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Static and Dynamic Tests of Polyvinyl Alcohol Cryogels

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Abstract

Laboratory set-up was developed on the basis of Reokinetika stand for the static and dynamic determination of the elastic modulus. Static and dynamic tests of polyvinyl alcohol cryogels were carried out, and the dependences of the output signals of force sensors on sample deformation were obtained. Dynamic measurements were made using a device with piezoceramic force sensor and an electromechanical source of mechanical oscillations. Laboratory balance was used as a force sensor in static measurements. Sample deformation was set with a micrometer. The absolute values of the static elastic modulus are obtained. A linear correlation of the results of static and dynamic measurements is demonstrated. The ratio of the slopes of the considered dependences is equal to the ratio of the absolute values of static and dynamic elasticity moduli of the samples.

Keywords: static elastic modulus, dynamic elastic modulus, polyvinyl alcohol, cryogel, correlation

INTRODUCTION

In many technological processes, with time or under the action of the varying external conditions, Newton liquids with low viscosity are transformed into viscoelastic objects (for example gels), with mechanical properties differing from those of the initial systems. To control the dynamics of gel formation, vibration viscosimetry may be used [1, 2], while the rheological characteristics of the formed gel may be determined using the static or dynamic method of measuring the elastic modulus [3].

The indicated methods imply simultaneous registration of deformation and strain, and their ratio, taking into account geometric factors, is proportional to the shear elasticity modulus (G). Under periodic deformation in the mode of dynamic tests (DT), the complex elastic modulus (G^*) is determined; its imaginary component describes the dissipative properties of the sample under examination. Under static tests (ST), the static elastic modulus (G_{stat}) is determined; it is not connected directly with dissipative characteristics. Deformation regimes differ from each other strongly in these two cases. It seems interesting and practically relevant to study the correlations between the results of these measurements.

In the present work, we consider the results of DT and ST of cryogels based on polyvinyl alcohol (PVA), which are widely used, especially under the conditions of Siberia and Arctic [4, 5], and are rather well studied using traditional methods [6–8].

The goal of the paper was to develop the design of an installation for the DT of cryogels on the basis of a piezoceramic force sensor and to determine elastic modulus using the static and dynamic methods.

EXPERIMENTAL

Cryogel samples were obtained from the aqueous solutions of PVA with molecular mass $M = 150 \cdot 10^3$, containing not more than 1 % residual acetate groups [9]. The samples under investigation were poured into cylindrical metal cells, frozen, kept for 24 h at a temperature of −20 °C, and then defrosted at 20 °C. After freezing-thawing cycle, the cylindrical samples of elastic cryogels possessed rubber-like properties up to a temperature of 70 °C.

To characterize the quality of the used cryogels, we studied the dependence of the static elastic modulus G_{stat} of the cryogels on PVA concentration (C_{PVA}) under relative deformation $\gamma = 0.1$ (Fig. 1). One can see that G_{stat} increases with an increase in PVA concentration, which is evidence of gel strengthening with an increase in polymer concentration [10].

Measurements were carried out using a laboratory set-up specially arranged on the basis of Reokinetika stand so that the samples for both cases (DT and ST) would be prepared in similar ways and were chemically and geometrically similar to each other, and identical deforming punches would be used (8 mm in diameter) [11, 12]. Measuring cells (10 mm in diameter) and the levels of their filling during DT and ST were identical, too.

The stand for dynamic tests

Three horizontal platforms are mounted at different levels on the rods of the holder (Fig. 2). An electromechanical unit with two electrodynamic transducers is mounted on the lower platform. These transducers are composed of coils placed in a magnetic gap at the opposite ends of a cylindrical permanent magnet with a magnetic path. One of the coils serves to excite mechanical oscillations, while the other is used to record the amplitude of the arising motion. The coils are connected through a rod passing inside the channel in the body of the magnet. The holder of the measurement cell is attached to this rod from the outer side. Together they form a mechanical oscillating system. The latter is attached to the immobile housing of the magnetic path with the help of flat springs. The immobile magnet and housing are tightly fixed together.

Alternating voltage was supplied from the generator of acoustical frequency to one of the coils, and it started to vibrate in the gap between the magnet and magnetic path. The axial rod, measuring cell and the coil of the measuring transducer were oscillating synchronously with this coil. Electromotive force (EMF) proportional to the amplitude and velocity of the motion was thus generated in the coil of the measuring transducer. The induced EMF was measured with a voltmeter.

A similar installation was used by A. B. Kaplun to construct a viscosity sensor with immersed probe operating in the resonance mode [13]. In the device considered in the present work, the electromechanical unit operates at non-resonant frequency, drives the entire sample into oscillatory movement and determines the amplitude of deformation. This amplitude was varied during the

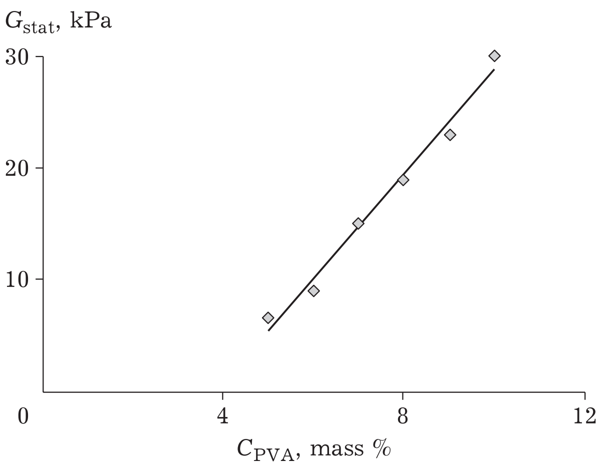

Fig. 1. Dependence of the static elastic modulus (G_{stat}) of cryogels on the concentration of polyvinyl alcohol (C_{PVA}) for relative deformation $\gamma = 0.1$.

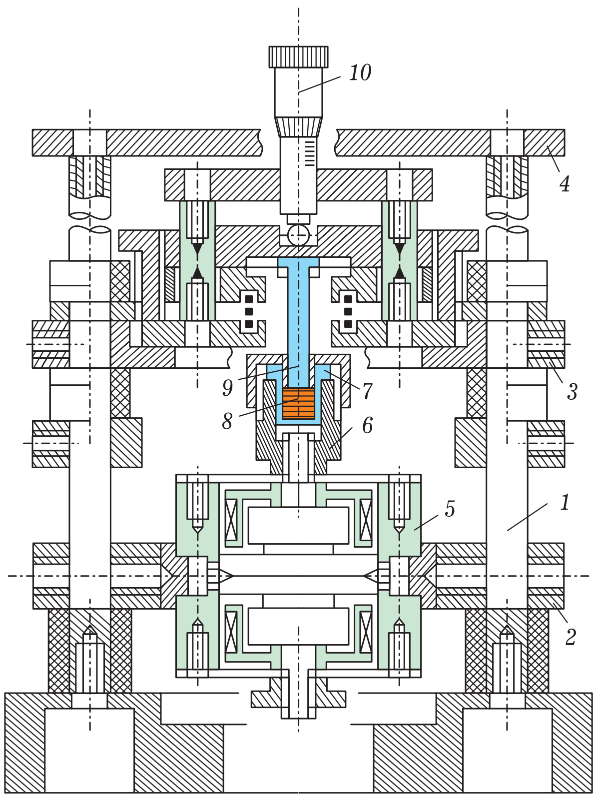

Fig. 2. Device for the dynamic tests of cryogels: *1* – vertical rods; *2* – lower platform; *3* – platform for mounting the dynamic force sensor; *4* – upper platform of the holder; *5* – the unit of electromechanical transducers; *6* – cell holder; *7* – cell; *8* – sample; *9* – punch probe; *10* – micrometer.

experiment regulating the voltage supplied to the coil exciting the motion.

During measurement, the sample is in contact with the test body (punch) in the form of a rod (probe), which is connected with the rigid sensitive element of the force sensor – a plate made of piezoceramics. The housing of the force sensor is spring-biased and may move vertically on the guide bars with the help of a micrometer. The cylindrical spring is mounted between an immobile middle platform and the housing of the sensor, while the micrometer is fixed in the upper immobile platform and connected with the force sensor housing through a ball-and-socket bearing. Measuring cell, force sensor, ball-and-socket bearing, and micrometer are mounted on the common vertical axis.

The force sensor readings were recorded at different positions of the punch gradually drawing the sample down into the measuring cell. As a result, the dependence of the output signal of the dynamic force sensor ($U_{F_{dyn}}$) on punch position was obtained. Mechanical strain (τ) and deformation (γ) of the sample are proportional to the force (F), the amplitude of displacement (ξ) and the values of the corresponding electrical signals – voltage values (U), and the τ/γ ratio is proportional to the dynamic elastic modulus, taking into account the formfactor.

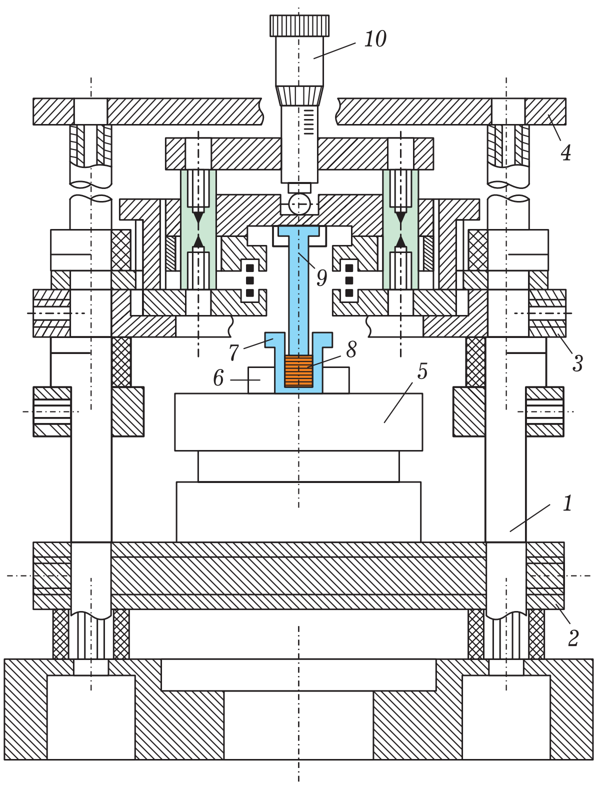

Fig. 3. Schematic of the installation for elastic modulus measurements using the static method: *1* – vertical rods; *2* – platform of the force sensor; *3* – vertical mobile platform; *4* – the upper platform of the holder; *5* – static force sensor; *6* – cell holder; *7* – cell; *8* – sample; *9* – punch; *10* – micrometer.

Stand for static tests

Similarly to the case of DT, the installation for ST is based on Reokinetika stand (Fig. 3). A static force sensor (electronic balance) is mounted on the lower platform. Displacement of the punch arranged on top was performed with the help of the micrometer.

During measurement, the sample was deformed to the required value (γ_0). Thus initial strain (τ_0) was formed in the sample; as a consequence of the internal rearrangement of the substance structure, it decreased (relaxed) with time (t) to τ.

Gel layer h_0 thick (the height of the sample) was placed in the measuring cell. The cell was placed in the centre of the balance pan, and the balance reading was brought to zero. The oriented punch was driven to the sample surface by gliding on the vertical rods of the holder. Then their contact was achieved by rotating the head of the micrometer, and deformation was created by means of the continuing vertical movement.

After the contact of the punch with the sample surface, balance reading m_1 was recorded, which corresponded to the initial (maximal) strain τ, arising in the material at the initial moment of time corresponding to deformation h_1. Then the deformation was increased discretely with a step of 0.1 mm (h_2, h_3, ..., h_n). Each next balance reading (m_2, m_3, ..., m_n) was recorded 10 s after recording the corresponding position of the micrometer. As a result, the dependence of the signal from the static force sensor (F) on punch position was recorded.

From the known initial sample height $h_{0,}$ its change under deformation, and the corresponding balance reading, elastic modulus (kPa) was calculated according to Hooke's formula: $G_{stat} = \tau/\gamma$, where $\tau = mg/s$ is strain arising at the given relative deformation value γ; $\gamma = (h_0 - h)/h_0$; g is the acceleration of gravity; $s = pr^2$ is the area of the end surface of the punch [14, 15].

RESULTS AND DISCUSSION

Figure 4 shows the dependences of the signal from the dynamic force sensor on the depth of punch immersion recorded for cryogel sample

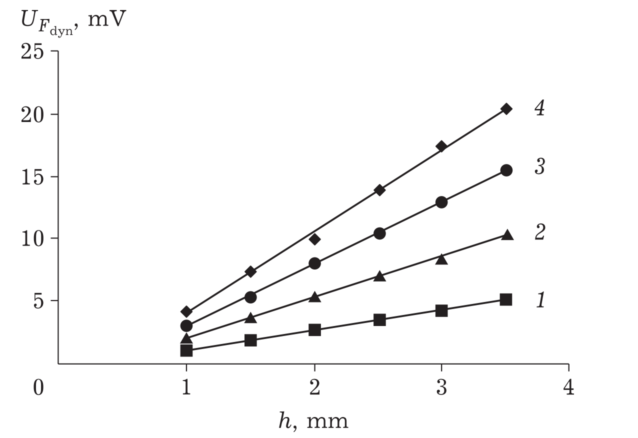

Fig. 4. Dependence of the signal from the dynamic force sensor ($U_{F_{dyn}}$) on the depth of punch immersion (h) for different values of probe oscillation amplitude: 0.2 (*1*); 0.4 (*2*); 0.6 (*3*); 0.8 mm (*4*).

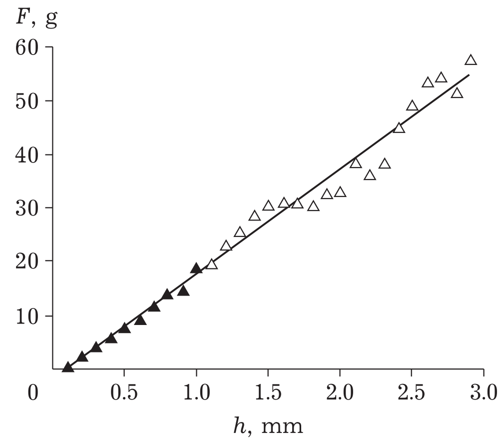

Fig. 5. Dependence of the signal on the static force sensor on the depth of punch immersion (h).

(C_{PVA} = 10 mass %) at different oscillation amplitude values. The plot is a family of ascending lines which are approximated by the linear regression equations: $U_{F_{dyn}} = hB_{dyn} + A$ with correlation coefficient R not less than 0.98, where B_{dyn} is the angular coefficient of correlation dependences of the signals from the dynamic force sensor; A is a constant. A hypothetic region of their intersection, which is not shown in the Figure, corresponds to the moment when the punch touches the sample.

The dependence of the signal from the static force sensor on the depth of punch immersion recorded for an identical sample is shown in Fig. 5. The initial region corresponding to the linear reversible deformation (the depth of punch immersion h from 0 to 1.5 mm) may be distinguished on the plot of the dependence. This part of the dependence is also satisfactorily approximated by the linear regression equation: $F = hB_{stat} + C$, where B_{stat} is the angular coefficient of the correlation dependences of signals from the static force sensor; C is a constant.

The angular coefficients of correlation dependences of the signals from dynamic and static sensors depending on the position of punches in the cells with gel samples (C_{PVA} = 6, 7 and 10 mass %) are shown in Table 1. In this case, the minimal frequency (20 Hz) was used for DT.

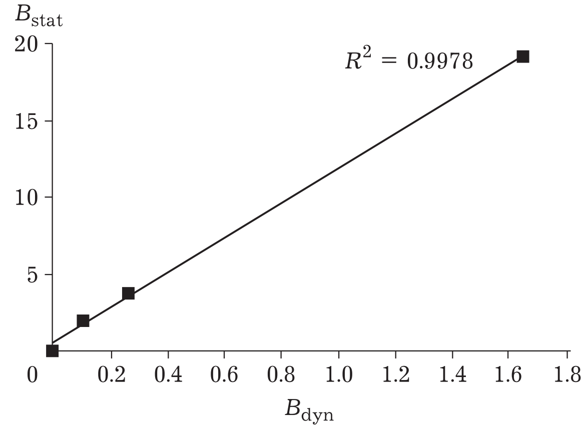

Fig. 6. Correlation between the results of static (B_{stat}) and dynamic measurements (B_{dyn}) of the elastic modulus of cryogels.

The dependence of angular coefficients B_{dyn} on B_{stat} is shown in Fig. 6. It is rather close to a straight line, approximation parameters of equation $B_{stat} = AB_{dyn} + B$, where A and B are constants, are presented in Table 2.Correlation coefficient is $R = 0.99891$.

Results of the static measurements according to Hooke's law give the absolute value of the static elastic modulus G_{stat}. Measurement of $|G_{stat}|$

TABLE 1

Effect of cryogel composition on the angular coefficients of the correlation dependences of the signals of dynamic (B_{dyn}) and static (B_{stat}) force sensors

Sample	PVA concentration, mass %	B_{dyn}	B_{stat}
1	10	1.65	19.20
2	7	0.26	3.83
3	6	0.10	1.98
4	0	0	0

TABLE 2

Approximation parameters for the equation of B_{dyn} dependence on B_{stat}

No.	Parameter	Value	Mean square error
1	A	0.55223	0.31383
2	B	11.34381	0.37509

by means of the proposed version of the dynamic method is relative. it is possible to obtain the absolute values of the dynamic elastic modulus $|G_{dyn}|$ using a reference sample with known elasticity. The ratio of the absolute values of static and dynamic elastic moduli of different cryogel samples is equal to the ratio of angular coefficients of the considered correlation dependences.

CONCLUSION

The design of a device for dynamic tests of cryogels is developed. The main elements of this device are a piezoceramic force sensor and an electromechanical source of mechanical oscillations. A linear correlation of the results of static and dynamic measurements of elastic modulus of polyvinyl alcohol cryogels is demonstrated.

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REFERENCES

1 Krutin V. N., Oscillatory Rheometers, Mashinostroenie, Moscow, 1985, 160 p. (in Russ.).

2 Koleshko V. M., Sunka V. Ya., Polynkova E. V., Krupskaya E. V., Design of Intellectual Sensor Systems to Measure Viscosity, Minsk, Izd-vo BNTU, 2010, 81 p. (in Russ.).

3 Ferry J. D., Viscoelastic Properties of Polymers, J. Wiley, New York, 1980, 582 p.

4 Altunina L. K., Kuvshinov V. A., Dolgikh S. N., Cryogels – promising material for underground works in permafrost, in: Advances in the Geological Storage of Carbon Dioxide, S. Lombardi, L.K. Altunina, S.E. Beaubien (Eds.), NATO Science Series. IV. Earth and Environmental Sciences, Springer, 2006, Vol. 65, P. 103–110.

5 Altunina L. K., Kuvshinov V. A., Dolgikh S. N., Cryogels for plugging in permafrost regions, *Gidrotekhnika*, 2010, No. 3, P. 56–60. (in Russ.).

6 Deville S., Freezing Colloids: Observations, Principles, Control, and Use, in: Applications in Materials Science, Life Science, Earth Science, Food Science, and Engineering, Springer, 2017, 598 p.

7 Peppas N. A., Reinforced uncross–linked poly (vinyl alcohol) gels produced by cyclic freezing-thawing processes: A short review, *J. Contr. Release,* 1991, Vol. 16, No. 4. P. 305–310.

8 Altunina L. K., Manzhai V. N., Fufaeva M. S., Mechanical and thermal properties of cryogels and foamed cryogels produced from aqueous solutions of poly(vinyl alcohol), *Russ. J. Appl. Chem.*, 2006, Vol. 79, No. 10, P. 1669–1672.

9 Lozinsky V. I., Cryostructuring of polymeric systems. 55. Retrospective view on the more than 40 years of studies performed in the A.N. Nesmeyanov Institute of Organoelement Compounds with respect of the cryostructuring processes in polymeric systems, *Gels,* 2020, Vol. 6, No. 3, Article 29, P. 1–59.

10 Fufaeva M. S., Kashlach E. S., Manzhay V. N., Altunina L. K., A new criterion for the evaluation of the rheological properties of viscoelastic cryogels, *Chemistry for Sustainable Development*, 2020, Vol. 28, No. 3, P. 305–310.

11 Kozhevnikov I. S., Bogoslovsky A. V., Altunina L. K., Stasyeva L. A., Double resonance method for determination of gel point, *Journal of Siberian Federal University, Chemistry,* 2019, Vol. 12, No. 2, P. 160–165.

12 Bogoslovsky A. V., Kozhevnikov I. S., Altunina L. K., Double-probe viscometer for rheokinetic measurements, AIP Conference Proceedings of the International Symposium on the Hierarchical Materials: Development and Applications for New Technologies and Reliable Structures. 2018, Tomsk, 01–05 October, 2018, P. 020036-1–020036-4.

13 Author's Certificate, USSR, 609078, 1978, Kaptul A. B., Vibratory device for the determination of physical properties of substances. (in Russ.).

14 Malkin A. Ya., Foundations of Rheology, TsOP Professiya, St. Petersburg, 2018, 336 p. (in Russ.).

15 Malkin A. Ya., Isayev A. I., Rheology: Concepts, Methods and Applications, ChemTec, Toronto, 2006, 474 p.