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TEMPERATURE DEPENDENCE OF THE SHEAR MODULUS IN CONCENTRATED POLYMER GELS: MOLECULAR MECHANISM

In addition to the conventional entropic mechanism of the temperature dependence of the shear modulus in polymer gels, another one has been found. It is implemented in concentrated rigid-chain gels. Such gels were shown to consist of two phases: a network and fibers, with the former phase determining the magnitude of the gel shear modulus. If the temperature increases, the fibers are destroyed; some chains come off the fibers and increase the network phase fraction, thus increasing the shear modulus. Temperature dependences of the shear modulus for gelatin gels with gelatin concentrations $c = 12\%$, 20%, 30%, and 40% were measured in a temperature interval of 34–42 °C. They are consistent with the proposed mechanism. We will also show that this mechanism of the temperature dependence of the shear modulus is responsible for the temperature effect on the regeneration of damaged cartilage tissue.

Keywords: polymer gel, shear modulus, cartilage tissue.

1. Introduction

In recent years, the rapid progress in gel research has been observed (see, e.g., review [1]). This occurs, because gels are components of the human body, and they are widely used as medicines (see, e.g., works [2, 3]).

As is known, the gel is a solution, where the dissolved substance forms a framework. A gel is called the polymer gel, if the dissolved substance is a polymer, and the hydrogel, if the solvent is water. A system, where the dissolved substance does not form a framework, is called a sol. Accordingly, the gel formation process is called the "sol-gel transition".

It is generally accepted (see, e.g., work [4]) that the framework of a polymer gel is a network formed by polymer chains that are interconnected by nodes (Fig. 1). The shear modulus plays the role of a parameter that determines whether a substance belongs to the class of gels on the basis of the deformation properties of the substance. Namely, the shear modulus G of the gel must satisfy the relationships

$$0 < G \ll G_S, \quad (1)$$

where G_S is the shear modulus of a solid.

Due to the special status of the shear modulus, attention in gel physics is focused on the mechanisms that govern the behavior of the shear modulus under the influence of various factors, in particular, temperature. Based on the model depicted in Fig. 1, it is accepted (see, e.g., work [4]) that the shear modulus changes under the temperature influence are caused by the entropy variation, which gives rise to the relationship

$$G \sim T, \quad (2)$$

where T is the absolute temperature.

In this paper, we will describe a mechanism of the temperature-induced change of shear modulus in polymer gels that is different from the conventional one [4].

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2. Experimental Part. Formulation of the Problem

In work [4], gelatin hydrogel is mentioned among the systems whose structure should correspond to Fig. 1, so, whose temperature dependence of the shear modulus should be described by formula (2). We experimentally determined the temperature dependence of the shear modulus of gelatin hydrogel. For this purpose, gelatin hydrogel with concentrations $c = 12\%$, 20%, 30%, and 40% was studied.

The technology of specimen manufacture and the method of the shear modulus measurement were described in work [5]. Before the measurements, the specimens were kept at a temperature of 20 °C for 24 h. The experimental results are presented in Fig. 2, where, besides the experimental points, the plots of the theoretical dependence (2) are shown for comparison. As one can see from Fig. 2, dependence (2) does not agree with the obtained experimental data.

The aim of this work was to determine the molecular mechanism that is responsible for the experimentally obtained temperature dependence of the shear modulus.

3. Phase States of the "Gelatin–Water" System

This paper continues the series of works [6–10]. Their novelty consists in that the sol-gel transition is considered a phase transition of the first kind. This idea is used in this work as well. According to this concept, four phases can exist in the "gelatin–water" system: phase a is the solvent, i.e., water ($c = 0$); phase b is the solid polymer ($c = 1$); phase q is the solution (sol-phase); and the phase m is a mesophase (an intermediate phase between the solution and the solid polymer). The phase diagram corresponding to this concept is schematically illustrated in Fig. 3 (the scale is not preserved). Here, the area above the curve ABF is the region of existence of the q-phase, the area bounded by the curve ADLE is the region of existence of the m-phase, the area bounded by the curve ABDA is the region of coexistence of the q- and m-phases, the area bounded by the curve FBDH is the region of coexistence of the q- and b-phases, and the area bounded by the curve ELDHN is the region of coexistence of the m- and b-phases.

If the temperature decreases along the line QV, then the sol-gel transition takes place. Accordingly, the m-phase is identified with the model depicted in Fig. 1.

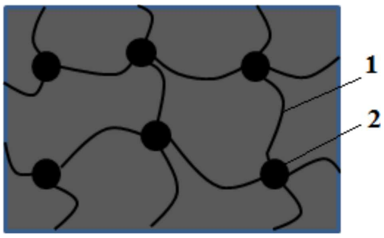


Fig. 1. Model of polymer network: chain (*1*), node (*2*)

Gelatin is formed by collagen chains in the absence of water. In this case, the chains form fibers (see, e.g., work [11]), i.e., the b-phase is formed by collagen fibers.

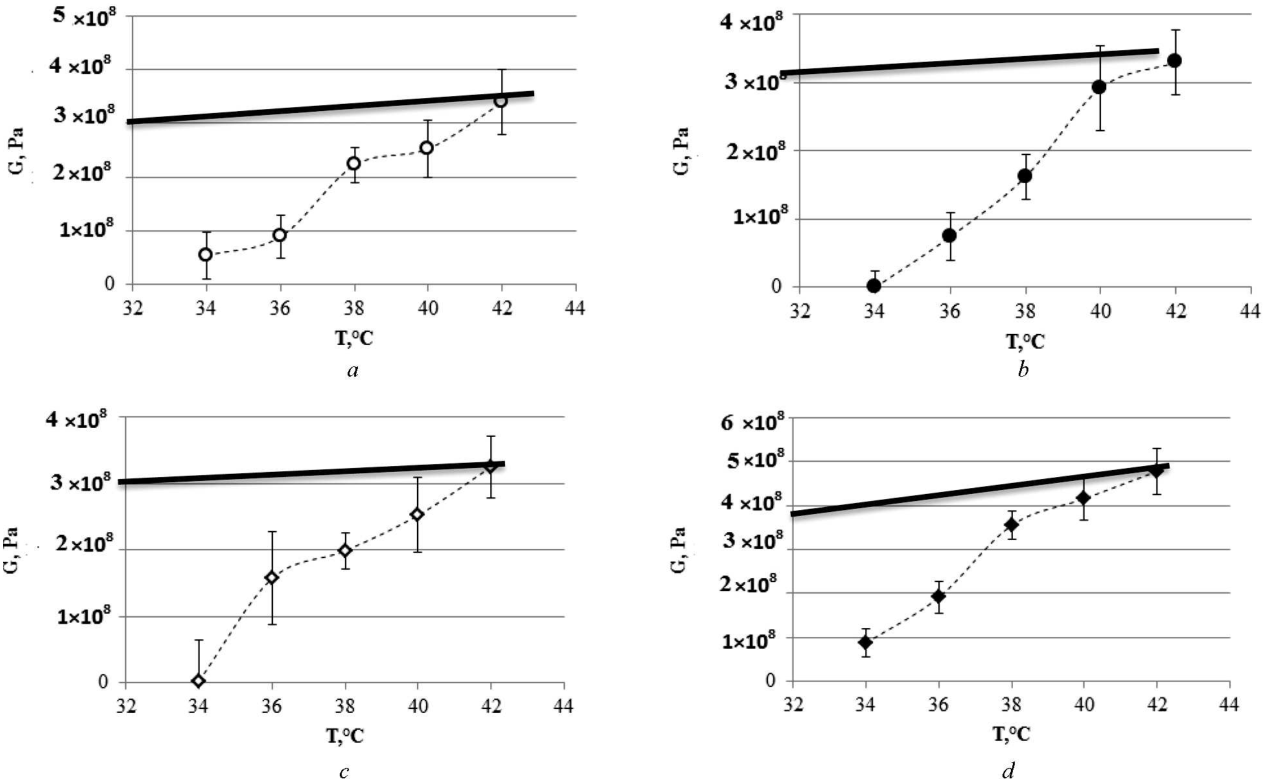
In the experiment (its results are presented in Fig. 2), we studied gels with rather high polymer concentrations. So, it is reasonable to assume that it is the area ELDHN in the $T - c$ plane that was studied experimentally. Below we will discuss gels corresponding to the area ELDHN, i.e., the region, where gel is a mixture of the m- and b-phases.

4. Model of Gel Structure

From the thermodynamical viewpoint, the gel is a non-uniform elastic continuum. We characterize such a continuum by the tensor function $\mathbf{S}(\mathbf{r})$, where $\mathbf{S}$ is the compliance tensor, and $\mathbf{r}$ is the radius vector of a point in the space occupied by the continuum. By definition (see, e.g., work [12]), a mathematically infinitesimal volume $d\mathbf{r}$ in the continuum actually corresponds to some finite-volume region, which is called the physically infinitesimal volume. The latter is a region, where a local equilibrium is established. Every such region is characterized by a certain value of the tensor function $\mathbf{S}$. The microscopic model of gel structure is schematically exhibited in Fig. 4, *a*. Here, the solid lines represent the fibers, and the dashed curves mark the boundaries of the local equilibrium regions. The cross-section of a local equilibrium region is shown in Fig. 4, *b*.

5. Influence of Phase Transition on the Gel Shear Modulus

Generally speaking, the function $\mathbf{S}(\mathbf{r})$ has a random character. Considering the $\mathbf{S}$-function values corresponding to different $\mathbf{r}$'s as independent random



a *b*

c *d*

Fig. 2. Temperature dependences of the shear modulus G in gelatin hydrogel with various gelatin concentrations 12% (*a*), 20% (*b*), 30% (*c*), and 40% (*d*)

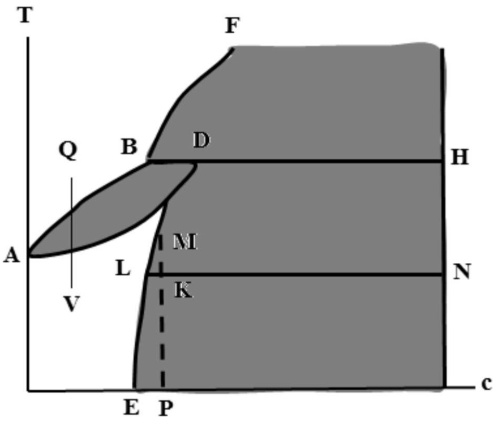
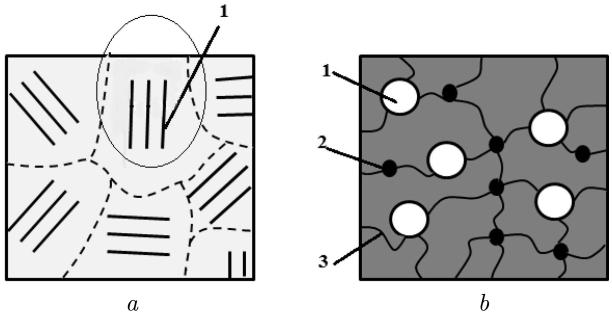


Fig. 3. Phase diagram for the “gelatin–water” system

quantities, we have the following formula for the gel compliance tensor:

$$\bar{S} = \frac{1}{V}\int\limits_{V} \mathbf{S}(\mathbf{r})\, d\mathbf{r}, \tag{3}$$

where V is the volume of the system.



a *b*

Fig. 4. Schematic diagrams of the gel structure (*a*) and the local equilibrium region (*b*): fiber (*1*), network node (*2*), and chain (*3*)

The orientation of fibers in the local equilibrium regions also has a random character. Let us assume those orientations to be equally probable. As a result, the gel as a whole will behave as an isotropic continuum, and the tensor $\bar{S}$ has two independent components; one of them is the shear modulus.

Let an external load create a stress tensor field $\sigma(\mathbf{r})$ in the gel. For the local strain tensor $\varepsilon(\mathbf{r})$, we have the formula

$$\varepsilon\left(\mathbf{r}\right)=\mathbf{S}\left(\mathbf{r}\right)\sigma\left(\mathbf{r}\right). \tag{4}$$

The components of tensor $\mathbf{S}\left(\mathbf{r}\right)$ depend on both the network compliance and the compliance of the fibers entering the local equilibrium region. The network compliance is determined by isolated chains. The fiber is a bundle of chains. Therefore, the network compliance substantially exceeds the fiber compliance. This fact gives grounds to consider a fiber as absolutely solid and leave in formula (4) only the components depending on the network compliance.

The deformation of network chains is mainly reduced to their bending. This type of deformation is accompanied by the smallest increase in the potential energy, if the deformation occurs in the form of rotations of the bonds connecting the chain links to one another. The mentioned energy increase is associated in this case with the force constant β of torsional vibrations.

The local compliance $\mathbf{S}\left(\mathbf{r}\right)$ depends on the size L of the local equilibrium region. Accordingly, the shear modulus G, whose value is obtained according to formula (3) by averaging over the volume V of the system, must also depend on L. Based on the dimensionality of the quantities that G depends on, we have the estimate

$$G\sim\frac{\beta}{L}. \tag{5}$$

Taking the values $\beta\approx 1$ N/m [13] and $L\approx 10^{-7}$ m [14], we obtain the numerical estimate

$$G\approx 10^{7}\ \text{Pa}, \tag{6}$$

which is consistent by order of magnitude with the shear modulus values obtained in our experiment.

Let the line PM in Fig. 3 describe the temperature increase in this experiment, and let the temperature reach a value corresponding to the point K. According to the lever rule (see, e.g., work [15]), the relative amount ξ_m of the m-phase equals

$$\xi_m=\frac{Z}{Z+y}, \tag{7}$$

where $Z=KN$, and $y=LK$ (see Fig. 3). As one can see from Fig. 3, the value of ξ_m should increase as the temperature grows (upwards along the line PM). Accordingly, the value of G should also increase, which was really observed in the experiment. Hence, the temperature dependence of the shear modulus, which was revealed in our experiment, is a consequence of the existence of two gel phases, the *m*- and *b*-phases.

As already mentioned, the fiber compliance practically equals zero, i.e., it is the *m*-phase that is responsible for shear elasticity. As the temperature increases, the fibers are destroyed: the collagen chains come off the fibers and join the network. As a result, the fraction of the *m*-phase increases, which, in turn, leads to the shear modulus growth.

The phase transition occurs when a certain concentration value is exceeded (in Fig. 3, this concentration is marked by the EM line). The probability of the *b*-phase formation increases as the chain stiffness grows.

The collagen chains composing gelatin have considerable stiffness. The gelatin concentration in the researched gel was tens of percent. Therefore, from the above considerations, the emergence of a specific temperature dependence of the shear modulus in such gel seems reasonable. Following the same logic, a similar mechanism should take place, in general, in concentrated rigid-chain gels.

6. Temperature Effect on the Cartilage Tissue Regeneration

In Introduction, we mentioned the gels that are the constituents of the human body. They include cartilage tissue [3]. When treating cartilage tissue (see, e.g., work [16]), applications of heat carriers (paraffin, ozokerite, mud therapy) are widely used. At the action of heat carriers, the tissue temperature in a certain area increases. Such a growth is believed to stimulate the regeneration of damaged cartilage tissue. The mechanism of the aforementioned stimulation remains uncertain.

In our opinion, the mechanism proposed above, which stimulates the temperature dependence of shear modulus in concentrated rigid-chain gels, can play this role. Indeed, as is known [3], the main components of hyaline and fibrous cartilage tissue are collagen (10–12%), proteoglycans (7–8%), and water (75–80%). In work [17], we proposed a model for the cartilage tissue structure, which actually coincides with the model depicted in Fig. 4, *a*. The only difference is that the network is now composed of proteoglycans, but the fibers, as earlier, consist of collagen chains.

Among the objects studied in our experiment was gelatin gel with a gelatin concentration of 12%. Such a solution is a toy model that corresponds to the amount of collagen in cartilage tissue. In this case, the behavior of cartilage fibers should be similar to that of gelatin gel fibers.

It was shown that the temperature growth led to the destruction of gelatin gel fibers. It is reasonable to assert that the same effect should be observed for cartilage fibers as well. Collagen chains that come off cartilage fibers join the proteoglycan network, increase the shear modulus of cartilage tissue, and thereby restore the ability of damaged cartilage tissue to resist the action of external loads. Actually, this process is one of the stages of the cartilage tissue regeneration.

7. Conclusions

It is accepted in the gel physics [4] that the temperature dependence of the shear modulus in polymer gels is determined by the entropy change. However, as [s shown in this paper, for concentrated and rigid-chain gels, there exists a different molecular mechanism governing the temperature dependence of the shear modulus. This mechanism is as follows.

- The mentioned gels consist of two phases, the network and fiber ones. As the temperature increases, a transition from the fiber phase into the network one takes place.
- This transition is accompanied by the destruction of the fibers. As a result, some chains come off the fibers and join the network; so, the fraction of the network phase increases.
- The compliance of the fibers is substantially lower than that of the network. In effect, the shear elasticity of gels is determined by the network. Accordingly, the growth of the network phase fraction as the temperature increases leads to larger shear modulus values. Just such a behavior is observed in the experiment.

The proposed mechanism explains the positive effect of increasing temperature on the cartilage regeneration process. Namely, the temperature growth increases the fraction of the network phase and, therefore, the shear modulus value; i.e., it restores the supporting function of cartilage tissue.

1. M. Karg *et al.* Nanogels and microgels: From model colloids to applications, recent developments, and future trends. *Langmuir* **35**, 6231 (2015).
2. E. Caló, V.V. Khutoryanskiy. Biomedical applications of hydrogels: A review of patents and commercial products. *Eur. Polym. J.* **65**, 252 (2014).
3. J. Eschweiler *et al.* The biomechanics of cartilage – An overview. *Life* **11**, 302 (2021).
4. P.-G. Gennes. *Scaling Concepts in Polymer Physics* (Cornell University Press, 1979) [ISBN: 978-0801412035].
5. L.A. Bulavin, Yu.F. Zabashta, L.Yu. Vergun, O.S. Svechnikova, A.S. Yefimenko. Interfacial layers and the shear elasticity of the collagen-water system, *Ukr. J. Phys.* **64**, 35 (2019).
6. Yu.F. Zabashta, V.I. Kovalchuk, L.A. Bulavin. Kinetics of the first-order phase transition in a varying temperature field. *Ukr. J. Phys.* **66**, 978 (2021).
7. Yu.F. Zabashta, V.I. Kovalchuk, O.S. Svechnikova, L.A. Bulavin. Determination of the surface tension coefficient of polymer gel. *Ukr. J. Phys.* **67**, 365 (2022).
8. Yu.F. Zabashta, V.I. Kovalchuk, O.S. Svechnikova, L.A. Bulavin. Application of the light scattering method to study the hydrogel surface structure, *Ukr. J. Phys.* **67**, 463 (2022).
9. Yu.F. Zabashta, V.I. Kovalchuk, O.S. Svechnikova, M.M. Lazarenko, O.M. Alekseev, A.V. Britan, L.Yu. Vergun, L.A. Bulavin. Clustering in solutions as a process of mesophase formation. *Zh. Fiz. Dosl.* **28**, 1602 (2024) (in Ukrainian).
10. Yu.F. Zabashta, V.I. Kovalchuk, O.S. Svechnikova, L.Yu. Vergun, L.A. Bulavin. The sol-gel transition in hydrogels as the first-order phase transition. *Ukr. J. Phys.* **69**, 409 (2024).
11. A. Miller, J. Wray. Molecular packing in collagen. *Nature* **230**, 437 (1971).
12. L.D. Landau, E.M. Lifshitz. *Fluid Mechanics* (Elsevier, 2013).
13. C. Liang *et al.* Infrared spectra of high polymers. I. Experimental methods and general theory. *J. Chem. Phys.* **25**, 543 (1956).
14. L.A. Bulavin, Yu.F. Zabashta. Local Maxwellian distribution in fluids. *Ukr. J. Phys.* **57**, 1156 (2012).
15. L.D. Landau, E.M. Lifshitz. *Statistical Physics* (Elsevier, 2013).
16. O.A. Bur'yanov *et al. Osteoarthrosis* (Lenvit, 2009) (in Ukrainian).
17. Yu.F. Zabashta, V.I. Kovalchuk, O.S. Svechnikova, L.Yu. Vergun, L.A. Bulavin, Deformation and the structure of cartilage tissue. *Ukr. J. Phys.* **69**, 329 (2024).

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ТЕМПЕРАТУРНА ЗАЛЕЖНІСТЬ МОДУЛЯ ЗСУВУ КОНЦЕНТРОВАНИХ ПОЛІМЕРНИХ ГЕЛІВ: МОЛЕКУЛЯРНИЙ МЕХАНІЗМ

Встановлено, що для полімерних гелів, окрім загальноприйнятого ентропійного, існує ще інший механізм температурної залежності модуля зсуву. Цей механізм реалізується у випадку концентрованих жорстколанцюгових гелів. Показано, що такі гелі складаються з двох фаз: сітки та волокон, причому величину модуля зсуву геля визначає сітка. При підвищенні температури відбувається деструкція волокон. При цьому частина ланцюгів відщеплюється від волокон, збільшуючи кількість сіткової фази, що, в свою чергу, приводить до зростання модуля зсуву. В інтервалі 34–42 °C отримано температурні залежності модуля зсуву для желатинового гелю з концентрацією $c = 12$, 20, 30 і 40% желатини. Отримані залежності узгоджуються із запропонованим механізмом. Показано, що вказаний механізм температурної залежності модуля зсуву зумовлює вплив температури на регенерацію пошкодженої хрящової тканини.

Ключові слова: полімерний гель, модуль зсуву, хрящова тканина.