 versus shear rate.

Adding nanoparticles to drilling fluid

Viscosity and rheology of drilling fluids are essential for their application. Since the pressure loss during flushing-out of the well, well cleanup efficiency, borehole stability and many other drilling factors depend on them. Drilling fluids generally have an extremely complex composition. In this paper we studied the effect of nanoparticles on the viscosity and rheology of drilling fluids. The usual clay solution was taken as a base. Silicon oxide particles (5, 10 and 50 nm) and nanodiamonds (5 nm) were used as nanoparticles. The study of rheology of the created drilling fluids was carried out using a rotational viscometer OFITE HPHT. The rotation speed range is from 3 to 600 rpm (this corresponds to a range of shear rates from 5 to 1022 s^{-1}).

The clay mud was prepared by adding clay particles to distilled water and intense stirring for 30 minutes with the use of high-speed 20000 rpm stirrer (OFITE 152-18 – Prince Castle). The clay suspension was kept for two days after preparation for the final clay swelling and stabilizing the properties. The colloidal stability of suspensions was monitored by using the optical stability analyzer TURBISCAN. Then, the necessary amount of nanosuspension was added to clay suspension. The same amount of distilled water was added to the base clay suspension in order to provide the same mass concentration of clay particles in all the investigated solutions. A standard two-step method was used for the preparation of nanosuspension. The required amount of nanopowder was added to the fluid and the resulting suspension was thoroughly mechanically stirred. The suspension was treated in ultrasonic bath "Sapphire SC-10338" or disperser "Volna-M" to destroy the nanoparticle conglomerates.

A significant feature of the drilling fluids viscosity is the fact that these solutions are usually viscoplastic non-Newtonian fluids even without the addition of nanoparticles. The results showed the addition of nanoparticles to drilling fluids could significantly change effective viscosity at very low concentrations. It was shown the nanoparticles addition leads to an increase in the effective viscosity of drilling suspensions in most of the considered cases. This can be seen in the example of adding nanodiamonds to the drilling fluid (see Fig. 2).

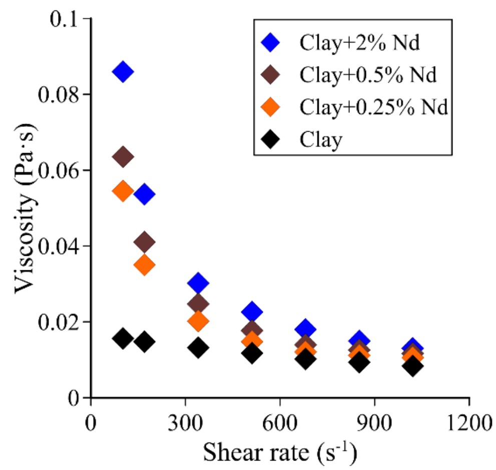


FIGURE 2. The viscosity of a soda-modified mud versus shear rate at different volume concentration of diamond nanoparticles.

The dependence of solutions viscosity modified by nanoparticles on the nanoparticles size was investigated (see Fig. 3a). It was found the viscosity of the studied suspensions depends significantly on added nanoparticles size. It was established the effective viscosity of drilling muds increases with decreasing nanoparticle size. It was found the nanoparticles of 50 nm (at 2 wt.%) don't have noticeable effect on effective viscosity of suspensions. The rheological properties of the solution are enhanced with decreasing nanoparticle size. In this case, the yield stress is increased (see Fig. 3b).

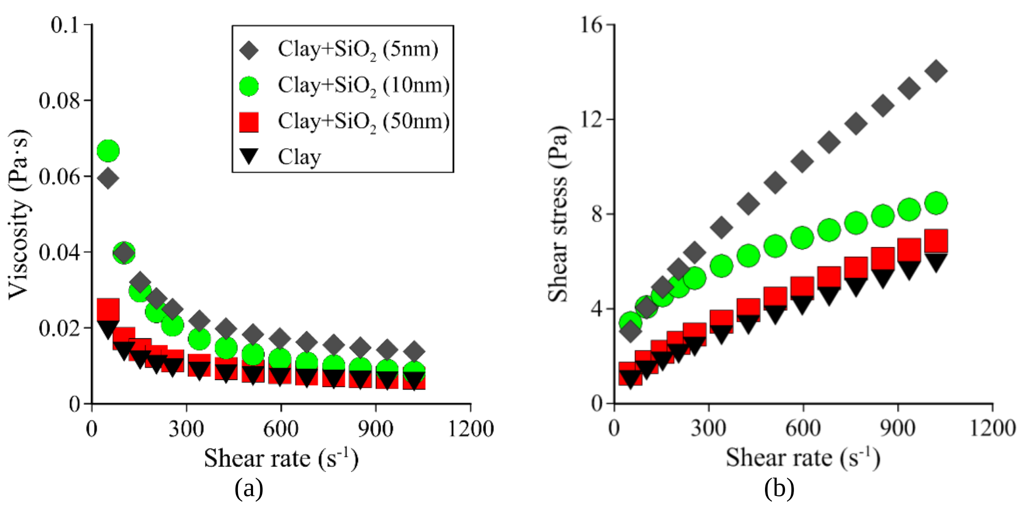


FIGURE 3. The effect of SiO_2 particle size on viscosity (a) and shear stress (b) of drilling fluid at 2wt.%.

CONCLUSION

Rheological of nanofluids based on water, ethylene glycol, machine oil with various oxide particles and nanodiamonds was investigated experimentally. In all cases, the base fluids were Newtonian and the dispersants (surfactants) were not used. It was found the rheology changed with increasing nanoparticle concentration in about a fifth of all studied nanofluids. Nanofluids showed pseudoplastic or viscoplastic behavior. In all the studied cases the rheology was well described by the model of power fluid (1) or Herschel-Bulkley fluid (2). Fluid index decreases as particles concentration increases, while consistency factor rises.

Particle size is another parameter determining rheological behavior of nanofluid. It is revealed that the transition from Newtonian behavior to non-Newtonian one in some cases occurs at a given volume concentration with decreasing size of nanoparticles. Apparently we can argue that nanofluids with fairly small particles will always obey non-Newtonian rheological behavior, if only their concentrations are not too small.

It was found the nanoparticles addition affects effective viscosity of drilling fluids. However, viscosity of drilling fluid also depends on size and concentration of nanoparticles.

The change in rheology of nanofluids is associated with structural changes occurring as nanoparticles concentration increases and their size decreases. However, neither the extent nor the nature of change in this structure is clear. Significantly, nanoparticles material also affects the nature of rheology, because nanofluids based on the same fluid with same particles size and same concentration, but different particles material can have different rheology. Further systematic investigations of nanofluids structure need to predict possible changes of nanofluids rheological properties.

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