Thermal conductivity and heat capacity of nanofluid based on water modified by hybrid material of composition detonation nanodiamonds-carbon nanotubes

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ABSTRACT
For the first time, the rheological and thermophysical properties of stable nanofluids based on water and ethylene glycol modified by the DND-CNT hybrid material and obtained without surfactants have been investigated. It was found that at the maximum concentration of the DND-CNT hybrid material 0.5 wt. % for water and 0.3 wt. % for ethylene glycol was increased in thermal conductivity at 50°C to 84% and 44%, respectively, without changing the dynamic viscosity. It is shown that the use of a hybrid material can reduce the freezing point by 11°C in the case of water and by 7°C in the case of ethylene glycol.

1. Introduction
Carbon nanomaterials (CNT) such as detonation nanodiamonds (DND) and carbon nanotubes (CNT) are actively used to create nanofluids. The choice of these very CNT is due to their high thermophysical properties. So the DND thermal conductivity is estimated at 2300 W/(mK),[1] and the CNT thermal conductivity at 3000 W/(mK).[2] Based on the high thermal conductivity of DND and CNT, the researchers expect to significantly increase the thermal conductivity of base fluids (for example, water or ethylene glycol) using these carbon nanostructures as modifying additives. Many experimental studies have shown that using DNDs or CNTs when creating nanofluids it is possible to obtain a significant increase in thermal conductivity compared to the base liquid.[3-5] For example, in work,[6] the authors found that the presence of multi-walled CNT (MWCNT) and gum arabic enhanced the thermal conductivity of the nanofluids based on solar glycol by 30.59% at 0.6 vol.% MWCNT and 1.25 gum arabic wt. % at 50°C.

However, for several reasons, it has not yet been possible to fully unleash the potential of these carbon nanostructures and create nanofluids with record thermal conductivity. Because the properties of nanofluids depend on many factors: the materials used, the characteristics of the nanomaterials used, their ratio, the nanofluid synthesis techniques used, the concentration of the hybrid material, and so on. For example, in ref. [7] the authors noted that the dynamic viscosity of aqueous nanofluids with CNT dependent on the time of sonication. It was found that the lowest dynamic viscosity was shown by the samples with the shortest (20 min) and longest (120 min) ultrasonic treatment time.

Therefore, to create nanofluids, researchers actively use hybrid materials based on carbon nanomaterials (DND, CNT and graphene nanostructures) and nanoparticles of metals and their oxides.[8] By combining the properties of these materials, the authors hope to obtain a synergistic effect, which will make it possible to obtain higher thermophysical properties of final nanofluids. However, as in the case of conventional CNT, there are problems of obtaining a stable nanofluid, a strong dependence of the final thermophysical properties on the characteristics of the starting materials, the method of obtaining nanofluids, and so on, which does not allow to reveal the potential of hybrid nanofluids fully.[9] It should also be noted that in most cases, researchers use conventional mechanical mixtures rather than chemically bonded hybrid materials.

In ref. [10] the authors used a mechanical mixture of multilayer graphene and multi-walled carbon nanotubes in a ratio of 1:1 (vol. fraction) at a concentration of up to 0.07 vol. % to increase the thermal conductivity of ethylene glycol. The authors found that the use of a hybrid material makes it possible to obtain an increase in thermal conductivity at 50°C by 50%, while the use of initial MWCNTs and low-layer graphene at the same concentration made it possible to achieve growth only by 22% and 37%, respectively. According to the authors, the enhancement was attributed to the combination of high thermal conductivity of CNT and multilayer graphene and high surface area of multilayer graphene-CNT hybrid structure.

In[11] the authors investigated the thermophysical properties of a hybrid material graphene-multi-walled CNT. It was found that the synthesized hybrid material in a
concentration of up to 0.04 vol. % forms stable suspensions in water without surfactants and makes it possible to achieve an increase in thermal conductivity by 11.3% and 97.5% at 25 and 50°C, respectively. A comparative test showed that using 1 vol. % MWCNT, the authors managed to increase thermal conductivity by only 6% at 25°C.

This work presents for the first time the results of a study of the rheological and thermophysical properties of nanofluids based on water and ethylene glycol, where a DND-CNT hybrid material was used as an additive.

2. Experimental

2.1. Initial materials

Deionized water (electrical conductivity \( q \) was 5.5 \( \mu S/cm \)) and ethylene glycol were used as base fluids. A DND-CNT hybrid material was used as an additive. MWCNT were synthesized on the surface of DND aggregates by the CCVD method. The volume fraction of MWCNTs was 44%. The synthesis procedure is described in detail in ref. [12].

2.2. Nanofluids preparation

To obtain stable suspensions, the hybrid material DND-CNT was placed in portions (0.1 of the total weight of the sample) into the initial liquid (filtered water, ethylene glycol) preheated to 70°C with constant stirring using an overhead stirrer. The time interval between the additions of the next portion was 10 minutes. After adding the entire mass of the hybrid material, the liquid was subjected to ultrasonic treatment in an ultrasonic bath for 60 min with constant stirring using an overhead stirrer and a temperature of 70°C. The maximum concentration of the DND-CNT hybrid material in nanofluids based on water and ethylene glycol was 0.5 wt. % and 0.3 mass. %, respectively. The maximum concentration of reference samples (DND, SWCNT, and mechanical mixture of DND and SWCNT) was 0.2 wt. %.

3. Experimental technique

The measurement of the particles size and zeta potential was performed with a dynamic light scattering (DLS) method on the device ZetaSizer Nano ZS Malvern (USA).

The boiling point of liquids was determined using an ebulliometer, the measurement error was \( \pm 0.3 \) °C. The freezing point of liquids was investigated using a hydrometer-refractometer and a climatic chamber CM-30/100-80 TX (RF), the measurement error was \( \pm 0.5 \) °C.

Thermophysical properties (thermal conductivity and heat capacity) were measured by the method of monotonic cooling on a KITT "nanofluids" device (KB “Teplofon,” Novomoskovsk, RF), the error in measuring thermal conductivity and heat capacity was no more than 5%.

2.3. Nanofluids properties

The rheological and thermophysical properties of nanofluids were measured by the method of monotonic cooling on a KITT "nanofluids" device (KB “Teplofon,” Novomoskovsk, RF), the error in measuring thermal conductivity and heat capacity was no more than 5%.

4. Results and discussion

Figure 1 shows a photograph of the initial liquids (water, ethylene glycol) and nanofluids with a DND-CNT hybrid material.

It was found that the DND-CNT hybrid material forms stable suspensions in water and ethylene glycol without the formation of a precipitate at a concentration of 0.5 wt. % and 0.2 wt. %, respectively, without the use of surfactants. These results were confirmed by measuring the zeta potential, which was 47 and 44 mV for nanofluids based on water and ethylene glycol, respectively. Similar values of the zeta potential were obtained for lower concentrations of the hybrid material.

Figure 2 shows the results of measuring the particle size of the DND-CNT hybrid material in water and ethylene glycol.

As can be seen from Figure 2, the average particle size of the hybrid material in water is about 40–50 nm, while the particle size in ethylene glycol is 90–100 nm. This discrepancy can be explained by the fact that water is a polar medium compared to ethylene glycol, which contributes to the better dispersion of particles of the DND-CNT hybrid material.

Figure 3 shows the results of measuring the change in the boiling point of nanofluids based on water and ethylene glycol with a DND-CNT hybrid material.

As shown in Figure 3, the addition of a DND-CNT hybrid material has practically no effect on the boiling point of the base liquids, both water and ethylene glycol. At the maximum concentration of the hybrid material (0.5 wt. % for water and 0.3 wt. % for ethylene glycol), the change in boiling point was 4% and 2% for water and ethylene glycol, respectively. At the same time, the hybrid material has a much more significant effect on the freezing point of water and ethylene glycol than on their boiling point (Figure 4).

The introduction of the hybrid material made it possible to reduce the freezing point by 11°C in the case of water, and by 7°C in the case of ethylene glycol. Such changes in the freezing temperature can already expand the applicability of nanofluids when used at negative temperatures. In ref.

![Figure 1](image1.png)

**Figure 1.** Photograph of the initial liquids and nanofluids based on them with a DND-CNT hybrid material after holding for 30 days. (1) initial water, (2) water-based nanofluid with 0.5 wt. % of hybrid material DND-CNT; (3) ethylene glycol; (4) nanofluid based on ethylene glycol with 0.3 wt. % of hybrid material DND-CNT.
the authors also noted the ability of CNT to lower significantly the freezing point of liquids (by 5–6°C). The authors also found that the freezing point of nanofluids was in direct proportion to the concentration of nanocarbons.

Figure 5 shows the results of measuring the dynamic viscosity of the obtained nanofluids. As shown in Figure 5, the introduction of a hybrid material practically did not lead to a change in the dynamic viscosity of the initial fluids. The absence of a significant change in the viscosity of liquids at relatively low concentrations of modifying additives was observed, for example, in ref. [14] where CNTs were used as a modifying additive to water.

Figures 6 and 7 show the results of studying the thermal conductivity of nanofluids based on water and ethylene glycol. It was found that the introduction of a hybrid material of the DND-CNT composition as an additive makes it possible to increase the thermal conductivity of both water and ethylene glycol. As shown in Figures 6 and 7, the thermal
Figure 5. Dependence of the dynamic viscosity of nanofluids on the concentration of the hybrid material. (a) nanofluid based on water; (b) based on ethylene glycol.

Figure 6. Thermal conductivity of water-based nanofluid. (a) dependence on the concentration of the hybrid material at 50 °C, (b) dependence on temperature (0.5 wt.% of the hybrid material), where (1) thermal conductivity of water, (2) thermal conductivity of nanofluid.

Figure 7. Thermal conductivity of ethylene glycol-based nanofluid. (a) dependence on the concentration of the hybrid material at 50 °C, (b) dependence on temperature (0.3 mass% of the hybrid material), where (1) thermal conductivity of ethylene glycol, (2) thermal conductivity of nanofluid.
conductivity of nanofluids is directly dependent on the concentration of the hybrid material. Thus, at the maximum concentration of the DND-CNT hybrid material, which is 0.5 wt. % for water and 0.3 wt. % for ethylene glycol, we managed to increase thermal conductivity at 50°C up to 84% and 44%, respectively. It was found that the thermal conductivity of nanofluids also increases with increasing temperature.

Figure 8 shows the results of a study of the specific heat capacity of nanofluids based on water and ethylene glycol.

As shown in Figure 8, introducing a DND-CNT hybrid material as an additive lead to an insignificant decrease in the heat capacity of both water and ethylene glycol.

5. Conclusions

It has been shown experimentally that the DND-CNT hybrid material even at low concentrations (no more than 0.5 wt. %) is an effective additive in the creation of nanofluids and allows a significant increase in the thermal conductivity of the base fluids without changing their dynamic viscosity. An important advantage of using a DND-CNT hybrid material is the possibility of obtaining stable nanofluids without the use of surfactants. In addition, a hybrid material of the DND-CNT composition allows reducing the freezing point of liquids, which expands the possibility of their application at low temperatures.

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