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*O.V. Suberlyak, N.M. Baran, Yu.Ya. Melnyk, G.V. Yatsulchak***FORMATION OF COMPOSITE HYDROGEL MEMBRANES****Lviv Polytechnic National University, Lviv, Ukraine**

The patterns of modifying the surface of hydrogel films by the diffusion deposition of thin layers of polycapraamide–polyvinylpyrrolidone (PA-6/PVP) from a formate solution have been established. The relationship between the composition and properties of hydrogel membrane substrates, which are intended for the formation of composite membranes, was shown. An increase in the PVP content results in an increase in elasticity and a decrease in the mechanical strength of hydrogels. The effects of the composition of formate solution, contact time with the surface, temperature and conditions of subsequent evaporation of formic acid on the surface adsorption of PA-6/PVP have been determined. The influence of the surface adsorption of PA-6/PVP mixture on the physical and mechanical properties of the synthesized films has been investigated. An increase in the modification time of hydrogel membranes, and, consequently, an increase in the PA-6/PVP adsorption lead to an increase in the strength of membrane with asymptotic deceleration. The permeability of the synthesized composite hydrogel membranes based on 2-hydroxyethyl methacrylate (HEMA) and PVP copolymers modified by a layer of PA-6/PVP has been determined during the osmosis of sodium chloride from an aqueous solution. The osmotic permeability of the synthesized composite membranes in the case of sodium chloride somewhat decreases as compared with the hydrogel matrix, especially if the PA-6/PVP concentration in the modifying formate solution increases.

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

Introduction

Current studies in the field of membrane technologies are focused on innovations which allow improving the properties of known synthetic membranes. The production of advanced composites or hybrid membranes from functional polymer hydrogels takes the leading place in these studies [1]. Despite numerous advantages, polymeric hydrogels also have some disadvantages. Their porous structure enables absorbing solutions, but makes them vulnerable to mechanical stress [2]. An insufficient strength of hydrogels does not allow them to be used under conditions of high pressures and loads, and it actually reduces the area of their application.

Various methods of hydrogel modification with organic and inorganic fillers [3], polymers and their mixtures are used to increase the strength of existing membranes based on polymer hydrogels [4]. A successful combination of various materials allows creating composite materials with unique properties. Therefore, the formation of composite polymeric membranes by modifying the hydrogel membranes

with polymers to improve their performance seems to be an urgent problem.

The physicochemical modification of hydrogel films and the formation of multilayered composite membranes are of special attention. Recently, the development of combined membranes has become increasingly expanded, since their formation makes it possible to simplify the manufacturing process by removing certain operations from the technological cycle, such as mixing or gluing [5].

The formation of composite polymer membranes is associated with two following technological processes: the production of a porous base and the application of a thin, dense, fine-porous, and selective layer [6,7].

The application of thin polymeric films by deposition from solutions is an effective method for modifying the surface of polymeric membranes, which allows considering it as a promising technology for the creation of specially designed membranes. The application of a layer is possible due to PA-6/PVP films deposition with water that is contained in the

free volume of hydrogel.

Previously, the authors of works [8,9] developed a method for the formation of selectively permeable membranes based on polyamide-polyvinylpyrrolidone mixtures obtained from formate solutions. It was shown that the synthesized films have sufficiently high physical and mechanical properties, which makes them possible to use under conditions of high pressures and temperatures. Such solutions were used to modify the surface of hydrogel films in order to strengthen them.

Hydrogel film membranes were synthesized via radical polymerization of 2-hydroxyethyl methacrylate with polyvinylpyrrolidone in an aqueous solution [10]. To form high-strength composite polymer membranes, a thin layer of PA-6+PVP interpolymer complex was applied on one side of the hydrogel film, it was obtained via the diffusion deposition of the polymeric mixture from the formate solution due to its contact with the surface of the hydrogel sample.

Materials and methods

To form a porous matrix, namely a hydrogel membrane-substrate, we used vacuum-distilled HEMA (Bisomer trademark), high-purity PVP with a molecular weight of 12,000 g/mol, potassium persulfate (PPS), purified by double recrystallization from an aqueous solution as an initiator, and distilled water as a solvent. For the formation of a thin modifying layer, we used polycapromide (PA-6) (Tarnamid-27 trademark), PVP and formic acid of pure grade with 90% content of the basic substance. To determine the osmotic permeability of the synthesized membranes, sodium chloride dissolved in distilled water ($C_{\text{NaCl}}=4$ wt.%) was used.

The hydrogel membranes as films were obtained in glass forms via polymerization of HEMA-PVP compositions in the presence of potassium persulfate (0.5 wt.%) in an aqueous medium [10]. The form was kept in an air thermostat with an accuracy of temperature control of $\pm 1^\circ\text{C}$. Three-stage process was used as follows: $55^\circ\text{C} - 3$ hours, $75^\circ\text{C} - 1.5$ hours, $85^\circ\text{C} - 1.5$ hours. Before the modification, the films were hydrated in water to an equilibrium swollen state.

The thin reinforcing modifying layer was applied via diffusion deposition of the polymeric mixture PA-6/PVP from the formic solution due to its contact with the surface of the hydrogel sample for a definite period of time (1–10 minutes).

Evaporation of the formic acid from the modifying layer was carried out in a dry-air thermostat at 80°C for 30 minutes. Hydration of the resulting composite films was carried out in three following stages: keeping for 0.5 hours in 1.5% aqueous solution

of sodium bicarbonate (50°C), in distilled water (50°C) and in distilled water for 12 hours (20°C), providing the formation of equilibrium swollen hydrogel in water.

The value of surface adsorption (A , kg/m^2) was determined as the ratio of the formed modifying layer weight to the area of the surface to be modified:

$$A = \frac{(m_0 - m_1)}{S}$$

where m_0 is the initial weight of hydrogel film (kg); m_1 is the weight of the hydrogel film after application of the modifying layer (kg) and S is the area of the surface to be modified (m^2).

The thickness of the films was measured by means of the thickness indicator TP 10-60 with an accuracy of ± 0.01 mm.

The physical-mechanical properties of the synthesized film membranes in the hydrated state were determined by a breakthrough method using the film fixed in a ring-shaped clip, under the action of a pin indenter. Kimura machine of 050/RT-6010 type was used with a strain rate of 25 mm/min. The procedure is described elsewhere [11].

The permeability of the synthesized membranes for the dissolved in water model substance (NaCl) without the application of external pressure was measured using the osmosis method proposed by Karelin [5]. Since the osmotic process is long-term, 4% aqueous solution of sodium chloride was chosen as a model which provided an increase in the method sensitivity. The amount of salt penetrated through the membrane was determined by the evaluation of electrical conductivity of distilled water into which the electrolyte penetrated through the membrane. The conductivity was measured using a conductivity meter «HANNA» of DIST-1 type. After definite periods of time, the measurements were recorded on the device scale. Based on the obtained results, the amount of salt penetrated through the membrane was determined using a calibration graph. Then the G/S ratio was calculated, where G is the amount of salt penetrated through the membrane for a definite time and S is the effective area of the membrane.

Results and discussion

We investigated the effect of PA-6/PVP concentration in solution, formic acid concentration, application time, temperature and evaporation time of the acid from the composite film on the surface adsorption and, consequently, on physicochemical properties and permeability of the obtained membranes.

The studies were carried out in two stages. At

the first stage, the conditions of the hydrogel substrate formation were studied, namely, the ratio of the polymeric and aqueous phases, the temperature regime of the matrices hardening (three stages of temperature increase) and the hydration conditions of hydrogel films with the thickness of 0.35 mm and 0.5 mm were determined. The obtained hydrogel films were used further to determine the effect of conditions on the hydrogel modification by a thin layer on the basis of PA-6/PVP.

We established the relationship between the composition, the amount of solvent and the properties of hydrogel membranes-substrates intended for the formation of composite membranes (Table).

Physical-mechanical properties of hydrogel membranes based on HEMA-PVP copolymers [11]

No	Contents of the components, wt. %			Strength during a breakthrough, σ , MPa	Relative elongation at breakthrough, ε , %
	HEMA	PVP	H ₂ O		
1	45	5	50	0.46	190
2	40	10	50	0.40	235
3	26.65	6.65	66.7	0.38	245
4	35	15	50	0.31	270

The obtained results showed a clear regularity: an increase in the PVP concentration leads to an increase in the elasticity and a decrease in the mechanical strength of hydrogels which is caused by the formation of a polymer network with enlarged chain segments between two cross-linking centers due to the introduction of PVP macromolecules into the polymeric network. On the other hand, a non-grafted part of PVP, which was washed out during hydration, also contributes to the expansion of the polymer network and facilitates the mobility of individual segments in it. Under the action of tensile force, long chain segments between cross-linking centers become stronger than those with short segments, providing the increased elasticity of the polymer. An increase in the PVP concentration decreases the strength during a breakthrough. The reason is the decrease in the number of macromolecular chains per unit of swollen polymer volume, which counteract the failure strain. The wash-out of PVP, as well as the expansion of its structure occurs with the increased PVP concentration in the initial composition. Thus, these phenomena contribute to the increase in water amount in the hydrogel which may be the reason for the increase in the adsorbed layer size.

The surface adsorption increases with an

increase in the modification duration of the combined membranes (Fig. 1), as well as with an increase in the formate solution concentration (Fig. 1, curves 2, 3). At the same time, it was found that the surface adsorption slightly grows with increasing the thickness of hydrogel layer (Fig. 1, curve 2).

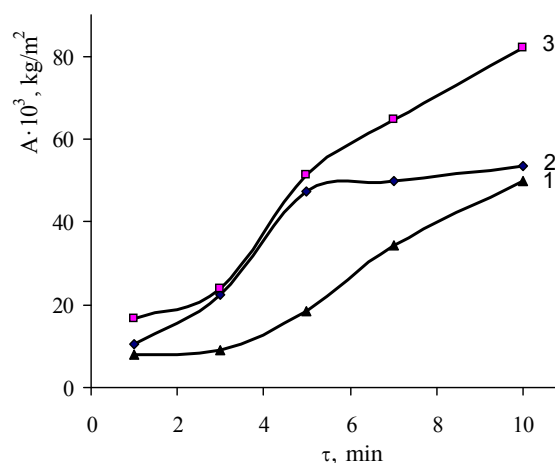


Fig. 1. Surface adsorption (A) of composite hydrogel films vs. modification time (τ). HEMA:PVP:H₂O=48:12:40 wt.%, PA-6:PVP=95:5 wt.%; C_{HCOOH}=80 wt.%; PA-6/PVP:HCOOH, wt. %: 1, 2 – 7:93; 3 – 10:90; the thickness of hydrogel layer (δ), mm: 1 – 0.35; 2,3 – 0.5

It is known [8] that PA-6/PVP mixtures form films characterized by high mechanical strength. They are also permeable for water and low molecular substances dissolved in it. According to the experimental results [12], the optimal concentration of formate solution was found to be 7 wt. %.

The effect of the of PA-6/PVP adsorption on physical-mechanical properties of the synthesized composite films is shown in Fig. 2.

It is obvious from Fig. 2 that with an increase in the hydrogel membranes modification time, and, consequently, the PA-6/PVP adsorption, the strength increases with asymptotic deceleration. The significant increase in strength is observed for the adsorption value of up to $25 \cdot 10^{-3}$ kg/m².

A further increase in time and adsorption only slightly affects the strength. Therefore, the increase in the modification time, at which the value of adsorption is greater than $25 \cdot 10^{-3}$ kg/m², is inexpedient.

Hydrogel membranes-substrates based on HEMA-PVP copolymers are characterized by high osmotic permeability for water and low molecular substances dissolved in it [11]. We investigated the permeability of the composite hydrogel membranes synthesized on the basis of HEMA-PVP copolymers

and modified by PA-6/PVP layer during osmosis of sodium chloride from the aqueous solution (Fig. 3).

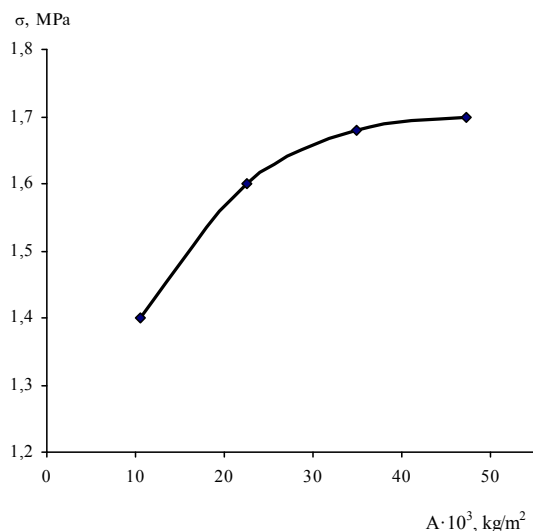


Fig. 2. Strength during a breakthrough (σ) vs. surface adsorption (A). HEMA:PVP:H₂O=48:12:40 wt.%, PA-6:PVP=95:5 wt.%; $C_{\text{HCOOH}}=80$ wt.%; PA-6/PVP:HCOOH=7:93 wt.%; the thickness of hydrogel layer $\delta=0.5$ mm

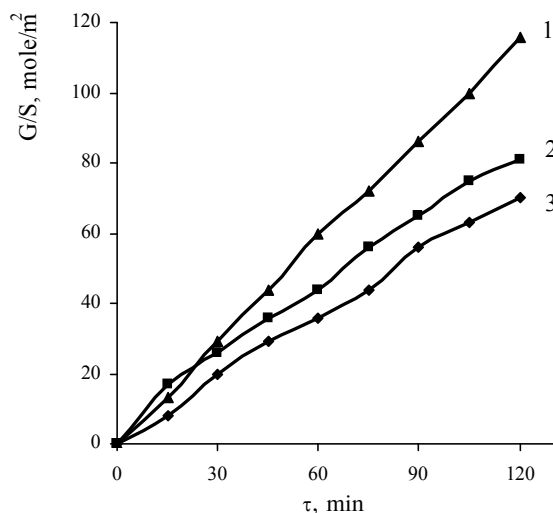


Fig. 3. Permeability (G/S) of composite hydrogel membranes for sodium chloride vs. osmosis duration (t).

HEMA:PVP:H₂O=48:12:40 wt.%; PA-6:PVP=95:5 wt.%; $C_{\text{HCOOH}}=80$ wt.%; $C_{\text{PA-6/PVP}}$, wt.%; 1 – 0; 2 – 5; 3 – 7; $C_{\text{NaCl}}=4$ wt.%

It has been established that the osmotic permeability of membranes is slightly reduced if PA-6/PVP concentration in the modifying formate

solution increased (Fig. 3). The osmotic permeability for sodium chloride of the synthesized composite membranes, which were modified with PA-6/PVP films, in comparison with hydrogel membranes-substrates is less by 28% of the osmotic permeability at the content of 5 wt.% of modifying blend in formic solution, and is less by 40% at the content of 7 wt.%. A decrease in permeability is caused by the formation of a dense film based on PA-6/PVP, but this decrease is slightly noticeable, therefore it cannot limit the area of the application of the obtained membranes.

Conclusions

We have formed the composite hydrogel membranes on the basis of 2-hydroxyethyl methacrylate/polyvinylpyrrolidone copolymers, which were reinforced with polycapraamide-polyvinylpyrrolidone nanolayers. The strength of hydrogel membranes increased 3–5 times due to the formation of PA-6/PVP thin layer via diffusion deposition using formate solution. It was shown that the synthesized composite hydrogel membranes modified with PA-6/PVP films are characterized by less than 28–40% osmotic permeability in comparison with hydrogel membranes that does not narrow the possible areas of their application.

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ФОРМУВАННЯ КОМПОЗИЦІЙНИХ ГІДРОГЕЛЕВИХ МЕМБРАН

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Встановлені закономірності модифікування поверхні гідрогелевих плівок методом дифузійного осадження тонких шарів полікапроамід–полівінілпіролідон (ПА-6/ПВП) із форміатного розчину. Наведений взаємозв'язок між композиційним складом і властивостями гідрогелевих мембран–підкладок, призначених для формування композиційних мембран, який свідчить, що зі збільшенням вмісту ПВП підвищується еластичність і знижується механічна міцність гідрогелів. Визначені межі зміни складу форміатного розчину, часу його контакту з поверхнею гідрогелевої плівки, температури та умов наступного упарювання мурашиної кислоти і встановлений їх вплив на величину поверхневої адсорбції ПА-6/ПВП. Досліджено вплив величини поверхневої адсорбції суміші ПА-6/ПВП на фізико-механічні властивості синтезованих композиційних плівок. Встановлено, що зі збільшенням часу модифікування гідрогелевих мембран, а отже, і зростання величини адсорбції суміші ПА-6/ПВП, міцність зростає з асимптотичним сповільненням. Досліджено проникність синтезованих композиційних гідрогелевих мембран на основі кополімерів 2-гідроксіетилметакрилату (ГЕМА) з ПВП, модифікованих шаром ПА-6/ПВП у процесі осмосу натрію хлориду з водного розчину. Виявлено, що осмотична проникність синтезованих композиційних мембран для натрію хлориду дещо знижується у порівнянні з гідрогелевою матрицею, в більшою мірою у випадку збільшення концентрації ПА-6/ПВП у складі модифікувального форміатного розчину.

Ключові слова: гідрогель, 2-гідроксіетилметакрилат, полівінілпіролідон, полікапроамід, композиційна мембрана.

FORMATION OF COMPOSITE HYDROGEL MEMBRANES

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Keywords: hydrogel; 2-hydroxyethyl methacrylate; polyvinylpyrrolidone; polycapraamide; composite membrane.

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