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ПРИРОДА ЭЛЕКТРОРЕОЛОГИЧЕСКОГО И ЭЛЕКТРОФОРЕТИЧЕСКОГО ЭФФЕКТОВ В СУСПЕНЗИЯХ ДЕТОНАЦИОННЫХ НАНОАЛМАЗОВ В МИНЕРАЛЬНОМ МАСЛЕ

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На основе ряда ротационных и осцилляционных тестов установлены качественные различия в характере электрореологического отклика суспензии наноалмазов детонационного синтеза в минеральном масле, в зависимости от типа функционализации поверхности частиц. Тип модификации и химический состав поверхности для частиц гидрированных и карбоксилированных наноалмазов исследовали методом инфракрасной спектроскопии. Морфологию частиц и структурную организацию в среде минерального масла исследовали методом малоуглового рентгеновского рассеяния. Обнаружено, что суспензии гидрированных и карбоксилированных частиц под действием электрического поля проявляют электрореологический и электрофоретический эффекты, соответственно. Проведен анализ причин электрофоретического движения карбоксилированных наноалмазов в среде минерального масла, в сравнении с наблюдаемым ранее эффектом в среде слабо-дифильного полидиметилсилоксана (силиконовое масло). Содержание воды на поверхности как гидрированных, так и карбоксилированных частиц наноалмазов было определено методом титрования суспензий по Карлу Фишеру. Была предположена взаимосвязь электрофоретического эффекта с содержанием адсорбированной на поверхности частиц воды. Методом ротационной вискозиметрии определены значения статического предела текучести суспензий, наполненных гидрированными и карбоксилированными наноалмазами, при различной напряженности электрического поля. Кривые течения вне и под действием электрического поля жидкости, наполненной гидрированными частицами, аппроксимировали реологическими моделями Бингама и Cho-Choi-Jhon. Проведен анализ соответствия используемых моделей практическим результатам. На основе зависимостей модулей накопления и потерь от амплитуды деформации выявлен линейный диапазон вязко-упругих свойств жидкости. Обнаружен рост значений модулей накопления и потерь, а также сужение линейного диапазона с увеличением напряженности поля.

Ключевые слова: стимул-чувствительные материалы, коллоиды, электрореологические жидкости, наноалмазы детонационного синтеза, минеральное масло, элекрофорез

THE NATURE OF THE ELECTRORHEOLOGICAL AND ELECTROPHORETIC EFFECTS OF DETONATION NANODIAMONDS SUSPENSIONS IN MINERAL OIL

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Qualitative differences in the nature of the electrorheological response of a detonation nanodiamonds suspensions in mineral oil depending on the type of particle surface functionalization were established from a number of rotational and oscillation tests. The type of modification and the chemical composition of the surface for particles of hydrogenated and carboxylated nanodiamonds were studied by infrared spectroscopy. Particles morphology and their structural organization in a mineral oil medium were studied by small-angle X-ray scattering method. It was found that suspensions of hydrogenated and carboxylated particles under an electric field exhibit an electrorheological and electrophoretic effects, respectively. The reasons for the electrophoretic motion of carboxylated nanodiamonds in a mineral oil medium were analyzed in comparison with the previously observed effect in the medium of weakly amphiphilic polydimethylsiloxane (silicon oil). The water content on the surface of both hydrogenated and carboxylated nanodiamond particles was determined by Karl Fischer titration of suspensions. The correlation between the electrophoretic effect and the adsorbed water content on the surface of the particles was suggested. The method of rotational viscometry revealed the dependences of the static yield stress for suspensions filled with hydrogenated and carboxylated nanodiamonds at various electric field strength. The flow curves of the fluid filled with hydrogenated particles without and under an electric field were fitted by Bingham and Cho-Choi-Jhon rheological models. An analysis of the used models matching to practical results was performed. Based on the dependences of the storage and loss moduli on the deformation amplitude, a linear range of the viscoelastic properties of the fluid was revealed. An increase in the values of the storage and loss moduli, as well as a narrowing of the linear viscoelasticity range with an increase in the electric field strength was detected.

Key words: stimulus-responsive materials, colloids, electrorheological fluids, detonation nanodiamonds, mineral oil, electrophoresis

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INTRODUCTION

In recent years, the exceptional interest of the scientific community related with the development and research of "smart" materials that are capable for the fast and controllably change of properties. Such materials include electrorheological fluids (ERFs), suspensions reversibly changing their rheological behavior under an electric field. Typically, ERFs are suspensions of easily polarizable or semiconducting particles in a dielectric liquid. ERFs exhibit Newtonian properties without electric field, but when an electric potential is applied, the behavior typical for Bingham liquids is observed. Due to such specific properties, these materials can potentially be used in a wide range of applications: electronics, hydraulics, robotics, crude oil transportation, sensors, etc. [1].

Suspensions filled by nanosized particles can exhibit a giant electrorheological effect. They have a high yield stress and are promising materials in applied studies of the electrorheological effect [2]. Besides the concentration and size of the filler, the efficiency of ERFs is affected by the shape of the particles [3, 4], the nature and viscosity of the dispersion medium [5, 6], the presence of low molecular weight activation additives [7], etc. One of the nanosized fillers exhibiting a pronounced electrorheological response even at low concentrations is detonation nanodiamonds (DNDs) [8]. DNDs as filler for ERFs have a number of positive features: commercial availability, lack of toxicity, and the possibility of the particle surface modifying [9, 10].

The synthesis of DNDs is extremely fast, which theoretically favors the formation of small particles with sizes from 4 to 5 nm. However, the resulting particles tend to aggregate [11]. There are several ways to break aggregates to individual particles, but the most commonly used are mechanical grinding by zirconium dioxide balls [12] and the temperature annealing methods [13]. It is well known that the method of mechanical grinding leads to adverse graphitization of the DNDs surface [14]. In turn, DND particles can be functionalized during thermal annealing depending on the gas atmosphere [15]. Particles annealed in a hydrogen flow have CH-groups on the surface. At the same time, particles annealed in an oxygen or ozone atmosphere have carboxyl groups on their surface [16]. Here and after such types of functionalized particles denote as hydrogenated and carboxylated, respectively. It was recently found that the type of functionalization of the DNDs surface affects the electrorheological response of their suspensions in polydimethylsiloxane. Thus, ERFs filled by hydrogenated DNDs form columnar structures under an electric field and a positive electrorheological effect is observed. Suspensions of carboxylated DNDs reveal an electrophoresis: the motion of particles is observed [17]. It is extremely important to understand the nature of different DNDs behavior under an electric field for practical application. Although today there are studies on the mechanism of the positive electrorheological effect of hydrogenated DND particles [18, 19], much less is known about the reasons for the electrophoresis of particles with a carboxylated surface. Since particles must be charged for electrophoresis, two hypotheses have been proposed in previous study to explain this phenomenon [20].

The first hypothesis explains the phenomenon of electrophoresis by the chemical nature of the previously used dispersion medium. It is known that polydimethylsiloxane exhibits weak amphiphilic properties due to the presence in the molecule of both hydrophobic methyl groups and a hydrophilic oxygen-silicon bond [21, 22]. The interaction of polydimethylsiloxane molecules with carboxyl groups on the surface of DND particles can lead to a weakening of the oxygen-hydrogen bond, resulting in charge separation and the formation of an electric double layer. The particles acquire a negative charge and electrophoresis is observed under an electric field.

The second hypothesis is in the adsorption of water on the surface of particles. Note, that a small amount of water can enhance the electrorheological effect [23, 24]. However, even a relatively low water content can lead to charge redistribution, due to interaction with functional groups on the particles surface [25].

The aim of this study is to verify the hypotheses about the reasons of electrophoresis of carboxylated DND particles under an electric field. The mineral oil is a mixture of high molecular weight hydrocarbons was considered as dispersion media, excluding the possible effect of the chemical nature of polydimethylsiloxane on the electrorheological behavior of suspension.

MATERIALS AND METHODS

In the study, hydrogenated and carboxylated DNDs were used as filler for ERFs. The powders of corresponding DNDs provided by the Ioffe Institute (St. Petersburg, Russia). The particle size of 4-5 nm has been repeatedly determined earlier by dynamic light scattering and X-ray scattering methods [26]. The powders were dried in a VD 23 vacuum oven (Binder, Germany) at 200 °C for 24 h before dispersing into the oil to remove water adsorbed on the surface of particles. The study of the chemical nature of particles was carried out by infrared spectroscopy on an FTIR spectrometer Nicolet iS5 (Thermo Scientific, USA).

Mineral oil RTM14 (Sigma-Aldrich, USA) with a dynamic viscosity of 101.4 mPa·s (25 °C) was used as the dispersion medium. ERFs were prepared by dispersing a powder of corresponding DND particles type (hydrogenated or carboxylated) into mineral oil. Suspensions with a filler concentration of 4 wt% were used for studies. Homogenization was carried out using a MR Hei-Tec magnetic stirrer (Heidolph, Germany) at a stirring rate of 300 rpm for three days with following sonication with an UP400S immersion disperser (400 W, 24 kHz) (Hielscher Ultrasonics, Germany). An additional ultrasonic treatment of suspensions was performed in an ultrasonic bath UZV-4.0/1 TTTs (RMD) (150 W, 35 kHz) (OOO "Sapphire", Russia) before each measurement.

The rheological properties of suspensions at various electric field strength were studied by rotational viscometry on a Physica MCR 501 rheometer (Anton Paar GmbH, Germany) with a measuring system of two coaxial cylinders (measuring cell CC-27E). An electric field was formed by FuG HCP 14 – 12500 MOD constant high voltage source (FuG Elektronik GmbH, Germany). The electric field strength was varied in the range of 0-5 kV/mm. The measurements were performed in rotational mode of control shear stress (CSS) and control shear rate (CSR) while finding the static yield stress and flow curves, respectively. A series of amplitude sweep tests were carried out to determine the linear range of viscoelastic properties.

The structural organization of DND particles in suspensions was studied by small-angle X-ray scattering. Two-dimensional X-ray scattering images were obtained using the Kurchatov synchrotron radiation source (NRC "Kurchatov Institute", Russia) at the BioMur beamline (λ = 1.445 Å) and 2D detector Dectris Pilatus3 1 M. Small-angle X-ray scattering curves were obtained by image integration using fit2D open source software (ESRF, France). The data are plotted in terms of scattering vector $q = 4\pi \sin\theta/\lambda$ (nm^{-1}).

The water content in suspensions of DNDs was determined by Karl Fischer titration using a coulometric titrator Compact KF C10S (Mettler Toledo, USA). Suspensions of the hydrogenated or carboxylated DND particles with a concentration of 1 wt% in a mineral oil/n-hexane mixture medium were used as samples for titration. The n-hexane was added to reduce the viscosity of the suspension during the titration. The n-hexane was pre-dehydrated using molecular sieves, the measured water content is beyond the sensitivity of the instrument. The content of the solvent varied in the range of 60-70 wt% and was taken into account for a corresponding sample for the calculations. To determine the water content of mineral oil, the sample with a 1:1 ratio of oil to n-hexane by weight was prepared as well.

RESULTS AND DISCUSSION

A qualitative analysis of the chemical composition of the DND particles surface of various modification type was performed by infrared spectroscopy (Table 1). Thus, specific bands for carboxylated particles can be distinguished. The wave number range 3200-3600 cm^{-1} corresponds to O–H stretching vibrations, and the peaks in the range from 1450 to 800 cm^{-1} related to ether and epoxy groups. The peak at ~1791 cm^{-1} indicate the presence of carbonyl groups (>C=O). For hydrogenated particles, the band in the region of ~1620 cm^{-1} is due to bending vibrations of O–H bonds. The absorption bands at 2919 and 2881 cm^{-1} correspond to stretching (symmetric and asymmetric, respectively) vibrations of C–H bonds [27].

Table 1

FTIR spectroscopy of DNDs

Таблица 1. **ИК-Фурье спектроскопия детонационных наноалмазов**

Absorbance frequency (cm^{-1})	Hydrogenated DNDs	Carboxylated DNDs
O-H (stretching)	3414	3417
O-H (bending)	1623	1623
C-H (stretching symmetric)	2919	–
C-H (stretching asymmetric)	2881	–
>C=O (stretching)	–	1791
C-O-C (stretching asymmetric)	1112	1134
C-O (bending)	1316	1274
>C=O (symmetric stretching)	–	1413

The structural organization of the filler particles was studied by small-angle X-ray scattering method (Fig. 1). The scattering curves of suspensions filled by both types of DND particles in double logarithmic scale show two characteristic slopes. Such scattering is typical for DND suspensions and is related with the formation of loose agglomerates. The first slope in the region of small values of the scattering vector corresponds to the spatial structure of agglomerates. The second slope in the region of higher values of scattering vector indicates the scattering on the surface of compact individual particles. The first slope of the scattering curve in double logarithmic scale of 2.1 is the characteristic dimension of the mass fractal. The dependence of the surface fractal of individual particles established by Porod's law:

$$I(q) \sim q^{-(6-k)} \quad (1)$$

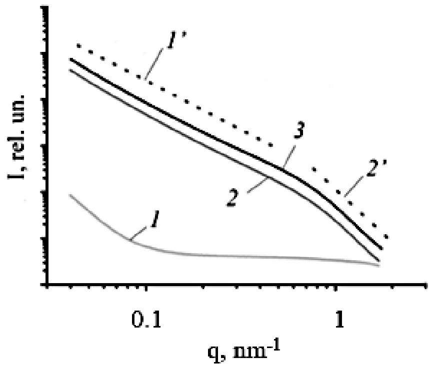

Fig. 1. Small angle X-ray scattering curves obtained for: 1 – mineral oil, 2 – 4 wt% suspension of hydrogenated DNDs in mineral oil, 3 – 4 wt% suspension of carboxylated DNDs in mineral oil. 1′ and 2′ – characteristic slopes for scattering levels -2.1 (agglomerates) and -3.7 (individual particles)

Рис. 1. Кривые малоуглового рентгеновского рассеяния для: 1 – минерального масла, 2 – 4 масс.% суспензии гидрированных детонационных наноалмазов, 3 – 4 масс.% суспензии карбоксилированных детонационных наноалмазов. 1′ и 2′ – характерные наклоны для уровней рассеяния - 2,1 (агломераты) и - 3,7 (индивидуальные частицы)

The slope (k) of this part of the curve is 3.7 ($3 < 3.7 < 4$) and corresponds to the surface fractal with a dimension of 2.3 [28]. Thus, there is no fundamental differences in the structural organization of hydrogenated and carboxylated DND particles in a mineral oil medium.

It is interesting to compare the electrorheological behavior of suspensions in mineral oil with previously studied fluids based on silicone oil [17]. Fig. 2 shows the flow curves for a suspension filled with hydrogenated DND particles. The suspension at the studied concentration has a yield stress even without an electric field: the shear stress values are constant in wide shear rate range (the region of low shear rate). An increase in the yield stress values is observed with an electric field. The values of the shear stress increase and the "plateau" range expands to the region of higher shear rates. Hence, an electrorheological effect caused by the polarization of the filler particles and the formation of a columnar structure is observed. More significant increase in the shear rate leads to the destruction of the sample structure. Thus, the values of the shear stress at different field strengths practically coincide at the highest shear rate under study. Thus, the rheological behavior of the fluid filled by hydrogenated DND particles in mineral oil is similar to corresponding suspension in silicone oil. The nature of the dispersion medium has no qualitative effect on the response of fluids. Note the fluctuation of the experimental values in the yield stress region, especially for the flow curve obtained at a high electric field strength. Various rheological models can be used to describe the rheological behavior of fluids. The Bingham model is the simplest model for describing materials with a yield stress:

$$\tau = \tau_0 + \eta_{pl}\dot{\gamma} \qquad (2)$$

where τ is shear stress, τ_0 is yield stress, $\dot{\gamma}$ is shear rate and η_{pl} is plastic viscosity. The fitting results are plotted in Fig. 2.

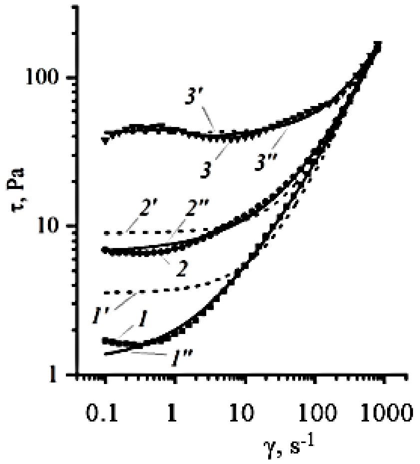

Fig. 2. Flow curves obtained in CSR mode at various electric fields (1 – 0 kV/mm, 2 – 1 kV/mm, 3 – 3 kV/mm). The data fitted by Bingham (dotted line, 1′ – 0 kV/mm, 2′ – 1 kV/mm, 3′ – 3 kV/mm) and CCJ models (solid line, 1′′ – 0 kV/mm, 2′′ – 1 kV/mm, 3′′ – 3 kV/mm)

Рис. 2. Кривые течения, полученные в режиме CSR при разных напряженностях электрического поля (1 – 0 кВ/мм, 2 – 1 кВ/мм, 3 – 3 кВ/мм). Данные аппроксимированы моделями Бингама (пунктирная линия, 1′ – 0 кВ/мм, 2′ – 1 кВ/мм, 3′ – 3 кВ/мм) и CCJ (сплошная линия, 1′′ – 0 кВ/мм, 2′′ – 1 кВ/мм, 3′′ – 3 кВ/мм)

The disadvantage of this model for describing the rheological behavior of the ERFs is an imprecise approximation of shear stress values at low shear rates, due to dynamic nature of fluid structure. The prolonged formation of equilibrium columnar structures related with the balance between polarization and hydrodynamic forces [29]. A Cho-Choi-Jhon (CCJ) model was developed for a more accurate description of the ERFs behavior [30]:

$$\tau = \frac{\tau_0}{1+(t_1\dot{\gamma})^{a}} + \eta_\infty\left(1 + \frac{1}{(t_2\dot{\gamma})^{\beta}}\right)\dot{\gamma} \qquad (3)$$

where τ is shear stress, τ_0 is yield stress, $\dot{\gamma}$ is shear rate, t_1 and t_2 are time constants, the exponent a is related to the decrease in shear stress at low shear rates, the exponent β is related to the increase in shear stress ($d\tau/d\dot{\gamma} \geq 0$) and ranges from 0 to 1, η_∞ is the viscosity at high shear rate.

The Bingham model does not allow evaluating structural changes in a suspension under an electric field. Of the two models considered, the best agreement with experimental data is observed for the six-parameter CCJ model.

The linear range of the viscoelastic properties of the material (LVE-range) can be distinguish by amplitude sweep tests and the level of deformation leading to the flow of the sample can be determined. Fig. 3 shows the dependence of the storage and loss moduli on the deformation amplitude for a suspension of hydrogenated DNDs. One can see an increase in the values of both moduli and decrease of the LVE range with an electric field. An increase in the deformation amplitude by more than 1% leads to the destruction of the sample structure and a nonlinear response to the applied deformation. At the higher amplitude the crossover of the storage and loss moduli is observed, the sample flows. The loss modulus starts to prevail over the storage modulus with a further increase in the amplitude. Thus, the sample exhibits a viscous response. The cross-over point corresponds to the dynamic yield stress of the suspension and shifts along the amplitude deformation axis to the region of high values with increasing electric field strength. These results are in full agreement with the rotational measurements and indicate about electrorheological effect. The magnitude of effect depends on the value of the applied electric field.

A qualitatively different behavior is demonstrated by a suspension of carboxylated particles. The dependence of the static yield stress on the electric field strength for DND suspensions with variously functionalized surface is shown in Fig. 4. There is no significant changes in the values of the yield stress for the suspension of carboxylated particles over the whole studied electric field range. Moreover, after the experiment, the sample has split into a dispersion medium and a filler. Thus, electrophoresis obviously occurs. In turn, suspensions of particles with a hydrogenated surface demonstrate an increase in the yield stress with electric field. Such behavior is explained by the formation of strong columnar structures and confirms the results obtained in other modes. The linear approximation of dependence plotted in double logarithmic scale results in slope of 1.6. The value of the slope indicates the mechanism of the electrorheological effect and is the exponent (*n*) in the following equation:

$$\tau \sim E^n, \qquad (4)$$

where τ is shear stress and E is electric field strength. The obtained value of the exponent corresponds mainly to the conductive mechanism of the electrorheological effect, and correlates with the values previously obtained for suspensions based on polydimethylsiloxane [17].

Since, mineral oil is a mixture of non-polar high-molecular hydrocarbons, it does not reveal amphiphilic properties. Thus, the first hypothesis about the effect of the dispersion medium leading to electrophoresis does not stand up to scrutiny and is not correct. Apparently, the possible presence of adsorbed water on the surface of carboxylated DND particles remains the main reason for the electrophoretic effect. To verify this second hypothesis, the water content in the suspensions, components was determined by the Karl Fischer titration method (Table 2). The water content in mineral oil was measured as 0.00167 ± ± 0.00017 wt%. One can note, that the main amount of water in the suspensions is introduced with the filler.

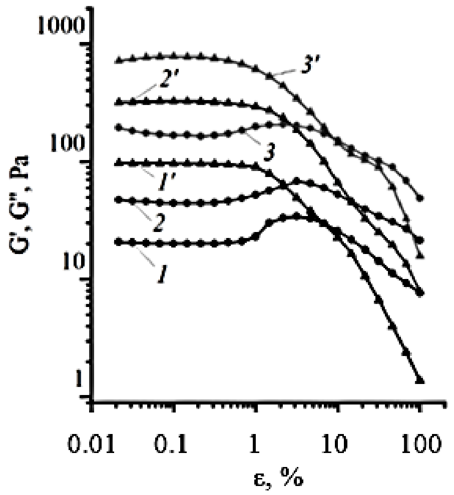

Fig. 3. Amplitude sweep of storage (1′, 2′, 3′) and loss (1, 2, 3) moduli of 4 wt% hydrogenated DND suspension at various electric fields (1′/1 – 0 kV/mm, 2′/2 – 1 kV/mm, 3/3′ – 3 kV/mm)

Рис. 3. Амплитудные зависимости модулей накопления (1′, 2′, 3′) и потерь (1, 2, 3) 4 масс.% суспензии гидрированных ДНА при разных напряженностях электрического поля (1′/1 – 0 кВ/мм, 2′/2 – 1 кВ/мм, 3/3′ – 3 кВ/мм)

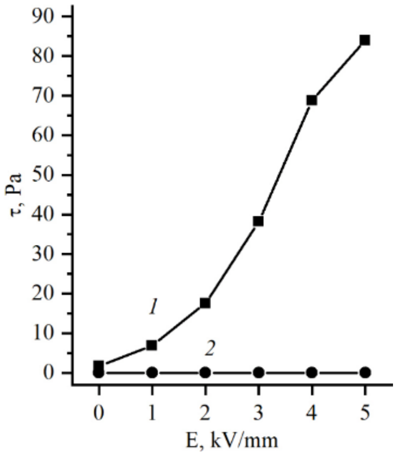

Fig. 4. The yield stress as a function of electric field for 4 wt.% DND suspension filled with CH-terminated (1) and COOH-terminated (2) particles

Рис. 4. Зависимость предела текучести от напряженности электрического поля для 4 масс.% суспензий ДНА, наполненных CH- (1) и COOH-терминированными частицами (2)

Table 2

Results of Karl Fischer titration

***Таблица 2*. Результаты титрования по Карлу Фишеру**

	Hydrogenated DNDs	Carboxylated DNDs
Filler concentration, wt%	1.00	1.00
Water content in the suspension, wt%	0.0127±0.00054	0.00381±0.00001
Water content on the DNDs surface, wt%	1.213±0.030	0.325±0.003
Ratio of water molecules to functional groups	~3:2	~2:5

The results show that the suspensions of both hydrogenated and carboxylated particles contain low amount of water, but the suspension of hydrogenated particles contains almost 3 times more water than that of carboxylated ones. Note that the water content in the suspensions of polydimethylsiloxane was much higher. Nevertheless, the amount of water in the studied samples turns out to be sufficient for a possible charge redistribution in the suspension [31]. Next, let us try to estimate the number of water molecules per functional group of particle. To simplify the calculations, we will consider the shape of the particles as spherical. Thus, taking into account the average particle size (5 nm) and the density of diamond (3.52 g/cm^3), the ratio is determined as:

$$\frac{N_{H_2O}}{N_{fun.gr.}} = \frac{\left({m_{H_2O}}/{M_{H_2O}} \right) * N_A}{\frac{m_{DND}/\rho_{DND}}{\frac{1}{6}\pi D^3} * n_{fun.gr.}}, \qquad (5)$$

where N_{H_2O} is the total number of water molecules in the sample, $N_{fun.gr.}$ is the total number of functional groups in the sample, m_{DND} is the mass of the dispersed phase (DND particles), ρ_{DND} is the density of DND, D is the diameter of the particle, $n_{fun.gr.}$ is the number of functional groups on the particle surface, m_{H_2O} is the mass of water in suspension, M_{H_2O} is the molar mass of water and N_A is Avogadro constant.

The average number of carboxyl groups on the surface of DND particles was calculated previously and is about 67 groups per particle [32]. Since carboxylated and hydrogenated particles are obtained from the same raw material using the same method, we believe that the number of functional groups in different types of particles (hydrogenated and carboxylated) is the same. The results of calculations according to equation (5) are shown in Table 2. Thus, trace amounts of water can lead to the formation of a charge around particles or their clusters leading to electrophoresis of carboxylated DND particles in mineral oil.

CONCLUSIONS

Rheological studies of suspensions filled by hydrogenated and carboxylated DND particles in the mineral oil under an electric field made it possible to verify hypotheses about the nature of the electrorheological and electrophoretic effects. The role of the DNDs surface functionalization on the particles behavior under an electric field, which was previously revealed in a weakly-amphiphilic silicone oil, is valid for hydrophobic mineral oil as well. Thus, the chemical nature of the dispersion medium has weak effect on the properties of ERFs. An increase in the values of the yield stress with an increase in the electric field strength is observed in suspensions of hydrogenated DNDs. An analysis of the dependence indicates a typical contribution of conductivity to the mechanism of the effect. The values of the yield stress does not significantly changes for suspensions of carboxylated particles under an electric field, i.e. electrophoresis occurs. A probable factor leading to the electrophoretic motion of carboxylated DNDs in a dielectric liquid is the presence of water mainly adsorbed on the particles surface. The interaction of carboxyl groups with water can lead to the formation of a charge on the surface of nanoparticles. Nevertheless, the mechanism of charge formation around a DND particle in a liquid dielectric medium is still not perfectly clear.

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The authors declare the absence a conflict of interest warranting disclosure in this article.

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