*JOURNAL OF NANO- AND ELECTRONIC PHYSICS*
Vol. **12** No 4, 04026(5pp) (2020)

*ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ*
Том **12** № 4, 04026(5cc) (2020)

# Peculiarity of Elastic and Inelastic Properties of Radiation Cross-linked Hydrogels

A.P. Onanko, V.V. Kuryliuk, Y.A. Onanko, A.M. Kuryliuk, D.V. Charnyi, M.P. Kulish, O.P. Dmytrenko

*Department of Physics, Taras Shevchenko National University of Kyiv,*
*64/13, Volodymyrska St., 01601 Kyiv, Ukraine*

(Received 25 May 2020; revised manuscript received 15 August 2020; published online 25 August 2020)

The dependences of efficiency of the radiation cross-linking hydrogels by the elastic and inelastic characteristics were investigated. The static elastic module $E$ at compression and extension, elastic limit $\sigma_E$, effective fluidity limit $\sigma_{fl}$, strength limit at compression $\sigma_{st}$ for the radiation cross-linked hydrogel with 5, 6, 8, 10 % polyvinyl alcohol were measured. The values of static module $E$, elastic limit $\sigma_E$, effective fluidity limit $\sigma_{fl}$, strength limit at compression $\sigma_{st}$ of the radiation cross-linked hydrogels are determined by the formation of the polyvinyl alcohol molecules nanoclusters. The optimum compositions of initial hydrogels and electronic irradiation regimes, which allow making the radiation cross-linked hydro polymeric composites with the necessary characteristics at the radiation doses, were found. The modified polymer real network has the large number of different defects, which do not participate in the transfer of the strains $\sigma$ in the network, and, therefore, do not contribute to its elastic module $G$, $E$. It is important that the radiation destruction of the polyvinyl alcohol molecules main chains, which contain the double C=C bonds, influences the formation of the formed hydrogels network. The bandages based on the radiation cross-linked hydrogels are elastic thick films of transparent jelly sterile material that consists of $C = 85 \div 90$ % distilled water. Such bandages must be biologically compatible and not stick to the wounds for the grant of the urgent help at bleeding or burns. They can contain some antiseptic, anesthetic, hemostatic drugs. The nature of the interaction of the polymer hydrogel with the body, its permeability to various substances and cells, the period of biodegradation, its mechanical properties are determined by the parameters of the three-dimensional polymer network that is formed during the formation of the hydrogel. The prediction and control of hydrogels mechanical properties is very important in assessing the applicability of hydrogels.

**Keywords:** Elastic module, Strain, Deformation, Hydrogel.

DOI: 10.21272/jnep.12(4).04026 PACS numbers: 82.33.Ln, 82.70.Gg, 83.80.Kn

## 1. INTRODUCTION

Hydrogels are network polymeric materials in which the polymer chains are very hydrophilic so that they can bind to large quantities of water without dissolving. Because of the large water content, hydrogels are quite biocompatible, and they can be used in many applications. Super absorbers, such as diapers [1] and contact lenses [2] are well established examples. Other interesting applications such as drug delivery systems [3] or tissue engineering [4] are discussed.

Bandages based on the radiation cross-linked hydrogels (CLHG) are elastic 2÷4 mm thick films of the transparent jelly sterile material, that consists of $C = 85 \div 90$ % distilled water. Such bandages must be biologically compatible and not stick to the wounds for the grant of the urgent help at bleeding or burns. They can contain some antiseptic, anesthetic, hemostatic drugs [5-10]. The prediction and control of mechanical properties in hydrogels is of great importance in assessing their applicability.

The properties of a specific hydrogel are extremely important in selecting which materials are suitable for a given application. It is known, that upon annealing of such mixtures, the yield of vacancies from the material is observed. Defect annealing leads to a change in the shape of the temperature spectrum of internal friction (IF) $Q^{-1}(T)$ [11]. To fully exploit the potential of hydrogels, it is crucial to understand, describe, and predict their mechanical properties. As hydrogels are materials that have relatively small values of elastic modulus and which exhibit neither the behavior of something solid nor something liquid, both the measurement and interpretation of mechanical data present significant challenges for the researchers.

The anharmonic effects can be studied by measuring the elastic characteristics of materials, because elastic constants $C_{ijkl}$ are determined through the second derivative of the atomic bonding energy $F$ with respect to the strain $\varepsilon$: $C_{ijkl} = \partial^2 F / \partial \varepsilon^2$. Strain effect on a phonon spectrum is described by means of the Grüneisen parameter $\gamma$. A change in the Grüneisen parameter $\gamma$ shows up in the anharmonicity phenomena.

In this paper, we present a systematic study of the elastic and inelastic mechanical properties of radiation cross-linked hydrogels and their dependence on concentration of polyvinyl alcohol (PVA) $(C_2H_4O)_n$. In particular, elastic modules $E$, elastic limit $\sigma_E$, effective fluidity limit $\sigma_{fl}$, and strength limit at compression $\sigma_{st}$ were estimated based on ultrasonic measurements.

## 2. MATERIALS AND METHODS

The processes of the radiation cross-linking were probed in water solutions of different compositions of the many-component mixtures of water dissoluble polymers in a wide range of the molecular masses. The ionization of hydrogels with layer thickness $h = 2 \div 4$ mm was carried out by the relativistic electron radiation with energy $W \approx 1$ MeV. The dependences of efficiency of the radiation cross-linked hydrogels after mechanical characteristics on the irradiation fluence dose were investigated. The CLHG hydrophilicity and gas-penetrability were investigated as functions of chemical composition and in terms of electron irradiation [12]. The optimum compositions of initial hydrogels and

 

electron irradiation regimes, which allow to make the radiation cross-linked hydro-polymeric composites with the necessary characteristics at the radiation doses $D = 2.5 \div 10$ Mrad, were found. It allows attaining the surgical sterility level ($10^{-6}$) of the made material without substantial influence on pharmaceutical facilities properties at RSHG composition.

The mechanical characteristics (static elastic module $E$, elastic limit $\sigma_E$, effective fluidity limit $\sigma_{fl}$, strength limit at compression $\sigma_{st}$) of the fabricated samples were measured by means of the construction of stress-strain diagram $\sigma(\varepsilon)$ at brief uniaxial circulating compression with utilizing extension of the modernized „ALA-TOO" (IMASH-20-75) setup [13].

The ultrasound (US) measurements were carried out by using the computerized device KERN-4 (Fig. 1) with frequencies $f_{\parallel} \approx 1$ MHz and $f_{\perp} \approx 0.7$ MHz [14]. The measuring error of the elastic module relative to the change was $\Delta E/E \approx 0.1$ %. The measured velocity error was equal to $\Delta V/V = 0.5 \div 1.5$ %.

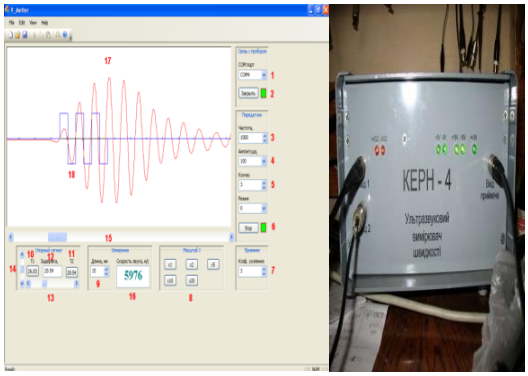


**Fig. 1** – The window of data treatment of elastic-wave velocity measurements in expanded polystyrene $C_8H_8$ by echo-impulse method at frequencies $f_{\parallel} \approx 1$ MHz, $f_{\perp} \approx 0.7$ MHz and the presence of computer device KERN-4

The samples structures were investigated using the "LOMO MVT" optical microscope with "Olympus SP-510UZ" digital photocamera, inverting metallographic microscope "GX51", and atom-force microscopy (AFM) of high resolution.

Molecular simulation techniques have also been utilized in the present work to study the mechanical properties of the hydrogel. The modeled hydrogel is built up of poly (N-isopropylacrylamide) (PNIPAAm) and is cross-linked with N, N′-methylenebisacrylamide (MBA). The molecular simulations were based on the OPLS force field with LAMMPS simulation package [15]. Newton's equations of motion were numerically solved with the Verlet integrator. To calculate elastic modules of the nanocomposites, we used a static method based on Hook's law. After potential energy has been minimized, 12 acts of deforming the structure have been made including three pairs of single-axis stretching-compression deformations followed by three pairs of pure shear deformations. Next, the second minimization procedure for potential energy has been performed retaining cell's dimensions unchanged. The maximal strain's amplitude under modelling was ± 0.002. Elastic strain components have been calculated by using the relation:

$$\sigma_{ij} = \frac{1}{V}\sum\left[ m^k \left( v_i^k v_{ij}^k \right) + \frac{1}{2} r_i^{kl} f_j^{kl} \right], \qquad (1)$$

where $i = x, y, z$; $m^k$, $v^k$ are the mass and velocity of the $k$-th atom, respectively, $r^{kl}$ is the distance between the atoms $k$ and $l$, $f^{lk}$ is the strength applied to the $l$-th atom from the $k$-th atom. The components $C_{ij}$ of the elastic constant matrix have been calculated as derivatives $\partial\sigma/\partial\varepsilon$, and the elastic modules have been evaluated as described in [16].

## 3. RESULTS AND DISCUSSION

The 3D polymeric network is the sponge with the pores size $d \leq 10^3$ nm. Due to the presence of pores, it contains distilled water and assumes the diffusion of solutions, but does not skip the bacterium. The micro-structures of radiation cross-linked hydrogels with 10 % $(C_2H_4O)_n$ were obtained by means of IMASH-20-75 microscope.

Fig. 2a shows the stress-strain curve of radiation cross-linked hydrogel with 5 % $(C_2H_4O)_n$. The calculated mechanical parameters from this curve are as follows: $E \approx 231$ kPa for static elastic module at compression, $E \approx 272$ kPa for static elastic module at tension, $\sigma_E \approx 73$ kPa for elastic limit, $\sigma_{fl} \approx 108$ kPa for effective fluidity limit, and $\sigma_{st} \approx 135$ kPa for strength limit at compression. This result correlates with our molecular dynamics data. In particular, the calculated elastic modulus of the hydrogel is $E = 252$ kPa, which is consistent with the experiment.

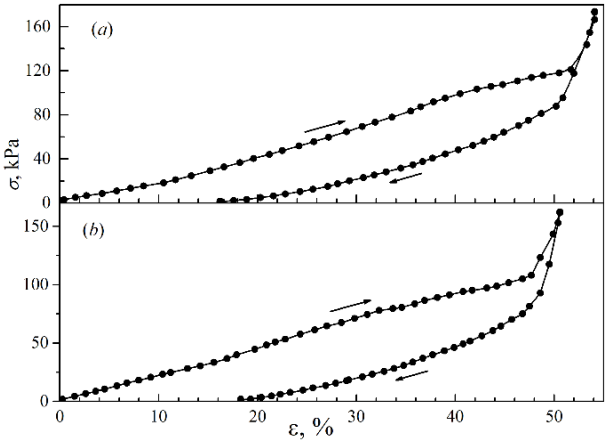


**Fig. 2** – Stress-strain curve for radiation cross-linked hydrogel with 5 % (a) and 8 % (b) $(C_2H_4O)_n$

The obtained mechanical parameters from strain-stress curve for radiation cross-linked hydrogel with 6 % polyvinyl alcohol $(C_2H_4O)_n$ are as follows: $E \approx 131.5$ kPa for static elastic module at compression, $E \approx 69.0$ kPa for static elastic module at tension, $\sigma_E \approx 43$ kPa for elastic limit, $\sigma_{fl} \approx 48$ kPa for effective fluidity limit, and $\sigma_{st} \approx 155$ kPa for strength limit at compression. At the same time, molecular dynamics calculation gives the elastic modulus value $E = 174$ kPa.

The following mechanical parameters for a material with the $(C_2H_4O)_n$ concentration of 8 % were obtained: $E \approx 243$ kPa for static elastic module at compression, $E \approx 249$ kPa for static elastic module at tension, $\sigma_E \approx 78$ kPa for elastic limit, $\sigma_{fl} \approx 94$ kPa for effective fluidity limit, and $\sigma_{st} \approx 152$ kPa for strength limit at

compression (Fig. 2b). According to molecular dynamics, the elastic modulus of such a sample is $E = 287$ kPa.

With an increase in $(C_2H_4O)_n$ concentration up to 10 %, the mechanical parameters are equal to: $E \approx 147$ kPa for static elastic module at compression, $E \approx 105$ kPa for static elastic module at tension; $\sigma_E \approx 38$ kPa for elastic limit, $\sigma_{fl} \approx 82$ kPa for effective fluidity limit, and $\sigma_{st} \approx 145$ kPa for strength limit at compression. The calculated value of the elastic modulus is $E = 182$ kPa.

According to the measurement results, the concentration dependences of the elastic modules were established. The concentration dependences of the static elastic module $E$, strength limit at compression $\sigma_{st}$, and elastic limit $\sigma_E$ for radiation cross-linked hydrogel with $(C_2H_4O)_n$ are represented in Fig. 3, Fig. 4, Fig. 5, respectively. It is seen, that the concentration dependences of the mechanical parameters are nonlinear. An explanation of these features is beyond the scope of the present work and requires additional research. However, these results imply that the range of elastic properties of radiation cross-linked hydrogel can be controlled by variations of concentration of polyvinyl alcohol $(C_2H_4O)_n$.

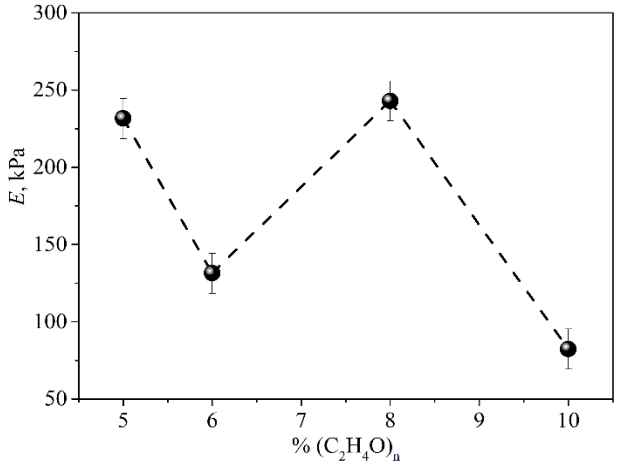


**Fig. 3** – Concentration dependence of static elastic module $E$ for radiation cross-linked hydrogel with $(C_2H_4O)_n$

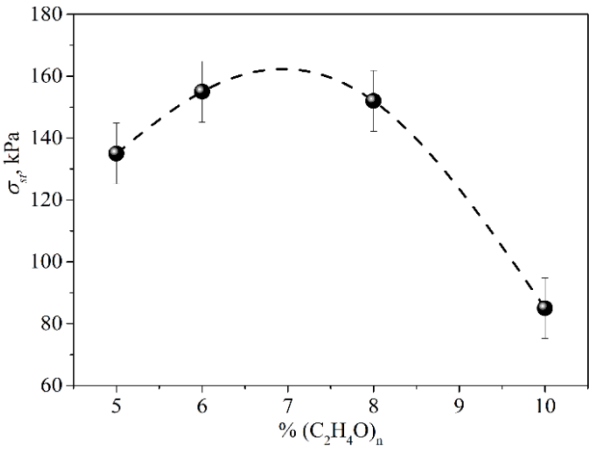


**Fig. 4** – Concentration dependence of strength limit at compression $\sigma_{st}$ for radiation cross-linked hydrogel with $(C_2H_4O)_n$

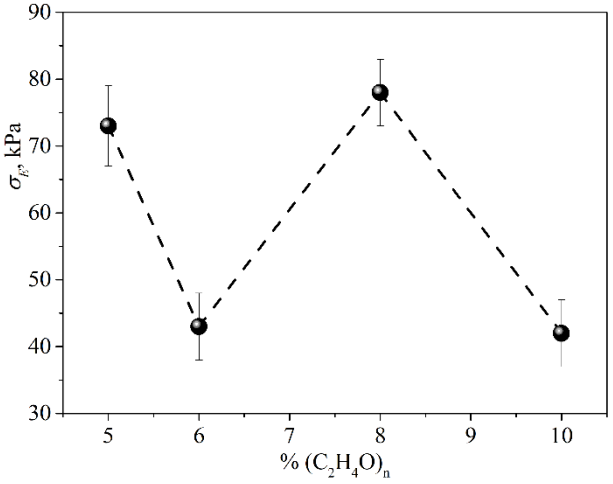


**Fig. 5** – Concentration dependence of elastic limit $\sigma_E$ for radiation cross-linked hydrogel with $(C_2H_4O)_n$

No less important characteristics of the studied materials are the sound velocity $V$ and the dynamic elastic modulus $E$. Using ultrasonic measurements, we found the following parameters for radiation cross-linked hydrogels with 10 % $(C_2H_4O)_n$: the quasilongitudinal ultrasound velocity $V_\parallel = 9$ m/s, elastic module $E = \rho V_\parallel^2 = 82$ kPa; "fast" quasitransversal US velocity $V_\perp = 5$ m/s, and shear module $G = \rho V_\perp^2 = 25$ kPa. Fig. 6 and Fig. 7 show the typical waveforms from which these parameters were determined.

It is known that the Poisson coefficient $\mu$ is equal to the ratio of relative transversal compression to relative longitudinal lengthening [11]:

$$\mu = \frac{\varepsilon_\perp}{\varepsilon_{II}} = \frac{1}{2}\left[1 + \frac{1}{1 - \left(\frac{V_{II}}{V_\perp}\right)^2}\right]. \quad (2)$$

In this work, the Poisson's ratio was determined using the automated system "KERN-DP". The obtained experimental results were processed using the Surfer 10 program for the numerical and graphic analysis and visualization in the automatic regime. The experimental value of the Poisson's ratio for the radiation cross-linked hydrogels with 10 % $(C_2H_4O)_n$ is $\mu = 0.276$.

The equilibrium shear modulus $G_{prep}$ of the hydrogel network chains is directly proportional to the concentration of interstitial cracks in the preparation state, which are elastically active, hydrogel network chains [2]:

$$G_{prep} = RTn_c\varphi_0, \quad (3)$$

where $R$ is the universal gas constant, $T$ is the temperature, $n_c$ is the concentration of the elastic active chains in the dry network, $\varphi_0$ is the polymer volume fraction.

We can calculate the average degree of polymerization of interstitial chains $N$ from the value of $n_c$ assuming that the hydrogel network is perfect and it does not contain any structural defects (the cycles, the hanging chains):

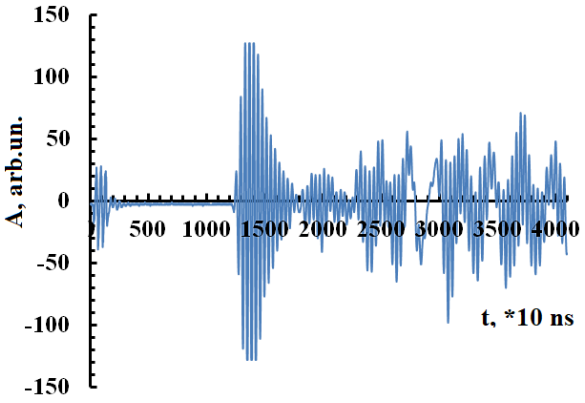


**Fig. 6** – Pulse waveform with quasilongitudinal polarization $V_{\parallel}$ for radiation cross-linked hydrogels with 10 % $(C_2H_4O)_n$

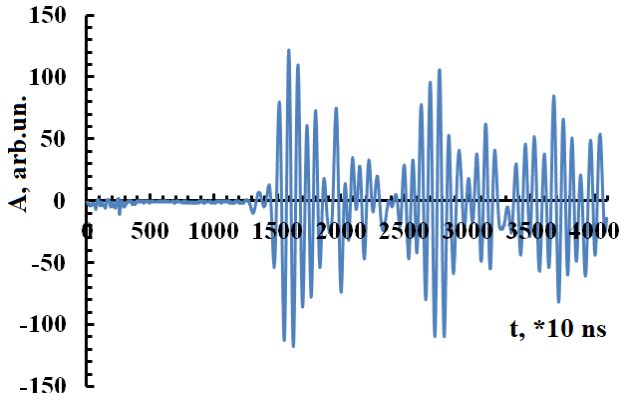


**Fig. 7** – Pulse waveform with quasitransversal "fast" polarization $V_{\perp}$ for radiation cross-linked hydrogels with 10 % $(C_2H_4O)_n$

$$N = \frac{1}{n_c V_m}, \tag{4}$$

where $V_m$ is the links molar volume in the network chains. The value of $N$, which is determined according to (4), gives the overestimated value of the chains length between the nodes, and this error is higher, the higher the defects concentration in the case of the imperfect networks containing the structural defects – the cycles and the hanging chains.

The modified polymer real network has a large number of different defects which do not participate in the transfer of the strains $\sigma$ in the network and, therefore, do not contribute to its shear module $G$ [2]. It is important that the radiation destruction of the polyvinyl alcohol molecules main chains, which contain double C=C bonds, influences the formation of the formed hydrogels network.

One of the most important indicators, which characterizes the system "cross-linked polymer – solvent", is the ratio of the elastic module $G$ and the swelling degree $Q$ of the polymer gel during its equilibrium swelling. This ratio allows us to judge about the solvent quality in the case of the neutral gel and the presence in the surrounding solvent of mobile ions in the case of the polyelectrolyte gels. The equations can be obtained from the equilibrium condition of their free swelling theoretically for the polymer hydrogels of this kind, which can be written as follows:

$$\sigma_{osm} = -\sigma_{del}, \tag{5}$$

where the elastic pressure $\sigma_{el}$ is directly proportional to the hydrogel shear module $\sigma_{el} = G$, the shear module $G$ is a characteristic of its osmotic pressure with equilibrium swelling of the gel. As can be seen from the equilibrium swelling condition (5), the values of $\sigma_{osm}$ and $G$ are equal only under the condition that the elastic pressure $\sigma_{el}$ is equal in absolute value to the shear module $G$: $\sigma_{el} = G$. Thus, the correlation between the shear module $G$ and the equilibrium swelling degree of the polymer gel $Q$ is the dependence of the gel osmotic pressure $\sigma_{osm}$ on its equilibrium swelling degree for equilibrium swelling.

## 4. CONCLUSIONS

1. The static elastic module $E$ at compression and tension, elastic limit $\sigma_E$, effective fluidity limit $\sigma_{fl}$, and strength limit $\sigma_{st}$ in radiation cross-linked hydrogels with various concentrations of $(C_2H_4O)_n$ are experimentally measured.

2. The concentration dependences of static elastic module $E(C)$, elastic limit $\sigma_E(C)$, strength limit at compression $\sigma_{st}(C)$ are represented in consequence of the formation of the PVA molecules nanoclusters.

3. The concentration $C = 5$ % of PVA radiation cross-linked hydrogel with the maximum absolute values of the static module $E(C)$ at compression and tension, elastic limit $\sigma_E(C)$, effective fluidity limit $\sigma_{fl}(C)$, strength limit at compression $\sigma_{st}(C)$ is discovered in consequence of the formation of the PVA molecules nanoclusters.

4. The large number of defects are present in the resulting hydrogel network, such as those formed by the closure of chains on each other and "hanging" double bonds C=C, which have the low ability for radical polymerization due to spatial difficulties, at low concentrations of the reaction system. The number of defects decreases with an increase in the concentration of the system, which naturally leads to the increase in the shear module $G$, elastic module $E$ and degree of crosslinking.

## REFERENCES

1. H.A.A. El-Rehim, *Radiat. Phys. Chem.* **74**, 111 (2005).
2. V.N. Pavlyuchenko, O.V. Sorochinskaya, S.S. Ivanchev, S.Y. Khaikin, V.A. Trounov, V.T. Lebedev, E.A. Sosnov, I.V. Gofman, *Polym. Adv. Technol.* **20**, 367 (2009).
3. N. Peppas, P. Bures, W. Leobandung, H. Ichikawa, *Eur. J. Pharm. Biopharm.* **50**, 27 (2000).
4. B.V. Slaughter, S.S. Khurshid, O.Z. Fisher, A. Khademhosseini, N.A. Peppas, *Adv. Mater.* **21**, 3307 (2009).
5. Y.G. Chernezkaya, A.I. Jebentyaev, P.T. Petrov, *Pharmacy Bull.* **3**, 57 (2011).
6. S.A. Lermontov, N.A. Sipyagina, A.N. Malkova, A.E. Baranchikov, V.K. Ivanov, *Russ. J. Inorg. Chem.* **59**, 1392 (2014).
7. Y.T.A. Al-Ademi, Y.V. Smirnov, T.A. Pulko, N.V. Nasonova, *BGUIR Rep.* **4**, 93 (2014).
8. T.A. Bayburdov, A.B. Shipovskaya, *Synthesis, Chemical and Physics-chemical Properties of Acrylamide Polymers* (Saratov:

FGBOU VPO: 2014).
9. V.I. Sevastyanov, N.V. Perova, *Practical Medicine* **8**, 110 (2014).
10. O.V. Moroz, V.A. Trush, K.O. Znovjyak, I.S. Konovalova, I.V. Omelchenko, T.Y. Sliva, O.V. Shishkin, V.M. Amirkhanov, *J. Molec. Struct.* **1007**, 109 (2012).
11. M.S. Blanter, I.S. Golovin, H. Neuhauser, H.R. *Sinning Internal Fiction in Metallic Materials* (A Handbook Series: Springer Series in Materials Science: 2007).
12. O. Nadtoka, V. Syromyatnikov, *French-Ukr. J. Chem.* **1**, 111 (2013).
13. A.P. Onanko, *Metallophys. Adv. Technol.* **33**, 253 (2011).
14. Y.A. Onanko, G.T. Prodayvoda, S.A. Vyzhva, A.P. Onanko, N.P. Kulish, *Metallophys. Adv. Technol.* **33**, 529 (2011).
15. B. Gorelov, A. Gorb, A. Nadtochiy, D. Starokadomsky, V. Kuryliuk, N. Sigareva, S. Shulga, V. Ogenko, O. Korotchenkov, O. Polovina, *J. Mater. Sci.* **54**, 9247 (2019).
16. B. Arab, A. Shokuhfar, *J. Nano- Electron. Phys.* **5** No 1, 01013 (2013).

## Особливості пружних та непружних властивостей радіаційно зв'язаних гідрогелів

А.П. Онанко, В.В. Курилюк, Ю.А. Онанко, А.М. Курилюк, Д.В. Чарний, М.П. Куліш, О.П. Дмитренко

*Київський національний університет імені Тараса Шевченка, вул. Володимирська, 64/13, 01601 Київ, Україна*

Шляхом вимірювання пружних та непружних механічних характеристик досліджено залежності ефективності радіаційного зв'язування гідрогелів. Експериментально виміряно статичний пружний модуль $E$ при стисненні та при розтягуванні; межу пружності $\sigma_E$, межу ефективної плинності $\sigma_\eta$ та межу міцності $\sigma_{st}$ при стисненні для радіаційно зв'язаних гідрогелів з концентраціями 5, 6, 8, 10 % полівінілового спирту. Встановлено, що абсолютні значення статичного модуля $E$, межі пружної $\sigma_E$, межі граничної ефективності текучості $\sigma_\eta$, межі міцності при стисненні $\sigma_{st}$ в радіаційно зв'язаних гідрогелях визначаються утворенням нанокластерів молекул полівінілового спирту. В результаті досліджень визначено оптимальні склади початкових гідрогелів та режими їх електронного опромінення, які дозволяють виготовити радіаційно зв'язаний гідрополімерний композит з необхідними характеристиками при дозах опромінення. Сітка ланцюгів молекул модифікованого полімеру має велику кількість різних дефектів, які не беруть участі в передачі напружень $\sigma$ в сітці, і, отже, не вносять вклад в її модуль пружності $G$, $E$. Важливо, що радіаційна деструкція основних ланцюгів молекул полівінілового спирту, які містять подвійні C=C зв'язки, впливає на формування сітки утворюваних гідрогелів. Пов'язки на основі опромінених гідрогелів являють собою еластичні товсті плівки з прозорого желе стерильного матеріалу, що складається з $C = 85 \div 90$ % дистильованої води. Такі пов'язки повинні бути біологічно сумісними і не прилипати до ран для надання невідкладної допомоги при кровотечах або опіках. Вони можуть містити деякі антисептичні, знеболюючі, кровоспинні ліки. Характер взаємодії полімерного гідрогелю з організмом, його проникність для різних речовин і клітин, термін біодеградації, його механічні властивості визначаються параметрами тривимірної полімерної сітки, яка утворюється при формуванні гідрогелю. Прогнозування та контроль механічних властивостей гідрогелів має велике значення при оцінці їх застосування.

**Ключові слова:** Модуль пружності, Напруження, Деформація, Гідрогель.