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MEASUREMENT OF THE SHEAR ELASTICITY OF POLYMETHYLSILOXANE LIQUIDS

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The paper concerns the shear mechanical properties of a number of polymethylsiloxane liquids by a dynamic method at the frequency of shear oscillations of the order of 10^5 cps (Hz). Three different methods for determining the complex shear modulus follow from the theory of the method. The first method is realized when the film thickness is much smaller than the shear wavelength. The second method involves the measuring of the shear wavelength on the basis of maxima of the frequency shifts of an oscillatory system. The third method is based on measuring the parameters of the oscillatory system when the shear waves are completely extinguished in the liquid bulk. All the three methods provide satisfactory coincidence of the results. This proves amply that the experiment determines the bulk values of shear elasticity.

Polymethylsiloxane liquids find wide application in the modern technics. A wide range of the working temperature and good lubricating properties allow their use as greases, instrument oils, polishing substances, as well as hydraulic brake liquids. Therefore, investigation of the shear mechanical properties of these liquids is of obvious interest.

In studies [1–4], a resonance method using a piezoquartz crystal was applied to measure low-frequency (10^5 Hz) complex elasticity shear moduli of different liquids. It was shown that all the liquids, including the low-viscosity ones, possess the modulus of shear elasticity on the order of 10^5 to 10^6 dyn/cm^2.

A major advantage of the present method of measuring the shear mechanical properties resides in that it has no limitations with regard to the viscosity of the liquids being investigated. It enables one to investigate the liquids whose viscosity lies within the range of hundredths to 10^6 P. The viscosity of a number of polymethylsiloxane liquids varies within a vary wide range; therefore, the present investigation method can successfully be applied to their examination. The main shortcoming of the method consists in the difficulty of varying the experimental frequency of shear oscillations due to technical reasons.

The resonance method for measuring the shear elasticity consists in the following. A piezoquartz crystal performs longitudinal (axial) oscillations at the basic resonance frequency, and its horizontal surface performing tangential oscillations supports a liquid interlayer covered by a solid cover plate. The cover plate with the liquid film is disposed on one end of the piezoquartz crystal (fig. 1). In this case, the liquid interlayaer undergoes a shear deformation, and standing shear waves should be induced in it. The parameters of the resonance curve of the piezoquartz crystal vary depending on the interlayer thickness.

The complex shift, Δf^*, of the resonance frequency of the piezoquartz crystal due to its interaction with the liquid interlayer has the form [4]

$$\Delta f^* = \frac{S\kappa^* G^*}{4\pi^2 M f_0} \frac{1+\cos(2\kappa^* H - \varphi^*)}{\sin(2\kappa^* H - \varphi^*)}, \qquad (1)$$

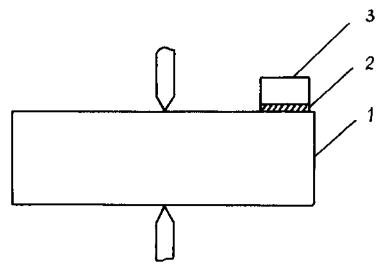

Fig. 1. Piezoquartz crystal (1) with a liquid film (2) covered by a cover plate (3).

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where S is the area of the base of the cover plate; $\kappa^* = \beta - i\alpha$ is its complex wave number, $G^* = G^1 + iG^{11}$ is the complex shear elasticity modulus of liquid, H is the thickness of the liquid interlayer; φ^* is the complex (shift) of the phase when the wave is reflected from the liquid–cover plate interface, M is the mass of the piezoquartz crystal; f_0 is its resonance frequency. Under the condition when the cover plate because of a weak bond with the piezoquartz crystal, which is realized by the liquid interlayer, is at rest ($\varphi^* = 0$), the expressions for the real and the imaginary components of the shift of the resonance frequency will be as follows:

$$\Delta f' = \frac{S}{4\pi^2 M f_0} \times \frac{(G'\beta + G''\alpha)\sin 2\beta H + (G'\alpha + G''\beta)\sinh 2\alpha H}{\cosh 2\alpha H - \cos 2\beta H}, \quad (2)$$

$$\Delta f'' = \frac{S}{4\pi^2 M f_0} \times \frac{(G''\beta - G'\alpha)\sin 2\beta H + (G''\alpha + G'\beta)\sinh 2\alpha H}{\cosh 2\alpha H - \cos 2\beta H}. \quad (3)$$

By the use of these formulas, the dependences of Δf^1 and Δf^{11} on the liquid interlayer thickness were computed for the case where $G^1 = 10^6$ dyne/cm^2 and tg $\theta = 0.5$ (fig. 2). It can be seen that the dependencies of the resonance frequency shifts on the liquid interlayer thickness give the decaying oscillation. With small thicknesses, when $H \ll \lambda$, the frequency shifts are inversely proportional to the interlayer thickness. The first decay maximum will be observed when the liquid interlayer thickness is equal to half of the shear wave length. With a further increase in the thickness, when $H \gg \lambda$, the shear wave undergoes the complete decay, and the frequency shifts tend to their limit values.

From fig. 2 it can be seen that under the aforementioned parameters the shear wave undergoes practically the complete decay with the interlayer thickness of about 250 μm.

Analyzing the expressions (2) and (3) gives three methods for measurement of the shear modulus of liquids. The first method is realized with small thicknesses of the liquid interlayer, when $H \ll \lambda$. In this case, both the real and the imaginary components of the resonance frequency shift are proportional to the inverse value of the liquid interlayer thickness. For the real shear modulus, G^1, and for the mechanical losses angle, $\tan\theta$, the following calculating formulas are derived [5]:

$$G' = \frac{4\pi^2 M_{f0} \Delta f' H}{S}, \quad (4)$$

$$\tan\theta = \frac{\Delta f''}{\Delta f'}. \quad (5)$$

Fig. 3 shows the experimental dependencies of

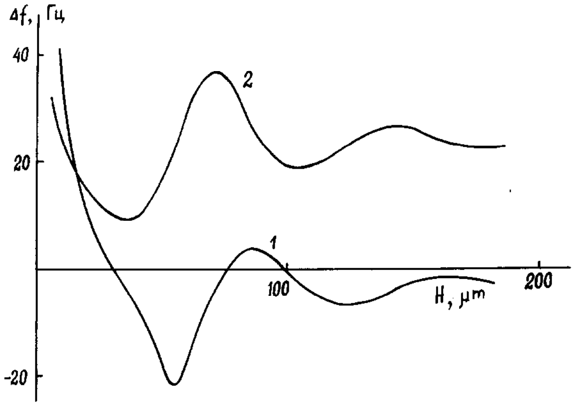

Fig. 2. Calculated dependencies of Δf^1 (*1*) and Δf^{11} (2) on the liquid interlayer thickness.

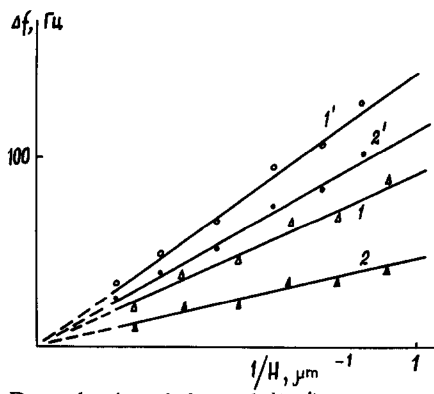

Fig. 3. Dependencies of the real $(1, 1^1)$ and the imaginary $(2, 2^1)$ frequency shifts on the inverse thickness of PMS-200 and PMS-900 interlayers.

Table I

	With $H \ll \lambda$		In terms of the wavelength		With $H \gg \lambda$	
Liquid	tan θ	$G' \times 10^{-6}$ (dyn/cm^2)	λ (μm)	$G' \times 10^{-6}$ (dyn/cm^2)	$\Delta f''_\infty$ (cps)	$G^1 \times 10^{-6}$ (dyn/cm^2)
PMS-200	0.5	0.86	–	–	20	0.66
PMS-400	0.75	1.24	–	–	23	0.88
PMS-900	0.8	1.35	170	1.08	25	1.04
PMS-5 384	0.6	2.12	200	1.8	29	1.4
PMS-20 000	0.55	2.36	210	1.93	33	1.82
PMS-52 000	0.5	2.6	220	2.4	37	2.2

the real and imaginary components of the frequency shift on the inverse value of the liquid interlayer thickness for PMS-200 and PMS-900 polymethylsiloxane liquids. Linear dependencies are obtained, which means, in accordance with the aforesaid, that these liquids possess a certain complex shear modulus. Similar results are also obtained for other investigated liquids. The calculated values of G^1 and tr θ are presented in table I.

The second method for determination of G^1 involves measuring the length of the shear wave, λ, on the basis of the decay maxima. Using the relationship $\kappa^{*2} = \omega^2\rho/G^*$, where ρ is the density of the liquid being investigated, it is possible to show that

$$G' = \lambda^2 f^2 \rho \cos\theta \cos^2\theta/2\,. \qquad (6)$$

The mechanical losses angle, θ, is determined by measuring the distance between the position of the first minimum of the real component of the shift of frequency and that of the first decay maximum [5].

Fig. 4 shows the experimental curves of real and imaginary dependencies of the shifts of frequencies on the thicknesses of a liquid interlayer for PMS-900 polymethylsiloxane liquid. It is obvious that the curves give decaying oscillations that are in good agreement with the theoretical curves shown in fig. 2. Thus, it is possible to determine that the shear wave length, λ, is equal to 170 μm for PMS-900. Using formula (6), we obtain the value for $G^1 = 1.08 \times 10^6$ dyn/cm^2.

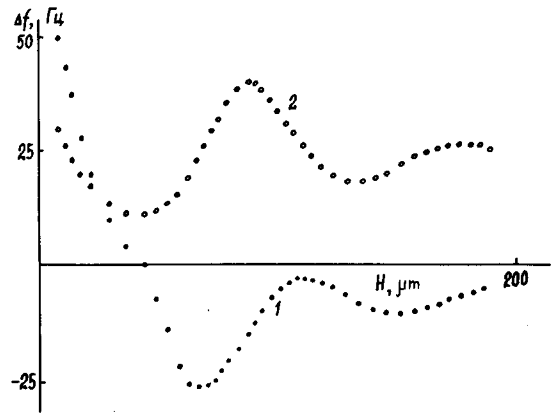

Fig. 4. Experimental dependencies of the real (1) and imaginary (2) frequency shifts on the thickness of PMS-900 interlayer.

Oscillating curves are obtained only for viscous PMS liquids. For low-viscosity liquids, there are observed no oscillations; because, owing to the presence of a normal component on the working surface of the piezoquartz crystal, causing considerable compression and tension deformations in the film, the maxima are levelled out [5]. Table I shows the measured values of wave lengths and the values of G^1, determined by formula (6) for viscous PMS liquids.

The third method is based on the measurement of limit values of Δf^1_∞ and Δf^{11}_∞, to which these parameters tend as the liquid interlayer thickness increases further, when the shear wave undergoes the complete decay. In this case, taking into account that the liquid covers the entire horizontal surface of the piezoquartz crystal, we obtain for the real shear modulus, G^1 and tg θ, the following expressions:

$$G' = \frac{16\pi^2 M^2}{S^2 \rho} [(\Delta f^{11}_{\infty})^2 - (\Delta f^{1}_{\infty})^2] , \quad (7)$$

$$\tan \theta = -\frac{2\Delta f^{1}_{\infty} \cdot \Delta f^{11}_{\infty}}{(\Delta f^{11}_{\infty})^2 - (\Delta f^{1}_{\infty})^2} . \quad (8)$$

Inasmuch as with $H \gg \lambda$, the shear wave undergoes the complete decay, there is no necessity in using a solid cover plate. In the present method of determining the value of G^1, the horizontal surface of the piezoquartz crystal is loaded by a thick layer of the liquid being investigated. Here S is the area of the horizontal surface of the piezoquartz crystal. From formula (7), it appears that $\Delta f^{11}_{\infty} > \Delta f^{1}_{\infty}$, when the liquids possess the bulk shear elasticity. Now, if the liquid is Newtonian at the experimental frequency, then $\Delta f^{11}_{\infty} = \Delta f^{1}_{\infty}$.

Yet, with tg $\theta < 1$ when calculating the value of G^1 by use of formula (7), it is possible to neglect the real component of the frequency shift; for its contribution does not exceed 3%. Therefore, the present method was applied to determine the real components of the complex shear modulus on the basis of measuring Δf^{11}_{∞} for any sort of the liquids investigated. The data thus obtained are also given in Table I.

In the experiments, there was used $x - 18.5°$ cut-off piezoquartz crystal possessing the resonance frequency of 74 kHz (kcps), the mass of 6.24 g, and dimensions of $34.7 \times 12 \times 5.5\ \text{mm}^3$. In measuring the value of G^1 by the first method, when $H \ll \lambda$, a cover plate was used having mass 0.2 g and contact area $S = 0.2\ \text{cm}^2$.

In measuring the shear wave length, there was used a cover plate provided with a magnetic suspension, for the purpose of precluding the influence of the normal component of vibrations on the results obtained [5].

The experiment was carried out as follows. On cleaning the piezoquartz crystal and the cover plate by the use of organic solvents, they were exposed to the treatment by hydrogen flame. After that, the piezoquartz crystal was placed into a special holder and coated by the liquid being investigated, which was covered by the cover plate. Then an optical method was applied to determine the thickness of the liquid interlayer [3], and the real shift of the resonance frequency and the width of the resonance curve were measured, half of the change in the latter being equal to the imaginary frequency shift.

When applying the third method to measure the value of G^1, the horizontal surface of the piezoquartz crystal, after being treated by the hydrogen flame, was coated by a thick layer of the liquid to be investigated. Then the widening of the resonance curve was determined.

From table I it can be seen that the maximum values of the shear modulus are obtained when measuring by the first method. This is explained by the fact that here the only factor influencing the results is the cleanness of working surfaces and this condition was well fulfilled. Now, in this case the normal component does not exert any influence, for the cover plate was chosen to be rather light.

In the second case, a cover plate with a magnetic suspension was used, whose mass was many times larger than that in the first case. Therefore, due to considerable stresses set up in the film by the normal component, the measurable values of the shear modulus are somewhat smaller. These differences increase as the viscosity decreases, and for the low-viscosity liquids it proves to be in general impracticable to measure the wavelength because of the smearing out of the decay maximum. The least values of the shear modulus are obtained when measuring by the third method. This is explained by the fact that the borders of the working surface of the piezoquartz crystal are used not to the full extent, for the liquid layer thickness at the borders is smaller than it should be for determining the value of Δf^{11}_{∞}. Taking into account the aforementioned factors influencing the experimental results, one may consider the coincidence between the data obtained by the three methods to be quite satisfactory.

Among numerous works on the viscous-elastic behaviour of liquids, of special interest to use are the works by T. Lamb and A.T. Barlow et al. [6, 7] involving the measurement of the complex shear modulus of four polydimethylsiloxane liquids within the wide range of frequencies. Thus at the frequency of the present experiment the values of $G^1 = 1.7 \times 10^6$ dyn/cm^2 and tan θ = 0.6 were obtained for a polydimethylsiloxane liquid having the viscosity value of 100 000 cst. If the differences in the liquids investigated are accounted for, then the agreement with the results of the present work proves to be sufficiently good.

It will have to be taken into consideration that in a rough approximation, the detected properties of liquids may be interpreted on the basis of the theory of relaxation of Maxwellian bodies, according to which

$$\text{tr}\ \theta = \frac{G^{11}}{G^1} = \frac{\omega\eta_\mu}{G_\mu}, \tag{9}$$

where G_μ is the Maxwellian body shear modulus; η_μ its viscosity. However, the real liquid cannot undoubtedly be interpreted by using a model with single relaxation time. In connection with this, the viscosity value obtained from eq. (9) does not by far coincide with the tabular values, but is much larger, especially for low-viscosity liquids. This problem is considered in more detail in paper [8].

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