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A New Criterion for the Evaluation of the Rheological Properties of Viscoelastic Cryogels

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Abstract

Rubber-like elastic cryogels were formed from a two-component solution of polyvinyl alcohol in water after a freezing-thawing cycle, and their rheological properties are investigated. The interest in such environmentally friendly polymer cryostructures having viscoelastic properties is due to the fact that they are currently in high demand in the northern regions of the country. Cryogels are promising structural materials used for the development of new arctic technologies for oilfield engineering and for strengthening seasonally thawing soil in the permafrost zone, as well as for the construction and arrangement of hydraulic structures. As a result of the studies of the properties of cryostructuring agents, it was revealed that due to the mechanical action of external loads, elastic moduli of deformed cryogel samples decrease monotonously with time. Elastic moduli are traditionally used to quantitatively characterise the physical and mechanical properties of Hookean materials. The results of comparative experiments conducted by different researchers using the same cryogel samples are interpreted ambiguously due to the inconstancy of the elastic moduli of viscoelastic systems. In this work, the possibility and necessity to use cryogel relaxation time values as a quantitative criterion for describing the rheological properties of polyvinyl alcohol cryogels are experimentally substantiated. The values of the relaxation time of cryogels are proposed to be used instead of cryogel elasticity moduli to evaluate the viscoelastic properties of polymer systems in future design calculations.

Keywords: polyvinyl alcohol, aqueous polymer solution, concentration, rheology, viscosity, cryogel, elastic modulus, relaxation time

INTRODUCTION

After freezing an aqueous solution of polyvinyl alcohol (PVA) at a negative temperature ($T < 0\text{ }^{\circ}\text{C}$) and subsequent defrosting of the glacial (rigid and fragile) sample at a positive temperature ($T > 0\text{ }^{\circ}\text{C}$), elastic cryogel is formed, that is, phase transition of the viscous-flow system from the liquid aggregate state to an elastic polymer body occurs (Fig. 1). The loss of fluidity in the polymer system proceeds not due to the chemical linkage of macromolecules into a continuous spatial framework with the help of additionally introduced reagents but after a cycling change of

the thermodynamic parameter (temperature). Cryogels formed under the conditions of solvent crystallization are thermally reversible but, unlike for the case of low-molecular compounds, they do not exhibit a fixed phase transition point and melt at a temperature of (T_m) $\sim 70\text{ }^{\circ}\text{C}$, which is higher by several ten degrees than the structuring temperature ($T_{cr} \sim 0\text{ }^{\circ}\text{C}$) of the initial aqueous solutions of the polymer. Cryogels have a caoutchouc-like consistency, besides, two-component cryogels (PVA – water) include non-toxic and ecologically safe components, so they are used in medicine, biotechnologies and in the food industry [1–3].

Stages of cryogel formation

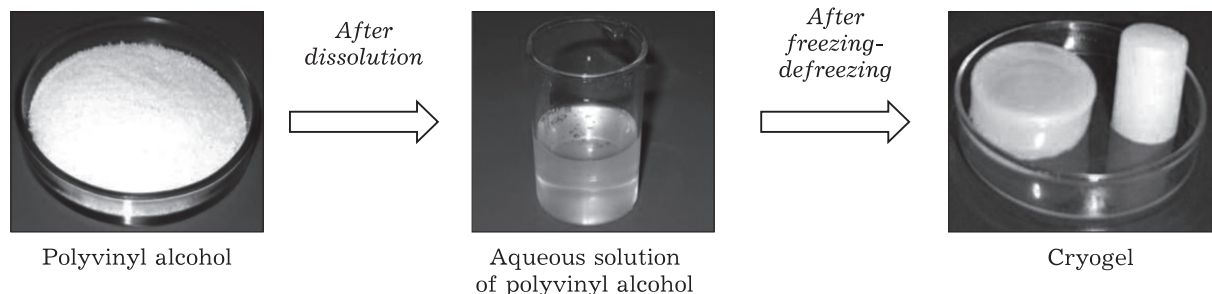


Fig. 1. Stages of cryogel formation from the aqueous solution of PVA.

One of the promising directions is the application of cryogels as a binding material for strengthening various earthy basements in seasonally freezing ground in the northern latitudes of our country or for preventing soil erosion under steppe conditions in the regions with sharply continental climate [4, 5]. The polymeric matrix of cryogel filled with the particles of ground with the seeds of perennial grass is sufficiently strong to endure the action of external erosion processes (wind, storm overflows, *etc.*) but at the same time it is sufficiently elastic to allow the growth of plants.

Mechanical, physicochemical and thermal physical characteristics of cryogels may be varied through preliminary introduction of additional fine ingredients as fillers (solid or liquid) [6–11], and subsequent freezing-thawing cycle. Due to specific properties of these multicomponent cryogels, they have found broad-ranged applications in oil mining, the construction industry and in the construction of hydraulic facilities in the northern regions [12–14].

The development of the natural resources of the Arctic is complicated by extreme climatic conditions, which put forward higher requirements to the technologies and materials in use. Promising construction materials for the development of new arctic technologies are cryogels with their viscoelastic (elastic) properties. However, mechanical characteristics of polymer systems should be evaluated relying not on such a traditional criterion for ideally elastic (Hook-type) systems as elastic modulus (E), which is a coefficient of proportionality in Hook's equation $\sigma = E\gamma$, but on another parameter – relaxation time (θ), which is incorporated into Maxwell's equation: $\sigma = \sigma_0 \exp(-t/\theta)$. This requirement is due to the fact [15] that initial mechanical strain (σ_0) arising in a body made of a viscoelastic polymer material af-

ter its rapid (instantaneous) deformation (γ), relaxed (weakens) with time (t) according to the exponential law. Maxwell hypothetically modeled the viscoelastic properties of the materials by combining sequentially connected spring and a cylinder filled with a viscous liquid (Fig. 2, *a*). It may be expected that the elastic modulus of an elastic cryogen sample would be not constant ($E \neq \text{const}$) and would vary with time according to the exponential law: $E = \sigma/\gamma = (\sigma_0 \exp(-t/\theta))/\gamma$.

In the present work, a quantitative criterion to describe the rheological properties of polyvinyl alcohol cryogels is suggested. We substantiate experimentally the possibility and necessity to carry out design calculations involving not the elastic modulus of a cryogel but the relaxation time of cryogel, which is a characteristic of the viscoelastic properties of polymer systems.

EXPERIMENTAL

To prepare initial aqueous solutions of different concentrations, we used two PVA samples with molecular masses (M) equal to $150 \cdot 10^3$ and $240 \cdot 10^3$. The content of acetate groups remaining after the hydrolysis of polyvinyl acetate [6], from which PVA is commercially obtained, was not more than 1 %. To form cryogel samples, the aqueous solutions of PVA were poured into cylindrical metal cells, frozen and kept for 24 h at $T = -20^\circ\text{C}$, and then defrosted at $T = 20^\circ\text{C}$.

Experiments were carried out with a laboratory set-up functioning on the basis of Maxwell's rheological model (see Fig. 2, *b*). An instantaneous compressing deformation ($\gamma = \Delta h/H_0$) was imposed on the formed elastic cryogel samples with the initial linear size (H_0), and elastic stress (σ_0) instantaneously arising in the material during compressing was measured [15]. Hook's equation

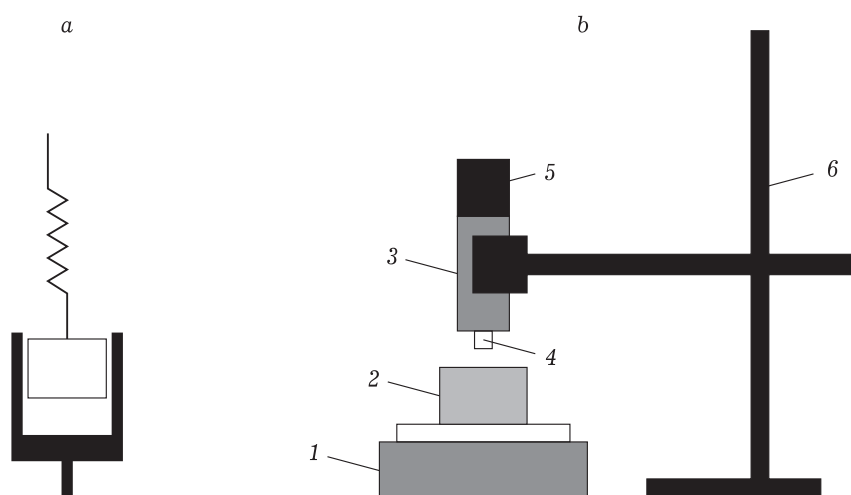


Fig. 2. Mechanical analogy of Maxwell's rheological model: spring and plunger (a); laboratory set-up (b) based on Maxwell's model: balance (1), cryogel sample (2), micrometer housing (3), micrometer rod (4), micrometer head (5), support (6).

($E = \sigma_0/\gamma$) is usually used by researchers to calculate the elastic modulus of cryogels (E) and to plot the dependence of this parameter on various parameters: concentration and molecular mass of PVA, the number of freezing-thawing cycles and some other variables [1, 6]. Experimentally measured values of elastic modulus are further on used to carry out technological calculations of various physicochemical processes occurring in industrial practice or necessary for designing new products with required properties.

We used the following equations in the work:

$$E = \sigma/\gamma$$

$$\gamma = \Delta h/H_0 = (H_0 - H)/H_0$$

$$\sigma = P/S = mg/\pi r^2$$

where E is elastic modulus; γ is relative deformation; σ is elastic stress in the sample; H_0 and H is the height of initial and compressed sample, respectively; $P = mg$ is the force of sample compressing; $S = \pi r^2$ is the area of the edge surface of micrometer rod.

RESULTS AND DISCUSSION

Results of laboratory investigations of the mechanical properties of cryogels confirmed the assumption made by us in the introductory section of the paper, concerning the dependence of stress arising in the sample during its deformation on observation time (Fig. 3, a). One can see that the experimental data are approximated with good reliability ($R^2 = 0.99$) by the exponent ($\sigma =$

$45.6 e^{-0.00149t}$), which is an analogue of the theoretical curve for Maxwell's equation. A similar picture is also observed for the elastic modulus of cryogel (see Fig. 3, b), which also decreases with time according to the exponential law with the negative exponent. It was established that the inconstancy of elastic modulus during observation in experiments is an accompanying factor independently of the physicochemical nature and component composition of various cryogel samples. In this connection, in our opinion, it is insufficient to characterize the mechanical properties of cryogels only by elastic modulus E , since its experimental measurement gives a subjective value because it depends on the moment of time t_x after sample deformation which is chosen by the operator of the set-up at will (see Fig. 2, b) to fix the value of varying stress σ_x . Therefore, different experimenters will obtain different values of E for the same sample, which cannot be considered as a satisfactory result of investigations.

So, relaxation time θ (that is, a value included in Maxwell's equation) serves as a more objective quantitative criterion to evaluate the physical-mechanical properties of cryogels. Mathematically, relaxation time is numerically equal to the time during which the stress σ will decrease by a factor of e (≈ 2.72). In addition to the mathematical interpretation, θ has also a physicochemical basis: under the external action on the polymer matrix of cryogel, its deformation occurs, which is accompanied at the nano-level by the transition of macromolecular tangles from more probable

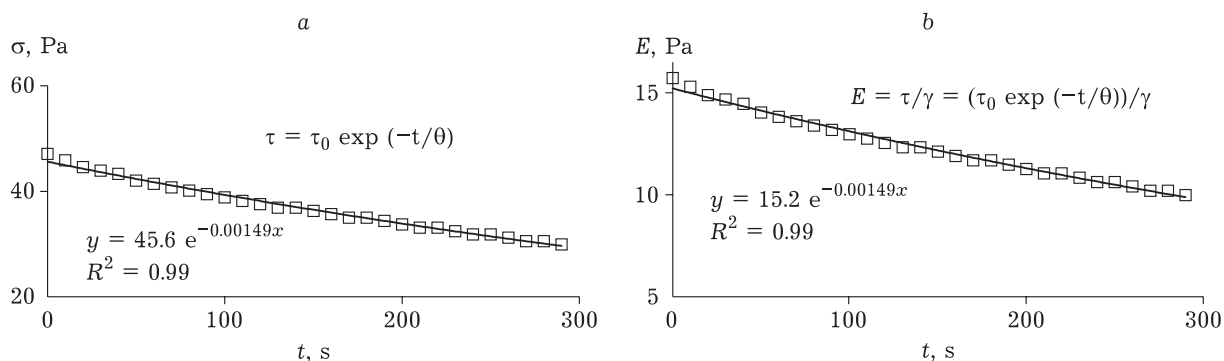


Fig. 3. Changes of stress in cryogel sample (a) and changes of the elastic modulus of cryogel (b) ($C_{PVA} = 100 \text{ kg/m}^3$; $M = 150 \cdot 10^3$) on the time of its residence in the deformed state.

states (equilibrium spherical balls) into less probable conformations (ellipsoids). Due to this, the elasticity of polymer systems, unlike for materials composed of low-molecular compounds, has the entropy-based nature [16, 17], while θ is a characteristic time within which the system returns to the equilibrium state. Recurrence to the spherical shape of tangles is due to the rotation of monomer links around covalent bonds connecting them into polymer chains [18], and is accompanied by segmental shift (flow) if macromolecules with respect to each other [19]. Therefore, mechanical (rheological) properties of polymer materials depend not only on elasticity (E) but also on viscosity (η) of the system, so cryogels belong to viscoelastic systems occupying an intermediate position between liquids and solids, while the numerical value of relaxation time depends on the ratio of viscous and elastic properties: $\theta = \eta/E$.

After finding the logarithms of the left and right parts of Maxwell's equation, it may be written as $\ln(\sigma_0/\sigma) = (1/\theta)t$. If the results of the experimental measurements of stress relaxation in one and the same cryogel sample at different deformation degrees are represented by a linear dependence $\ln(\sigma_0/\sigma) = f(t)$, then, we obtain a set of straight lines (Fig. 4, a), for which the cotangents (ctg) of slope angles will be numerically equal to the time θ of sample relaxation at different values of deformation parameter γ . It follows from Fig. 4, b that the larger is sample deformation, the longer time (relaxation time) will be necessary for the sample to return to the equilibrium (unstrained) state.

It was established unambiguously in the works published previously [1, 2, 11] that the elastic modulus E of cryogels increases with an increase in the number (n) of freezing-defrosting cycles, that is, it is logical to expect a decrease in the time of stress relaxation accompanying an

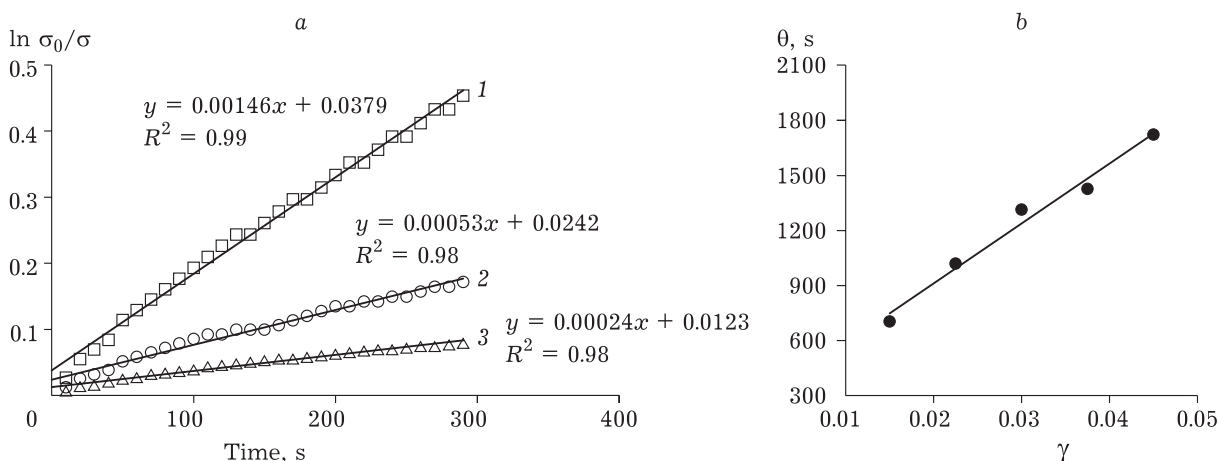


Fig. 4. For PVA cryogel sample ($C_{PVA} = 100 \text{ kg/m}^3$; $M = 150 \cdot 10^3$): a – the dependence of $\ln(\sigma_0/\sigma)$ on time (t) for different sample deformations: 0.015 (1), 0.05 (2), 0.1 (3); b – dependence of relaxation time (θ) on sample deformation.

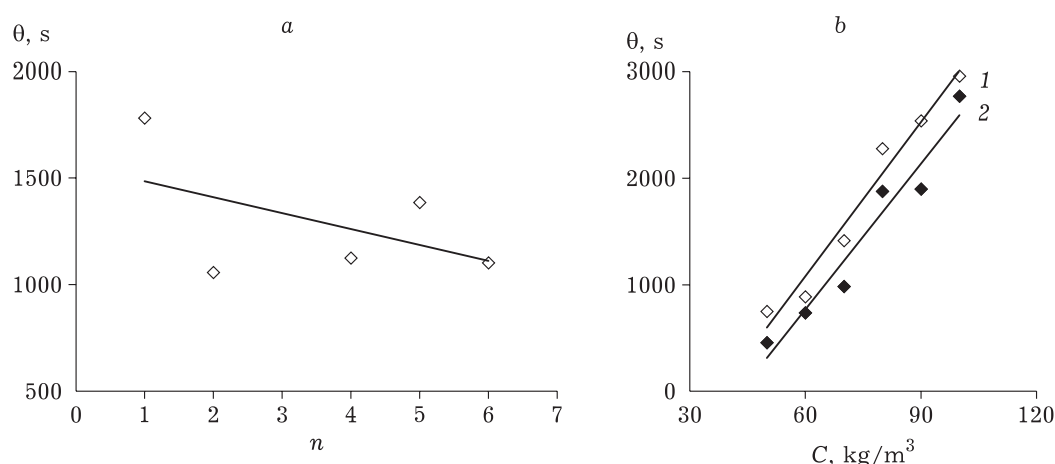


Fig. 5. Dependence of relaxation time θ on: a – number of cycles (n) of PVA cryogel freezing-defrosting ($M = 240 \cdot 10^3$; $C_{\text{PVA}} = 70 \text{ kg/m}^3$); b – concentration of PVA samples with different molecular masses M : $240 \cdot 10^3$ (1), $150 \cdot 10^3$ (2).

increase in sample rigidity with an increase in the number of cryo-treatment cycles, which was confirmed experimentally (Fig. 5, a). With an increase in the molecular mass of polymer samples and PVA concentration in the initial aqueous solution, not only elastic modulus of the formed cryogels increases [2, 6], but also relaxation time increases (see Fig. 5, b).

An increase in relaxation time (see Fig. 5, b) with an increase in PVA concentration and the molecular mass of polymer samples is a consequence of the viscoelastic properties of cryogels, for which the relaxation time is described by the analytical formula: $\theta = \eta/E$. After substituting the known formulas into this equation [16, 20]:

a) the viscosity of the polymer solution $\eta_p = \eta_s(1 + [\eta]C + \chi[\eta]^2C^2 + \dots)$;

b) the viscosity of polymer systems $E = CRT/M$;

another equation will be obtained for qualitative predictions of the dependence of cryogel relaxation time on concentration and molecular mass:

$$\theta \approx ACM^{(1+\alpha)}$$

where η_p is the viscosity of polymer solution; η_s is the viscosity of the solvent; C is concentration of solution; χ is the Huggins constant; $[\eta]$ is the characteristic viscosity of polymer sample depending on its molecular mass (M) and thermodynamic quality of the solvent, that is, $[\eta] = KM^a$; T is temperature; R is gas constant; $A =$

$\eta_s \chi K / (RT)$ is the product of constants, so this is a constant value.

CONCLUSION

It is established that a change in elastic modulus is observed in deformed cryogel sample, so the possibility and necessity to use relaxation time (usually used to characterize the viscoelastic properties of polymer systems) as the quantitative criterion to describe the rheological properties of polyvinyl alcohol cryogels are substantiated experimentally.

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