Rheological properties of “Vaseline – Carbon nanoparticles” model systems under conditions of non-destructive deformations

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Abstract. The paper presents experimental data on the rheological properties of “Vaseline – Carbon Nanoparticles” systems, which were obtained through oscillation tests. The nanoparticles used are multi-layered oxidized graphene (Gr), single- (SWCNTs) and multi-walled (MWCNTs) carbon nanotubes, as well as shungite nanocarbon (Sh). It was demonstrated that when carbon nanoparticles were added to the Vaseline (VM) at concentrations from 0.5 to 1.5 wt.%, the elasticity of the systems increased as compared with the pure VM, wherein the system containing 1.0 wt. % of MWCNTs was characterized by the greatest elasticity. All the studied carbon nanoparticles proved to be rheomodifiers. However, Gr, SWCNTs and MWCNTs acted essentially depending on their concentration in the vaseline system, resulting in both shortening and lengthening of the relaxation time. The natural shungite nanocarbon always led to the decrease of the relaxation time within the studied concentration range. The obtained results form an experimental basis for the development of scientific approaches to the production of lubricants operating in various friction modes

1. Introduction
One of the most effective ways of ensuring the reliability and durability of machine moving parts is the use of lubricating materials (LMs) as components of these parts. If designers try to reduce the LM specific input into the friction unit to extend the entire service life, it is necessary to use plastic lubricating materials (PLMs). They consist of at least two components – base oil (dispersion medium)
and thickener (dispersed phase). The thickener forms a structural lattice and determines the PLM properties. Industry-grade PLMs contain modifiers that make the optimal LM lattice and additives (poorly soluble compounds) that impart the lubricant the required functional properties. Defining the functionality of specific additives in PLMs is complicated by their possible interaction with surface molecules of a solid object as well as with other lubricant components [1].

Modern PLMs contain additives of both organic and inorganic nature [2,3]. It is known that addition of different carbon nanoparticles (CNPs) can improve the tribological properties of LMs [4,5]. However, all those studies were carried out on commercially produced PLMs, which makes it impossible to isolate the effect of certain CNP additives on tribological properties of PLMs, regardless of other components. Rheological characteristics are among important operational properties of LMs. Managing the viscoelastic properties of LMs allows to optimize the LM composition scientifically. Flow curves seem to be a useful tool for studying the lubricant internal lattice and registering its changes.

Considering the aforementioned, the objective of the present research was to determine the dependence of the rheological properties of “Vaseline-CNPs” model systems on the type and concentration of CNPs in non-destructive (oscillation) tests. The main goal was to develop a scientific selection of additives to LMs operating under various loads. It is known that different viscosity of LMs is required for heavy- and light-load machines [1]. The secondary goal was to study the effect of the shear frequency on the characteristics of the viscoelastic flow of the analyzed model systems.

2. Materials and methods

Medical vaseline (VM) (Pharmaceutical Warehouse Himfarmprodukt LLC, St.-Petersburg, Russia), manufactured according to the Federal standard requirements LSP-005886/08-230708, was used as the base for VM/CNPs model systems.

The following CNPs, representing various allotropic carbon modifications, were introduced as additives (at concentrations ranging from 0.5 to 1.5 wt.%):

- multi-layered oxidized graphene (Gr) (NanoTech Center LLC, Tambov, Russia) representing 3-5-nm thick nano-sized layered platelets. The number of graphene layers ranges from 5 to 10, on the periphery of which hydroxyl and carboxyl groups are available;
- single-walled (SWCNTs) and multi-walled (MWCNTs) carbon nanotubes (Arry GmbH, Weiher, Germany): SWCNTs are 1–2 nm in diameter, ~20 µm in length, their purity exceeds 90 wt.%; whereas MWCNTs are 3–10 nm in diameter, ~20 µm in length, the purity exceeds 95 wt.%);
- shungite carbon nanoparticles (Sh), obtained from high-carbon Shungit I rock (Shunga deposit), Russia). The particles have multi-level fractal structure resulting from the sequential aggregation of ~1 nm graphene fragments. Turbostratic stacks of ~1.5–2.5 nm and globular stack formations averaging ~6 nm in linear size determine the secondary and tertiary levels of the structure. Globule aggregates of tens of nanometers in size complete the structure [6-8]. It was demonstrated that the Sh basic element is a reduced graphene oxide [9]. In our tests, we used a condensate of water dispersion of Sh nanoparticles [10], which was placed into chloroform and then dried.

The VM/CNPs systems were obtained by mechanical mixing. The VM and CNPs components were weighed with 0.1 mg accuracy using analytical balance.

To determine the rheological characteristics of the samples, a StressTech rheometer by REOLOGICA Instruments AB (Lund, Sweden) was used. It included a digital interface rotational viscosimeter and a personal computer with a preinstalled control- and experiment-data-processing software suite. As a sensor element, we used a plane-plane system of the following geometry: 2r – 20 mm, the in-plane gap was 0.4 mm. The shaft was rotated by a compressed-air low-friction turbine. We used a precision automatic micrometer to set the gap between the sensor elements. To maintain constant temperature, a 0.1 °C accuracy thermostat was used. Oscillation tests were done at constant temperature of 30 °C and constant torque $M_{trq} = 2.094 \text{ N} \cdot \text{mm}$. The viscoelastic properties were estimated by varying the shear frequency in the 0.1 - 12 Hz frequency range. To preserve the system structure at the beginning of the test, the stress and strain values were significantly lower than the yield strength and amounted to $\tau_0 = 1 \text{ Pa}$ and $\gamma_0 = 2.5 \cdot 10^2 \text{ Pa}$.
In non-destructive tests, we measured the following parameters: the complex shear modulus \((G^*)\) as well as its components – elastic (or storage) modulus \((G')\) and viscous (or loss) modulus \((G'')\) components, the phase angle \((\delta)\) and the phase angle tangent \((\tan \delta)\). A decrease in the phase angle \(\delta\) over the entire range \((0 - 90^\circ)\), depending on the frequency, indicates a decrease in the viscous and, accordingly, an increase in the elastic inputs into the sample characteristics.

3. Results and discussion

In [1], nanoparticles are considered as rheo-improvers and specifically viscosity modifiers. According to their Working Site Category, they relate to bulk agents, whereas, according to their Working Mechanism Category, they belong to physical additives. By functionality, the rheo-improvers could be categorized as “indirect” tribo-improvers. Therefore, we began our study with such values as the phase angle and the complex shear modulus, which together determine the viscoelasticity map of the VM/CNPs systems. The map is shown in figure 1. In this map, the shift from left to right represents the increase in viscosity, whereas the shift from bottom to top represents the solid-to-liquid transition.

![Viscoelasticity Map](image)

**Figure 1.** A viscoelasticity map.

The performed tests demonstrated that the general trend for all the VM/CNPs systems studied in the considered range of phase angles \(\delta \ (0^\circ < \delta < 90^\circ)\) and frequencies \(f \ (0.1 \text{ Hz} < f < 12 \text{ Hz})\) is a gradual decrease of \(\delta\), which leads to an increase of the elastic component \(G'\) and a decrease of the viscous component \(G''\) of the complex shear modulus \(G^*\) as compared to the pure VM. The corresponding formula for calculating \(G^*\) is given below:

\[
G^* = G' + iG''.
\]

The experimental data on the oscillation tests for the pure VM and VM/CNPs systems are summarized in the viscoelasticity map in figure 2. When drawing the map, we used numerical data for the complex shear modulus \(G^*\) and phase angle \(\delta\) at the test end time \(t = 65 \text{ s}\).
When the studied carbon allotropes were added to VM, the $G^*$ value increased over time in all the samples, except the VM/SWCNTs (1.0 wt %) system. The $G^*$ value for the latter system was 682 Pa, i.e. close to that of the pure VM – 731 Pa. In general, in the VM/CNP systems, we observed a tendency for increasing $G'$ and $G^*$ and decreasing $G''$ as compared with the pure VM (figure 2). However, the $G''$ value in the systems turned out to exceed that of the pure VM. The greatest increase in the $G^*$ value (figure 2) was caused by addition of the MWCNTs (1.0 wt.%).

All the tested systems demonstrated a decrease in the phase angle $\delta$ values. Moreover, this decrease depended on the CNPs concentration and lay within the limits of $\delta \approx 46-38^\circ$ when adding 0.5 wt.% of the CNPs and 35-30° – for the systems containing 1.0 wt.% of the CNPs. The increase in the additive concentration up to 1.5 wt.% in the VM/Gr system reduced $\delta$ value to 18°. Thus, according to the $G''$ and $\delta$ values, an increase in the system elasticity with the increase of the CNP concentration took place.

As examples given in figures 3 and 4, we show the dependence of the VM and VM/MWCNTs (1.0 wt.%) viscoelastic properties on the oscillation time. Evidently, once the values of the elastic $G'$ and viscous $G''$ components of the complex shear modulus $G^*$ crossed the equilibrium point, a sharp increase of the $G^*$ value was recorded, which for the VM/MWCNTs (1.0 wt.%) system reached 7300 Pa ($\delta = 31^\circ$, figure 4), whereas the corresponding value for the pure VM was 731 Pa ($\delta = 52^\circ$, figure 3).

In his classic monograph, Schramm [11] demonstrated that it was possible to register structural rearrangements within the system at low frequencies of the 1 Hz order by the relaxation times $\lambda_i$. That is why we took this indicator to analyze the effect of the structure and concentration of CNPs in the studied systems. We established certain correlations between the relaxation time and the angular velocity of the systems. In these systems, time is one of the most important factors signaling that the system returns to its original state once the external load is removed (figure 5). As it is shown in Figure 5, within the entire angular velocity range, a decrease of the $\lambda_i$ values was recorded. However, the steady exponential decrease observed for the VM was characteristic only of the VM/CNPs systems in the following sequence of additive: SWCNTs (1.0 wt.%) > Gr (0.5 wt.%) > MWCNTs (0.5 wt.%) > SWCNTs (0.5 wt. %).
Figure 3. Changes in the viscoelastic properties of the pure VM at $T = 30 \, ^\circ\mathrm{C}$, where $G^*$ – complex shear modulus, $G'$ – elastic and $G''$ – viscous components of the complex shear modulus, $\text{Phase}$ – phase degree, $\text{Viscosity}^*$ – complex viscosity.

For the other systems, the curves (figure 5) demonstrated a definite knee-bend in the 30–55 rad/s angular velocity range. The introduction of the MWCNTs (1.0 wt.%) into the VM caused the greatest $\lambda_i$ decrease, making the relaxation time half the value of that for the pure VM. The maximum increase in the relaxation time was observed when 1.0 wt. % of the SWCNTs was introduced: the relaxation time increased by 2.6 times as compared to the pure (pristine) VM.
Based on Schramm's evaluation of the relaxation time $\lambda_i$ given the $G' = G''$ equation, the quantitative values for $\lambda_i$ and the corresponding frequencies satisfying this equation were obtained (table 1). The oscillation frequency was measured in the tests.

It was found that the CNPs presence in vaseline in any of the studied concentrations resulted in a shift of the intersection point of the curves, representing the elastic and viscous components ($G' = G''$) of the system and the change of $\lambda_i$. In all the systems, that point was reached earlier than in the pure VM.

The relaxation time at a low oscillation frequency (about 1 Hz) was calculated according to equation (2):

$$\lambda_i = \frac{1}{\omega G''_i},$$

where $i$ is the ordinal number of relaxation time value, $\omega$ is the angular velocity (rad/s), and $G''_i$ is the loss modulus.

### Table 1. Dependence of the relaxation time $\lambda$ on the CNPs concentration and structure.

| Vaseline/CNPs system | CNPs | CNPs concentration (wt.%) | Relaxation time, $\lambda_i$ (µs) | Oscillation frequency, $f$ (Hz) at $G' = G''$ |
|---------------------|------|---------------------------|----------------------------------|-----------------------------------------------|
| −                   | −    | −                         | −                                | −                                             |
| Gr                  | −    | 0                         | 540                              | 1.5                                           |
| Gr                  | −    | 0.5                       | 830                              | 0.9                                           |
| Gr                  | −    | 1.0                       | 500                              | 0.5                                           |
| Gr                  | −    | 1.5                       | 340                              | 0.4                                           |
| SWCNTs              | −    | 0.5                       | 500                              | 0.7                                           |
| SWCNTs              | −    | 1.0                       | 1420                             | 0.9                                           |
| MWCNTs              | −    | 0.5                       | 640                              | 1.0                                           |
| MWCNTs              | −    | 1.0                       | 260                              | 0.5                                           |
| Sh                  | −    | 0.5                       | 310                              | 0.9                                           |
| Sh                  | −    | 1.0                       | 450                              | 0.6                                           |
The decrease in the system relaxation time corresponded to the destruction of the VM internal organization, whereas the increase of the relaxation time meant the formation of a new structure, the dimensions of which exceed those of the basic one. Analyzing the data in table 1, we could establish the following correlations between the structure-forming and structure-destructive CNPs effect and the CNPs type as well as the CNPs concentrations (for the concentrations of 0.5 and 1.0 wt.% the correlations are presented in figure 6).

Figure 6. Viscoelastic properties of the VM/CNPs systems depending on the type and concentration of added nanoparticles. The relaxation time \( \lambda, \mu s \) is given in brackets.

Figure 6 illustrates that only Sh at both studied concentrations behaves as a structure-destructive factor, whereas the other CNPs additives can act in two ways depending on their concentrations: both as structure-destructive and as structure-forming agents.

4. Conclusion

The experimental study of the viscoelastic properties of Vaseline and its CNP-containing systems through oscillatory deformation showed that with the introduction of the studied carbon nanoparticles the model systems shift from the low-viscosity liquid zone to that of a viscoelastic solid. At the same time, the elasticity of the systems increases over the entire range of the frequencies studied. The maximum increase in the elastic properties was observed in the VM/Gr (1.5 wt.% system). The least effect on the increase of the \( G' \) component of the \( G^* \) complex shear modulus was found after introducing SWCNTs (1.0 wt.%).

The analysis of the relaxation times \( \lambda_i \) of the VM/CNP model systems demonstrated a steady decrease of \( \lambda_i \) with an increase of the angular velocity \( \omega \). Comparing \( \lambda_i \) of the \( G^* \) complex shear modulus at the equilibrium point of the elastic \( G' \) and viscous \( G'' \) components, it was found that the introduction of MWCNTs (1.0 wt.%) has the greatest effect upon diminishing the relaxation time.

All the studied nanoparticles acted as rheo-modifiers, however, the multi-layered oxidized graphene, single- and multi-walled carbon nanotubes acted essentially depending on their concentration in the vaseline system, which resulted in both shortening and lengthening of the relaxation time. In contrast, the natural shungite nanocarbon added in all the concentrations studied always led to the decrease in the relaxation time. The obtained results form the experimental basis for the development of scientific approaches to the production of lubricants operating in various friction modes.
5. Acknowledgments
The work was supported in the framework of the program of the Ministry of Science and Higher Education of the Russian Federation [Grant No. 16.1037.2017/4.6] and the Russian Foundation for Basic Research [Grant No. 18-29-19150_mk].

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