Viscosity and rheology of the ethylene glycol based nanofluids with single-walled carbon nanotubes

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Abstract. The work is devoted to the experimental study of the viscosity and rheology of nanofluids based on ethylene glycol with single-walled nanotubes. Polyvinylpyrrolidone is used as a dispersant. The weight concentration of nanotubes ranged from 0.01 to 1%. In all cases, the weight concentration of the dispersant was controlled. The measurements were carried out in the temperature range from 20 to 40°C. It was shown that at all weight concentrations the solution of ethylene glycol and dispersant is a Newtonian liquid, and at a maximum concentration (4%) the viscosity of the solution is two and a half times higher than the viscosity of ethylene glycol. At the same time, all the studied nanofluids turned out to be non-Newtonian and have a pseudoplastic character. It was established that ultrasonic treatment of nanofluids leads to partial degradation of the dispersant and a decrease the base fluid viscosity. The degree of this degradation increases with increasing ultrasonic processing power. With the considered low weight concentrations of nanotubes, the dependence of the viscosity coefficient of the nanofluid on temperature is determined by the corresponding dependence of the base fluid.

1. Introduction

Dozens of groups in different countries of the world have actively studied the thermophysical properties of nanofluids for about a quarter of a century. At present, many thermophysical properties of nanofluids with spherical particles are systematically studied. Today it has been established that these properties are not described by classical theories. In particular, the viscosity of nanofluids depends not only on the concentration of particles, but also on their size and material (see, for example, [1, 2] and the literature cited there).

However, in practice, liquids with non-spherical particles are often encountered. The most typical of such nanofluids are the dispersed fluids with carbon nanotubes (CNT), which are the sheets of graphene rolled into a cylinder. The carbon nanotubes possess exceptional mechanical, electrical, and thermal properties [3]. Usually, for practical use, CNT should be dispersed in liquids. Water, ethylene glycol, various oils, etc. can be used as the base fluid. The unique properties of CNT make it natural to expect special properties for the corresponding nanofluids.

Possible and already used practical applications of such nanofluids initiated numerous studies of their thermophysical properties [4–8]. However, the structure of these nanofluids differs significantly from the structure of fluids with spherical particles. The CNTs are essentially the heterogeneous formations. Their diameter is of the order of nanometer or several nanometers, whereas the length varies from tens...
to hundreds of nanometers (or more). Therefore, even at relatively low concentrations, CNTs actively interact with each other in the medium, forming large conglomerates. To make the corresponding nanofluid as homogeneous as possible, on the one hand, various surface-active substances (surfactants) are used, and on the other hand, the nanofluid is subjected to ultrasonic treatment. Various polymers are often used as surfactants. In the general case, the thermophysical properties of these nanofluids can vary considerably depending on the way of their treatment.

The purpose of this work is to study experimentally the viscosity and rheology of nanofluids based on ethylene glycol (EG) with single-walled CNT (SWCNT). The SWCNTs produced by OCSiAl, Novosibirsk were used. Polyvinylpyrrolidone ((C\(_6\)H\(_9\)NO\(_n\))\(_n\) PVP) was used as a dispersant. About two dozen different nanofluids have been studied. Weight concentrations of SWCNT ranged from 0.01 to 1%. At the same time, PVP concentrations varied from 0.01 to 4%.

2. The methodology of the experiments

Nanofluids were prepared using the standard two-step method. First, a specified amount of SWCNT was added to the base fluid (EG+PVP), then this suspension was mechanically mixed. In order to destroy the formed CNT conglomerates, the suspension obtained after mechanical mixing was subjected to ultrasonic treatment (UST). For this, a UZTA-0.4 / 22-OM disperser with a maximum power of 400 W and ultrasonic oscillation frequency of 22 \(\pm\) 1.65 KHz was used.

The viscosity and rheology of fluids were studied using a Brookfield DV3RV rotary viscometer with a UL spindle. Testing conducted on measuring the viscosity of ethylene glycol and its dependence on temperature showed that the accuracy of measuring the viscosity coefficient is about 2%. The measurements were carried out in the temperature range from 20 to 40°C.

3. Base fluid properties

Since the objective of this work is a systematic study of thermophysical properties of nanofluids based on ethylene glycol (EG) with a single-walled carbon nanotube with PVP as a dispersant, as a first step it was necessary to study the properties of the base fluid used EG+PVP.

The measurements have shown that with high accuracy, the viscosity of both pure ethylene glycol and all EG+PVP solutions is almost independent of the spindle speed and, therefore, of the shear rate. Thus, these fluids are the Newtonian ones. Table 1 shows the average values of the viscosity coefficient \(\mu\) of the EG+PVP solution for different weight concentrations of PVP. The EG+PVP solution with the maximum concentration of PVP (4%) exceeds the viscosity of the pure EG by two and a half times. Nevertheless, it is a Newtonian fluid. The dependence of the viscosity coefficient on the weight concentration \(w\) of PVP turns out to be linear and is well described by the correlation

\[
\mu = 16.62 + 6.1w. \tag{1}
\]

| \(w\) | 0% | 0.2% | 0.4% | 0.8% | 1% | 2% | 4% |
|---|---|---|---|---|---|---|---|
| \(\mu,\text{cP}\) | 16.62 | 17.42 | 18.76 | 20.12 | 21.06 | 27.02 | 41.66 |

The active interaction of the SWCNTs leads to formation of their conglomerates. As a result, the distribution of SWCNTs in the dispersion turns out to be extremely non-uniform, which significantly changes its physical and mechanical properties. As it was already mentioned, the standard methods for creating more homogeneous dispersions and controlling conglomerates are those using UST of the suspensions obtained. In order for the UST to be effective, it is necessary to pump sufficiently high energies into the suspension. This has a little effect on the structure of simple liquids, which are commonly used as base fluids. However, various polymers with a complex structure and often quite weakly bound groups are usually used as a dispersant. Such polymers under the influence of UST can significantly change their structure, and hence the structure of the entire base fluid. This fact has long
been established [9–11]. Naturally, it is therefore necessary to study the viscosity and rheology of the base fluid after the UST, varying the energy supplied for processing.

It is established that the investigated solutions after the UST are Newtonian. However, the viscosity of the solutions after the UST was lower than that of solutions not subjected to UST. Figure 1 clearly demonstrates this. The viscosity of the solution after UST increases linearly with increasing PVP concentration, and the difference between the viscosity of two solutions (with and without UST) is greater, the higher the PVP concentration. With a maximum concentration of PVP (4%), this difference exceeds 10%.

![Figure 1. Comparison of the viscosity coefficient of EG+PVP solutions with (triangular labels) and without (square labels) UST.](image)

| w (%) | μ (cP) | N (W·h/l) | w (%) | μ (cP) | N (W·h/l) |
|-------|--------|-----------|-------|--------|-----------|
| 0,1%  | 17,25  | 1500      | 1%    | 21,16  | 1500      |
| 0,1%  | 17,29  | 1000      | 1%    | 21,27  | 1000      |
| 0,1%  | 17,35  | 500       | 1%    | 21,45  | 500       |
| 0,4%  | 18,38  | 1500      | 4%    | 36,98  | 4480      |
| 0,4%  | 18,48  | 1000      | 4%    | 38,43  | 2800      |
| 0,4%  | 18,59  | 500       | 4%    | 40,15  | 1120      |

Since it was shown that UST significantly changes the viscosity of solutions, it was necessary to understand how the applied power N affects the viscosity value. The concentration of PVP varied from 0.1 to 4%, and the input power varied from 500 to 4800 W·h/l. The obtained measurement data are shown in table 2. The measurements show that at weight concentrations of PVP of 0.1, 0.4 and 1%, the viscosity coefficient changes within 1%, but in all cases there is a systematic decrease in viscosity with an increase in input power. This indicates the degradation of PVP even at low concentrations. This degradation is particularly well seen at the maximum concentration of PVP. Here, at maximum power, the viscosity coefficient changes by about 8%. It is important to emphasize that in the studied range of power input, the viscosity of the solution decreases linearly with increasing power.

To study the effect of temperature, three solutions of different concentrations were studied: pure EG and EG solutions + 0.4% PVP; EG + 1% PVP. The viscosity and rheology of each solution were studied at 25, 30 and 40°C. First of all, it can be stated that in all cases the solutions studied had the Newtonian rheology. The viscosity of both ethylene glycol and EG+PVP solutions decreases with increasing temperature. However, at the considered concentrations of PVP, the relative viscosity coefficient of the
solution \( \mu_r = \mu / \mu_{EG} \) does not depend on temperature, it is constant within the limits of measurement accuracy (here \( \mu_{EG} \) is the viscosity coefficient of the pure ethylene glycol). This means that at given concentrations of PVP, the dependence of the viscosity of solutions under consideration on temperature is determined by the corresponding dependence of ethylene glycol.

4. Viscosity and rheology of nanofluids

In the experiments, the weight concentration of SWCNTs varied from 0.01 to 1%. In this case, the weight concentration of the dispersant was either equal to the concentration of single-walled carbon nanotubes, or it was twice greater. An example of the dependence of the viscosity coefficient of nanofluid on the spindle speed \( N \) of the rotational viscometer (or shear rate \( \dot{\gamma} \)) is shown in Fig. 2, and the dependence of the stresses \( \tau \) on the shear rate is shown in Fig. 3. In all cases, nanofluids have the non-Newtonian rheology. Their rheology is well described by the power fluid model

\[
\mu = k \dot{\gamma}^{n-1}.
\]  

In all cases, with an increase in the concentration of SWCNTs, the liquid index \( n \) decreases, and the consistency parameter \( k \) increases.

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Figure 2. Dependence of the viscosity coefficient of nanofluids at different concentrations of single-walled carbon nanotubes on the shear rate.
Conclusion

We will formulate the main results. First of all, it is shown that all base fluids are Newtonian. However, the addition of PVP to ethylene glycol significantly increases the viscosity of the resulting solution. This increase is well described by equation (1) and at 4% PVP concentration, the viscosity of the resulting solution is two and a half times higher than the viscosity of pure ethylene glycol. On the other hand, the studied nanofluids with OWCNTs are non-Newtonian and their rheology is well described by model (2).

The ultrasonic treatment leads to degradation of PVP, which affects the viscosity of the corresponding solution of EG+PVP. It is important to emphasize that the degree of PVP degradation also grows almost linearly with pumping the ultrasonic energy into the solution. Degradation of PVP leads to a decrease in the viscosity of the solution. Bearing in mind the future applications of PVP, it is necessary to understand how the degradation of PVP with UST reduces the efficiency of destruction of SWCNT conglomerates. The lifetime of nanofluids and dispersions with SWCNTs is their most important characteristic. Usually, in order to return to nanofluid its properties some time after preparation, it is “stirred up”, that is, it is first mechanically mixed and then subjected to additional UST. However, with a high degree of certainty, it can be predicted that such an operation in the general case will not return the original properties of the nanofluid. When using PVP, this occurs due to the fact that PVP links, degraded during nanofluid creation, are not restored, and additional UST leads to further degradation of PVP. As a result, such a recovered nanofluid will have a deliberately lower viscosity as compared with the initial one.

Re-mixing and ultrasonic processing can be effective in two cases. First, if dispersant was not used in the preparation of nanofluid. And secondly, when using dispersants with stable molecular bonds, which are practically not destroyed at a given power of the UST. It is clear that the systematical study of the stability of dispersant used should be carried out previously.

The studied dependence of viscosity on temperature is extremely important from a practical point of view. The dependences obtained, however, are fairly typical. Since the concentrations of SWCNTs are low, the nature of the dependence of nanofluid viscosity on temperature is determined by the corresponding dependence for the base fluid. This is generally typical of nanofluids with spherical particles [12–14].
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