

Regularities of strengthening of film hydrogel membranes based on 2-hydroxyethylmetacrylate copolymers and polyvinylpyrrolidone

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The results of the research of a surface adsorption magnitude and tensile strength of composite polyamide-hydrogel membranes, depending on the content of the hydrogel lining membrane are presented in the article. It was found that a change in the molecular weight of PVP, both in the structure of the copolymer and in the modifying mixture, as well as the residence time of the hydrogel film in the modifying solution, makes it possible to directly control the properties of composite membranes, in particular, their strength and permeability. The feasibility of using the compositions to obtain medical films is experimentally substantiated.

Keywords: hydrogel membrane, 2-hydroxyethyl methacrylate, polyvinylpyrrolidone, polycapraamide, permeability.

Приведены результаты исследований величины поверхностной адсорбции и прочности при прорыве композиционных полиамид-гидрогелевых мембран в зависимости от состава гидрогелевой мембраны-подложки. Установлено, что варьирование молекулярно й массы ПВП, как в структуре сополимера так и в модифицирующей смеси, а также времени выдержки гидрогелевой пленки в модифицирующем растворе, позволяют направленно регулировать свойства композиционных мембран, в частности, их прочность и проницаемость. Экспериментально доказана целесообразность использования композиций для получения пленок медицинского назначения.

Закономірності зміцнення плівкових гідрогелевих мембран на основі кополімерів 2-гідроксиетилметакрилату і полівінілпіролідону. *О.В.Суберляк, Н.М.Баран, Ю.Я.Мельник, О.М.Гриценко, Г.В.Яцульчак*

Наведено результати досліджень величини поверхневої адсорбції та міцності при прориві композиційних поліамід-гідрогелевих мембран залежно від складу гідрогелевої мембрани-підкладки. Встановлено, що варіювання молекулярної маси ПВП як у структурі кополімеру так і в модифікувальній суміші, а також часу витримки гідрогелевої плівки у модифікувальному розчині, дозволяють прямою регулювати композиційних мембран, зокрема, їх міцність і проникність. Експериментально доведено доцільність використання композицій для отримання плівок медичного призначення.

1. Introduction

Last years the hydrogels have been of great interest to researchers due to their increasing use in medicine and biotechnology [1–5]. The possibilities of using hydro-

gels in medical practice are expanding due to their unique properties. Porous polymer hydrogels are particularly perspective for applications in the drug delivery processes, like medications for binding and controlled drugs release, also for tissue engineering

and regenerative medicine, anti-burn bonds, as well for separation and purification of proteins as implants [6–17].

The hydrogels are obtained on the basis of hydrophilic cross-linked polymers that are able to swell in water and form an insoluble volumetric hydrated grid [18]. The insoluble structure and volumetric structure is the result of cross-linking the polymers. The chemical composition and molecular weight determine the density of the cross-links, which in turn affects the swelling and pore size of the gel [19]. Besides, the cross-linking determines the characteristics of the hydrogels. In terms of practice, the most interesting are hydrogels with the maximum amount of water. A significant disadvantage of such hydrogels is their insufficient mechanical properties. The problem of their increasing is extremely relevant [20]. This problem can be solved by the creation of new polymer composite films, which are characterized by increased strength due to the effective reinforcement of the porous lining membrane by a dense surface layer [21].

The authors [22] obtained composite polymer membranes by a method consisting in the formation of a thin reinforcing layer on the polymer lining membrane by precipitation from a thermoplastic polymer solution with further evaporation of the solvent. Hydrogels based on copolymers of 2-hydroxyethyl methacrylate (2-HEMA) with polyvinylpyrrolidone (PVP) were applied as polymer lining membranes; and aliphatic polyamide (PA-6) and polyvinylpyrrolidone which are solved in formic acid with the different amount of water were used to obtain a thin reinforcing layer. Such solutions were used for modification of the surface of hydrogel films in order to strengthen them [23]. It is known [24] that the strength of polymers depends on the molecular weight. The strength of polymers is determined by the bond breaking energy and the degree of inter-macromolecular interactions.

The purpose of the work is to determine the regularities of strengthening the film hydrogel membranes based on copolymers of 2-hydroxyethyl methacrylate and polyvinylpyrrolidone by thin polycapramid films and to form on their base the composite hydrogel membranes with the required osmotic permeability and strength as well as to determine the effect of the polyvinylpyrrolidone molecular weight on the properties of membranes.

2. Research methods

The composition membranes were formed in two stages according to the following technology: in the first stage, hydrogel films were synthesized by initiating radical polymerization [25]; in the second stage, the hydrogel films were modified with a thin layer of PA-6/PVP mixture, precipitating them with water from the solution in formic acid.

For the formation of a lining membrane, the following components were used: 2-HEMA of Bisomer brand (USA); PVP with $MM = 12 \cdot 10^3$ g/mol medical of high purification of SIAL "Sigma-Aldrich" (USA) brand and PVP with $MM = 360 \cdot 10^3$ g/mol of AppliChem GmbH brand (Germany) qualification "pharm."; distilled water. The polymerization of 2-HEMA with PVP was initiated by potassium persulfate, which was recrystallized from an aqueous solution. The polymerization was carried out in flat-parallel forms made of the glasses, using a three-stage process mode: $55^\circ\text{C} - 3$ h, $75^\circ\text{C} - 1.5$ h, $85^\circ\text{C} - 1.5$ h. Before reinforcing, the synthesized films were hydrated in water until an equilibrium swollen state at room temperature for 24 h.

To make the reinforcing layer, PA-6 of "Tarnamid-27" brand (Poland); PVP $MM = 12 \cdot 10^3$ and $360 \cdot 10^3$ g/mol (properties above); formic acid labeling "h"; distilled water were used. The thin reinforcing layer was applied unilaterally to the surface of the hydrogel films by contacting the surface of the hydrogel film with PA-6 solution in the mixture containing PVP in formic acid for a certain time with further evaporation of the solvent at a temperature of $75-80^\circ\text{C}$ for 30 min. The obtained composite hydrogel membranes were hydrated for 24 h in distilled water before determining the properties at room temperature. Hydration of both hydrogel substrates and composite membranes was carried out under the same conditions.

The surface adsorption value and mechanical properties of the composite polyamide-hydrogel membranes were determined by the methods described previously [20]. The permeability of the obtained composite membranes was measured by the osmosis method [26]. A 4 % of sodium chloride solution was applied as the model substance.

Table 1. Properties of composite hydrogel membranes PA-6/PVP:HCOOH = 7:93 wt. %, [HCOOH] = 80 wt. %, PA-6:PVP (MM PVP = $12 \cdot 10^3$) = 95:5 wt. %

Properties	Contents of components HEMA:PVP (MM PVP = $360 \cdot 10^3$):H ₂ O, wt %.		
	32:8:60	40:10:50	48:12:40
Surface adsorption (A·10 ³ , kg/m ²)	111	134	163
Breaking strength (σMPa)	0.9	1.0	1.18

3. Results and discussion

An important requirement for the operational properties in the case of membranes is the combination of high physical, mechanical and diffusion-transport characteristics [27]. However, for hydrogels, the increase in water content and permeability is usually accompanied by a significant deterioration of mechanical properties, and vice versa. Therefore, the search for effective methods for the directed formation of the structure of copolymers is of great scientific and practical importance.

The production of combined films is considered as a method of modification of polymer films, which allows obtaining a material with desired properties. The choice of individual films for the combination is determined by a complex of properties of individual constituents for use in specific conditions provided by available methods.

To improve the physical-mechanical properties, the hydrogel films were modified with a thin layer of PA-6/PVP blend obtained from formic solution, taking into account the insolubility of polyamide in water contained in the volume of the hydrogel. As for the production of coatings and various combined materials, the main qualitative parameter is the adhesion of the modifying layer to the hydrogel substrate, which depends on the technological process conditions [28].

The analysis of experimental data shows (Table 1) that with an increase in the amount of HEMA-PVP in the hydrogel membrane, the surface adsorption and the breaking strength of the composite polyamide-hydrogel membranes increase. Obviously, it is due to the intermolecular interactions and the conformational changes caused by them, which occur when the surface of the hydrogel is saturated with polyamide polyvinylpyrrolidone macromolecules [29].

It was found that with an increase in the holding time in the modifying solution, the strength of hydrogel films increases but their elongation decreases (Table 2). At the

Table 2. The dependence of braking strength (σ, MPa) and elongation (ε, %) on the modification time for composite hydrogel membranes: HEMA:PVP (MM PVP = $12 \cdot 10^3$):H₂O = 48:2:40 % wt., PA-6/PVP:HCOOH = 7:93 % wt., [HCOOH] = 80 % wt., PA-6:PVP (MM PVP = $360 \cdot 10^3$ g/mol) = 95:5 % wt., δ = 0.5 mm

Mechanical properties	Time of exposition in modifying solution, min				
	1	3	5	7	10
σ, MPa	0.41	0.57	0.72	1.0	1.47
ε, %	–	400	360	347	335

same time, it is observed that the strength increases by almost 5 times, while the elongation decreases by 1.2 times. Such behavior is a characteristic of the skin. These changes are associated with an increase in the adsorption value of the PA-6/PVP blend by the surface layer of the hydrogel. The rise in the adsorption is confirmed by the increase in the thickness of the precipitated film of higher strength. The described film is more wire-wound due to the formation of intermolecular physical bonds.

An important feature of membranes for medical use is the ability to sufficiently diffuse aqueous solutions of salts and drugs. The osmotic permeability of the synthesized composite membranes was determined depending on the time of holding of the hydrogel film in the modifying solution, as well as depending on MM PVP. The results of the osmotic permeability of the modified composite membranes are shown in Fig. 1 and 2. Based on the above graphs (Fig. 1a, c), the permeability of the composite polyamide-hydrogel membranes decreases with increasing exposure time of the hydrogel film in the modifying polyamide solution; but this decrease is different, depending on the molecular weight of the polyvinylpyrrolidinyrrole both in the matrix structure and in the PA-6 blend in the solution of formic acid.

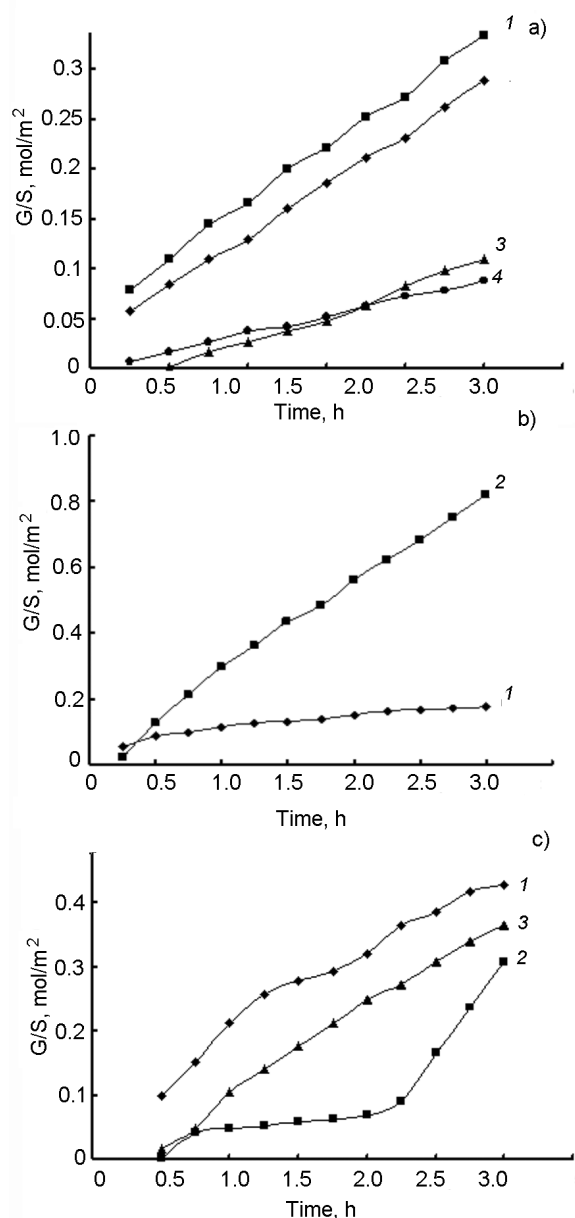


Fig. 1. The dependence of the osmotic permeability of composite hydrogel-polyimide membranes on the molecular weight of PVP:

Hydrogel:HEMA:PVP:H₂O = 48:12:40 wt. %, Solution: (PA-6/PVP):HCOOH = 7:93 wt. %, PA-6:PVP = 95:5 wt. %, [HCOOH] = 80 wt. %, $\delta = 0.5$ mm

a) Hydrogel:MM PVP = $12 \cdot 10^3$ g/mol; solution: MM PVP = $360 \cdot 10^3$ g/mol. Exposure time in modifying solution, min: 1 - 1; 2 - 3; 3 - 5; 4 - 7.

b) Hydrogel:MM PVP = $360 \cdot 10^3$ g/mol; solution: MM PVP = $12 \cdot 10^3$ g/mol. Exposure time in modifying solution, min: 1 - 3; 2 - 5.

c) Hydrogel:MM PVP = $360 \cdot 10^3$ g/mol; solution: MM PVP = $360 \cdot 10^3$ g/mol. Exposure time in modifying solution, min: 1 - 3;

2, 3 - 5. δ , mm: 1, 2 - 0.5; 3 - 0.25.

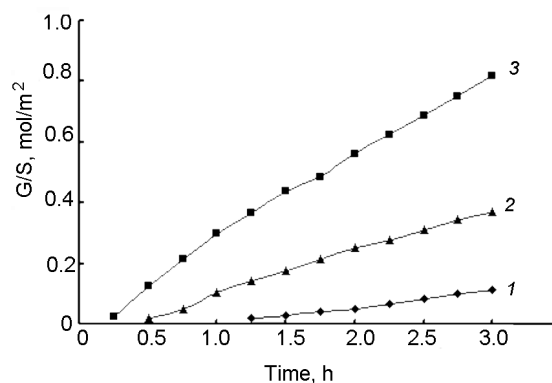


Fig. 2. The dependence of the osmotic permeability of composite hydrogel-polyimide membranes on the molecular weight of PVP:Hydrogel:HEMA:PVP:H₂O = 48:12:40 wt%, MM PVP, g/mol: 1 - $12 \cdot 10^3$, 2, 3 - $360 \cdot 10^3$.

Solution: (PA-6/PVP):HCOOH = 7:93 wt%, [HCOOH] = 80 wt. %, PA-6:PVP = 95:5 wt%, MM PVP, g/mol: 1, 2 - $360 \cdot 10^3$, 3 - $12 \cdot 10^3$, $\tau = 5$ min.

4. Conclusions

Summarizing the results of experimental studies, it can be affirmed that the use of polyvinylpyrrolidone of $12 \cdot 10^3$ g/mol (molecular weight) in the PA-6 reinforcing layer and $360 \cdot 10^3$ g/mol of polyvinylpyrrolidone in the lining membrane provides effective diffusion of the solution into the surface layer of the hydrogel film. This provides a dense surface film and the formation of a high strength composite hydrogel membrane with the possibility of directional control of its diffusion permeability. Such membranes can be applied in medicine.

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