

Relaxation of Mechanical Stress in Poly(vinyl alcohol) Cryogels of Different Compositions

Vladimir N. Manzhai, Maria S. Fufaeva, and Ekaterina S. Kashlach*

Institute of Petroleum Chemistry of the Siberian Branch of the Russian Academy of Sciences, Tomsk 634055, Russia

Abstract The study presents the experimental results of measurements of the relaxation time of cryogels formed from various colloid-dispersed systems based on a poly(vinyl alcohol) aqueous solution. It is shown that the value of relaxation time, which characterizes the relationship between the viscosity and elasticity of real bodies, describes the rheological properties of materials more objectively than the traditional assessment of their physical and mechanical characteristics only by the elasticity modulus of the samples.

Keywords Cryogel; Relaxation processes; Viscoelasticity; Rheological properties

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INTRODUCTION

Cryostructuring of aqueous solutions of poly(vinyl alcohol) (PVA), keeping such samples in a crystalline state at negative temperatures ($T < 0$ °C) for several hours, and their subsequent thawing in the region of positive temperatures (at $T > 0$ °C) leads to the formation of elastic cryogels, i.e., a transition of two-component solutions from a liquid state of aggregation to a solid state without the use of 'crosslinking' chemical reagents. Therefore, the manufacturing of new composite materials from true solutions of PVA in water and the formation of cryogels from suspensions, emulsions, and foams, whose dispersion medium is an aqueous PVA solution for the purpose of their practical application is an urgent task for specialists in the field of colloidal chemistry.

At present, PVA cryogels are widely used in medicine, biotechnology, and the food industry due to their non-toxicity and environmental safety.^[1,2] They could be used in oil production and transportation and for creation waterproofing screens to prevent unwanted water filtration through the walls and bottoms of hydraulic structures,^[3,4] as well as in industrial and road construction.^[5–7] To make cryogels waterproof, such hydrophobic fillers as mineral and vegetable oils, petroleum resins, soot, etc., are used.^[8–12] Introduced into the polymer matrix of cryogels, they cause significant changes in their structural-mechanical and physicochemical properties.^[13–15]

Cryostructures, the dispersion medium (polymer solution) of which is filled with various fine ingredients before the

freezing stage, after the thawing stage become promising construction materials for the development of new Arctic technologies.

Formed cryogel samples have viscoelastic properties, hence, the mechanical properties of such systems should be assessed not only upon the traditional criterion, which is the elastic modulus (E) for ideally elastic (Hooke) bodies and which is the proportionality coefficient in Hooke's formula $\sigma = E \cdot \varepsilon$, where σ is the stress, and ε is the deformation, but also by another parameter, which is the relaxation time (θ) included in Maxwell's rheological equation $\sigma = \sigma_0 \cdot \exp(-t/\theta)$.

Hence, the purpose of this work was to carry out experimental measurements of the relaxation times of cryogel samples formed from various colloidal dispersed systems.

EXPERIMENTAL

To prepare a series of initial aqueous solutions in the concentrations range from 50 kg/m³ to 100 kg/m³, a PVA sample with a molecular mass $M = 100 \times 10^3$ was used. To form samples of two-component cryogels (Fig. 1), aqueous PVA solutions were poured into metal cells of a cylindrical shape, frozen and kept for 24 h at a temperature of $T = -20$ °C, and then they were thawed at room temperature $T = 20$ °C. To prepare homogeneous three-component systems, pre-calculated amounts of glycerol and water were additionally introduced into a concentrated PVA solution ($C = 100$ kg/m³). After thorough mixing, homogeneous solutions with a fixed polymer concentration ($C = 50$ kg/m³) and different glycerol contents 100, 200, 400 and 500 kg/m³ were obtained. Then these solutions were underwent a freeze-thaw cycling. To form filled heterophase cryogels (Fig. 2), finely dispersed soot or quartz sand was preliminarily introduced into two-component

* Corresponding author, E-mail: kashlach.cat@yandex.ru

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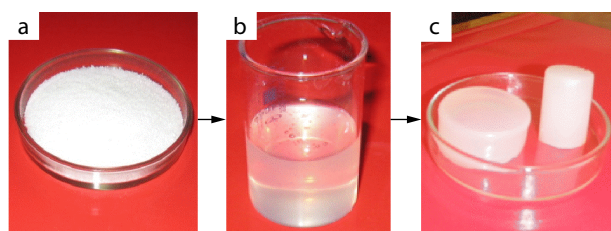


Fig. 1 Stages of cryogel formation: (a) PVA (powder), (b) aqueous solution of PVA, (c) elastic samples of cryogel.

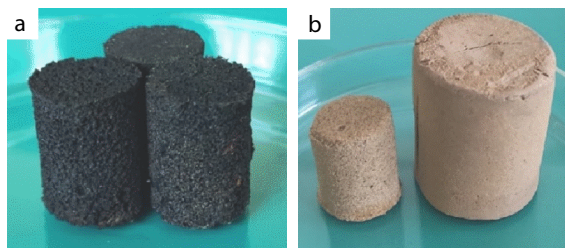


Fig. 2 Dried cryogels containing finely dispersed soot (a) and sand (b).

aqueous PVA solutions in order to obtain a suspension. To obtain an emulsion (Fig. 3), transformer oil was dispersed by mixing it with a polymer solution using a magnetic stirrer. A detailed description of the sequence of operations carried out in this case was presented in our studies.^[11,16–18]

To measure the elastic properties of cryogels, a laboratory setup for the compressive deformation of the samples was used (Fig. 4). In order to compress the samples by a preset value (Δh), a cryogel sample (5) with a height h_0 was placed on the center of the balance pan (1) and the balance readings were reset to zero. Then a micrometer (3) was brought perpendicular to the center of the cryogel and by rotating the micrometer head (2) the rod (4) was quickly lowered onto the surface of the sample. The compression strain was set to the sample ($\varepsilon = (h_0 - h_1)/h_0$) to measure the elastic stress (σ_0) instantly arising in the material. When the first readings of the scales appeared, we started to count the time with a stopwatch (t_n) and record the corresponding (decreasing) readings of the scales (m_n). Then, according to the Hooke formula, the instantaneous moduli of elasticity of cryogels (E_0) were calculated, i.e., $E_0 = \sigma_0/\varepsilon$, where $\sigma_0 = mg/S$ is the stress that arises in the sample at a given value of relative deformation $\varepsilon = (h_0 - h_1)/h_0$, g is the free fall acceleration, is the end surface area of the micrometer rod. Then, graphs of their de-

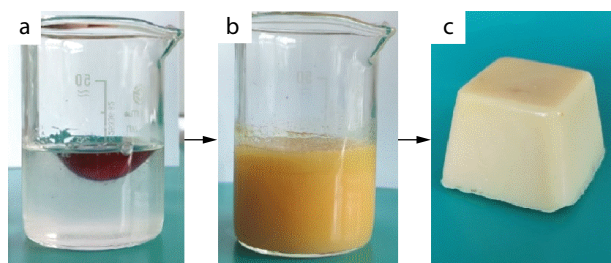


Fig. 3 Stages of formation of a cryogel containing mineral oil: (a) two-phase system of an aqueous polymer solution and mineral oil, (b) mineral oil emulsion in polymer solution, (c) elastic cryogel containing water, polymer, and mineral oil.

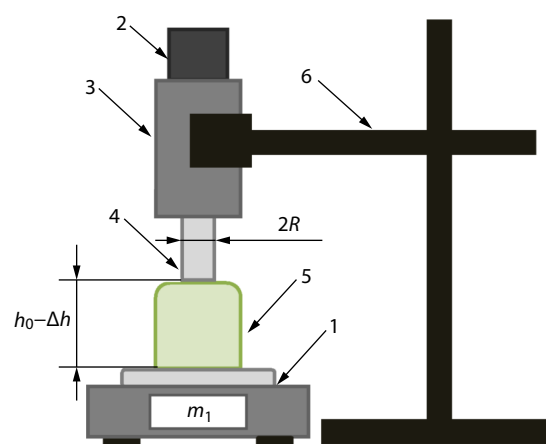


Fig. 4 Setup based on the Maxwell model: 1 – scale; 2 – micrometer head; 3 – micrometer; 4 – micrometer rod; 5 – cryogel sample; 6 – retort stand with a clamp.

pendence on following parameters were built: deformation (ε), concentration (C), the number of freeze-thaw cycles (n) and some other variable arguments.^[7,11,17,18] The experimentally measured values of the instantaneous moduli of elasticity were subsequently used to carry out the design calculations of new products with desired properties.

RESULTS AND DISCUSSION

In these experiments, when we set a known value of the absolute deformation (Δh) to the sample and calculated the relative deformation (ε), we recorded not only the value of the instantaneous stress in the sample (σ_0), but also the values of changed stress (σ) at certain time intervals (t). The results of our laboratory studies and those reported in the works of other researchers^[19,20] indicate that the value of the instantaneously arising internal stress in the cryogel samples after their deformation gradually decreases (relaxes) over time. As follows from Fig. 5(a), the experimental data (stress versus time dependences for different values of a given deformation) with good coefficients ($R^2 \approx 0.98$) are approximated by exponential equations, which are analogs of Maxwell's equation. A similar pattern was observed for the elastic moduli of cryogel (Fig. 5b), which also decreased with time according to the law of negative exponents. This behavior of viscoelastic bodies is due to the fact^[21] that after relative deformation by a constant value ε , an initial stress appears in the body (cryogel sample) at the initial moment of time ($t=0$). The stress decreases with time ($t \rightarrow \infty$). In the course of relaxation described by the relaxation function $\phi(t) = E_0 \cdot \exp(-t/\theta)$, the elastic modulus of the viscoelastic body decreases from the initial (instantaneous) value to the residual elastic modulus E_{res} which remains in the deformed body after the completion of the relaxation process. Thus, the change in the modulus of elasticity may be characterized by the analytical expression (Fig. 5b).^[22,23]

Therefore, in our opinion, it is not enough to characterize the mechanical properties of cryogels only by the instantaneous modulus of elasticity (E_0), experimentally measured value of which is a subjective quantity, since its quantitative value depends on the moment of time (t_x) after the deformation of the sample chosen by the operator of the experimen-

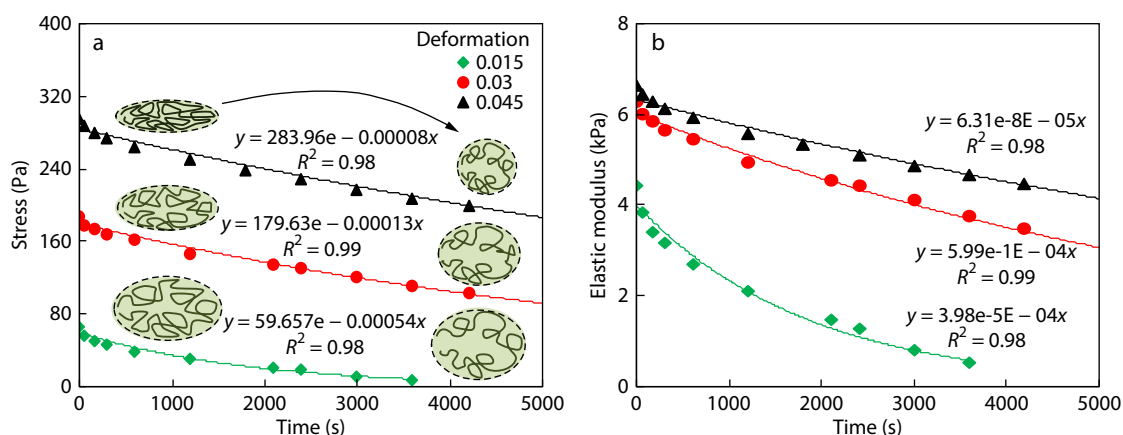


Fig. 5 (a) Cryogel stress ($C_{PVA}=100 \text{ kg/m}^3$ and $M=100 \times 10^3$) versus the residence time of the sample at different deformations; (b) Change in the elasticity modulus of the cryogel ($C_{PVA}=100 \text{ kg/m}^3$; $M=100 \times 10^3$) over time at different deformations.

tal setup to register the value of the changing stress (σ_x). Hence, the numerical values of the coefficient E registered by different experimenters for the same sample will be different, which cannot be considered a satisfactory result of investigation.

Therefore, the relaxation time (θ), i.e., the quantity included in Maxwell's equation is a more objective quantitative criterion for assessing the physical and mechanical properties of cryogels. It also indirectly characterized the rate of approach of the system to equilibrium.^[24] The presence of relaxation times in cryogels is a consequence of the formation of a fluctuation network in concentrated polymer systems. The fluctuation network consists of mutually entangled polymer chains randomly rolled into loose coils with a solvent (water) in their cavities. According to Graessley's theory,^[25] at certain points of the network, knots of engagement appear, which should be considered not only as points of mechanical entanglement of chains, but also as regions of intermolecular interactions between macromolecules. The most important parameter of the fluctuation network is the average lifetime of the knots, which determines the relaxation time of the material under mechanical action on it. The presence of a network in concentrated polymer systems not only increases the viscosity but also gives them elastic properties.

The interpretation of the value θ also has a physicochemical basis, which consists in the fact that the polymer matrix of cryogel deforms under externally applied forces. This deformation at the nanoscale is accompanied by the transfer of macromolecular coils from more probable states (equilibrium and chaotically folded spherical coils) into less probable conformations (ellipsoids) (Fig. 6). Therefore, the elasticity of polymer systems, in contrast to materials made from low molecular weight compounds, has an entropic nature^[26,27] and the value of the relaxation time (θ) is the characteristic time for the system to return to equilibrium.^[28] The return to the spherical shape of coils was realized by rotation of monomer units around covalent bonds connecting them into polymer chains.^[29,30] This is accompanied by segmental displacement (flow) of macromolecules relative to each other. Hence, the mechanical (rheological) properties of polymer materials depend not only on the elasticity (E) but also on the viscosity (η) of the system. Therefore, cryogels belong to viscoelastic sys-

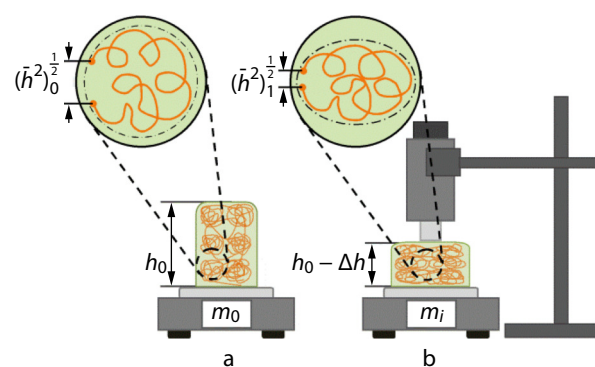


Fig. 6 (a) Cryogel sample in the initial equilibrium state, when the root-mean-square distance between the ends of the polymer chain of coils is equal to $(\bar{h}_0^2)$; (b) Cryogel sample under compression (deformation), when the root-mean-square distance between the ends of the polymer chain of coils ($\bar{h}_1^2$) deviates from the optimal value ($\bar{h}_0^2$), which leads to a decrease in the entropy of the system.

tems that occupy an intermediate position between liquids and solids. The numerical value of the relaxation time of sample depends on the ratio of viscous and elastic properties $\theta = \eta/E$.

Maxwell's equation taken its logarithm can be represented as a linear dependence $\ln(\sigma_0/\sigma) = (1/\theta) \cdot t$. The graph interpretation of the results of experiments with the same cryogel sample having different values of its deformation (ϵ) gave a set of straight lines (Fig. 7a). Cotangents (ctg) of their slope will be numerically equal to the relaxation times of the sample. The relaxation times of the same cryogel sample determined in this way at different deformation values are shown in Fig. 7(b). It is evident that with an increase in the sample deformation, a longer period of time is required to return the sample to an equilibrium (unstressed) state.

As follows from Fig. 8(a), the viscosity of the system increases with increasing PVA concentration. According to the formula $\theta = \eta/E$, the relaxation time of cryogels with a high polymer content in the matrix also expectedly increases from $\theta \approx 400 \text{ s}$ ($C_{PVA}=50 \text{ kg/m}^3$) to $\theta \approx 1500 \text{ s}$ ($C_{PVA}=100 \text{ kg/m}^3$).

An increase in the number of freeze-thaw cycles of cryogels is accompanied by an increase in the number of engagement knots in the polymer network^[31] and, consequently, an

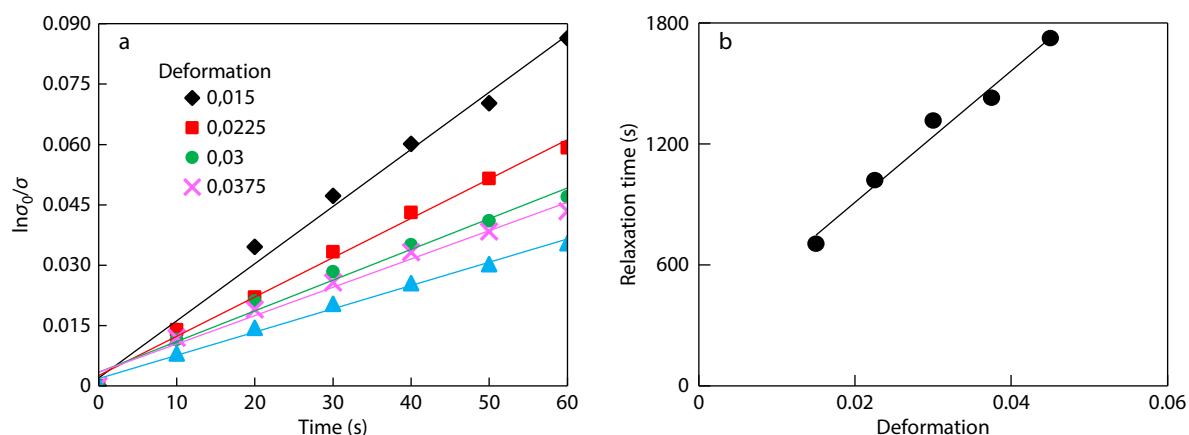


Fig. 7 (a) Dependence of the value $\ln\sigma_0/\sigma$ on the time of a PVA cryogel sample ($C_{PVA}=100 \text{ kg/m}^3$ and $M=100\times 10^3$) at different deformations; (b) Relaxation time of the PVA cryogel sample ($C_{PVA}=100 \text{ kg/m}^3$ and $M=100\times 10^3$) versus the value of sample deformation within the range from $\varepsilon=0.015$ to $\varepsilon=0.045$.

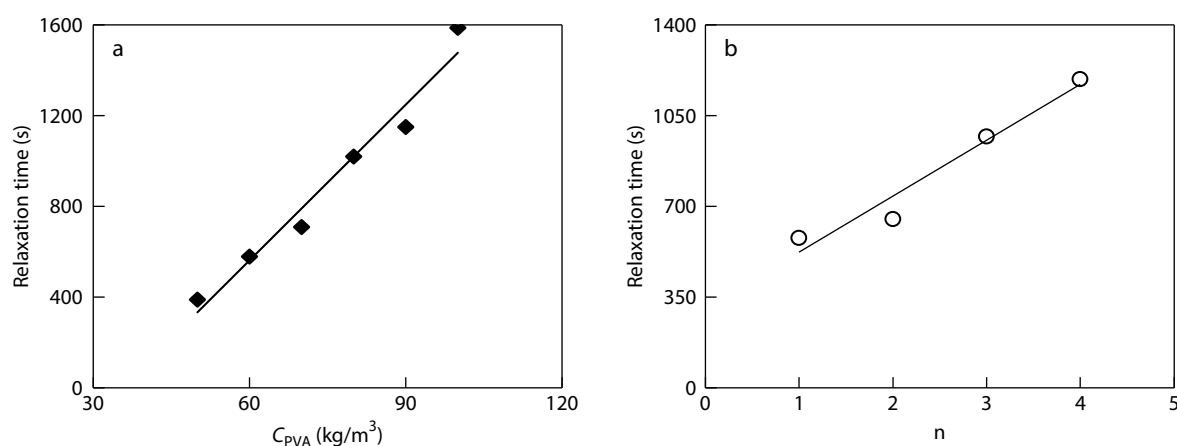


Fig. 8 (a) Relaxation time of cryogels versus the concentration of PVA ($M=100\times 10^3$) at their relative deformation by the value $\varepsilon=0.03$; (b) Relaxation time versus the number of freeze-thaw cycles (n) of PVA cryogel ($C_{PVA}=50 \text{ kg/m}^3$, $M=100\times 10^3$) at deformation $\varepsilon=0.03$.

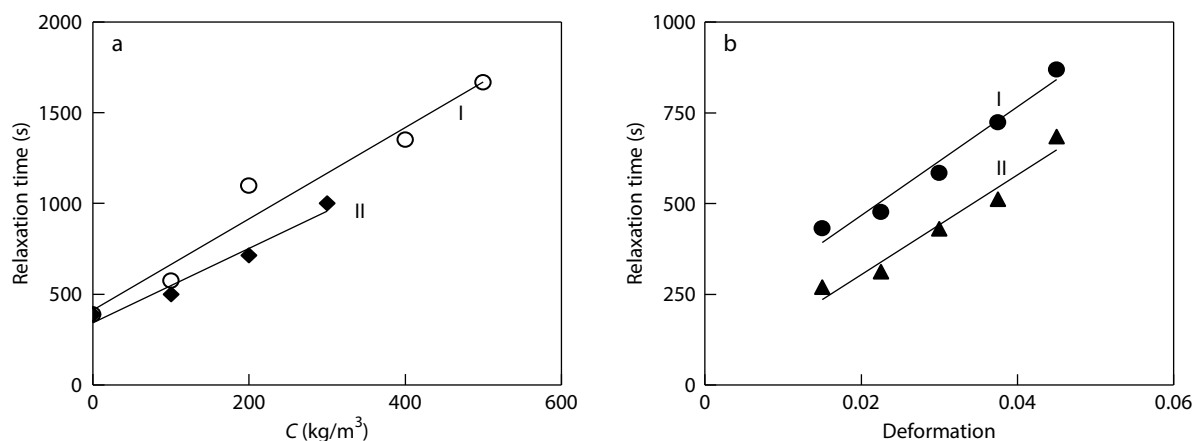


Fig. 9 (a) Relaxation time versus the content of glycerol (I) and mineral oil (II) in PVA cryogels ($M=100\times 10^3$, $C_{PVA}=50 \text{ kg/m}^3$) at their deformation $\varepsilon=0.03$; (b) Relaxation time on deformation of PVA cryogels ($M=100\times 10^3$, $C_{PVA}=100 \text{ kg/m}^3$) with soot (I) and sand (II) as a fillers.

increase in the relaxation time of the samples (Fig. 8b).

An increase in the concentration of glycerol in a homogeneous solution or an increase of the transformer oil content in a heterogeneous colloidal system is also accompanied by an increase in their viscosity and the expected increase in the relaxation time of cryogel samples (Fig. 9a). However, for

samples of cryogels formed from suspensions based on PVA solutions, where the dispersed phase completely filling the internal volume of the polymer matrix is fine soot or sand, the relaxation times of samples are noticeably shorter, than those for cryogels obtained from true solutions or hydrophobic emulsions (Fig. 9b).

It is known that the relaxation time of ideal elastic Hooke bodies after their deformation is infinitely small ($\theta \rightarrow 0$). Low values of relaxation times (θ) of cryogels formed from suspensions are due to very high values of elastic moduli of samples (E), whose framework in the polymer matrix is completely filled with contacting solid particles. In polymer rheology, an analytical expression $\theta = \eta/E$ is also known for the quantitative calculation of the relaxation time of a viscoelastic system. It depends on the ratio of viscosity (η) and high elasticity (E) of filled samples.

The rheological properties of viscoelastic samples (polymer systems), in contrast to ideal Hookean bodies, depend not only on the preset stress or strain, but they also change with time. Thus, in order to predict changes in the properties of viscoelastic bodies, it is necessary to calculate the values of these changes at any point of time. Hence, it is necessary to know the relaxation times of polymer samples of different molecular weights and different concentrations subjected to different deformations.

CONCLUSIONS

For a quantitative description of the rheological behavior of various cryogel samples the use of the relaxation time value, which characterizes the ratio of viscous and elastic properties of polymer bodies has been experimentally substantiated. The following patterns have been revealed:

- With increasing deformation of the cryogel sample, a longer period of time is required to return it to the equilibrium (unstressed) state;
- The relaxation time increases with increasing PVA concentration in the polymer matrix of cryogel;
- The relaxation time increases with increasing number of freeze-thaw cycles of cryogels;
- The relaxation time of the formed cryogel increases with increasing concentration of glycerin or transformer oil content in the initial colloidal system;
- The relaxation time of samples of cryogels formed from suspensions based on an aqueous PVA solution is shorter than that of cryogels obtained from true solutions or hydrophobic emulsions.

NOTES

The authors declare no competing financial interest.

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REFERENCES

- 1 Du Toit, J. P.; Pott, R. W. M. Transparent polyvinyl-alcohol cryogel as immobilisation matrix for continuous biohydrogen production by phototrophic bacteria. *Biotechnol. Biofuels* **2020**, *13*, 105–121.
- 2 Wan, W.; Bannerman, A. D.; Yang, L.; Mak, H. in *Poly(vinyl alcohol)*

- cryogels for biomedical applications*, Vol. 263, ed. by Okay, O., Springer, Cham, **2014**, p. 330.
- 3 Altunina, L. K.; Kuvshinov, V. A.; Dolgikh, S. N. *Cryogels—promising material for underground works in permafrost*. Advances in the Geological Storage of Carbon Dioxide. NATO Science Series. IV. Earth and Environmental Sciences. Springer, **2006**, 65, 103–110.
- 4 Lozinsky, V. I.; Podorozhko, E. A.; Vasil'ev, V. G.; Burmistrov, A. A.; Nikitina, Y. B.; Klabukova, L. F.; Kondrashov, Y. G.; Vasiliev, N. K. A study of cryostructuring of polymer systems. 45. Effect of porosity of dispersed filler on physicochemical characteristics of composite poly(vinyl alcohol) cryogels. *Colloid J.* **2017**, *79*, 497–507.
- 5 Manzhai V. N.; Altunina L. K.; Fufaeva M. S.; Bondaletov V. G.; Bondaletova L. I. **2016**, patent RF, 2605112.
- 6 Vasiliev, N. K.; Pronk, A. D. C.; Shatalina, I. N.; Janssen, F. H. M. E.; Houben, R. W. G. *A review on the development of reinforced ice for use as a building material in cold regions cold regions*. Cold regions science and technology. Eindhoven University of Technology, Eindhoven, Netherlands, **2015**, *115*, 56–63.
- 7 Altunina, L. K.; Fufaeva, M. S.; Manzhai, V. N.; Bondaletov, V. G.; Fisenko, D. V. Effect of an oxidized polymeric petroleum resin on the properties of cryogels. *Chem. Sustain. Dev.* **2019**, *27*, 120–125.
- 8 Lozinsky, V. I.; Savina, I. N. Study of cryostructuring of polymer systems: 22. Composite poly(vinyl alcohol) cryogels filled with dispersed particles of various degrees of hydrophilicity/hydrophobicity. *Colloid J.* **2002**, *64*, 336–343.
- 9 Lozinsky V. I.; Podorozhko E. A. **2006**, patent RF, 2326908.
- 10 Manzhai, V. N.; Fufaeva, M. S. Polyvinyl alcohol cryogels as an efficient spent-oil utilization method. *Chem. Tech. Fuels Oil.* **2015**, *51*, 487–492.
- 11 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). *J. Appl. Chem.* **2006**, *79*, 1669–1672.
- 12 Podorozhko, E. A.; Korlyukov, A. A.; Lozinsky, V. I. Cryostructuring of polymer systems. XXX. Poly(vinyl alcohol)-based composite cryogels filled with small disperse oil droplets: a gel system capable of mechanically induced releasing of the lipophilic constituents. *J. Appl. Polym. Sci.* **2010**, *117*, 1332–1349.
- 13 Kolosova, O. U.; Kurochkin, I. N.; Kurochkin, I. I.; Lozinsky, V. I. Cryostructuring of polymeric systems. 48. Influence of organic chaotropes and kosmotropes on the cryotropic gel-formation of aqueous poly(vinyl alcohol) solutions. *Eur. Polym. J.* **2018**, *102*, 169–177.
- 14 Podorozhko, E. A.; Ul'yabaeva, G. R.; Tikhonov, V. E.; Grachev, A. V.; Vladimirov, L. V.; Antonov, Yu. A.; Kil'deeva, N. R.; Lozinsky, V. I. A study of cryostructuring of polymer systems. 43. Characteristics of microstructure of chitosan-containing complex and composite poly(vinyl alcohol) cryogels. *Colloid J.* **2017**, *79*, 94–105.
- 15 Lozinsky, V. I.; Damshkaln, L. G.; Kurochkin, I. N.; Kurochkin, I. I. Cryostructuring of polymeric systems. 36. Poly(vinyl alcohol) cryogels prepared from solutions of the polymer in water/low-molecular alcohol mixtures. *Eur. Polym. J.* **2014**, *53*, 189–205.
- 16 Altunina, L. K.; Manzhai, V. N.; Stasyeva, L. A.; Fufaeva, M. S. **2006**, patent RF, 2288924.
- 17 Altunina, L. K.; Manzhai, V. N.; Stasyeva, L. A.; Fufaeva, M. S. Production of foamed cryogels by chemical gas generation in an aqueous solution of poly(vinyl alcohol). *J. Appl. Chem.* **2007**, *80*, 1647–1650.
- 18 Manzhai, V. N.; Fufaeva, M. S. Dispersity and stability of foams obtained from poly(vinyl alcohol) solution and the properties of resulting foamed cryogels. *Colloid J.* **2014**, *76*, 455–458.
- 19 Lozinsky, V. I.; Sakhno, N. G.; Damshkaln, L. G.; Bakeeva, I. V.; Zubov, V. P.; Kurochkin, I. N.; Kurochkin, I. I. Study of

- cryostructuring of polymer systems: 31. Effect of additives of alkali metal chlorides on physicochemical properties and morphology of poly(vinyl alcohol) cryogels. *Colloid J.* **2011**, 73, 234–243.
- 20 Watase, M.; Nishinari, K. Rheological and DSC changes in poly(vinyl alcohol) gels induced by immersion in water. *J. Polym. Sci. Polym. Phys. Ed.* **1985**, 23, 1803.
 - 21 Malkin, A. Ya.; Isayev, A. I., *Rheology: concepts, methods and applications*, ChemTec Publishing, Toronto, **2006**, p. 474.
 - 22 Montgomery, T. S., in *Introduction to polymer rheology*, John Wiley & Sons, Inc., **2012**, p. 416.
 - 23 Sunthar, P., in *Polymer rheology. Rheology of complex fluids*, Springer, New York, **2010**, p. 171–191.
 - 24 Christanti, Y.; Walker, L. M. Effect of fluid relaxation time of dilute polymer solutions on jet breakup due to a forced disturbance. *J. Rheol.* **2002**, 46, 733–748.
 - 25 Graessley, W. W. Elasticity and chain dimensions in gaussian networks. *Macromolecules* **1975**, 8, 865–868.
 - 26 Volkenstein, M. V., in *Entropy and Information*, Nauka, Moscow, **1986**, p. 191.
 - 27 Ravve, A., in *Principles of Polymer Chemistry*, Springer, New York, **2016**, p. 801.
 - 28 Barnes, H. A.; Hutton, J. F.; Walters, K., in *An Introduction to Rheology*, Elsevier, Amsterdam, **1989**, p. 199.
 - 29 Wang, J. P.; Yu, Y. H.; Guo, Y. Q.; Luo, W.; Hu, W. B. Local transient jamming in stress relaxation of bulk amorphous polymers. *Chinese J. Polym. Sci.* **2021**, 39, 906–913.
 - 30 Volkenstein, M. V. The configurational statistics of polymeric chains. *J. Polym. Sci.* **1958**, 29, 441–454.
 - 31 Lozinsky, V. I.; Damshkaln, L. G.; Kurochkin, I. N.; Kurochkin, I. I. Study of cryostructuring of polymer systems: 28. Physicochemical properties and morphology of poly(vinyl alcohol) cryogels formed by multiple freezing-thawing. *Colloid J.* **2008**, 70, 189–198.