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Viscoelastic properties of nanofluids with carbon tubes

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The method of diffusion wave spectroscopy is used to study the microrheology of several nanofluids based on water, ethylene glycol and isopropyl alcohol with single−wall and multi−wall nanotubes. Their viscosity and rheology have been previously investigated, and it has been shown that, starting with a certain concentration of carbon nanotubes, nanofluids are non−Newtonian and viscoplastic. At the same time, it was experimentally established that these nanofluids are viscoelastic. Various viscoelastic characteristics of these nanofluids have been systematically studied and compared.

Keywords: viscoelasticity, nanofluid, microrheology, carbon nanotubes.

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Nanofluids with carbon nanotubes (CNTs) have been intensely studied already for more than twenty years. This is first of all connected with already existing and potentially possible applications of such nanofluids in creating new materials, biomedical technologies, thermophysics, etc. [1–4]. By now, there have been published hundreds of papers devoted to studying thermophysical characteristics of these nanofluids. A significant part of those publications concerns investigation of viscosity and rheology of nanofluids with CNTs. Analysis of the obtained data is rather complicated because in absolute majority of works properties of different nanofluids were actually studied, namely, of those based on different basic fluids, containing dispersants or free of them, and, finally, containing either single−wall CNTs (SWCNTs) or multiwall CNTs (MWCNTs). Along with this, prediction of viscosity and rheology is extremely important for practical purposes. What is also crucial is to understand the differences in using nanofluids containing SWCNTs and MWCNTs. Therefore, to reveal characteristic features of rheology and viscosity of CNT−containing nanofluids, it is necessary to consider and analyze these properties for well−defined nanofluid classes. The first steps in this direction were made in papers [5–7] where SWCNT and MWCNT nanofluids based on the same base liquids were studied. Data obtained in this study, as well as those known from literature, enable formulation of two main conclusions. The first one is that most of CNT−containing nanofluids appear to be non−Newtonian, moreover, pseudo — and viscoplastic. The other states that viscosities of SWCNT nanofluids are essentially higher than those of MWCNT nanofluids.

The above−mentioned non−Newtonian behavior of those nanofluids evidences that they possess viscoelastic properties. To reveal the nature of these properties, microrheology of CNT nanofluids was studied in this work. For this purpose, optical contactless instrument Rheolaser MASTER^{TM} was used. The investigation procedure was based on one of dynamic light scattering methods referred to as diffusive wave spectroscopy [8,9]. Samples of suspensions in 20−ml glass vials were irradiated with a 650−nm laser beam. Radiation scattered from the sample particles gave rise, due to photon interference, to a speckle field. A CCD chamber detected the speckle field permanently varying due to Brownian movement of particles, and then the time dependence of their mean−square displacement (MSD) was calculated.

Nanofluids were prepared by the two−stage method. At the first stage, the necessary mass amount of CNTs was added to the base fluid and agitated mechanically. In a number of cases, dispersants were used: sodium dodecylbenzene-sulfate (SDBS), polyvynylpyrrolidon (PVP) and sodium dodecyl-sulfate (SDS). To prevent formation of CNT agglomerates at the second stage, the nanofluid was subject to ultrasound processing (USP) using setups „Volna“ UZTA-0.4/22-OM and UZTA-0.8/22-OM. The USP duration varied from 30 to 120 min. CNT size distributions in the prepared nanofluids were controlled by the dynamic light scattering and electroacoustic methods. This, for instance, allowed also choosing appropriate USP mode.

Nanofluids were prepared based on ethylene glycol (EG), EG + PVP, EG + SDBS, W + PVP, W + SDBS, W + SDS (W is water) and isopropyl alcohol (IPA). The CNT weight concentration varied from 0.025 to 1%. The dispersant weigh concentration was either equal to the CNT concentration or twice as high. In the process, SWCNTs produced by OCSiAl (Novosibirsk, Russia) were used; their mean diameter was 1.6 ± 0.4 nm, specific surface area determined by the BET (Brunauer−Emmett−Teller) method [10] was 510 m^2/g. As per the atomic−force

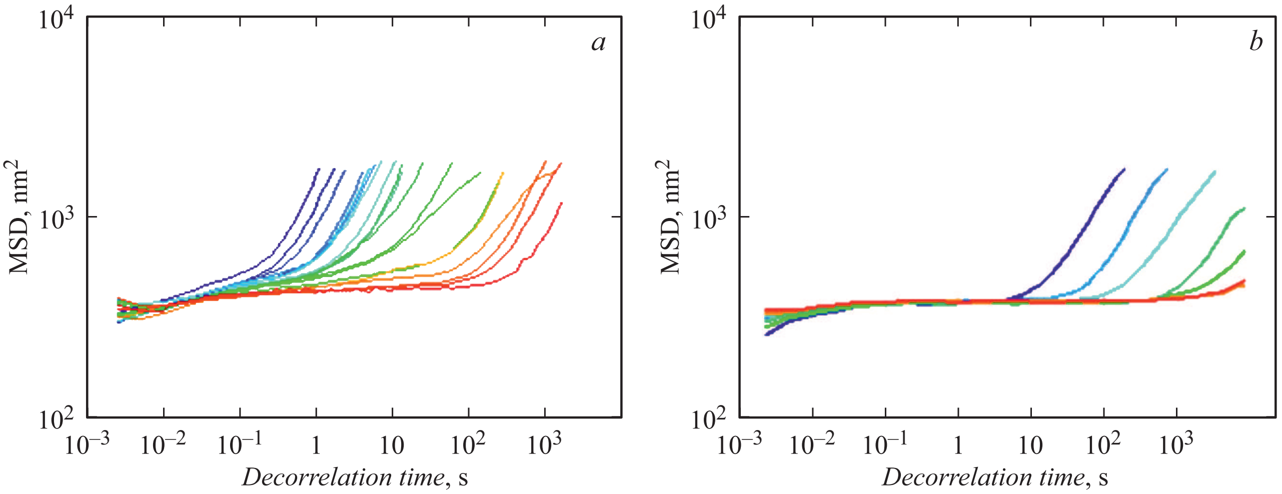

Figure 1. Mean–square displacement of EG–based SWCNT nanofluid at SWCNT weight concentrations of 0.05 (*a*) and 0.2% (*b*).

microscopy data, SWCNT length exceeded 4 μm, while their mean density was 1.8 g/cm^3. MWCNTs of two types were used: Taunite-M and Taunite-MD (produced by „NanoTechCenter“, Tambov, Russia). Inner diameter of those MWCNTs varied from 5 to 15 nm, while their outer diameter was 8 to 30 nm. Their specific surface area exceeded 270 m^2, while the length exceeded 5 μm. The main difference consisted in the number of carbon layers. This number was 6 to 10 for Taunite-M and 30 to 40 for Taunite-MD. Naturally, mean densities of these MWCNTs were also different: 1.4 g/cm^3 (Taunite-M) and 1.9 g/cm^3 (Taunite-MD).

Quality of the obtained nanofluid was controlled by its optical density (permeability) and stability. For this purpose, spectrophotometer UV-3600 and colloidal stability analyzer Turbiscan were used. Thermophysical properties of all the prepared nanofluids retained for at least several weeks.

The nanofluid viscosity and rheology were studied using Brookfield rotational viscometer LVDV-II + Pro. Measurement accuracy was no worse than 2%. It was established that nanofluids based on EG, EG + PVP, IPA, W + PVP, W + SDBS with SWCNTs were viscoplastic, and their rheology was well describable by the Herschel–Bulkley model: $\mu = \tau_0/\dot{\gamma} + k_\nu \dot{\gamma}^{n-1}$, where n is the fluid index, k_ν is the consistency parameter, μ is the viscosity coefficient, $\dot{\gamma}$ is the rate of displacement, τ_0 is the limiting stress. Nanofluids based on EG, EG + SDBS and IPA with MWCNTs were also viscoplastic with rheology describable by the Herschel–Bulkley model, while nanofluids with the same CNTs based on W + PVP, W + SDBS and EG + PVP appeared to be Newtonian.

In a viscos Newtonian fluid, diffusion of particles takes place, and their MSD increases linearly with time. The slope of the relevant straight line is proportional to the sample viscosity. When particles move in an ideally elastic fluid, MSD reaches a plateau corresponding to the equilibrium between thermal energy and elastic interaction energy [11]. Figs. 1, *a* and *b* present time dependences of MSD for EG–based nanofluids at two SWCNT weight concentrations *w* (0.05 and 0.2%). In Fig. 1, as well as in Fig. 2, curves are plotted in accordance with the decorrelation time increasing from left to right, the time steps are nonuniform and vary from a few seconds at the beginning to tens of minutes at the end. Curves representing MSD versus time have both a sloped section and a plateau, which corresponds to the viscoelastic behavior. The section of the nanofluid elastic behavior increases with increasing SWCNT concentration; vice versa, the viscous behavior section becomes less sloped, which corresponds to a decrease in the SWCNT diffusion coefficient.

Figs. 2, *a*, *b* illustrate the MSD evolution for nanofluids also based on EG but possessing MWCNT concentrations of 0.05 and 1%. At lower concentrations, viscous behavior is actually observed, while pronounced viscoelastic properties are fixed only at the concentration of 1% (Fig. 2, *b*). Comparison of Figs. 1, *b* and 2, *b* demonstrates that in both cases the MSD values appear to be close to each other, but the MWCNT weight concentration is 5 times higher. This complies with the obtained experimental data on rheology.

The height of the MSD(t) curve plateau characterizes the sample properties and is describable by the elasticity index (IE). The plateau height decrease is related with an increase in the sample elasticity. Elasticity index EI is proportional to elastic modulus G' on the plateau and enables observing the sample elasticity variation with time or comparing elasticities of same–type samples. On the other side, macroscopic viscosity index MVI is just the index characterizing the sample viscosity. Index MVI is inversely proportional to the MSD curve slope in linear coordinates. The higher is index MVI, the higher is the sample viscosity. Index MVI is proportional to the sample macroscopic viscosity and allows tracing the sample viscosity variation with time. One more index characterizing the fluid viscous properties is fluidity index FI. This parameter

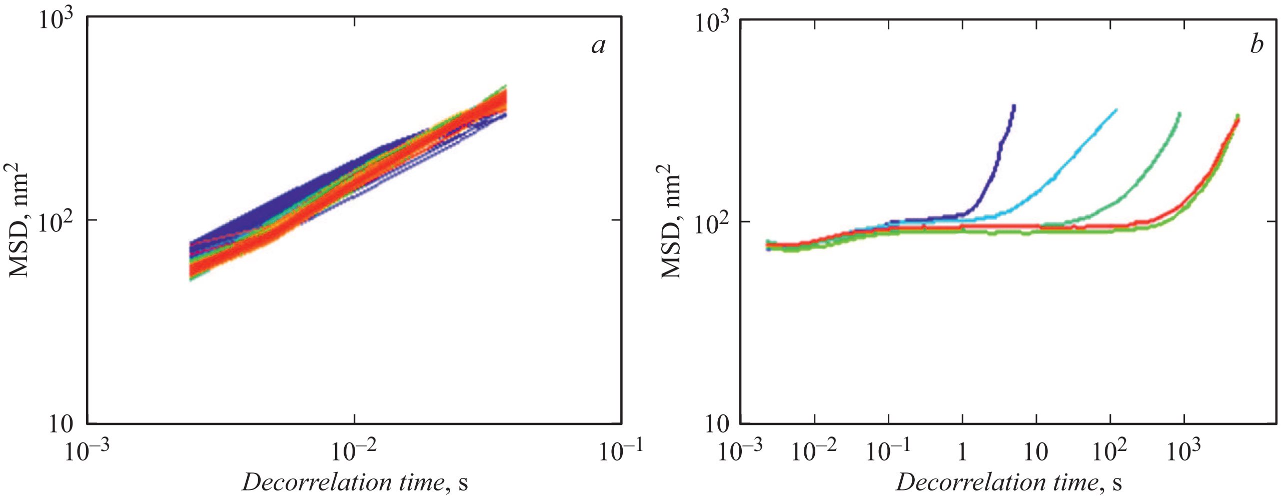

Figure 2. Mean–square displacement of MWCNTs in the EG–based nanofluid at the MWCNT weight concentrations of 0.05 (a) and 1% (b).

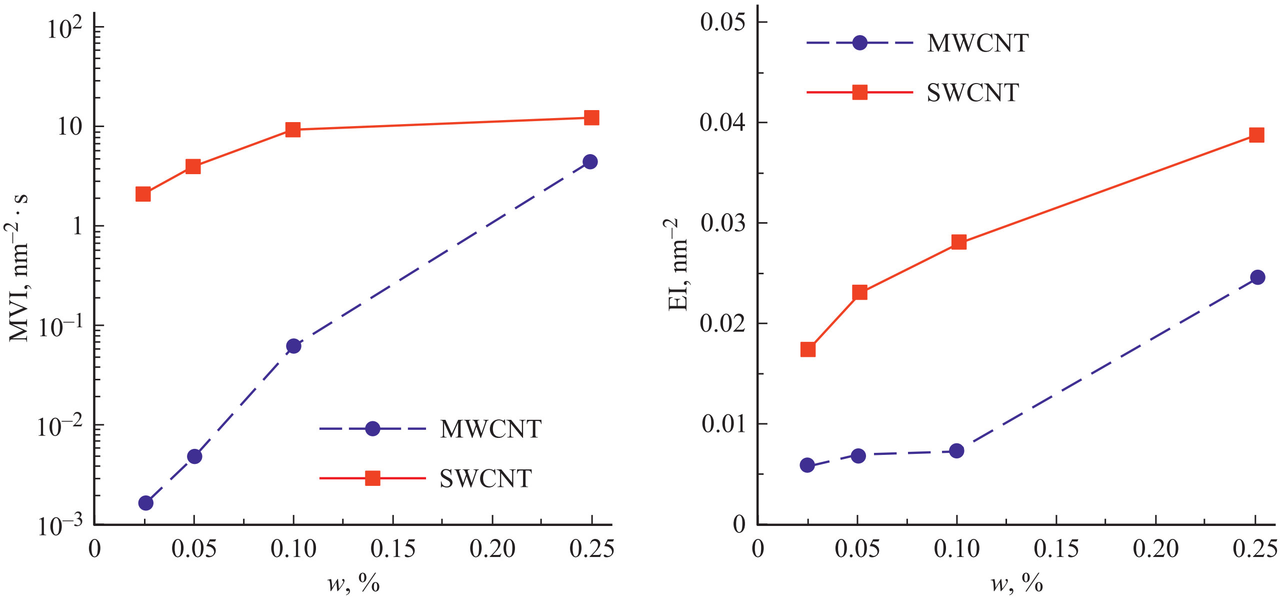

Figure 3. Comparison of MVI and EI indices for the SWCNT and MWCNT IPA–based nanofluids at different CNT concentrations.

that is inverse to the characteristic time of the speckle field decorrelation is measured in Hz. It is commonly believed that the sample is, in general, elastic/solid at low FI (about 10^{-2} Hz and lower) and viscous/liquid at high FI (about 10 Hz). The table presents values of the EI, MVI and FI indices for a number of studied nanofluids. These data allow one to compare viscoelastic properties of all the fluids mentioned here and evaluate the influence of the used dispersants on these properties. Fig. 3 clearly illustrates the comparison of the MVI and EI indices typical of IPS–based nanofluids containing SWCNTs and MWCNTs. Viscosity of nanofluids with SWCNTs is significantly higher than that of MWCNT nanofluids at all concentrations. However, notice that index MVI of MWCNT nanofluids increases thereat by more than three orders of magnitude, while that of SWCNT nanofluids increases by about 5 times.

The observed considerable difference in viscosities of nanofluids with SWCNTs and MWCNTs is connected with differences in their structures. Both the CNTs are characterized by a great aspect ratio (the length–to– diameter ratio). In addition, CNTs actively interact with each other [12]. After reaching a certain critical concentration, CNTs in nanofluids begin forming a percolation lattice. Estimates show that this critical concentration in SWCNT nanofluids is lower than that in MWCNT ones by about an order of magnitude. For SWCNTs, it is about 0.01%. Besides, it is useful to note that emergence of viscoelastic properties in nanofluids with CNTs differs in physical nature from that

EI, MVI and FI indices for nanofluids with different CNT concentrations

Nanofluid	w,%	EI, nm^{-2}	MVI, nm$^{-2}\cdot$ s	FI, Hz
SWCNT/EG	0.2	0.0028	78	0.000117
SWCNT/EG	0.1	0.0026	15	0.0005
SWCNT/EG	0.05	0.0026	2	0.0015
SWCNT/EG + PVP	0.2	0.011	227	0.000348
SWCNT/EG + SDBS	0.2	0.0032	7	0.0004
SWCNT/W + PVP	0.2	0.011	100	0.00036
SWCNT/W + SDBS	0.2	0.006	3	0.009
MWCNT/EG	1.0	0.012	24	0.00064
MWCNT/EG	0.2	0.0085	5.6	0.002
MWCNT/EG	0.1	0.0072	0.32	0.05
MWCNT/EG	0.05	0.006	0.0001	87
MWCNT/EG + PVP	0.2	0.0047	4	0.015
MWCNT/EG + SDBS	0.2	0.0115	8	0.002
MWCNT/W + PVP	0.2	0.0052	0.00034	80
MWCNT/W + SDBS	0.2	0.004	0.00026	80

in nanofluids with ordinary spherical particles. Rheology variations in nanofluids with spherical particles are first of all connected with the base fluid structuring near nanoparticles and formation of nanoparticle pseudo–lattice essentially depending on the particle sizes and concentration.

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Conflict of interests

The authors declare that they have no conflict of interests.

References

[1] K. Saeed, Ibrahim, Carbon Lett., **14** (3), 131 (2013). DOI: 10.5714/CL.2013.14.3.131

[2] C. Espinosa, I.C. Ortiz-Trujillo, J.A. Carlos-Cornelio, R.D. Zapata-Hernández, L.M. Hoyos-Palacio, DYNA, **84** (203), 24 (2017). DOI: 10.15446/dyna.v84n203.64132

[3] Hanif, G. Saxena, J. Raj, Int. J. Eng. Management Res., **7** (1), 304 (2017).

[4] I.M. Alarifi, J. Mater. Res. Technol., **8** (5), 4863 (2019). DOI: 10.1016/j.jmrt.2019.08.019

[5] V. Rudyak, A. Minakov, M. Pryazhniko, J. Mol. Liq., **329** (1), 115517 (2021). DOI: 10.1016/j.molliq.2021.115517

[6] V.Ya. Rudyak, D.S. Tret'yakov, J. Eng. Phys. Thermophys., **94** (5), 1208 (2021). DOI: 10.1007/s10891-021-02401-x

[7] V. Rudyak, G. Dashapilov, A. Shupik, J. Phys.: Conf. Ser., **1211**, 91117 (2021). DOI: 10.1088/1742-6596/2119/1/012117

[8] D.A. Weitz, D.J. Pine, in *Dynamic light scattering*, ed. by W. Brown (Clarendon Press, N.Y., 1993), p. 652.

[9] T.G. Mason, H. Gang, D.A. Weitz, J. Opt. Soc. Am. A, **14** (1), 139 (1997). DOI: 10.1364/JOSAA.14.000139

[10] S. Brunauer, P.H. Emmett, E.J. Teller, Am. Chem. Soc., **60** (2), 309 (1938). DOI: 10.1021/ja01269a023

[11] T.G. Mason, Rheolog. Acta, **39** (4), 371 (2000). DOI: 10.1007/s003970000094

[12] A. Cwirzen, K. Habermehl-Cwirzen, V. Penttala, Adv. Cem. Res., **20** (2), 65 (2008). DOI: 10.1680/adcr.2008.20.265