

Effect of NaCl and KCl solutions on deformation of PVA hydrogel – chemo-mechanical coupling

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DOI: [dx.doi.org/10.14314/polimery.2020.1.6](https://doi.org/10.14314/polimery.2020.1.6)

Abstract: This paper provides results of studies of chemically induced deformation of PVA [poly(vinyl alcohol)] hydrogels due to interaction with diffusing NaCl and KCl solutions. The experimental studies were carried out in the specially modified reservoir system, where simultaneously registration the changes in the reservoir salt concentration and the deformation under chemical load were applied. The linear model is used to determine the chemo-mechanical coupling parameter. The results showed that PVA hydrogels deform in the presence of salts in pore fluid and the higher the salt concentration the greater deformation is observed.

Keyword: hydrogels, PVA, chemo-mechanics, reservoir test, ultrasound.

Wpływ roztworów NaCl i KCl na deformację hydrożelu PVA – sprzężenie chemo-mechaniczne

Streszczenie: W pracy przedstawiono wyniki badań chemicznie indukowanej deformacji w hydrożelach poli(alkoholu winylowego) (PVA) pod wpływem oddziaływania z dyfundującymi roztworami NaCl i KCl. Badania obejmowały specjalnie zmodyfikowany test zbiornikowy, w trakcie którego rejestrowano jednocześnie zmiany stężenia soli w zbiorniku i deformację pod obciążeniem chemicznym. Do wyznaczenia parametrów sprzężenia chemiczno-mechanicznego zastosowano liniowy model chemo-deformacji. Stwierdzono, że hydrożele PVA deformują się w obecności soli w płynie porowym, w stopniu zależnym od stężenia soli.

Słowo kluczowe: hydrożele, PVA, chemo-mechanika, test zbiornikowy, ultradźwięki.

Hydrogels are materials that react mechanically (through deformations, change in stiffness, permeability, *etc.*) to a variety of factors of the surrounding environment and pore fluid composition. They may respond to physical stimuli (change of temperature, radiation, applied electric or magnetic field), change of chemical composition of pore and ambient fluid (pH, presence of salt) and biological environment (presence of microorganisms). Type of functional groups in hydrogels' polymers determines the environmental factors to which given polymers are sensitive [1, 2]. There are many experimental studies of the effect of salt on the deformation of different hydrogels such as poly(ethylene oxide) [3], poly(allylamine) (PAAm) [4], poly(4-vinyl pyridine) [5], poly(*N*-vinyl-2-pyrrolidone) [6, 7], poly(acrylic acid) [8]. Only a few are focused on the PVA hydrogel crosslinked by γ -ray irradiation [4, 9–10] or by freezing and thawing [2]. The last process of crosslinking results in the formation of hydrated gel of PVA with high tensile strength,

high water content and high light transmittance, which are important properties of the material, especially for biomedical and biotechnological applications [1, 11]. The polymers have many desirable characteristics such as low protein adsorption, biocompatibility, high water solubility, and chemical resistance. Some of the most common medical uses of PVA are soft contact lenses, eye drops, controlled drug delivery system, embolization particles, tissue adhesion barriers, artificial cartilage and scaffolds for tissue engineering [11]. Because of the applications of PVA as biomaterials, it is very important to have information on their response to particular salts, which are included in the body fluids. The issue of the diffusion process in hydrogels as well as transformation mechanism of the chemical and mechanical energy of the hydrogel is receiving more and more attention. For swelling gels the early fundamental work was laid by Flory and Rehner, who firstly developed an explicit free energy function for neutral gels. This classical model is still being used widely to model various chemo-mechanical couplings in polymer gels [12–15]. However it should be noted, that in the Flory and Rehner model, the stretching energy of polymer networks is represented by Neo-Hookean model for large deformation. In studies of salt on the deforma-

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tion Hong *et al.* [12, 13] used the chemical potential of the solvent and deformation gradient of the network as independent variable of the Flory-Rehner free energy function. By this theory the hydrogel can undergo time-dependent large deformation. In the transient deformation process, the solvent migration is driven by the chemical potential gradient. Further development of the theory is based on formulation a new hybrid energy function of neutral hydrogel by taking into account chain entanglements and junction functionality [14]. A theory of coupled diffusion and deformation relates not only to polymeric materials but also to biological tissues and chemical sensitive rock like clays. Pioneering works on the continual modeling of coupled chemo-mechanical issues appeared in the context of the description of biological systems [16]. The independent group of works is related to the development of chemo-mechanical description applied to clay materials [17–19]. Examples of such macroscopic models were proposed as extensions of the Biot's consolidation theory [20–22], which include parameters responsible for the chemo-mechanical coupling. Numerous couplings that characterize the behavior of reactive hydrogels cause that an effective determination of their properties require the use of relatively complex experimental procedure, ensuring control of external parameters, and the selection of a suitable mathematical model taking into account all the relevant effects.

The aim of this paper is to provide results of studies of chemically induced deformation of PVA hydrogels due to their interaction with salts (NaCl and KCl) that diffuse in pore fluid. The parameters of chemo-mechanical coupling were determined. The experimental studies were carried out in the modified reservoir system that had previously been applied for the determination of diffusion and sorption coefficients of hydrogels [23]. The changes in the reservoir salt concentration and the displacements of the upper base of a hydrogel sample were simultaneously registered. Due to the applied ultrasonic non-contact method to measure deformation of sample it remains in the same environment during tests. As the result the proposed method does not disturb thermal and chemical environment of samples and should be more precise compared to the contact methods applied in the previous papers [2, 4, 9, 10]. The tested materials are three types of poly(vinyl alcohol).

EXPERIMENTAL PART

Materials

Poly(vinyl alcohol) (PVA, $M_w = 146\,000\text{--}186\,000$ g/mol; degree of hydrolysis 99%, Du Pont, Elvanol) hydrogels were prepared by freezing-thawing according to the procedure described elsewhere [24].

The reservoir liquid solutions were physiological fluid (0.15 M NaCl, *i.e.* 0.9 wt % NaCl), one molar sodium chloride (1 M NaCl) and one molar potassium chloride (1 M KCl).

Samples preparation

PVA aqueous solutions were prepared at two concentrations: 22 wt % and 25 wt % in an oven at 90 °C during 12 hours. Prepared solutions were placed in cylindrical Teflon® molds (40 mm diameter, 100 mm height). Samples were subjected to freezing at -18 °C for 12 h and thawing at 18 °C for 12 h for 4 cycles. During this process, water acts as a porophor. In addition to the selected samples, the appropriate amount (5 parts by weight) of the crosslinking agent – gluconic acid was added. The cylinders were cut into homogeneous samples avoiding visible defects (pores) at their circumferential surface. This resulted in different heights of samples. The difference in diameters of samples was caused by different shrinking of hydrogels. The three types of materials tested differ in their initial concentration. Material containing 25% PVA is marked with the symbol H_4A; the material containing 22% PVA was marked as H_5A. In addition, H_4B material was used, in which 5% gluconic acid was added to the gel with 25% PVA. The basic characteristics of the samples taken for tests are presented in Table 1.

Table 1. Basic characteristics of PVA hydrogel samples

Hydrogel sample	Concentration of polymer PVA, %	Admixture	Sample height H , mm
H_4A	25	–	9.98 ± 0.16
H_4B	25	5% gluconic acid	10.11 ± 0.21
H_5A	22	–	8.60 ± 0.10

Methodology

The methodology known as the reservoir method with decreasing source concentration, used as the standard test for identification of diffusion and sorption parameters, was modified to measure the deformation of gel samples due to chemical loads on hydrogel materials. Schematic view of the test chamber and the components of the experimental setup are presented in Figs. 1 and 2.

The chamber shown in Fig. 2b is made from PMMA [*poly(methyl methacrylate)*] internal ring with an inner diameter of 40 mm, which contains a sample of hydrogel, over which there is 60 cm³ of solution. The internal ring is surrounded by an external ring of outer diameter 70 mm and the space between the rings is filled with liquid circulating between the chamber and the thermostat which allows to stabilize temperature. The upper base of the gel sample is in contact with the reservoir liquid (Fig. 1), which has uniform concentration because of mixing by mechanical stirrer. A miniature electric motor rotates the stirrer. The side walls of the sample are insulated against salt diffusion by a flexible membrane which has negligible effect on deformation induced by interaction of hydrogel with salts. The temperature of liquid solution

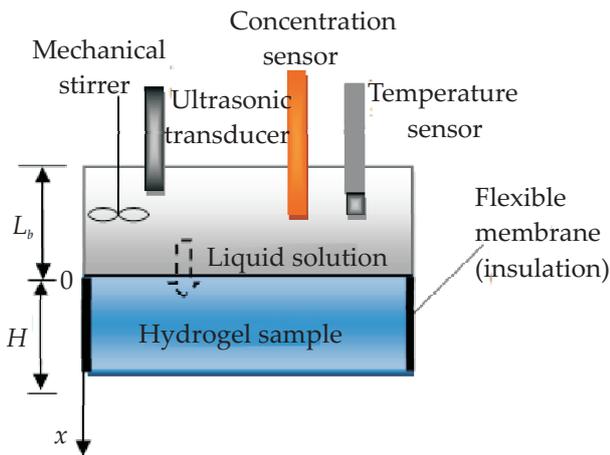


Fig. 1. Schematic of the test chamber in the applied modified reservoir method

and sample are stabilized during the tests by thermostat DC 30/DL30 (HAAKE, Vreden, Germany), Fig. 2a. The measured parameters are the concentration of salt in the reservoir $c_b(t)$, the displacement of the upper base of the sample $u(t)$, and temperature.

Methods of testing

In order to measure continuously salt concentration and temperature of reservoir liquid the conductometric multimeter CX-701 (Elmetron, Zabrze, Poland) is used.

The displacement of the upper base of the sample is recorded by ultrasonic echo method. The ultrasonic card OPCARD-01/100 (Optel, Wrocław, Poland) is applied to generate pulse signals exciting ultrasonic transducer and then acquire waves reflected from samples and propagating in liquid twice the path between the transducer and sample. The transducer with central frequency 5 MHz is fixed to the upper plate of the chamber and its face is immersed in liquid (see Fig. 1). The ultrasonic signals

Table 2. The values of wave propagation velocity in liquid solutions and temperatures applied in the tests

Liquid	Wave velocity m/s	Temperature of liquids, °C
Distilled water	1492	25.24
Physiological fluid	1506	25.20
1 M NaCl	1564	25.75
1 M KCl	1555	25.28

are registered every 60 s and transferred to PC. Then, the data are processed offline in order to determine increments of time of flight using correlation method. The displacement (u) of the upper base of the sample as the function of time (t) are calculated having the increments of time of flight (Δt) (found by correlation) and independently determined values of wave velocity in liquid (c). The appropriate dependence reads $u = c\Delta t/2$. Table 2 shows the values of wave propagation velocity of ultrasound in the applied liquids for appropriate concentration and temperature. From the results for displacement of the upper base and the initial height of samples (L_0) one can find evolution of their strains $\varepsilon = u/L_0$. All the measurements were conducted at 25 °C.

Macroscopic model of chemo-mechanical coupling

A change of chemical composition of a pore fluid in hydrogel and interactions of components of the pore fluid with hydrogel's matrix can result in chemically induced deformations. While the description of microscopic effects related to the interaction of chemicals with polymer chains is important for understanding of the observed behavior of materials the interest of engineers is mostly focused on macroscopic modelling in terms of measures of stress and deformation. In the mathematical description of chemically sensitive porous materials, the constitutive relations included in classical poromechanics (e.g. [25]) are

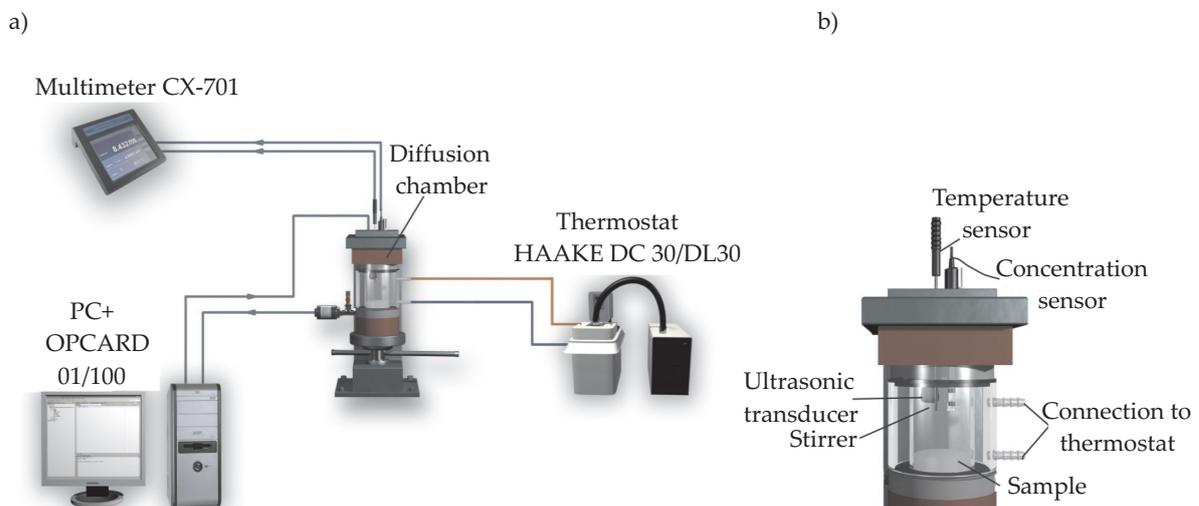


Fig. 2. The experimental system used to study chemically induced deformation of: a) hydrogels, b) diffusion chamber

complemented with contributions of variables representing chemistry of pore fluid, see e.g. [26] and references therein. We concentrate here on constitutive equations for equilibrium states of hydrogels in the case of a single substance in pore liquid. Then, the relations between stress and strain variables must be supplemented by a dependence on a chemical variable such as concentration. For the reservoir test this means that the results for the final or equilibrium state of the transient process of transport of salts and deformation of sample will be used.

Given the range of small deformations of studied hydrogel materials and low concentration of salts in pore liquid we consider linear constitutive relations which gather the total stress in porous material (\mathbf{T}) and change of pore liquid content (ξ) as dependent variables with strain (ε , pore pressure p and concentration c as independent variables) [26]:

$$\mathbf{T} = 2\mu_s \varepsilon + (\lambda_s tr \varepsilon - \alpha p + dc) \quad (1)$$

$$\xi = \frac{1}{M} p + \alpha tr \varepsilon - \frac{\gamma}{M} c \quad (2)$$

where: μ_s , λ_s , α , M – parameters of Biot poroelasticity (μ_s and λ_s are Lamé constants), d and γ – the chemo-mechanical parameters. In the considered case (reservoir test) we can simplify the equations for one dimensional problem. Moreover, neglecting gravity we can assume that hydrogel samples are not mechanically loaded and the total stress at any time and pore pressure for equilibrium states must be equal to zero, i.e.:

$$\mathbf{T} = 0, p(t \rightarrow \infty) = 0 \quad (3)$$

and from (1) we have

$$0 = E \varepsilon_\infty + dc_\infty \quad (4)$$

where: $E = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu}$ is the Young modulus, ε_∞ and

c_∞ the axial strain and concentration of salt in pore fluid at equilibrium.

Assuming that the tests are conducted as long as the hydrogels' deformation and transport reach equilibrium the appropriate values of strain of hydrogel sample ε_∞ and concentration of salt in fluid c_∞ are used along with the data for Young modulus (determined in mechanical tests) the parameter of chemo-mechanical coupling d can be found. Because the pore liquid content ξ is not controlled in the reservoir test the second chemo-mechanical parameter, γ , cannot be determined.

RESULTS AND DISCUSSION

The process of transport of salt into studied hydrogel material results in concentration changes of reservoir liquid and deformation of hydrogel samples. The results for three PVA materials and three salt solutions are reported

in Figs. 3 and 4. The plots in Fig. 3 show the temporal evolution of reservoir concentration for: a) physiological fluid, b) 1 M solution of sodium chloride, and c) 1 M solution of potassium chloride.

It is observed that the type of hydrogel material, particularly the polymer concentration, does not affect substantially the intensity of salt penetration. The final salt concentrations are about 10% lower than the initial ones. Larger difference between initial and final concentration of salt in reservoir for KCl than for NaCl means that for the three studied materials KCl is transported more intensively into the hydrogels than NaCl.

Figures 4 show the results of measurements of displacement of the upper base of the samples, which takes place due to interaction of salts with the hydrogel materials. Since the diffusion of salts into hydrogel is slow (see Fig. 3) the process of deformation of the materials is time dependent and reaches equilibrium at time comparable with time when the reservoir concentration becomes constant.

Table 3 compares the initial height of hydrogel samples, equilibrium concentration of reservoir liquid and equilibrium strains of the samples. The final reservoir concentrations for tests of samples H_4A and H_4B are comparable and higher concentration for tests of sample H_5A is at least partially related to its lower volume (height).

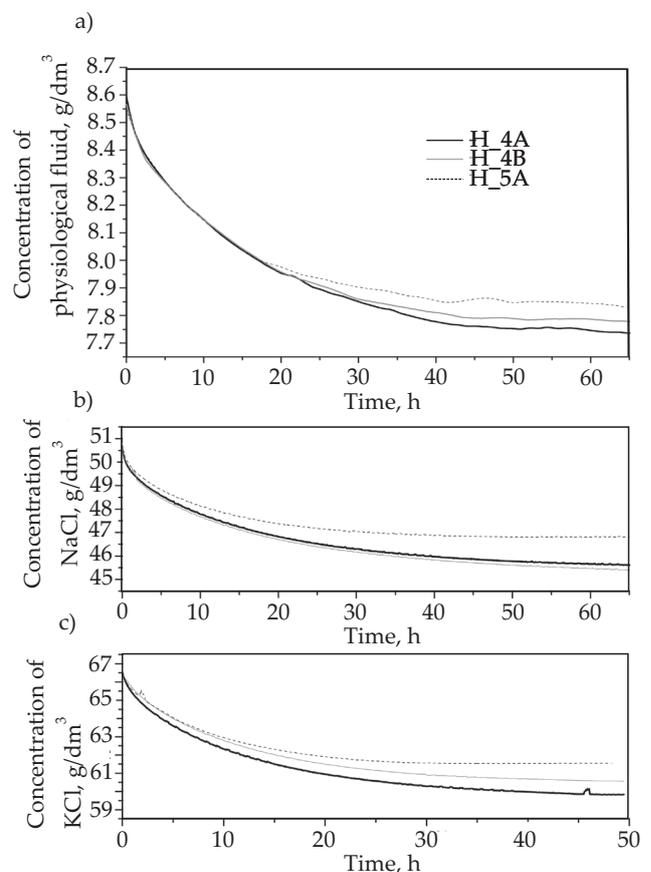


Fig. 3. The evolution of solute concentration in reservoir liquid for: a) physiological fluid, b) 1 M NaCl, c) 1 M KCl diffusing into three tasted hydrogels

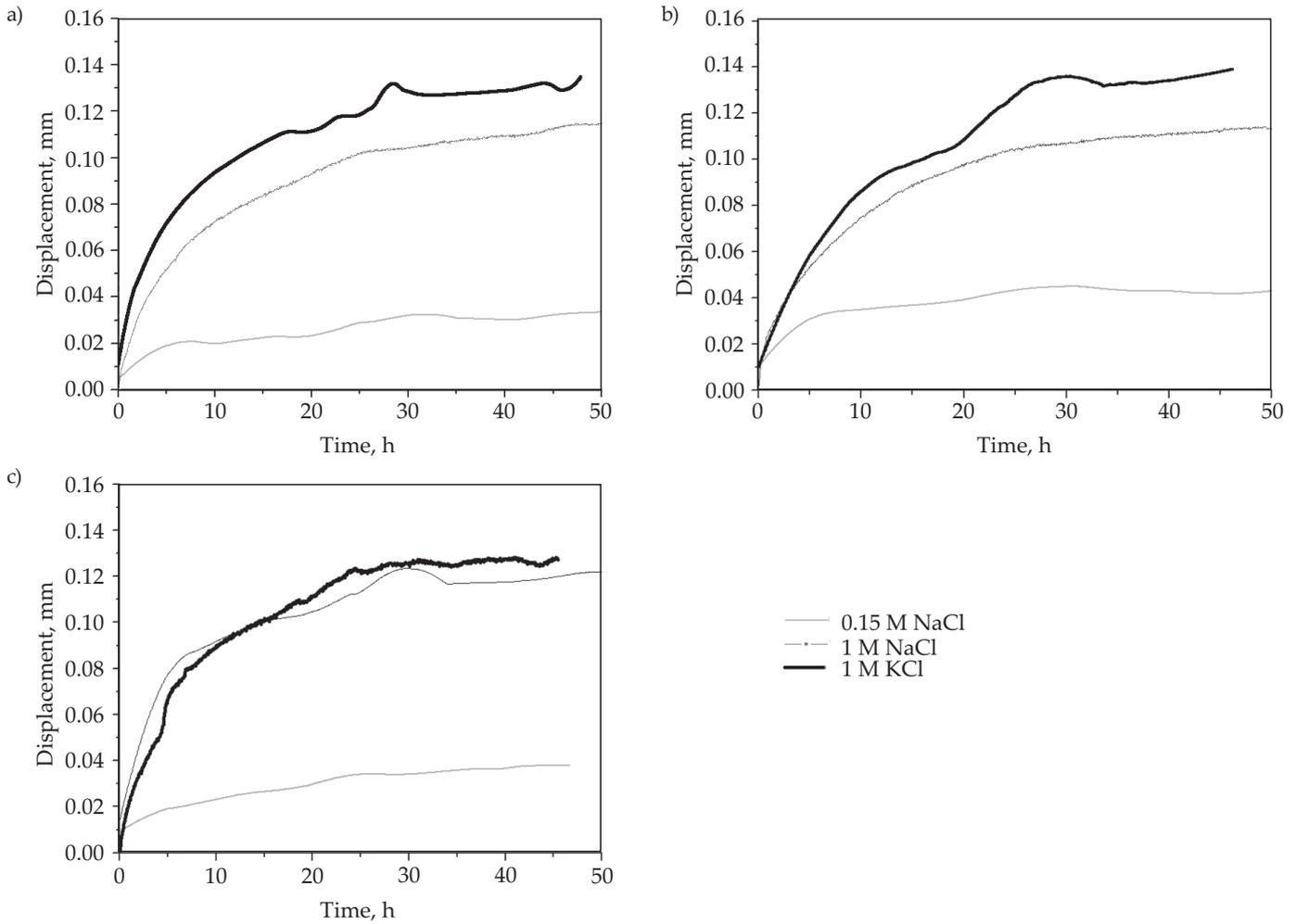


Fig. 4. Displacement of the upper base of the chemically loaded hydrogel samples: a) H_4A, b) H_4B, c) H_5A

The final strains of hydrogel samples amount approximately 0.4% in the presence of physiological fluid, and from 1.1% to 1.6% in the cases of 1 M NaCl and 1 M KCl. All the results show that the higher salt concentration the greater shrinkage of samples. It is worth noting that KCl causes a slightly greater deformation of PVA sample than NaCl. A review of the literature confirms similar results for PVA hydrogel [2] and also for other kinds of hydrogels, like for example poly(ethylene oxide) [3]. The activity of hydrogels to chemicals is related to complex role of water and its interactions with ions. In hydrogels three kinds of water can be distinguished [28]: bounded non-freezable water (about 30%), bounded freezable wa-

ter (about 26%), and free water (barely 3%). The transport process may take place both in free water and in bounded water. KCl electrolyte ions have greater impact on PVA hydrogel than NaCl [2, 10, 29]. It is supposed that K^+ ions decompose (break) the bond between water molecules and hydrogel polymer matrix and thus PVA polar areas are becoming more affordable for KCl.

The values of chemo-mechanical coefficient d can be found from Eq. 4 assuming that salt concentration in pore fluid is the same as the equilibrium concentration in the reservoir and using the data for c_∞ and ϵ_∞ from Table 3. The coefficient of axial strain ϵ_∞ and concentration of salt in pore fluid at equilibrium c_∞ were determined experi-

Table 3. The values of initial height of samples H_0 , equilibrium concentration and strain ϵ_∞ for the studied materials

Hydrogel sample	H_0 Mm	Physiological fluid		1 M NaCl		1 M KCl	
		c_∞ g/dm ³	ϵ_∞ [-]	c_∞ g/dm ³	ϵ_∞ [-]	c_∞ g/dm ³	ϵ_∞ [-]
H_4A	9.98 ± 0.16	7.78 ± 0.05	0.0037 ± 0.004	45.40 ± 0.06	0.011 ± 0.001	59.77 ± 0.07	0.013 ± 0.001
H_4B	10.11 ± 0.21	7.78 ± 0.01	0.0043 ± 0.003	44.89 ± 0.42	0.011 ± 0.001	61.50 ± 1.40	0.013 ± 0.000
H_5A	8.60 ± 0.10	7.85 ± 0.02	0.0039 ± 0.003	46.69 ± 0.21	0.015 ± 0.001	61.02 ± 0.31	0.016 ± 0.002

Table 4. The values of Young modulus E and chemo-mechanical parameter d for studied materials

Hydrogel sample	E	Chemo-mechanical parameter d , m ² /s ²		
		Physiological fluid	1 M NaCl	1 M KCl
H_4A	0.902 ± 0.030	765 ± 97	409 ± 54	367 ± 34
H_4B	0.778 ± 0.040	823 ± 27	289 ± 27	369 ± 0
H_5A	0.715 ± 0.046	947 ± 66	526 ± 57	428 ± 81

mentally from the curves presenting the displacement of the upper base and change of concentration over time, respectively, when the chemically loaded hydrogel samples approach steady state. Additionally, the values of Young modulus reported in the previous paper [27] are adopted. The results for Young modulus E and coefficient of chemo-mechanical coupling d for the studied hydrogels and salts are presented in Table 4.

Given the values of chemically induced strain and the chemo-mechanical coupling parameters it can be concluded that the chemo-mechanical response of hydrogel is affected both by the polymer concentration and the type of chemical load. Into 22% PVA sample penetrates less salt than into 25% PVA samples. On the other hand, deformation (induced by salt) and the coefficient d has a slightly higher value, which means that the samples with a lower polymer content (22% – H_5A) are more prone to deformation than 25% of PVA (H_4A and H_4B). Such a trend in the behavior of the hydrogels is observed for both salts.

CONCLUSIONS

This paper reports studies of chemically induced deformation of PVA hydrogels due to presence in pore fluid NaCl or KCl solutions. The methodology is based on application of the single reservoir test and ultrasonic non-contact method. During the tests, there was possible simultaneously register the changes in the reservoir salt concentration diffusing into the hydrogel sample and the displacement of the upper base of the sample under chemical load. The results show that PVA hydrogels are chemically sensitive materials and the higher salt concentration the greater shrinkage of hydrogel materials is observed. Moreover it is worth noting that 1 M KCl causes a greater deformation of PVA sample than 1 M NaCl. The obtained results along with the values of Young modulus found for the studied PVA hydrogels earlier allowed to determine parameter of the chemo-mechanical coupling. It can be concluded that the chemo-mechanical response of hydrogel is affected both by polymer concentration and type of chemical load.

One should be noticed that the applied methodology allowed not only to measure the parameter characterizing chemo-mechanical coupling but also to monitor the whole process (concentration in liquid chamber and deformation of sample) in time. As the result the process of approaching equilibrium can be noticed and proper values of deformation and concentration can be determined.

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Received 10 III 2019.

Revised version 25 VI 2019.