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Thermophysical properties of aqueous nanofluids modified with carbon nanostructures

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The results of the study of thermal conductivity and viscosity of water-based nanofluids modified with commercial detonation nanodiamond (DND) purified under self-propagating high-temperature synthesis conditions are presented, which made it possible to obtain a dispersion of up to 90 nm. Also, using this purification technique, it became possible to obtain stable nanofluids based on DND with a content of up to 1 vol.%, as well as to get an increase in thermal conductivity of up to 26% at 55°C, but the addition of DND led to an increase in the viscosity of the final nanofluid to 62%. The experimental data were compared with theoretical calculations using models to establish the most important parameters for obtaining high thermal conductivity. Another carbon nanomaterial, few-layer graphene, which has a thermal conductivity similar to DND, was also compared.

Keywords: nanofluid, nanodiamond, self-propagating high-temperature synthesis, viscosity, thermal conductivity.

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Introduction

Liquid cooling is one of the most widely used methods of removing excess heat from running machinery, powerful electronic devices and cutting tools during machining operations. Liquid that serves as heat-transfer fluid is the key element of liquid cooling. In addition to high heat-transfer properties, liquid shall have as low viscosity as possible because liquid is often forced via a system using pumps. However, despite the extensive technological development, well-known liquids such as water, alcohols, etc., that cannot remove heat with desired efficiency, are still used as heat-transfer fluids in liquid systems. Therefore, researchers make active efforts to obtain more effective cooling liquids — so-called nanoliquids — by creating stable suspensions of nanomaterials with high thermal conductivity such as nanodiamond (ND).

The diamond's record-breaking thermal conductivity that reaches 2000 W/(m·K) is the main reason why ND is used for nanoliquids [1].

There are many methods to determine thermal and physical properties of nanoliquids [2]. Work [3] used 1 vol.% of surface-modified ND with a dispersity of 11 nm to show that the growth of thermal conductivity was achieved compared with the initial water by 12.7% and 22.8% at 20°C and 60°C, while the dynamic viscosity grew by a factor of 1.5 and 1.8, respectively. In [4], the growth of thermal conductivity was achieved by using 3 vol.% ND of about 7.2% and 9% compared with the initial water at 30°C and 50°C, respectively. In [5], 6 nm 0.25 mass% ND were used to achieve the growth of thermal conductivity by 15% at 60°C compared with the initial water. The authors of [6] used 1 vol.% ND with a mean size of 11 nm to achieve the growth of thermal conductivity by 22.8% at 60°C, while the growth of dynamic viscosity was 79%. As shown in [7], despite the fact that the intuitively expected dependence of the final nanoliquid efficiency on ND dispersity and degree of aggregation cannot be achieved because the concentration and ND aggregate stability in suspension actually play the key role.

A unique method to create ND by way of detonation synthesis was developed in the USSR [8]. ND fabricated using this process were named „detonation nanodiamonds“ (DND). However, the detonation synthesis actually forms a so-called detonation charge, and treatment using various chemical techniques is required to extract ND from this charge [9]. Using a proprietary commercial DND disaggregation process, the Ioffe Institute research teams have developed a method of producing stable water-based suspensions of 4–5 nm DND [10].

This work describes the study of viscosity and heat-transfer properties of water-based nanoliquids with addition of commercial DND treated in the self-propagating high-temperature synthesis (SHS) conditions [11,12] to increase the DND aggregate dispersity.

1. Experiment

1.1. Feedstock

Commercial DND (Special Design and Technological Bureau „Tekhnolog“, Russia) was used as feedstock.

1.2. DND modification technique

Initial DND was treated in the SHS conditions. For this, the DND powder was mixed with ammonia nitrate (AR grade, Russia) in a tumbling drum homogenizer with mass ratio 1:2 during 30 min. Then the obtained mixture was heated to 200°C and held until the completion of gas release. The obtained powder was rinsed, dried at 200°C in the vacuum cabinet (10^{-3} Pa) until the completion of loss of weight.

2. Nanoliquid preparation procedure

Ultrasonic bath (22 kHz) was used to produce nanoliquids. Accurately weighed DND was dispersed in water volume heated to 50°C, then mechanical stirring was performed using an overhead stirrer (100 rpm). The prepared suspension underwent ultrasound treatment during 30 min. The dispersion process at 50°C was carried out to facilitate DND in the water volume by reducing water viscosity in half.

2.1. DND and nanoliquid characterization

Ash content of the initial DND (DNDi) and DND after the SHS process (DND-SHS) was determined by thermal annealing of samples (2 g) during 5 h at 1000°C in a muffle furnace, then the residue was weighed. To maintain the experimental integrity, the DNDi powder was rinsed and dried in the same conditions as the DND-SHS sample. Electronic images of DND-SHS particles were made by the TEM method using the FEI Tecnai G2 30 S-TWIN (100 kV) microscope. DNDi particle dispersity in water was measured by laser diffraction using the Mastersizer 2000 instrument (Malverin, UK). Dispersity of DND-SHS was determined by the DLS method using the Zetasizer Nano ZS instrument (Malverin, UK). The Zetasizer Nano ZS instrument was also used to measure the zeta potential for stability assessment of the produced liquids. Thermal conductivity of nanoliquids was studies by a hot disk method using the SKZ1061C instrument (SKZ, China). The methods uses a flat heating element — a probe, also known as a „hot disk“, that simultaneously serves as a heat source and sensor. According to the recommendations in [13,14], the following conditions were used for nanoliquid measurements: probe diameter 15 mm, measurement time 5 s, and the experiments were performed in a special cell to minimize convective liquid flows. Dynamic viscosity of nanoliquids was measured on the NDJ-9S rotational viscometer (XZBELEC, China).

3. Findings and discussion

Figure 1 shows an electronic image of the DND-SHS sample.

As shown in the figure, 4–5 nm DND particles form aggregates to 150–200 nm. The acquired data was validated by the DLS method (Figure 2).

As shown in Figure 2, the mean dispersity of the DNDi aggregates is 25 – 30 μm, while it is only 80 – 100 nm in the DND-SHS samples. These measurements may be caused by the fracture of DND aggregates due to release of a large amount of reactive gases (oxygen, nitrogen) during the SHS process that penetrate the whole accessible DND volume (including pores). The same mechanism was observed in [15], where a similar dispersity increase effect was achieved during reduction of cobalt nitrate deposited on the DND aggregate surface, the cobalt nitrate was reduced to pure cobalt with release of a large amount of gases. It is also likely that, due to the reactivity of gases released during the SHS process, various contaminations on the DND surface that prevent disaggregation are removed [16]. It was

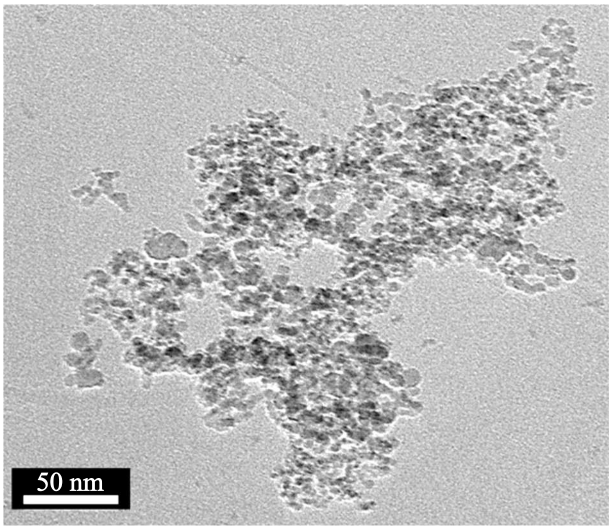

Figure 1. TEM image of the DNS-SHS sample.

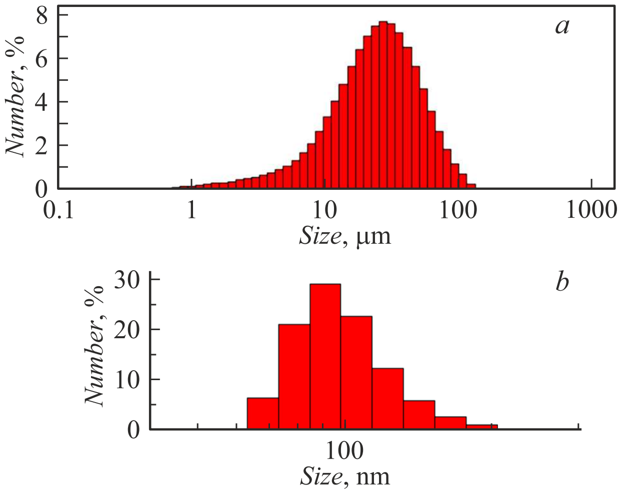

Figure 2. Dispersity measurements of DNDi (*a*) and DND-SHS sample (*b*).

Ash content measurements of DND samples

Sample	Ash content, %	Specific surface area, m^2/g
DNDi	7.4 ± 0.3	244 ± 4
DND-SHS	1.1 ± 0.3	196 ± 3

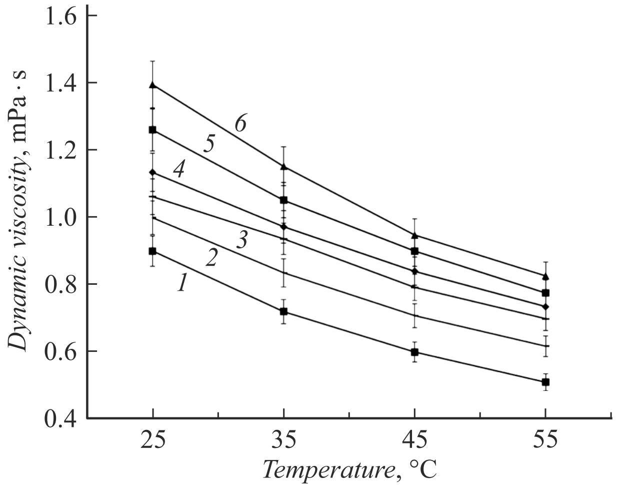

Figure 3. Dynamic viscosity of nanoliquids depending on the DNS-SHS concentration. *1* — initial water, *2* — 0.1, *3* — 0.2, *4* — 0.4, *5* — 0.8, *6* — 1 vol.%.

also established that the DNDi-based nanoluquid is unstable (particle precipitation during 2 h, zeta potential -11.2 mV), while no precipitation (zeta potential -32.5 mV) was observed for the DND-SHS particle nanoliquid.

The table shows ash content measurements (non-combustible residue) of the DNDi and DND-SHS powder.

The table shows that the DND-SHS ash content and specific surface area are much lower which may be caused by contamination removal during the SHS process.

Figure 3 shows the dynamic viscosity measurements of the prepared nanoliquids.

It follows from the figure that introduction of DND-SHS causes a significant increase in the dynamic viscosity of nanoliquids even with a minimum concentration (0.1 vol.%). As the fraction of DND-SHS increased, the growth of dynamic viscosity continued and reached 51% and 62% with 1 vol.% at 25 and 55°C, respectively.

Figure 4 shows the thermal conductivity measurements depending on the DND-SHS concentration at various temperatures.

It can be seen from the figure that the thermal conductivity of nanoliquids at 25 and 35°C is almost independent on the DND-SHS concentration, however, as the temperature grows,the effect of this additive is displayed at high concentrations of DND-SHS (0.4–1 vol.%). Thus, for 1 vol.% DND-SHS, the growth of thermal conductivity at 55°C was 26% compared with the initial water. Note that the obtained values are much lower than the expected and theoretical calculations using the known models such as the Maxwell model [17] (Figure 5) because temperature-induced phenomena such as additional liquid mixing cannot be accounted for in these models.

Figure 5 shows that, irrespective of the thermal conductivity of DND-SHS particles (20–2000 W/(m·K)) assumed for the evaluation, the thermal conductivity of nanoliquid calculated using the Maxwell model is almost unchanged. An assumption was made that the particle geometry, that gives rise to active water mixing, is the key factor affecting the thermal conductivity of nanoliquids at high temperatures. For this, few-layer graphene synthesized from cellulose in the SHS conditions [11,12], particles sizes of which are an order of magnitude larger than those of the DND-SHS particles (Figure 6), and the geometry differs drastically, was used as a reference sample. Thermal conductivity of such material is also estimated as a value up to 5000 [18].

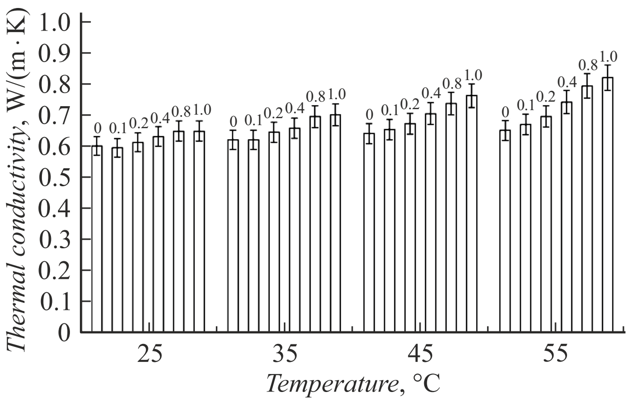

Figure 4. Thermal conductivity of nanoliquids depending on the DND-SHS concentration at various temperatures.

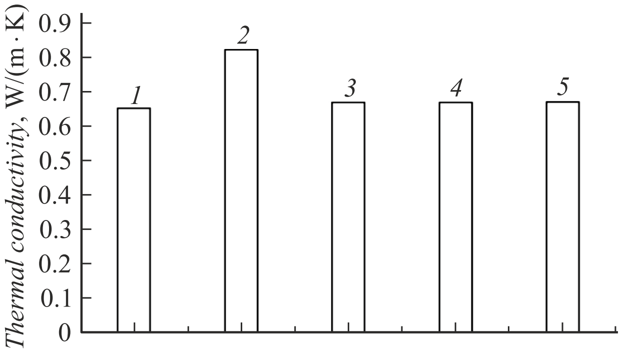

Figure 5. Thermal conductivity data for water and nanoliquid, and calculated thermal conductivities of nanoliquid with 1 vol.% DND-SHS at 55°C according to the Maxwell model (spherical approximation). *1* — thermal conductivity of water at 55°C; *2* — experimentally measured thermal conductivity of 1 vol.% DND-SHS nanoliquid at 55°C; *3* — calculated value according to the model with DND-SHS thermal conductivity = 20 W/(m·K); *4* — calculated value according to the model with DND-SHS thermal conductivity = 200 W/(m·K); *5* — calculated value according to the model with DND-SHS thermal conductivity = 2000 W/(m·K).

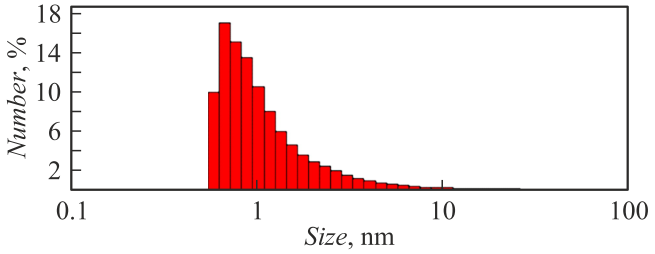

Figure 6. Dispersity measurements of the few-layer graphene sample.

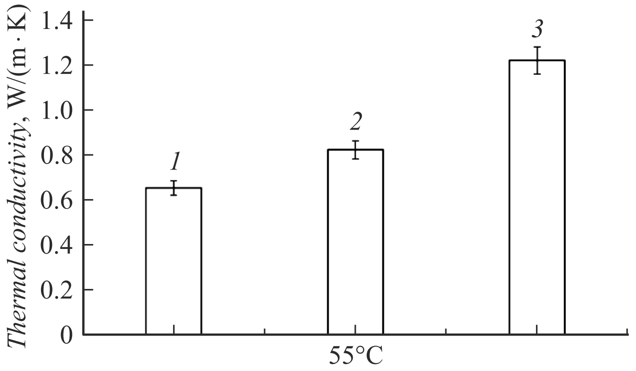

Figure 7. Thermal conductivity measurements of water-based nanoliquids at 55°C. *1* — initial water, *2* — 1 vol.% DND-SHS, *3* — 1 vol.% few-layer graphene.

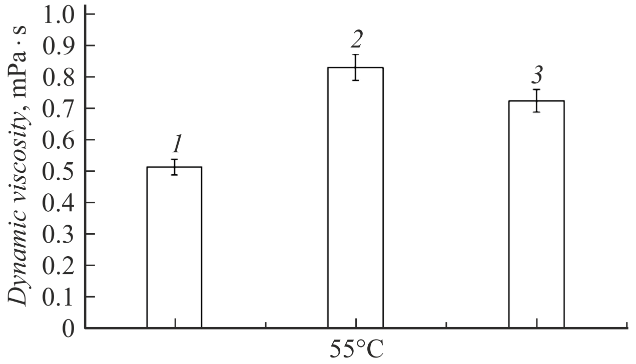

Figure 8. Dynamic viscosity measurements of water-based nanoliquids at 55°C. *1* — initial water, *2* — 1 vol.% DND-SHS, *3* — 1 vol.% few-layer graphene.

As shown in Figure 7, addition of the few-layer graphene particles gave the growth of thermal conductivity by 87% compared with the initial water, while the same amount of DND-SHS gave the growth of only 26%.

Figure 8 shows comparative dynamic measurements of nanoliquids modified with DND-SHS and few-layer graphene.

As shown in Figure 8, addition of few-layer graphene particles, as in the DND-SHS case, leads to the growth of dynamic viscosity. However, the growth of dynamic viscosity, when the few-layer graphene particles were added, was 41%, while for the DND-SHS particles the growth was 62%.

Conclusion

Stable water-based nanoliquids with a particle size of 80–100 nm were achieved by means of SHS treatment of commercial detonation ND. It was found that, despite the growth of dynamic viscosity with increasing particle concentration (to 62% compared with the initial water), the thus treated detonation ND increased the thermal conductivity by 26% at 55°C compared with the initial water. Experimental comparison of carbon nanomaterial efficiency with a similar order of magnitude of the expected thermal conductivity of particles, i.e. detonation ND and few-layer graphene, but with different dispersity, has shown that particles with lower dispersity should be preferably used to create nanoliquids with high thermal conductivity.

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Conflict of interest

The authors declare no conflict of interest.

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