MICROSTRUCTURAL, RHEOLOGICAL, AND CONDUCTOMETRIC STUDIES OF MULTIWALLED CARBON NANOTUBE SUSPENSIONS IN GLYCEROL

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Optical microscopy studies of electrical conductivity and rheological properties (in the cone-plate geometry) of glycerol suspensions filled with multiwalled carbon nanotubes (MWCNTs) have been fulfilled. The researches were carried out in the intervals of temperature $T = 283 \div 333$ K and MWCNT concentration $C = 0 \div 1$ wt%. MWCNTs in glycerol are demonstrated to have a strong tendency toward the aggregation, so that "primary" MWCNT aggregates persist even after the intensive ultrasound homogenization. Typical percolation phenomena accompanied by an enhancement of the electrical conductivity and the viscosity are observed at an increase of the MWCNT concentration. The concentration percolation threshold is identified at $C = C_p \approx 0.1$ wt%, and the scaling behavior in a vicinity of the percolation threshold is found to be characterized by the conductivity exponent $t = 2.7 \pm 0.3$, which is somewhat higher than a value typical of the random percolation problem. The introduction of MWCNTs in glycerol resulted in the appearance of thixotropic behavior related to the fracture of MWCNT aggregates under shear. An anomalous rheological behavior is observed at a high MWCNT concentration, $C = 1$ wt%, which testifies to the destruction of the H-bond network in glycerol induced by MWCNTs. The dependences of the activation energies of the ionic electric conductivity and a viscous flow on the MWCNT concentration are estimated.

1. Introduction

Carbon nanotubes (NTs) demonstrate a number of interesting mechanical, electrical, thermal, and other physical properties. Their potential applications became a focus of many experimental and theoretical researches, as well as industrial research programs in such branches as microelectronics, sensorics, materials science, biotechnology, and medicine [1]. Important "biological" implementations of NTs not only demand for them to be biocompatible, but also require that stable and well dispersed suspensions of NTs in water or other biologically compatible liquid systems should be created [2]. However, NTs reveal an extremely high tendency to the aggregation in liquid systems, which is associated with long-range – and strong enough – van der Waals forces, as well as with the intense Brownian motion [3]. For today, a number of researches on the behavior of NT suspensions have been fulfilled, and the relationships among the solubility parameters, dispersion ability, and nanotube dimensions in various liquid solvents including water [4], toluene and chloroform [5], liquid crystals [6–19], polyethyleneoxide [20], and others have been established.

Rather an interesting liquid medium for future biotechnological and medical NT applications can be glycerol. It is not biologically toxic and can be used as a liquid carrier in biologically attractive NT-based compositions. Note that glycerol is widely used in food industry (e.g., as an agent preventing the crystallization), biology and medicine (here, it is a component of tinctures, elixirs, anesthetics, as well as a medium for growing bacteriological cultures), cosmetics (creams, lotions, and tooth-pastes), and so forth [22].

Glycerol is also widely used as a solvent at the extraction of high-quality proteins from cells in biosuspensions. In this case, extracted proteins and glycerol form stable associates, for which the presence of hydroxyl groups in a glycerol molecule is responsible [23]. Note also that the introduction of NTs into a biosuspension can induce a substantial increase in the efficiency of the electroporation-induced destruction in a vicinity of bio/nano interfaces [24–26]. The novel electroporation technologies are rather promising from the viewpoint of elevating the degree of useful component extraction from cells [27, 28]. The phenomenon of enhanced electroporation was explained by a substantial (by a factor of 10 to 100) growth of the electric field strength near the NT surface owing to the so-called "lightening rod effect" [24]. Estimations testify that the efficiency of the enhanced electroporation stimulated by NTs can exceed even 80% already at fields of the order of 50 V/cm [26]. The application of an electric field to an NT-doped biosuspension of *Escherichia coli* stimulated a considerable concentration of biocells on the NT surface, which was explained by the dielectrophoresis phenomenon [29]. The enhanced electroporation associated with the presence of NTs allows the strategy of electroporation treatment to be changed [30]. Such an approach possesses a high potential for the creation of systems aimed at the local drug delivery and can be implemented in practice by stimulating the transport of drug molecules over the NT surface into electroporated cells [31]. Hence, the liquid systems on the basis of glycerol and NTs are promising media for future biophysical applications in electroporation technologies. Note also that aqueous glycerol solutions are successfully used in the centrifugal separation of different NTs [32]. However, practically no detailed structural researches of liquid systems on the basis of glycerol and NTs have been carried out till now.

This work aimed at carrying out the microstructural researches, as well as the study of electrophysical and rheological properties, of suspensions created on the basis of multiwalled carbon nanotubes and glycerol.

2. Materials and Methods

As a liquid system, we used glycerol, $C_3H_8O_3$ (GOST 6259-75, the Novokhim Company, Kharkiv, Ukraine), which was characterized by a molecular weight of 92.09, a melting point of 291.3 K, and a density of 1.261 g/cm^3 at a temperature of 293 K. Before being used, glycerol was kept under vacuum for 10 h at a temperature of 363 K to take away water admixtures.

Multiwalled carbon nanotubes, which were used in the experiments concerned, had been fabricated by the method of chemical sedimentation of graphite in the gas phase with the FeAlMo0.07 catalyst [33]. To separate MWCNTs from the catalyst and mineral additives, the obtained product was treated in an alkaline solution (NaOH) in order to dissolve aerosil and in hydrochloric acid (HCl) to dissolve metal oxides. Afterwards, the specimens were filtered to remove acid remnants and repeatedly washed out with distilled water until the value pH = 5.5 was attained. The residual weight concentration of mineral admixtures did not exceed a few per cent.

For researches, we prepared a suspension of MWCNTs in glycerol with a concentration of 1 wt%. The obtained suspension was mixed and homogenized for 5–10 min at a frequency of 22 kHz, by using an UZDN-2T ultrasonic disperser; then it was quickly (within 5–10 s) cooled down to its crystallization temperature. Note that the ultrasonic treatment is an adopted technique for the homogenization of MWCNT suspensions [34]. Suspensions with lower MWCNT concentrations were obtained by diluting the 1 %-suspension, followed by their ultrasonic treatment for 5 min.

Optical microscopic images were obtained using specimens 50 μm in thickness on an OI-3 UHL 4.2 microscope (LOMO, Russia). The dependences of the electric resistance and the viscosity on the temperature in the interval of 293–350 K were measured for every specimen. The rate of temperature variation in heating–cooling cycles was about 2 K/min. The electrical conductivity was measured on an LCR-819 (GW Instek) device in a temperature-controlled cell about 0.5 mm in thickness. To prevent suspension particles from the migration in the electric field and to reduce the influence of the capacitor component of a specimen on the results, the measurements were carried out by applying an alternate voltage of 0.25 V with a frequency of 1 kHz. Rheological researches were carried out with the use of a Rheotest R.V.2 (Rheotest Messgeräte Medingen, Germany), by applying the cone–plate technique. The shear velocity γ was varied within the range of 5.56–4860 s^{-1}, and the measurements of the shear stress τ were carried out. The shear viscosity η was calculated as the ratio τ/γ. Every measurement was repeated at least three times to calculate the average value and to determine the measurement error.

3. Results and Their Discussion

In Fig. 1, the micrographs of suspensions at various concentrations of MWCNTs in glycerol are shown. One can see that, in spite of the intense ultrasound-induced homogenization, aggregates, which are characterized by rather large dimensions – namely, 100 μm and more, – arise even at low MWCNT concentrations in the system. A high efficiency of the MWCNT aggregation in glycerol

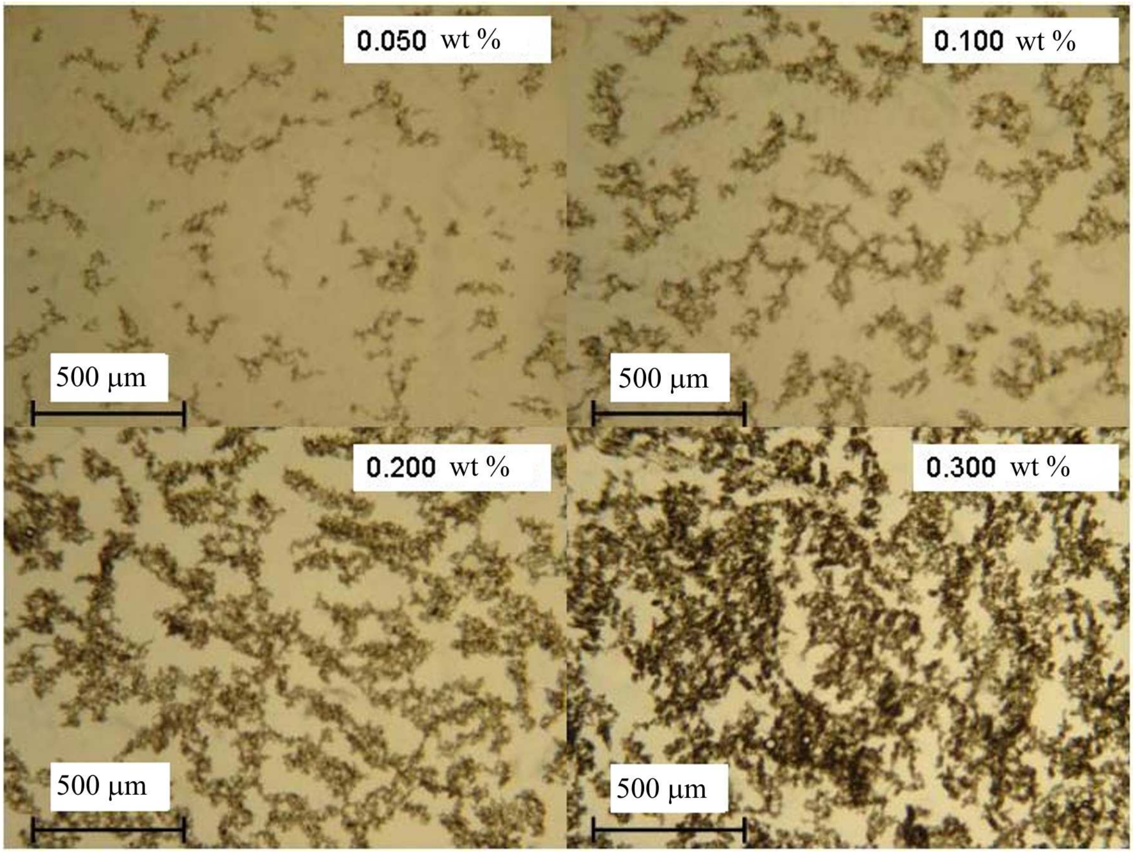

Fig. 1. Micrographs of MWCNT suspensions in glycerol at various MWCNT concentrations C (wt%)

can be stimulated by strong van der Waals interactions together with the Brownian motion.

For cylindrical nanoparticles, the half-aggregation time – i.e. the time interval, after which the concentration of primary particles becomes half as high – can be estimated by the relation [19]

$$\theta \approx 3\pi d^3\eta/(8kTC)(r/\ln r), \tag{1}$$

where d is the MWCNT diameter, η the viscosity of glycerol, kT the thermal energy, C the weight concentration of MWCNTs in the suspension, $r = l/d$ the NT aspect ratio ($r \gg 1$), and l the MWCNT length.

Taking into account that $\eta \approx 0.5$ Pa $\cdot$ s (glycerol), $d = 2$ nm, $r = 500$, $T = 303$ K, and $C = 0.05$ wt%, we obtain $\theta \approx 4500$ s. Therefore, the diffusion aggregation takes a rather long time (about 1.5 h) in such a viscous medium as glycerol. Within this time interval, the microscopic researches carried out at $T = 303$ K revealed no visual changes in the aggregate structure. Hence, a conclusion can be drawn that it is "primary" aggregates that were observed. They emerge owing to a low dispersion ability of MWCNT nanoparticles in glycerol, and this parameter cannot be improved by the ultrasonic dispersion. As the concentration is increased, those "primary" aggregates start to join with one another to form larger aggregates, and, in the concentration interval $C = 0.1 \div 0.2$ wt%, there emerges a percolation cluster that is extended over the whole space (Fig. 1).

A certain re-structuring of those "primary" aggregates was observed only after long enough holding times; at higher temperatures, this time interval became shorter (Fig. 2). When the temperature increased, the viscosity of glycerol decreased, which enhanced the intensity of the Brownian motion and stimulated a reduction of θ-value. As a result of the re-structuring, the aggregates formed by MWCNTs became more compact, so that an increase of the area free of nanotubes was observed visually.

Such a percolation behavior and a certain re-structuring were confirmed by the dependences of the electrical conductivity on the temperature (Fig. 3). The temperature growth was accompanied by a substantial increase of the electrical conductivity in both pure glycerol and glycerol-based suspensions with MWCNT ad-

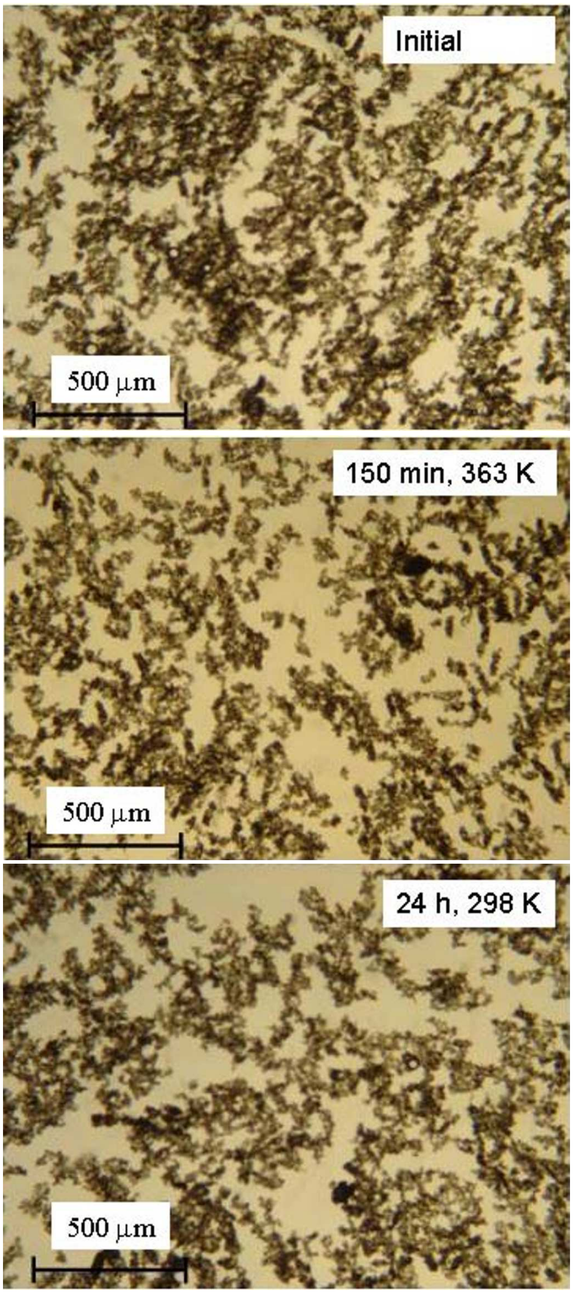

Fig. 2. Microstructural changes in MWCNT suspensions in glycerol at re-structuring; $C = 0.3$ wt%

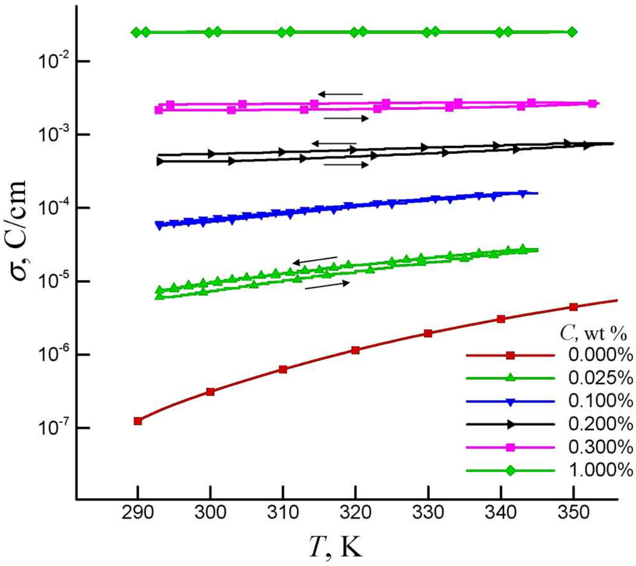

Fig. 3. Dependences of the electrical conductivity σ on the temperature T for MWCNT suspensions in glycerol at various concentrations C (wt%). Arrows denote the directions of the temperature variation

ditives, which testified to an enhancement of the ionic conductivity mechanism in the systems concerned.

In addition, the electrical conductivity demonstrated a certain growth, when the measurements were carried out in the heating–cooling regime. Such a hysteretic behavior of the dependence $\sigma(T)$ is also characteristic of other liquid systems filled with MWCNTs [10, 15]. It can be explained as a result of the re-structuring processes in MWCNT clusters accompanied by changes in the microstructure density of suspension and the formation of better electric contacts between individual nanotubes. It should be noted that an appreciable hysteresis was observed only when the MWCNT concentration was rather low ($C < 0.3$ wt%), whereas, at high MWCNT concentrations ($C \approx 1.0$ wt%), it was considerably suppressed. Such a behavior can be explained by the fact that a rather strong multidimensional MWCNT network is formed at high MWCNT concentrationS, so that the re-structuring processes are slowed down.

The influence of the concentration C on the suspension rheological properties is shown in Fig. 4. Pure glycerol is known to be a Newtonian liquid, for which the shear stress τ grows proportionally to the shear velocity γ, so that the viscosity $\eta = \tau/\gamma$ does not depend on γ [35]. However, in the case of composites, the Newtonian character of a flow was violated already at rather low C-values. A substantial reduction of the viscosity η was observed at an increase of γ, and such a thixotropic behavior evidently appeared owing to the processes of MWCNT aggregate destruction under shear. The attention is drawn by an anomalous thixotropic behavior which was observed at high MWCNT concentrations, $C = 1$ wt%, and high shear velocities, $\gamma > 10$ s^{-1}. Under those conditions, the measured viscosity of suspensions was substantially lower than that of pure glycerol

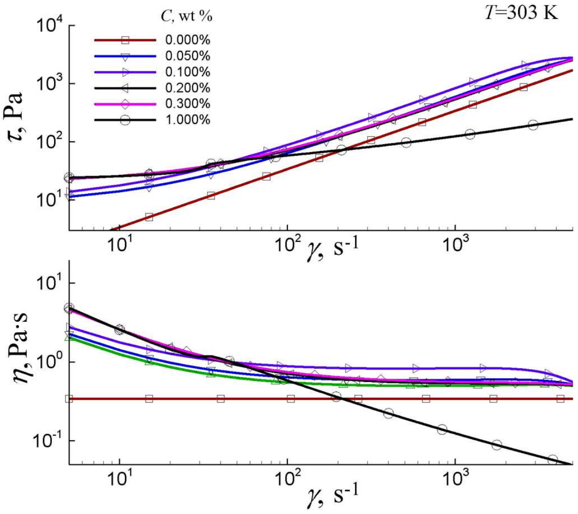

Fig. 4. Dependences of the shear stress τ and the viscosity $\eta = \tau/\gamma$ on the shear velocity γ for MWCNT suspensions in glycerol at various concentrations C and the temperature $T = 303$ K

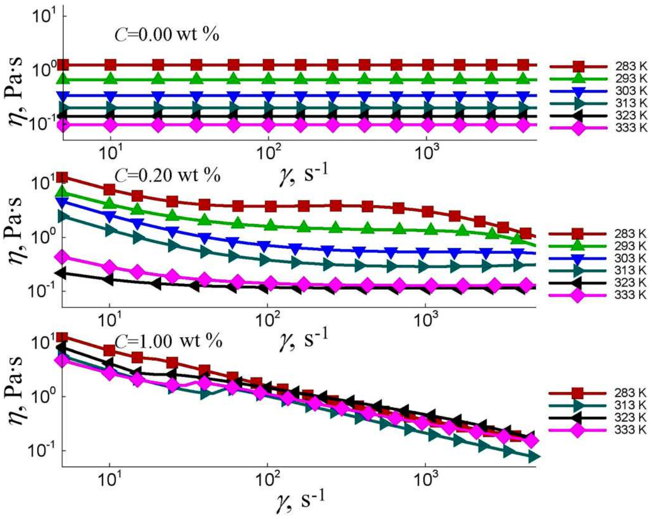

Fig. 5. Dependences of the viscosity $\eta = \tau/\gamma$ on the shear velocity γ for MWCNT suspensions in glycerol at various MWCNT concentrations $C = 0$ (pure glycerol), 0.2, and 1.0 wt% (panels from top to bottom) and various temperatures

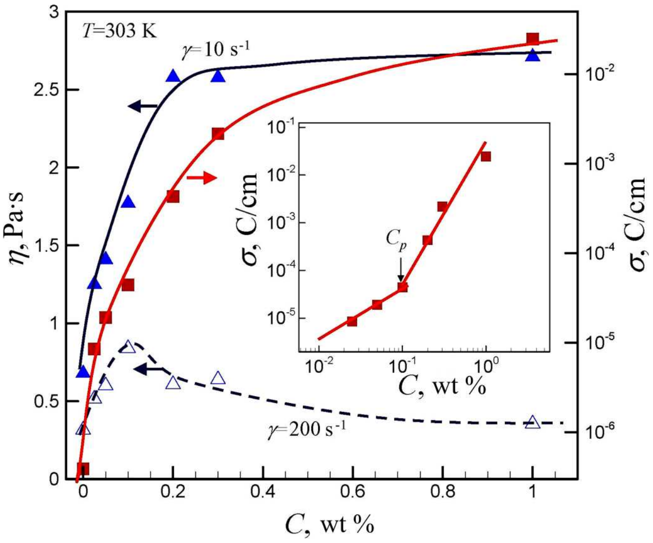

Fig. 6. Dependences of the viscosity η (at various shear velocities γ) and the electrical conductivity σ on the MWCNT concentration in glycerol C at the temperature $T = 303$ K. The inset shows the dependence $\sigma(C)$ on the log-log scale

(Fig. 4). This fact can be explained by the existence of specific formations in the structure of MWCNT suspensions in glycerol which give rise at high concentrations C to the destruction of the hydrogen bond network in glycerol and, in such a manner, promote a suspension flow. It is known that the viscosity of glycerol, the molecule of which (HOH_2C-$CHOH$-CH_2OH) includes three hydroxyl groups, is mainly governed by hydrogen bonds, so that their destruction can result in a substantial reduction of the viscosity [36–38].

In Fig. 5, the dependences of the viscosity $\eta = \tau/\gamma$ on the shear velocity γ are depicted for MWCNT suspensions in glycerol at various concentrations C and temperatures T. The figure shows that the temperature affects the behavior of the viscosity rather considerably at low MWCNT concentrations ($C < 1.0$ wt%), but practically no effect is observed at $C = 1.0$ wt%.

The typical dependences of the viscosity η and the electrical conductivity σ on the MWCNT concentration C in glycerol are shown in Fig. 6. The inset demonstrates the dependence $\sigma(C)$ on the log-log scale. The behavior of the electrical conductivity testifies to a percolation-induced transition from a low- to a high-conductivity state at $C = C_p \approx 0.1$ wt%. It is at this concentration in the system that the connected cluster is formed (Fig. 1). The behavior of the electrical conductivity above the percolation threshold is described by the classical scaling law

$$\sigma \propto (C - C_p)^t \tag{2}$$

with the exponent $t = 2.7 \pm 0.3$, which exceeds somewhat the value $t \approx 2.0$ typical of the random percolation.

Perhaps, this difference from the random percolation case may be associated with the fact that a percolation cluster in the systems concerned arises by means of the association of "primary" ones with a complicated, probably fractal structure. Note that a substantial (by a factor of about five) growth of the viscosity η measured at low

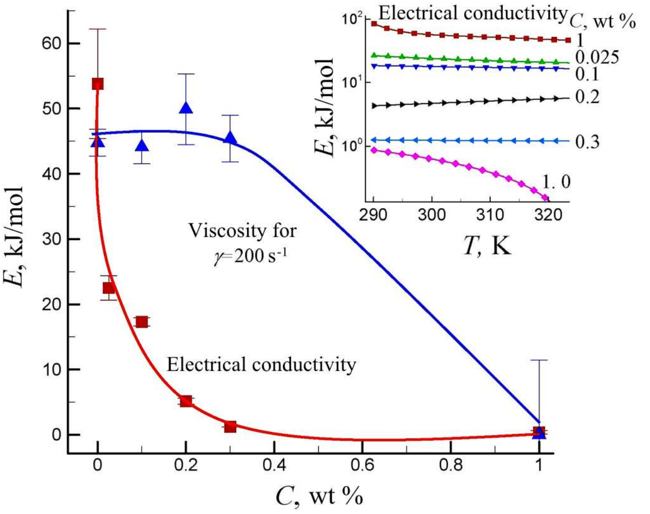

Fig. 7. Dependences of the activation energies E calculated from the temperature dependences of the viscosity η (at $\gamma = 200\ \mathrm{s}^{-1}$) and the electrical conductivity σ on the MWCNT concentration C in glycerol. The inset shows the temperature dependences of the effective activation energy E_e for the electrical conductivity ($E_e = d\ln\sigma/d(1/RT)$) at various C

shear velocities (at $\gamma = 10\ \mathrm{s}^{-1}$, see Fig. 6) is observed in a vicinity of the electric percolation point, if the concentration C increases. However, at high shear velocities (at $\gamma = 200\ \mathrm{s}^{-1}$, see Fig. 6), the viscosity η in a vicinity of the percolation point $C \approx C_p$ passes through a maximum. We may suppose that, at high shear velocities γ and high MWCNT concentrations C, the destruction of the hydrogen bond network in glycerol is the most effective, which is responsible for this anomalous effect.

The temperature dependence of the viscosity of pure glycerol η has a well-pronounced Arrhenius-like character with the activation energy $E = 47.0 \pm 0.3$ kJ/mol. The temperature dependence of the electrical conductivity in glycerol was not Arrhenius-like, and the value of activation energy E was calculated in this case by averaging the effective activation energy

$$E_e = d\ln\sigma/d(1/RT) \qquad (3)$$

within the temperature interval $T = 283 \div 333$ K. In Eq. (3), $R = 8.314$ J/(mol×K) is the universal gas constant.

Note that the non-Arrhenius behavior of the electrical conductivity is typical of glass-forming liquid systems, and, to approximate the temperature dependence in such cases, a more complicated Vogel–Tammann–Fulcher equation is usually applied (see, e.g., work [40]).

The dependences of the activation energies calculated in such a manner on the MWCNT concentration C are depicted in Fig. 7. The temperature dependences of the quantity E_e are shown in the inset. It should be noted that the activation energy of the ionic conductivity decreased with increase in the filling degree C and reached very low values above the percolation point, when a multiply connected MWCNT network had been formed, and the mechanism of ionic conductivity had lost its dominating role. Such a behavior is rather typical of nanocomposites filled with carbon nanotubes [5, 10, 14]. On the other hand, the activation energy of a viscous flow at low C (< 0.3 wt%) was practically independent of C, and its appreciable reduction was observed only at higher MWCNT concentrations. Thus, a considerable reduction of the activation energy was observed only at the formation of a multiply connected MWCNT network in glycerol, which can be explained by a substantial destruction of hydrogen bonds in glycerol due to the presence of nanotubes.

4. Conclusions

MWCNTs reveal a high tendency to the aggregation in glycerol, which is governed by strong van der Waals interactions and the Brownian motion. “Primary” aggregates survive in the system even after the intense ultrasonic homogenization. As the MWCNT concentration increases, those aggregates join with one another to form a percolation network at $C = C_p \approx 0.1$ wt%. An introduction of MWCNTs into glycerol resulted in a drastic increase of the electrical conductivity and a manifestation of the thixotropic behavior of suspensions, which testified to the processes of MWCNT aggregate destruction under shear. At high MWCNT concentrations, $C = 1$ wt% , and high shear velocities, $\gamma < 100\ \mathrm{s}^{-1}$, an anomalous rheological behavior was observed. Under those conditions, the measured values of viscosity in suspensions were substantially lower than that in pure glycerol. This fact testifies to the destruction of the hydrogen bond network in glycerol induced by MWCNTs. This conclusion is in accordance with the observed influence of the temperature on the suspension viscosity. The behavior of the electrical conductivity above the percolation threshold is described by a classical scaling law with the conductivity index $t = 2.7 \pm 0.3$, which is somewhat higher that the t-value characteristic of the stochastic percolation.

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МІКРОСТРУКТУРА, РЕОЛОГІЧНІ ТА КОНДУКТОМЕТРИЧНІ ДОСЛІДЖЕННЯ СУСПЕНЗІЙ БАГАТОШАРОВИХ ВУГЛЕЦЕВИХ НАНОТРУБОК У ГЛІЦЕРИНІ

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Резюме

Методами оптичної мікроскопії, проведено дослідження електропровідності і реологічних властивостей (метод конус-плита) суспензій гліцерину, наповненого багатошаровими вуглецевими нанотрубками MWCNT. Дослідження проведено в інтервалі температур 283–333 K і при ступенях наповнення $C = 0$–1% мас. Показано, що MWCNT у гліцерині проявляють високу схильність до агрегації і в системі зберігаються "первинні" агрегати MWCNT навіть при інтенсивній ультразвуковій гомогенізації. При збільшенні концентрації MWCNT спостерігалися типові перколяційні процеси, які супроводжувалися підвищенням електропровідності і в'язкості. Перколяційна концентрація ідентифікована при $C = C_p \approx 0,1\%$ мас., а скейлінгова поведінка поблизу точки перколяції характеризується показником провідності $t = 2,7 \pm 0,3$, який дещо перевищує значення, характерне для задачі випадкової перколяції. Введення MWCNT у гліцерин приводило до прояву тіксотропної поведінки суспензій, яка відображала процеси руйнування агрегатів MWCNT при зсувові. При високих концентраціях MWCNT, $C = 1\%$ мас., спостерігалася аномальна реологічна поведінка, яка відображала наявність руйнування сітки водневих зв'язків у гліцерині внаслідок присутності MWCNT. Проведено оцінку залежності енергій активації електропровідності і в'язкої течії від концентрації MWCNT.