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Viscosity of yttrium oxide (Y_2O_3) and magnesium-aluminum spinel ($MgAl_2O_4$) nanopowder suspensions in ethyl alcohol

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We report results of rheological experiments on suspensions of nanopowders. In this work we have used two ceramic nanopowders such as magnesium-aluminum spinel (S30CR Baikowski – $MgAl_2O_4$) and yttrium oxide (Y_2O_3) suspended in ethyl alcohol. Rheological studies have been carried out using several experimental systems including Haake Mars 2 rheometer (Thermo Electron Corporation, Karlsruhe, Germany) and Rheo-NMR (Bruker BioSpin, Rheinstetten, Germany). Measurements of dynamic viscosity in the range of shear rates from $0,01\ s^{-1}$ to $2000\ s^{-1}$ and the temperature range from $-15\,^{\circ}C$ to $20\,^{\circ}C$ has been conducted. Most of the samples exhibited a non-Newtonian nature.

Key words: rheology, rheo-NMR, viscosity, nanopowder, nanoparticles, nanofluids, nanosuspensions.

1. Introduction

Rheological studies of nanoparticles suspensions and nanofluids heve been conducted throughout the world, and their results can be successfully used in science and industry. Recently, the discovery of the thermal conductivity of these materials [1] has been of particular interest to researchers. There have been many studies on the phenomenon of thermal conductivity of nanofluids [2–7]. Their mechanical properties, particularly rheological properties, are also of great interest [8–12]. The nanomaterials used in our research have been used to produce high quality ceramics [13, 14]. Studies on nanomaterials that have been used for manufacturing of ceramics have been conducted in many research centers [15, 16]. Not only oxides nanopowders are of great interest to researchers. Various investigations have also been carried out into the use of nanopowders of silver [17, 18] and gold [19]. Nanofluids have been used in numerous industrial applications [20, 21].

Rheology is the study of the flow of matter, primarily in the liquid state, but also in 'soft solids' or solids under conditions in which they respond with plastic flow rather than deforming elastically in response to an applied force [22]. It applies to substances which have a complex molecular structure, such as muds, sludges, suspensions, polymers and other glass formers (e.g., silicates), as well as many foods and additives, bodily fluids (e.g., blood) and other biological materials.

Newtonian fluids can be characterized by a single coefficient of viscosity for a specific temperature. Although this viscosity will change with temperature, it does not change with the flow rate or strain rate. Only a small group of fluids exhibit such constant viscosity, and they are known as Newtonian fluids. But for a large proportion of fluids, the viscosity changes with the strain rate (or relative velocity of flow) and these are called non-Newtonian fluids. Rheology generally accounts for the behavior of non-Newtonian fluids, by characterizing the minimum number of functions that are needed to relate stresses to the rate of change of strains or strain rates. The research performed by our team, has produced new and practical results which could be used to produce nanomaterials with desirable properties in the future.

Many of the properties of nanomaterials (such as suspensions of nanopowders Y_2O_3 and $MgAl_2O_4$) have not been sufficiently studied rheologically. Our group at the Rzeszów University of Technology has undertaken research on the rheological properties of suspensions of ceramic nanopowders in ethanol. This is important for industry because the suspension is subjected to further technological processes that may lead to the manufacture of the ceramics with certain properties.

Some materials have been also tested in the research laboratories and companies of ThermoFisher Scientific and Bruker Biospin GmbH in Germany. This work presents a summary of the results obtained by us for two types of nanopowders suspensions. The use of Rheo-NMR [23, 24] and RheoScope systems has added a new dimension to our project.

Y. Rao in [25] pointed out "The study of the rheological behavior of a nanofluid also helps to understand the structure of the nanofluid. Therefore, significant amount of work has been done in this area, which provides a wealth of database on different nanofluid systems. Further effort is needed to consolidate the empirical observation into a better described science". This was an extra motivation for us to undertake research in the field of science.

2. Methodology

The materials that we used in our research were yttrium oxide (Y_2O_3) and magnesium-aluminum spinel ($MgAl_2O_4$) suspensions in ethyl alcohol.

2.1. Characterization of dry nanopowders

The sample of Y_2O_3 ceramic nanopowder was purchased from a commercial company and modified at Institute of Ceramics and Building Materials by grinding to smaller grains. The second type of nanoparticles used in our experiments was a commercially available nanopowder of magnesium-aluminum spinel ($MgAl_2O_4$) manufactured by Baikowski (Annecy, France). Several additional experiments have been performed on both samples including: (a) imaging with an electron microscope (SEM) (Fig. 1), (b) measurements of the size of grains with X-Ray Diffraction (XRD) and (c) elemental analysis with X-Ray Fluorescence (XRF). More information on applications and SEM pictures of used materials was presented in paper [26]. The approximate particle size measured with XRD was (31 ± 1) nm for Y_2O_3 and (40 ± 1) nm for magnesium-aluminum spinel.

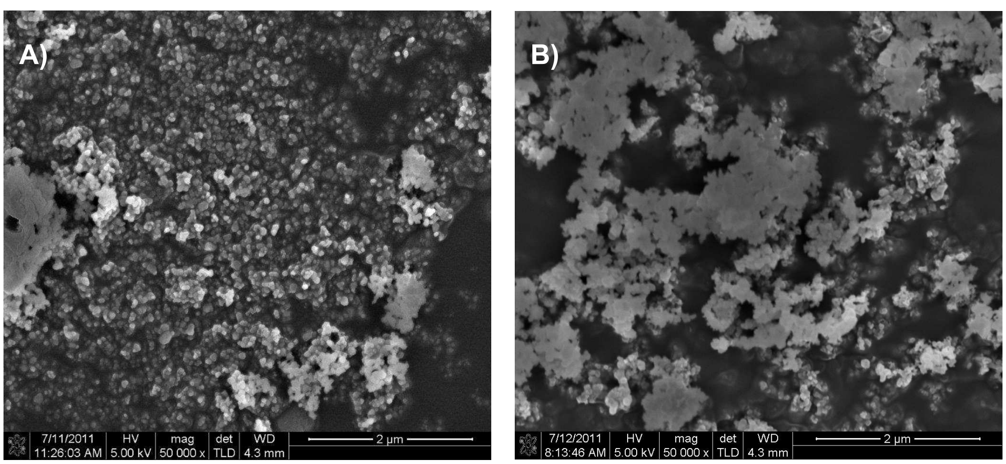

Fig. 1. Images of ceramic nanopowders taken with the SEM microscope: A) magnesium-aluminum spinel ($MgAl_2O_4$), B) yttrium oxide (Y_2O_3).

2.2. Preparation of the sample for rheological measurement

Experiments were carried out on samples containing different concentrations of ceramic nanoparticles in ethanol. SEM microscopy pictures showed a tendency for nanoparticles to form into agglomerates. Samples were prepared on the laboratory balance WAS 220/X (Radwag, Radom, Poland) by performing measurements with an accuracy of 0.1 mg. The first step in producing the nanosuspensions used in the experiments, the results of which are presented in this paper, was to place a desired amount of ceramic nanopowder in a glass container. The second step was to fill the container with 96% pure p.a. ethyl alcohol produced by POCH (Gliwice, Poland), CAS: 64-17-5 which created desired mass concentration of the nanopowder in the suspension. To avoid the existence of agglomeration one can use surfactants or destroy them mechanically by using ultrasounds. In our experiments we have used the later method. Then the sample was subjected to mechanical mixing for 30 minutes and placed in an ultrasound-wave bath U-505 (Ultron, Olsztyn, Poland) for 60 minutes to break up agglomerates of nanoparticles [27, 28]. We optically observed the process of sedimentation for two different nanofluids. Dimensions of nanoparticles of Y_2O_3 and $MgAl_2O_4$ were similar, however the speed of sedimentation was quite different. We attribute this difference to existence of agglomerates of nanoparticles Y_2O_3 and the lack of them in the case of other $MgAl_2O_4$ nanoparticles. The described method of sedimentation observation was discussed by Ghadimi *et al.* [29]. Unfortunately, this is only qualitative method.

2.3. Measurements carried out using HAAKE MARS 2 rheometer

The study of the rheological properties of the suspensions of nanopowders were made at the Rzeszow University of Technology on HAAKE MARS 2 rheometer (Thermo Electron Corporation, Karlsruhe, Germany) in the double cone measuring geometry (diameter 60 mm, cone angle 1°). Rheometer allows to control torques from 0.05 μNm to 200 mNm. To control the temperature, a Peltier system and thermostat Phoenix 2 (Thermo Electron Corporation) were used that allow us to control temperature with the accuracy of 0.1 °C. In addition, a measuring system was isolated from the environment by using glass rings. We performed measurements of dynamic viscosity in the range of shear rates from $0,01\ s^{-1}$ to $2000\ s^{-1}$ and the temperature range from $-15\,°C$ to $20\,°C$.

2.4. Experiments using RheoScope module

In the laboratory of ThermoFisher Scientific in Karlsruhe, Germany, rheological studies were performed on a rheometer HAAKE MARS 3 (Thermo Electron Corporation) equipped with a RheoScope module (Thermo Electron Corporation) which allows the optical observation of samples during the rheological tests. The RheoScope module measures the change in the rheological properties and the microscopic structure of the sample at the same time. Results have provided the information of both the mechanical properties of the material and allowed an optical observation of agglomerates in the samples. RheoScope module consists of an optical microscope, a digital video camera and the temperature controller used in combination with the HAAKE MARS platform.

To measure the plate-plate geometry, a diameter of 60 mm was used. We carried out research in the range of shear rates 1 s^{-1} to 1000 s^{-1} on samples of 1 wt.% and 5 wt.% concentration of Y_2O_3.

2.5. Measurments using Rheo-NMR system

In 1999, CALLAGHAN presented paper [24] where he described the use of nuclear magnetic resonance (NMR) in studies of rheological properties of fluids. Currently, the company Bruker BioSpin offers dedicated Rheo-NMR system, which allows to perform such a research on nanofluids. The Rheo-NMR system, in the Bruker BioSpin laboratory in Rheinstetten, Germany, has been used for experiments on Y_2O_3 nanosuspensions and ethyl alcohol. The Rheo-NMR experiments were performed on a Bruker AV III spectrometer with a 300 MHz wide bore magnet. Spectrometer with a NMR Microscopy accessory and a Micro2.5 gradient system (25 mT/mA) and a 25 mm 1H birdcage resonator was used. Rheo-NMR cell is driven by a drive shaft inserted in the magnet bore and rotated by stepper motor gear assembly mounted over magnet bore and NMR spectrometer controll the stepper motor. Cone and plate cell is placed into the 25 mm birdcage resonator to get NMR images of the sample material in the measuring cell. Standard NMR imaging methods provide spacially resolved velocity maps of the fluid in the cell. The velocity distribution inside the sample has been investigated based on the fact, that in this system, the lower plate is stationary while the upper cone is rotating. The measuring geometry of a plate-cone (diameter 16 mm, cone angle 7°) was used, and the flow velocity distribution of the 10 wt.% Y_2O_3 nanoparticle sample was studied at speeds of 2.5 rad/s and 5.0 rad/s.

3. Results and discussion

3.1. Yttrium oxide (Y_2O_3)

The rheological studies conducted using HAAKE MARS 2 rheometer were performed in CR (control rate) mode in the range of shear rates from $0,01$ s^{-1} to 2000 s^{-1}. The studies have shown that at low shear rates the dynamic viscosity of the suspension increases to a certain limiting value of shear rate and then starts to decrease. Figure 2 shows the comparison of the dynamic viscosity of a suspension of 10 wt.% Y_2O_3 in ethyl alcohol at different temperatures. Measurements performed with the use of HAAKE MARS 3 with RheoScope module have enabled us to optically observe the interior of the sample during rheological testing and we have observed sedimentation of the nanopow-

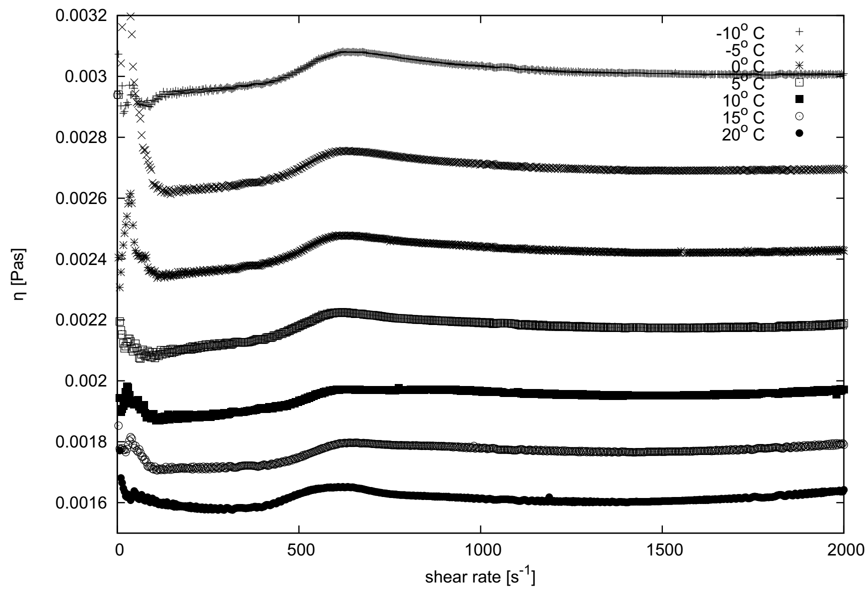

Fig. 2. Results of dynamic viscosity measurements of suspension of 10 wt.% Y_2O_3 in ethylen in various temperature.

ders. It was shown that there is a limit of shear rate at which nanoparticles are "picked up" from the bottom of the measuring cell. For the experimental geometry (plate-plate 60 mm) it was about 120 s^{-1} for 1 wt.% concentration. For the 5 wt.% concentration it was at about 530 s^{-1}. More detailed discussion of this effect and attempt to explain the basis of this phenomenon have been presented in [30].

In measurment with the use of a Rheo-NMR system, in Bruker Biospin Laboratory, we confirmed the non-Newtonian nature of the suspension of Y_2O_3 nanopowder. To study nanosuspensions a plate-cone (diameter 16 mm, cone angle 7°) measuring geometry was used. Suspension of 10 wt.% concentration of Y_2O_3 nanopowder was examined at two speeds of measuring geometry 2.5 rad/s and 5.0 rad/s. In Fig. 3 we presented the velocity distribution inside the sample volume at the distance from the stationary bottom plate of the measuring geometry to the rotating rotor. Newtonian fluids exhibit a linear velocity distribution in this study. In Fig. 3 it is clear that at rotor speed of 5.0 rad/s velocity between the rotor and the stationary plate is non-linear, which shows that the tested sample is a non-Newtonian fluid. Plot presents distribution of velocities in the volume of sample at the place marked on the insert by vertical line. We also made measurements dependent on the viscosity of the concentration of the nanopowder in suspension. We noticed that the dynamic viscosity increases with increasing concentration of the nanopowder, as presented in Fig. 4.

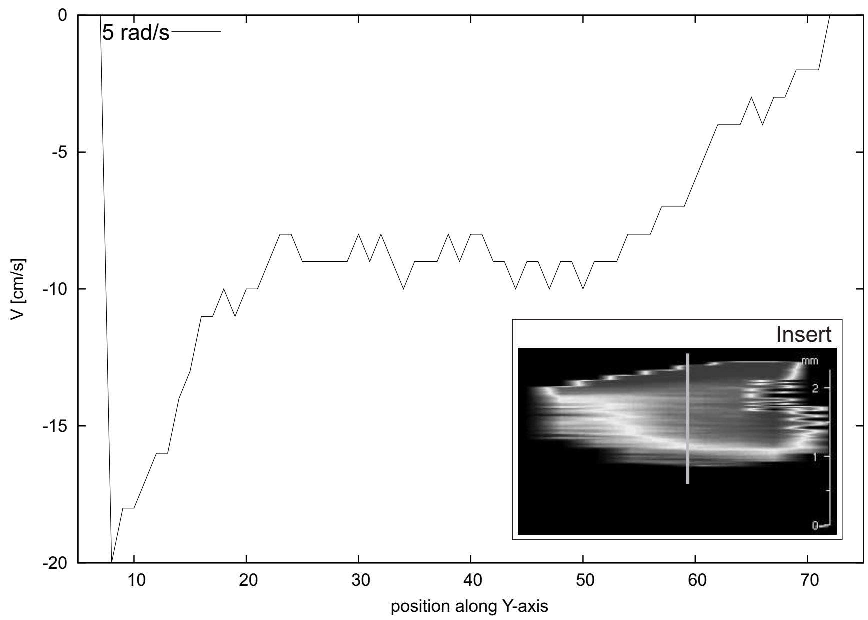

Fig. 3. Distribution of velocity in 10 wt.% Y_2O_3 in ethyl alcohol at rotor speed of 5.0 rad/s. Insert presents velocity map inside examined sample.

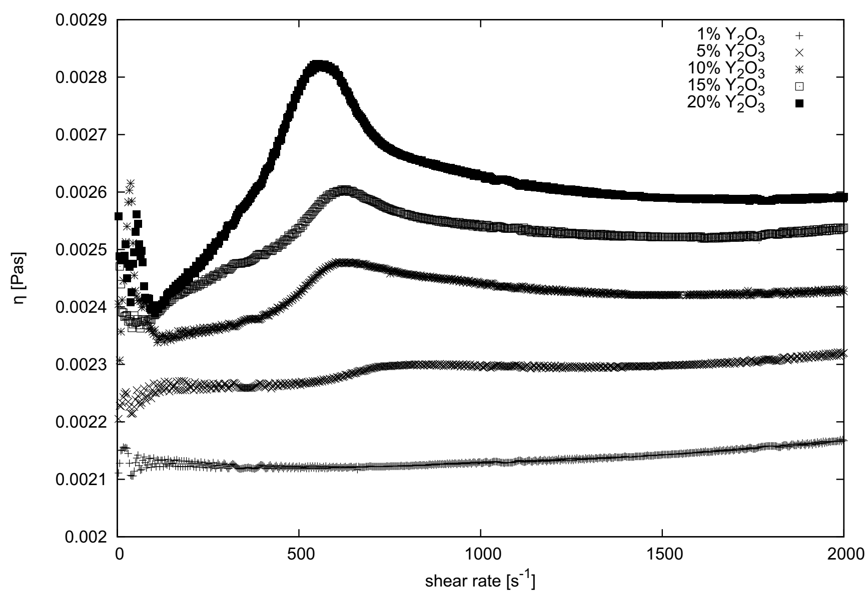

Fig. 4. Dependence of dynamic viscosity of the shear rate for various concentrations Y_2O_3 in ethyl alcohol at 0 °C.

3.2. Magnesium-aluminum spinel ($MgAl_2O_4$)

The viscosity of the nanopowder $MgAl_2O_4$ suspended in ethyl alcohol was measured using HAAKE MARS 2 rheometer, and performed under the same environmental conditions as research of suspensions of Y_2O_3. The results are decidedly different, depending on the type of nanopowder used in the study. In the case of Y_2O_3 we had to deal with sedimentation and a critical value of shear rate, leading to a "pick up" of nanoparticles from the bottom of the measuring geometry. Conversely, with the $MgAl_2O_4$ nanopowder we did not observe this phenomenon. Figure 5 summarizes the results of measurements of dynamic viscosity of $MgAl_2O_4$, depending on temperature. It is clear that temperature does not have as significant effect on the viscosity of the suspension as was observed with the suspension of Y_2O_3. We measured the viscosity dependence on several concentrations of $MgAl_2O_4$, as shown in Fig. 6. From the measurements it is clear that the concentration has a significant effect on the viscosity of the suspension. At lower concentrations (1 wt.%, 5 wt.%) after an initial non-linear dependence of viscosity the shear rate is linear. We can therefore determine that the suspension is a Newtonian fluid. In the case of higher concentration (15 wt.%, 20 wt.%) we observed a decrease of viscosity with increasing shear rate in the entire measuring range.

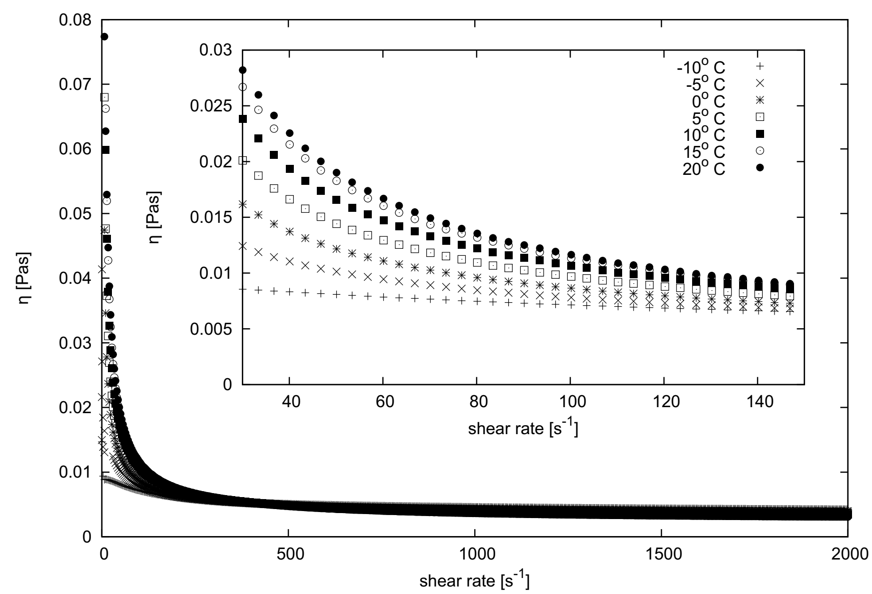

FIG. 5. Dependence of dynamic viscosity of 10 wt.% concentration of $MgAl_2O_4$ in ethyl alcohol for various temperatures.

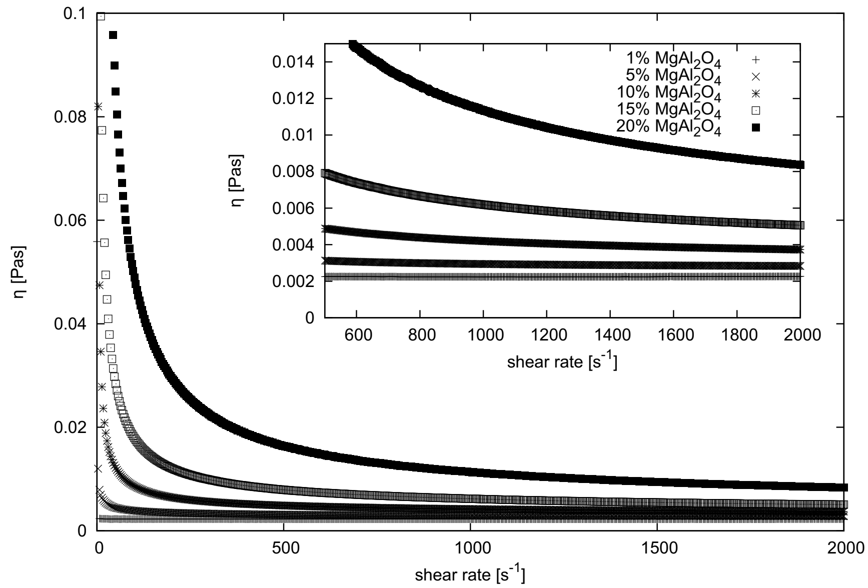

FIG. 6. Dependence of dynamic viscosity of $MgAl_2O_4$ in ethyl alcohol on concentration at 0 °C.

4. Conclusions

Due to the enormous impact of environmental conditions during sample preparation, studies of rheological properties of nanomaterials suspensions are difficult and require great precision. Paper presents the results of research on nanofluids involving various measuring apparatus:

- XRD and SEM at ICBM which allowed us to measure the average sizes of nanoparticles as well as obtain some information about porosity of them,
- HAAKE MARS 2 at RUT allowed us to characterize the viscosity of nanofluids,
- Rheo-NMR at BRUKER in Germany gave us a chance to determine that the measured nanofluid has non-Newtonian nature,
- RheoScope at ThermoFischer Scientific in Germany allowed us to observe sedimentation process during rheological measurements.

We observed differences between the properties of samples prepared under varied environmental conditions. Our research has shown that the rheological properties of suspensions of different nanopowders have significantly different properties. We noticed that for suspensions of nanopowder Y_2O_3 sedimentation is almost immediate. To prevent nanoparticples from falling to the bottom, the usage of higher shear rates is necessary. This is important for industry because it allows the specification of the minimal shear rate to be used in technological

processes. Experiments have shown that the temperature within the range tested had no significant effect on the viscosity of nanosuspension of $MgAl_2O_4$ in ethyl alcohol. On the other hand, the increase of concentration of nanoparticles causes an increase in dynamic viscosity of the nanopowder suspension, and change the nature of the nanosuspension from Newtonian to non-Newtonian.
Further research is needed in this area, which can provide experimental data that can be used to construct a theoretical model.

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