Investigation of physical-mechanical and tribological properties of suspensions of nanoparticles based on polyethylsiloxane liquid

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Abstract. The study of the physical-mechanical properties of suspensions of silica dioxide nanoparticles and fullerenes in polyethylsiloxane liquid was carried out. The shear modulus and effective viscosity of nanosuspensions were determined by the acoustical resonance method, the coefficient of friction with the base polyethylsiloxane lubricant and modified lubricants was determined, and an improvement of the tribological properties of the synthesized suspensions was shown due to increasing the strength of the lubricating film.

1. Introduction

One of the most effective methods to significantly increase of reliability and wear resistance of machines and mechanisms is to improve the quality of lubricants by introducing various additives into base lubricants that improve the tribological properties of the lubricant medium. The effectiveness of the use of nanomaterials and nano-functional additives is confirmed by numerous studies [1, 2].

This paper presents a study of shear mechanical properties of colloidal suspensions of silica dioxide nanoparticles and fullerenes. Polyethylsiloxane liquid was used as a base fluid. The wide range of working temperatures (from −60 to +150 °C) and good lubricating properties allow them to be used as greases, instrument oils, and hydraulic brake fluids. Silica dioxide nanopowder SiO₂ with particle sizes of 50 and 100 nm, obtained by gas-phase synthesis [3], and fullerenes C₆₀, purchased from Company “NeoTechProduct”, were used for suspensions.

2. Method

Viscoelastic properties of the synthesized suspensions are investigated by an acoustic resonance method using a piezoquartz resonator [4, 5]. Investigated liquid is placed between the surfaces of a piezoquartz oscillating at the resonant frequency and a resting solid cover-plate. A cut of X-18.5° piezoquartz provides pure shear deformations of the liquid and standing shear waves are established in it. The solution of the interaction problem of the resonator with liquid layer and a solid cover-plate gives for the complex shift of resonant frequency \( \Delta f^* = \Delta f' + i \Delta f'' \) the following expression:

\[
\Delta f^* = \frac{SG^* k^*}{4\pi^2 M f_o} \frac{1 + \cos(2k^* H - \phi^*)}{\sin(2k^* H - \phi^*)},
\]

where \( G^* = G' + iG'' \) – is the complex shear modulus of the liquid, \( S \) – is the cover-plate base area,
$H$ – is the thickness of liquid interlayer, $M$ – is the resonator mass, $f_0$ – is its resonance frequency, $k^*$ – is the complex wave number; $\phi^*$ – complex phase shift in the reflection of a shear wave from the liquid – cover-plate interface. In accordance to the theory of the method considering that the cover-plate is at rest due to a weak bond to the piezoquartz through the liquid layer ($\phi = 0$) and a thickness of liquid layer is much smaller than the shear wave length, the complex shear modulus and a tangent of the mechanical losses angle will be determined by the expressions:

$$G^* = \frac{4\pi^2 M f_0 \Delta f^* H}{S}, \quad \tan \theta = \frac{G^*}{G'} = \frac{\Delta f^*}{\Delta f'}.$$  \hspace{1cm} (2)

According to expression (2), the complex shift of the resonant frequency of piezoquartz $\Delta f^*$ should be proportional to the inverse value of the interlayer thickness. It is necessary to thorough clean of working surfaces when measuring the complex shear modulus [5]. The studied liquids should wet the surfaces of the piezoquartz and the cover-plate well to prevent slippage.

3. Results and discussion

We used the piezoquartz with size of $34.9 \times 12 \times 6$ mm$^3$ and a mass of 6.82 g, the main resonant frequency is of 73.2 kHz. The area of the cover-plate base $S = 0.2$ cm$^2$. Experimental dependences of real $\Delta f'$ and imaginary $\Delta f''$ parts of shift of the resonance frequency on the inverse value of liquid thickness $1/H$ for samples of silica dioxide suspensions with nanoparticles of 100 nm and fullerenes with a concentration of 1.25 wt.% in PES-2 polyethylsiloxane liquid turned out to be linear. It indicates that these suspensions possess the shear modulus, independent of the thickness of the liquid layer. The calculations of the real shear modulus and the tangent of the mechanical losses angle for these liquids give values $G' = 0.25 \times 10^3$ Pa, $\tan \theta = 0.35$ and $G' = 0.71 \times 10^3$ Pa, $\tan \theta = 0.38$, respectively. The study of the low-frequency shear elasticity of liquids by the acoustic resonance method showed that the shift of the resonance frequency of piezoquartz depends on the amplitude of shear deformation, indicating non-linear shear properties [6–8]. Determination of the amplitude $A$ of the shear oscillations of piezoquartz was carried out using the method based on the principle of the Fabry-Perot interferometer [9]. The ratio $A/H$ can serve as a measure of angular deformation. For convenience of analysis, experimental results are given depending on the square root of this ratio.

Figure 1 shows the dependences of the real (1) and imaginary (2) components of the shear modulus on shear strain for the suspensions studied. At small angles of deformations the components of the complex shear modulus $G^*$ are constant, then with increasing shear angle the real part $G'$ decreases, and imaginary part $G''$ begins to increase. At small shear deformation angles, the equilibrium structure of the suspension remains unchanged, and a region of linear elasticity is found.

It can be assumed that at some critical shear stress $P_\sigma$, the equilibrium structure of suspension begins to break and its mechanical properties change. The critical shear stress corresponds to a certain critical shear angle $\varphi_c$, which can be determined from the data of figure 1. The critical angles for SiO$_2$/PES-2 suspension, $\varphi_c = 1^\circ$, and for C$_60$/PES-2, $\varphi_c = 5^\circ$, are much higher than the value for PES-2, $\varphi_c = 8.4^\circ$. That indicates an increase in the structure strength of the suspension studied.

The effective viscosities $\eta_{\text{eff}}$ of the investigated suspensions at small angles of deformations have exceeded the viscosity value of the base liquid. The viscosity of polyethylsiloxane has been determined by a rotation method using a Physica Anton Paar MCR 302 rheometer and is equal to 0.01 Pa·s. Effective viscosities of suspensions was calculated using data of figure 1 according to Maxwell rheological model by the formula:

$$\eta_{\text{eff}} = \frac{G'(1 + \tan^2 \theta)}{2M f_0 \tan \theta}.$$ \hspace{1cm} (3)

Figure 2 presents the dependence of effective viscosity on the shear deformation angle for suspensions with silica dioxide particles of 50 and 100 nm, $c = 1.25$ wt.% and fullerenes, $c = 1.5$ wt.%. At angles not exceeding the value of $\varphi_c$, suspensions are characterized by a constant increased
viscosity. With a further increase in the shear angle, when the equilibrium structure is destroyed, the viscosity decreases to the smallest value.

**Figure 1.** Experimental dependences of real (1) and imaginary (2) parts of shear modulus on the shear deformation angle for suspensions: (a) – 100 nm SiO\textsubscript{2}/PES-2, 1.25 wt.%; (b) – C\textsubscript{60}/PES-2, 1.5 wt.%. Figures 2(a), (b) show that the critical shear angle $\phi_c$ is increased with decreasing silica dioxide particle size. Besides, the specific surface area of particles increases, which contributes to the formation of additional hydrogen bonds with the polymer which rise in viscosity.

**Figure 2.** Dependence of effective viscosity on the shear deformation angle for suspensions: (a) – 50 nm SiO\textsubscript{2}/PES-2; (b) – 100 nm SiO\textsubscript{2}/PES-2; (c) – C\textsubscript{60}/PES-2.

Polyorganosiloxanes have weak intermolecular interactions, because of which they are characterized by low mechanical characteristics, especially low tensile strength. The use of fullerenes and silica dioxide nanoparticles with hydroxyl groups on their surface leading to the formation of hydrogen bonds with the polymer increases the strength of the structure of nanosuspensions.

The friction coefficient of a steel-steel pair with lubrication was determined on Anton Paar MCR 302 rheometer using a tribological system operating on the ball principle on three planes. Normal load
was 5 N, measurements were carried out at –25 °C. Figure 3 presents the results of determining the coefficient of friction versus the sliding velocity for PES-2 liquid and the investigated suspensions of 50 nm size SiO$_2$ nanoparticles and C$_{60}$ in the base liquid as lubricants. The critical sliding velocity is revealed, upon reaching which destruction of the lubricating layer separating the rubbing surfaces occurs. From figure 3 it can be seen that the destruction of layer of the lubricant modified with nanoparticles occurs at higher sliding velocities as compared to the base lubricant. The addition of nanoparticles to the lubricating oil leads to increase in strength of the lubricant at break.

![Figure 3. Friction coefficient vs sliding velocity for steel – steel pair with lubricant: 1 – PES-2; 2 – 50 nm SiO$_2$/PES-2, 1.25 wt.%; 3 – C$_{60}$/PES-2, 1.5 wt.%; 4 – 50 nm SiO$_2$/PES-2, 0.5 wt.%.

4. Conclusion

Thus, the nanoparticles dispersed into the base liquid are a structure-forming element, varying the concentration and dimensions of which can simulate the properties of nanosuspensions. In particular, the tribological characteristics of polyethyilsiloxane liquids modified with nanoparticles significantly improve by increasing the strength of the lubricant film.

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