

Article

Features of the Formation of a Reinforcing Coating on Hydrogel Membranes Based on Polyvinylpyrrolidone Copolymers

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Abstract: This paper presents the study results of formation features of composite hydrogel/polyamide membranes obtained by modification of hydrogel films based on 2-hydroxyethylmethacrylate (HEMA) and polyvinylpyrrolidone (PVP) copolymers. The formation process of composite two-layer membranes was carried out in two stages: obtaining hydrogel membrane substrates followed by their modification with an ultra-thin layer based on a mixture of polyamide (PA) with PVP. The main task of the work was to investigate the possibility of forming a modifying PA/PVP coating on the surface of hydrogel films and to obtain composite hydrogel membranes with the required strength and osmotic permeability based on them. For the formation of composite two-layer membranes, PVP with $MM = 12 \times 10^3$ g/mol and $MM = 360 \times 10^3$ g/mol were used. Additional use of PVP in the modifying solution contributes to the process of its penetration into the hydrogel substrate. Together with the formation of a reinforcing layer, this ensures the obtainment of hydrogel films of increased strength, with the possibility of directional regulation of their diffusion permeability. It was found that the main factors affecting the nature of the interaction between the layers of the obtained composite films, as well as their physico-mechanical and sorption–diffusion properties, are the HEMA:PVP ratio in the original polymer–monomer composition (PMC), the formulation of the reinforcing layer, the duration of the modification process and the molecular weight of PVP in PMC and in the modifying solution. The strength and water content of two-layer composite hydrogel/polyamide membranes, as well as their salt and water permeability coefficients, are the highest in the case of using high-molecular weight PVP ($MM_{PVP} = 360 \times 10^3$ g/mol) and low-molecular weight ($MM_{PVP} = 12 \times 10^3$ g/mol) during the synthesis of the hydrogel substrate to obtain a PA-6/PVP solution for forming a reinforcing layer.

Keywords: hydrogel membranes; hydrogel composites; two-layer membranes; polyvinylpyrrolidone; 2-hydroxyethylmethacrylate; polyamide



Citation: Baran, N.; Grytsenko, O.; Dulebova, L.; Spišák, E. Features of the Formation of a Reinforcing Coating on Hydrogel Membranes Based on Polyvinylpyrrolidone Copolymers. *Appl. Sci.* **2024**, *14*, 3234. <https://doi.org/10.3390/app14083234>

Academic Editor: Vlasoula Bekiari

Received: 29 February 2024

Revised: 4 April 2024

Accepted: 8 April 2024

Published: 11 April 2024



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1. Introduction

Due to the intensively growing use in various fields of science and practice [1–4], synthetic hydrogel materials are of great interest to researchers. A significant part of modern research in the field of hydrogels is aimed at the development and synthesis of materials with improved properties with the possibility of use in medicine and biotechnology—tissue engineering, targeted drug delivery, the creation of implants, protective medical bandages, long-acting drugs, etc. [5–8].

Hydrogel materials are obtained on the basis of hydrophilic cross-linked polymers that can swell in water and form an insoluble volumetric hydrated network [9–11]. The ability to absorb water provides hydrogels with permeability to low-molecular substances, as well as a unique complex of valuable physico-chemical and medical-biological properties—widely adjustable sorption capacity, biocompatibility, soft tissue-like consistency, non-toxicity,

etc. [12,13]. Precisely because of the high permeability for liquids and gases, as well as the ability to absorb low-molecular substances, polymer hydrogels are widely used for the production of various types of diffusion membranes [14–16]. Important requirements for the operational properties of hydrogel membranes are a combination of high physico-mechanical and diffusion-transport characteristics [17]. For practice, of course, the most interesting are hydrogels with the maximum amount of water, the content of which depends on the porosity of the material. At the same time, there is a characteristic dependence for polymer hydrogels—as the porosity increases, the strength characteristics deteriorate [18]. Therefore, the search for effective methods of directional formation of the structure of copolymers and increasing the strength of hydrogel membranes, while maintaining their permeability to aqueous solutions of low molecular weight substances, is urgent and requires a solution. One of the ways to solve this problem is to create composite materials by modifying polymer hydrogels by various methods [19–21]. Among the methods of modification of polymer materials, physical methods have attracted attention because they allow for creating materials with specific properties without significant material costs. This modification provides an opportunity to purposefully change the individual characteristics of already used polymers and thereby expand the scope of their application. Modification of film products can be carried out both on the surface [20,22], that is, the creation of combined multilayer films, and in volume—for example, on the basis of multicomponent polymer solutions with their subsequent evaporation [23]. The formation of multilayer membranes is carried out in order to improve the strength characteristics of the films, reduce their thickness, obtain a defect-free surface layer, and provide special properties or a complex configuration. At the same time, multilayer membranes can be obtained either by applying a modifying hydrogel layer to an already existing substrate [24–27] or by forming a modifying layer on the surface of the hydrogel film. Polymer hydrogels are reinforced by applying a hydrogel layer on an already existing polymer substrate. Reinforcement provides hydrogels with high strength, rigidity, and shape stability and improves their heat resistance. The simplest method of increasing the strength of film hydrogels is their reinforcement with network materials and fibers of various nature, that is, applying a hydrogel layer on a reinforcing strengthening layer. In most cases, a thin hydrogel layer is formed by polymerization of monomers on a porous, strong substrate [18,28]. Reinforced hydrogel films demonstrate satisfactory mechanical properties, and at the same time, they are characterized by a heterogeneous structure, the necessary strength of which can be provided only by a chemical bond between the polymer matrix and the reinforcing network [29,30].

Membranes are obtained by modification in volume, for example, by deposition from multicomponent solutions, which is an effective and technologically simple method. This method was used to obtain membranes based on polyamide-6 (PA-6) by modifying them with polyvinylpyrrolidone (PVP). The polymers were mixed in a formic acid solution, followed by evaporation of the solvent [23]. However, this method is technologically limited in the case of obtaining membranes based on hydrogel materials. At the same time, the method of obtaining film coatings by deposition from multicomponent polymer solutions can be used to modify hydrogel membranes with thin heterolayers. The deposition method of modifying layers from solutions ensures the obtainment of thin films of uniform thickness, with the predicted structure and properties, on hydrogel membranes. This method also allows for changing the nature and formulation of the reinforcing layer within wide limits, while providing composite membranes with additional special properties.

During the preparation of composite two-layer membranes by the method of deposition of a modifying layer on a hydrogel membrane-substrate, great attention must be paid to the selection of the formulation of the modifying solution and the structure of the hydrogel substrate to ensure good adhesion between them. The connection of the modifying layer with the hydrogel substrate is carried out, mainly, as a result of the solution flowing into the pores of the substrate and its hardening in the form of “hooks”.

The currently existing assortment of hydrogel materials ensures the production of a huge number of different types of membranes based on them, which, depending on the required set of properties, are used in various fields of science and practice [14]. The set of properties of hydrogel membranes depends on the nature and porous structure of the polymer matrix. Hydrogels based on copolymers of 2-hydroxyethyl methacrylate (HEMA) and PVP are currently widely used in science and practice among hydrogel materials [31,32]. These hydrogels are considered promising materials for the production of medical bandages [33], contact lenses [34], vascular prostheses [35], materials for the regeneration of damaged tissues [36], enzyme immobilization systems [37], drug delivery systems [38], etc. Due to their unique properties, in particular, the ability to swell, high permeability to aqueous and other solutions, and biotolerance, hydrogel materials based on grafted copolymers of polyHEMA with PVP (pHEMA-gr-PVP) are effectively used for the manufacture of membrane devices, in particular for medical purposes [18,39]. However, a significant drawback that sharply limits the use of such membranes is their low mechanical strength. Therefore, the search for reinforcing materials, as well as the development of effective methods of modifying hydrogel membranes based on pHEMA-gr-PVP copolymers, remains relevant nowadays. In addition to increasing the physico-mechanical properties, the reinforcing material should provide the selective and penetrating characteristics of the hydrogel membrane. Solutions based on aliphatic polyamides with PVP are promising for modifying hydrogel membranes based on pHEMA-gr-PVP copolymers [23,40]. Polyamides, due to the presence of polar amide groups in macromolecules, which cause strong intermolecular interactions involving hydrogen bonds, are characterized by a complex of valuable properties, in particular wettability, chemical resistance, elasticity, and high mechanical strength [41,42]. PVP occupies a special place among a wide range of water-soluble polymers due to its unique properties—surface activity, high hydrophilicity, a wide range of solubility, and a pronounced tendency to complex formation [43]. In addition, PVP is widely used in membrane technologies [40,44–47]. Films formed on the basis of polyamide/PVP solutions in formic acid are characterized by hydrophilic properties and increased strength characteristics [23]. Good compatibility of PA-6 with PVP was also established [23].

The purpose of this work was to study the regularities of reinforcing hydrogel films based on pHEMA-gr-PVP copolymers, modifying them with a polyamide/PVP layer to form composite hydrogel membranes with the required strength and osmotic permeability.

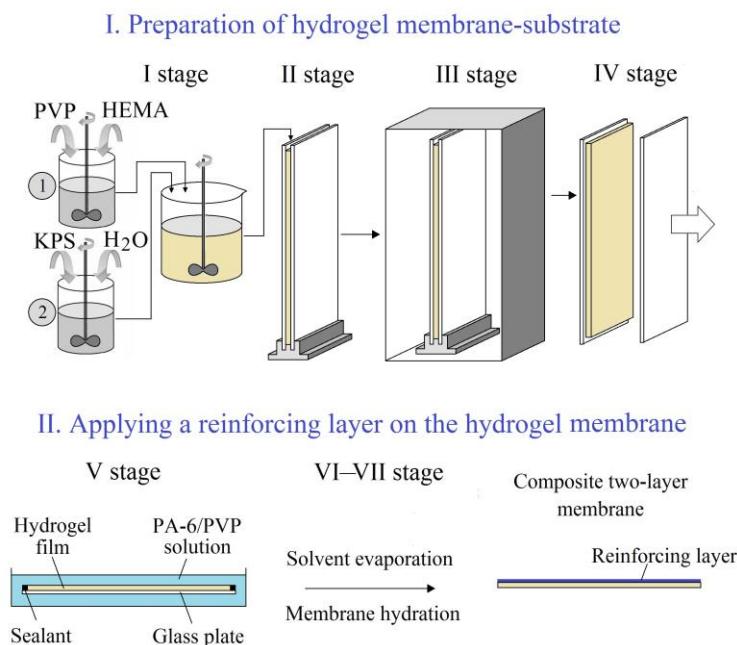
2. Materials and Methods

2.1. Materials

As hydrogel membrane substrates, hydrogel films based on copolymers of pHEMA and PVP were used [31], and a mixture of aliphatic polyamide (PA-6) with PVP dissolved in formic acid (FA) of different concentrations was used to obtain the reinforcing coating. Two-layer composite membranes were obtained using the following substances: 2-hydroxyethylmethacrylate (Sigma Chemical Co., Saint Louis, MO, USA), which was purified and distilled in a vacuum (residual pressure = 130 N/m², T_B = 351 K); high-purified polyvinylpyrrolidone with MM 12 × 10³ g/mol and 360 × 10³ g/mol (AppliChem GmbH, Darmstadt, Germany); polyamide PA-6 “Tarnamid-27” (Grupa Azoty S.A., Tarnów, Poland) specific gravity—1.08 g/cm³, melt flow—60 g/10 min, melting point—221 °C; potassium persulfate (PPS, 99%, Merck KGaA, Darmstadt, Germany); formic acid (Poch S.A., Gliwice, Poland), marking “h”.

2.2. The Method of Obtaining Two-Layer Films

The method consists in the formation of a thin reinforcing layer on the hydrogel membrane substrate by means of deposition from a thermoplastic polymer solution with subsequent evaporation of the solvent (Scheme 1).



Scheme 1. Schematic diagram of obtaining hydrogel membranes with a reinforcing polyamide/PVP coating. Stages of the technological process: I—obtaining the forming composition; II—dosage of the forming composition into the polymerization mold; III—polymerization; IV—opening the form and removing the hydrogel membrane-substrate; V—application of a reinforcing PA-6/PVP layer on the membrane; VI—evaporation of the solvent; VII—membrane hydration.

Hydrogel membranes in the form of films were obtained in glass molds by copolymerization of HEMA with PVP in the presence of $K_2S_2O_8$ ($[KPS] = 0.5 \text{ wt.}\%$). The polymerization process was carried out in a three-stage mode (I stage: $T = 55^\circ\text{C}$, $\tau = 3 \text{ h}$; II stage: $T = 75^\circ\text{C}$, $\tau = 1.5 \text{ h}$, III stage: $T = 85^\circ\text{C}$, $\tau = 1.5 \text{ h}$) with a temperature adjustment accuracy of $\pm 1^\circ\text{C}$. The obtained films were hydrated in water until they reached an equilibrium swollen state, placed on a glass plate and fixed at the edges with a special frame. After that, the frame with the hydrogel membrane was immersed into the formate PA-6/PVP solution and kept for $1 \div 10 \text{ min}$. A layer of polymer solution was applied to the hydrogel film on one side. Evaporation of methanoic acid from the reinforcing layer was performed by keeping the films in a dry-air thermostat ($T = 80^\circ\text{C}$, $\tau = 30 \text{ min}$). After that, the obtained composite films were hydrated in distilled water (room temperature, $\tau = 12\text{--}24 \text{ h}$).

2.3. Measurements and Characterization

2.3.1. Procedure for Determining the Specific Amount of Film on the Surface of Hydrogel Membranes

The hydrogel membrane was taken out from distilled water, excess surface moisture was removed, weighed and fixed with a frame on a glass plate. The frame with the hydrogel membrane was immersed in the formate PA-6/PVP solution. After that, the membrane was kept in a dry-air thermostat for 30 min at a temperature of 80°C . The resulting composite membrane was cooled to room temperature and placed in distilled water for 12–24 h for hydration to an equilibrium swollen state. Subsequently, the polyamide/hydrogel membrane was removed from the water, and the layer of surface moisture was removed and weighed.

The value of the specific amount of film (A , kg/m^2) was determined according to the following formula:

$$A = \frac{m_{\text{mod}} - m_0}{S_{\text{mod}}}, \quad (1)$$

where m_0 —mass of the membrane before modification with a polymer solution, kg;

m_{mod} —mass of the membrane after applying the modifying layer, kg;
 S_{mod} —area of the modifying surface, m².

2.3.2. X-ray Diffraction Analysis

The structure of the obtained materials was evaluated on the basis of the data of X-ray diffractometry (XRD), for which a DRON-4-07 X-ray Diffractometer (JSC «Burevestnik», Saint Petersburg, Russia) was used.

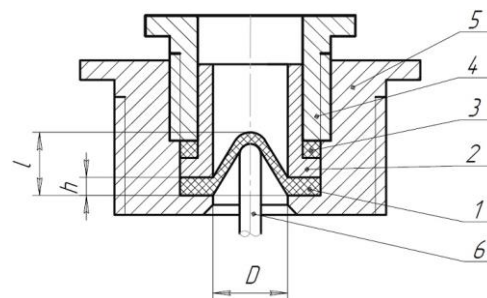
2.3.3. The Bursting Strength and the Percentage Elongation at Bursting

The physico-mechanical properties of the obtained film samples were studied on a tensile testing machine “Kimura” 050/RT-601U (Kimura Machinery, Ishinomaki, Japan). The bursting strength (σ , MPa) was characterized by destructive stress during burst, the elasticity (ε , %)—by relative elongation during breakthrough. The essence of the research is to burst a hydrogel film fixed in a ring-shaped clamp (the diameter of the clamp hole is 1×10^{-2} m, the radius of rounding of the indenter 2×10^{-3} m, the speed of movement of the indenter 25×10^{-3} m/min) with an indenter in the form of a pin. σ and ε were calculated using formulae:

$$\sigma = \frac{F}{D \cdot h} \cdot 10^{-6}, \quad (2)$$

$$\varepsilon = 257 \cdot \frac{l}{D} - 25, \quad (3)$$

where F —the force at which the film bursts, N; D —diameter of the hole of the ring-shaped clamp, m; h —thickness of the film sample, m; l —the path of movement of the indenter from the moment of contact with the film sample to the moment of the film burst, m (Scheme 2).



Scheme 2. Scheme of a device for assessing the physico-mechanical properties of film materials through bursting: 1—film sample; 2—ring-shaped clamp; 3—fluoroplastic seal; 4—clamping nut; 5—holder; 6—pin.

2.3.4. Boundary Water Absorption

The percentage of boundary water absorption (W , %) was calculated using the weight method as the difference between dry (m_0 , g) and swollen (m_1 , g) samples:

$$W = \frac{m_1 - m_0}{m_1} \cdot 100, \quad (4)$$

2.3.5. Membrane Permeability

The permeability of the synthesized membranes was measured without applying external pressure, using the osmosis method [23]. For the study, a 4% sodium chloride solution was used. The coefficient of osmotic salt permeability (α_{NaCl} , mol/(m²·h)) and the coefficient of osmotic water permeability ($K_{\text{H}_2\text{O}}$, L/(m²·h)) were calculated using the formulae:

$$\alpha_{\text{NaCl}} = \frac{G}{S \cdot \tau \cdot C}, \quad (5)$$

$$K_{H_2O} = \frac{Q}{S \cdot \tau \cdot C'} \quad (6)$$

where G —amount of salt that passed through the studied membrane, mol;

Q —amount of water that passed through the studied membrane, L;

S —effective membrane area m^2 ;

τ —duration of the osmotic process, h;

C —concentration of the original salt solution, ($C_{NaCl} = 4\%$).

3. Results and Discussion

The proposed method of obtaining composite hydrogel membranes based on pHEMA-gr-PVP copolymers includes two stages (Scheme 1)—obtaining a hydrogel membrane (Figure 1a) and forming an ultra-thin polymer layer on its surface (Figure 1b). A PA-6/PVP modifying solution in formic acid was used to obtain the reinforcing layer. To obtain composite membranes, the method of forming a polyamide film on the water-containing surface of the hydrogel was used. Deposition of the reinforcing layer based on the PA-6/PVP solution happens in the presence of a water swollen hydrogel membrane-substrate. Deposition is carried out as a result of a decrease in the solubility of the PA-6/PVP mixture caused by the mixing of free water from the volume of the hydrogel with formic acid.

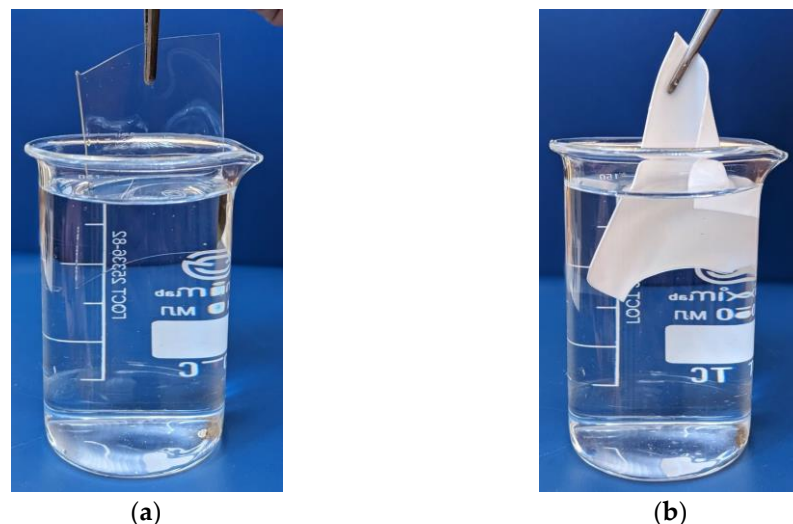


Figure 1. Hydrogel membrane-substrate based on pHEMA-gr-PVP copolymer (a) and hydrogel substrate with an applied ultra-thin reinforcing layer based on PA/PVP (b).

At the first stage of research, the formation conditions of the hydrogel substrate were established, namely—the water content in the original composition, the temperature regime of polymerization, as well as the hydration conditions of the obtained hydrogel films. The effect of the formulation of the original composition on the physico-mechanical properties of the obtained hydrogel films based on pHEMA-gr-PVP copolymers, which were used as substrates for the preparation of composite two-layer membranes, was established (Figure 2).

From the presented results, a clear regularity is observed—an increase in the content of polyvinylpyrrolidone in hydrogels is accompanied by an improvement in their elasticity and a deterioration in strength characteristics [31,48]. Previous studies have established that the effectiveness of polyvinylpyrrolidone grafting decreases with an increase in its content in the original composition [31,48]. Ungrafted PVP is washed out from the samples during their hydration, as a result of which the number of PVP chains that perceive the load decreases in the swollen polymer, which leads to a decrease in strength. At the same time, as a result of the leaching of ungrafted PVP, additional pores are formed, the presence of which facilitates conformational changes during sample deformation and, thus, the growth of relative elongation.

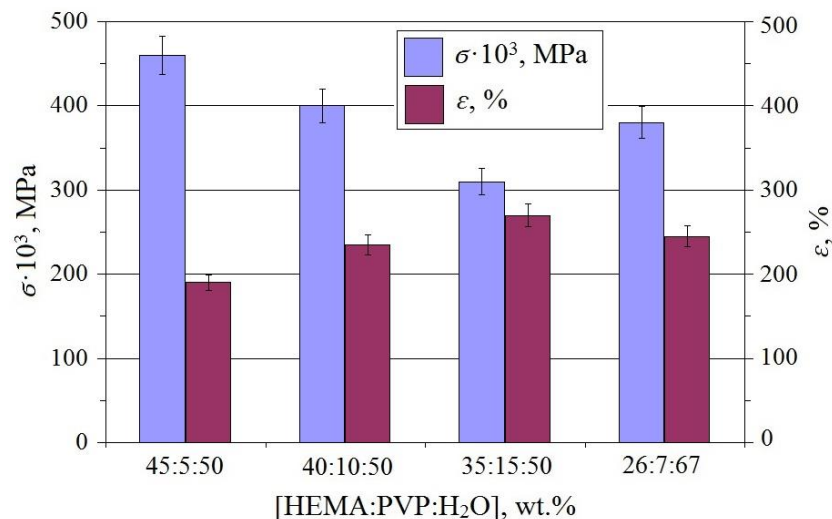


Figure 2. The effect of PMC formulation on the physico-mechanical properties of hydrogel membranes based on pHEMA-gr-PVP copolymers.

As can be seen (Figure 2), hydrogel film materials based on pHEMA-gr-PVP copolymers are characterized by insufficient strength characteristics, which significantly limit their suitability for the production of membranes, and their modification is required.

3.1. Study of the Adhesion of the Reinforcing Layer to the Hydrogel Substrate

When obtaining multilayer composite films, the main factor that affects their operational characteristics is adhesion between layers, which, of course, will depend on the technological parameters of the process of obtaining composites. In this case, the main factors affecting surface adsorption are the composition and thickness (δ , mm) of the hydrogel membrane substrate, the composition of the modifying solution, as well as the duration of the modification stage (τ_{mod} , min), i.e., the time the hydrogel substrate is kept in the modifying solution.

In the work, the adhesion strength of the reinforcing layer to the hydrogel substrate was estimated based on the study of the value of the specific amount of modifying film (A , kg/m²) on the surface of the hydrogel substrate.

First of all, the influence of the composition of the hydrogel substrate, in particular the content of PMC and water (solvent) in the original composition, on the specific amount of the modifying film was investigated (Figure 3). In Figure 3, the results of the study of a composite membrane with a hydrogel substrate (thickness $\delta = 0.5$ mm) are presented, for the synthesis of which PVP of $MM_{\text{PVP}} = 360 \times 10^3$ was used. A solution with the following characteristics was used as a modifying solution: (PA-6/PVP):FA = 7:93 wt.%; PA-6:PVP = 95:5 wt.%; $MM_{\text{PVP}} = 12 \times 10^3$; [FA] = 80 wt.%; $\tau_{\text{mod}} = 5$ min. It was found that with an increase in the amount of PMC in the hydrogel, the A value (with the same formulation of the modifying layer) increases, which is caused by intermolecular interactions and the resulting conformational changes that occur during saturation of the hydrogel surface with polyamide macromolecules.

At the same time, this is due to the fact that the part of the PVP that did not take part in the grafting reaction is washed out during hydration [31,48], which leads to the formation of additional pores that are filled with a modifying solution. However, an increase in the solvent content causes a decrease in the adhesion of the reinforcing layer to the hydrogel substrate and correspondingly, the reduction of A . The best value of the specific amount of modifying film has hydrogel films obtained on the basis of the original composition HEMA:PVP:H₂O = 48:12:40 wt.%. An increase in the amount of polyvinylpyrrolidone in the original composition negatively affects its technological properties (flowability and dosage deteriorate) and polymerization conditions (the time of PVP dissolution and air removal from the composition increases).

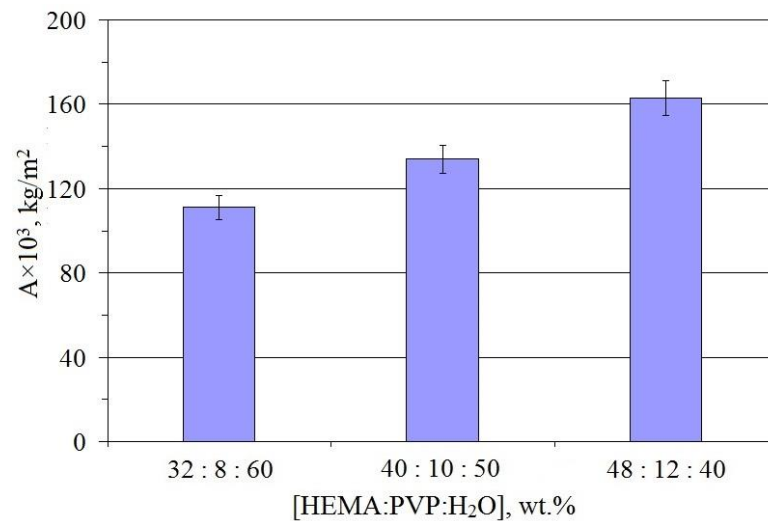


Figure 3. The effect of the HEMA:PVP:H₂O ratio in the hydrogel substrate on the value of the specific amount of the modifying film (A , kg/m²).

The connection of the reinforcing layer with the hydrogel substrate is ensured, mainly, due to the sorption of the modifying solution by the hydrogel pores. Therefore, it is natural that the adhesion of the reinforcing layer to the hydrogel substrate will depend on such a technological parameter of the process as the duration of the modification—the exposure time of the hydrogel substrate in the modifying solution (Figure 4). Composite membranes were studied, which consist of a hydrogel substrate based on the original composition HEMA:PVP:H₂O = 48:12:40 wt.% and a reinforcing layer, for the formation of which a modifying solution with a ratio of PA-6:PVP = 95:5 wt.% was used. According to the obtained results, an increase in the contact time of the hydrogel membrane substrate with the modifying solution causes an increase in the value of the specific amount of the modifying film. In particular, the influences of the thickness of the hydrogel substrate (Figure 4a), the concentration of the modifying solution (Figure 4b), the concentration of formic acid (Figure 4c) and the molecular weight of PVP (in PMC and the modifying solution) (Figure 4d) on A and its change over time were investigated. As can be seen (Figure 4a), with an increase in the thickness of the hydrogel layer, the value of the specific amount of modifying film slightly increases. The value of the specific amount of modifying film increases with an increase in the content of the PA-6/PVP mixture in the modifying solution (Figure 4b) and the concentration of HCOOH (Figure 4c). During the formation of the reinforcing layer on the hydrogel film, two processes take place—the deposition of the polyamide/PVP polymer mixture with water (the hydrogel substrate is in a swollen state) and the formation of physical intermolecular bonds between the polyamide and PVP of the deposited mixture and the functional groups of the pHEMA-gr-PVP copolymer of membrane substrate. It is obvious that increasing the content of the PA-6/PVP mixture in the modifying solution will contribute to the intensification of these processes. An increase in the concentration of HCOOH in the modifying solution may indicate the fact of a strong interaction of the acid, as a solvent, with polyamide, as a result of which the part of intermolecular interaction of PA-6 with PVP decreases, which affects the conformation of polyamide macromolecules. A decrease in the interaction of PA-6 with PVP causes the straightening of PA macromolecules and the strengthening of their interaction with the functional groups of the pHEMA-gr-PVP copolymer. In this case, water acts as a diluent of the solution and does not act as a co-solvent, weakening the acid solvation of polyamide macromolecules.

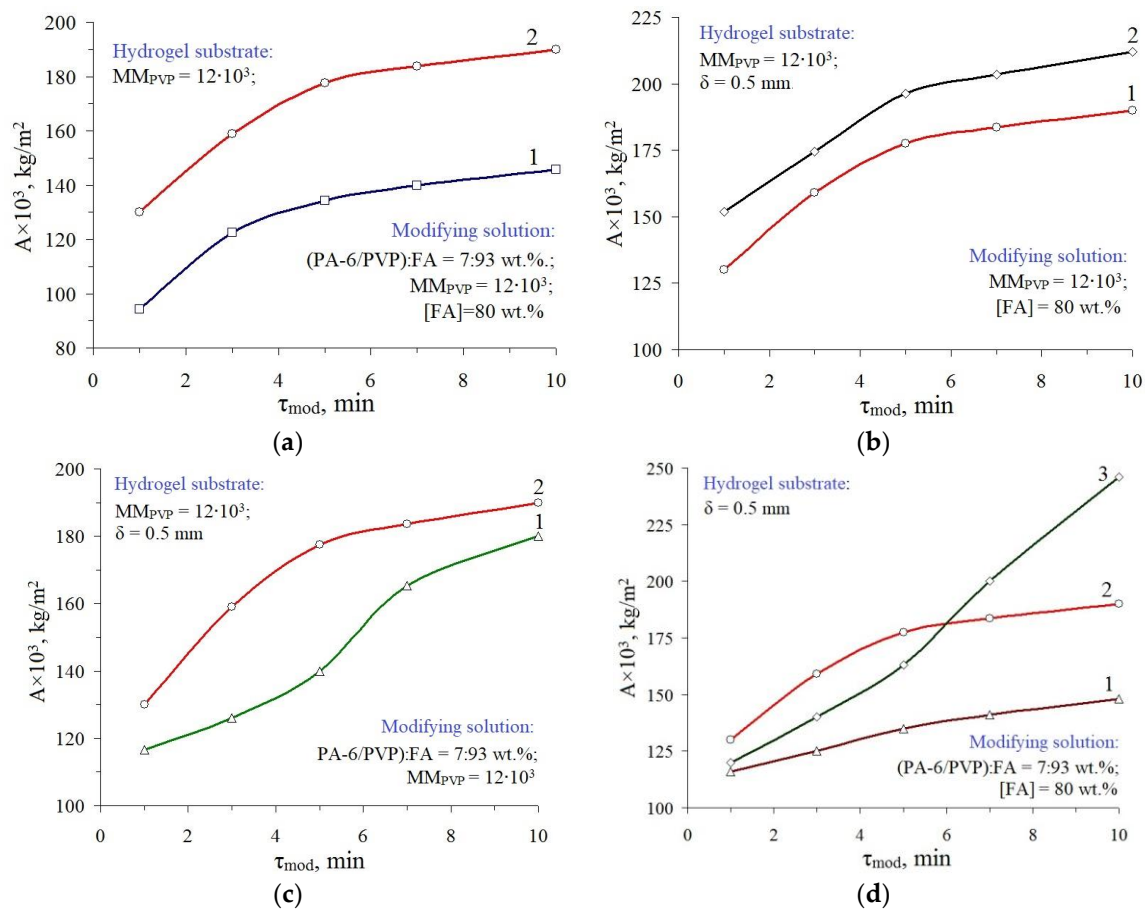


Figure 4. Change in the value of the specific amount of modifying film over time (A , kg/m^2) depending on the thickness of the hydrogel substrate (a), the concentration of the modifying solution (b), the concentration of formic acid (c) and the molecular weight of PVP (d); (a)— δ , mm: 1—0.35, 2—0.5; (b)—(PA-6/PVP):FA, wt.%; 1—7:93, 2—10:90; (c)—[FA], wt.%; 1—75, 2—80; (d)— MM_{PVP} , g/mol: Hydrogel substrate: 1, 2— 12×10^3 , 3— 360×10^3 ; modifying solution: 1— 360×10^3 , 2, 3— 12×10^3 .

A significant influence of the molecular weight of PVP on the value of the specific amount of modifying film was established. In particular, PVP of different molecular weights was used, both for obtaining a hydrogel substrate and in a modifying solution. The use in the original polymer–monomer composition of PVP with $\text{MM} = 360 \times 10^3$ contributes to the growth of A (Figure 4d, curve 3). In this case, the macrochains of the high-molecular-weight PVP loosen the polymer network (due to the grafting of polyHEMA to PVP and the formation of a polymer network with a lower cross-linking density), into the free space of which the formate solution of the PA-6/PVP polymer mixture diffuses. When using PVP with a lower molecular weight (12×10^3 g/mol) in a polymer–monomer composition, the value of the specific amount of modifying film is significantly lower (Figure 4d, curve 1). It is possible that the modifying solution penetrates into the surface layer of the hydrogel substrate in a smaller amount, forming a film on its surface. As the study results show, the adhesion of the layer based on PA-6/PVP is higher in composite membranes, for the reinforcement of which modifying solutions of PVP of lower molecular weight were used. At the same time, it can be noted that the modifying solution containing PVP with $\text{MM} = 12 \times 10^3$ g/mol diffuses into the hydrogel at a higher rate; however, the formation of a dense film based on PA-6/PVP reduces A (Figure 4d, curve 2).

On the basis of the analysis of the obtained experimental data, it is possible to present the dependence of the effect of the value of the specific amount of modifying film on the strength characteristics of the synthesized composite films, which were characterized by the ultimate tensile stress (Figure 5).

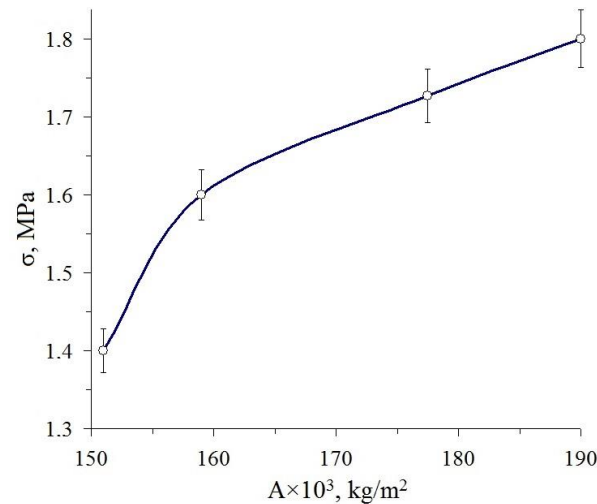


Figure 5. Dependence of break stress (σ , MPa) of composite hydrogel films on the value of a specific amount of modifying film (A , kg/m^3). Hydrogel substrate: HEMA:PVP:H₂O = 48:12:40 wt.%; $\text{MM}_{\text{PVP}} = 12 \times 10^3$; $\delta = 0.5$ mm. Modifying solution: (PA-6/PVP):FA = 7:93 wt.%; PA-6:PVP = 95:5 wt.%; $\text{MM}_{\text{PVP}} = 12 \times 10^3$; [FA] = 80 wt.%.

The increase in value of a specific amount of modifying film causes an increase in the strength of the obtained composite two-layer polyamide/hydrogel films, which confirms the formation of a dense, strong near-surface layer based on PA-6/PVP. The formation of such a layer is confirmed by the results of X-ray diffraction analysis of the obtained materials (Figure 6). The diffractogram of the hydrogel surface is characteristic of a completely amorphous material (Figure 6a), while the diffractogram of the modified surface (Figure 6b) shows reflections at angles $2\Theta = 12.2^\circ$; 19.8° ; 20.2° ; 24.6° , which are characteristic for the crystalline phase formed by polyamide [49], as well as the PA-6/PVP complex.

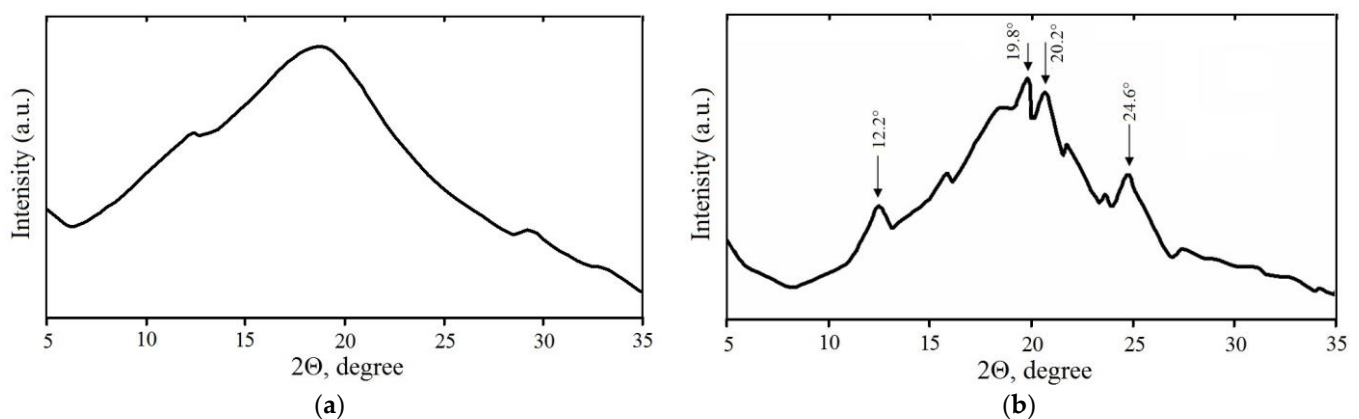


Figure 6. X-ray images of samples of hydrogel (a) and composite (b) membranes: (a)—hydrogel membrane: HEMA:PVP:H₂O = 48:12:40 wt.%; $\text{MM}_{\text{PVP}} = 12 \times 10^3$; $\delta = 0.5$ mm; (b)—composite membrane: hydrogel substrate: HEMA:PVP:H₂O = 48:12:40 wt.%; $\text{MM}_{\text{PVP}} = 12 \times 10^3$; $\delta = 0.5$ mm. Modifying solution: (PA-6/PVP):FA = 7:93 wt.%; PA-6:PVP = 95:5 wt.%; $\text{MM}_{\text{PVP}} = 12 \times 10^3$; [FA] = 80 wt.%; $\tau_{\text{mod}} = 1$ min.

3.2. Properties of Composite Two-Layer Polyamide/Hydrogel Membranes

3.2.1. Strength and Elasticity of Composite Membranes

One of the most important operational characteristics of polymer membranes is the physico-mechanical properties, which largely determine the areas of their use, as well as the operating conditions. The strength characteristics of the obtained two-layered films were characterized by the breaking stress (σ , MPa), elasticity—by the relative elongation at break (ε , %). Test samples were used in a swollen state.

It was found (Figure 4d) that increasing PVP content in the original composition and in the structure of the hydrogel substrate provides an increase in the value of the specific amount of modifying film. At the same time, an increase in the PVP content in the formulation of the copolymer of the hydrogel substrate causes a decrease in its mechanical strength and an increase in elasticity (Figure 2).

To establish the optimal content of the reinforcing layer, films were obtained from a modifying solution with the composition: PA-6:PVP = 95:5 wt.% with different concentrations of PA-6:PVP in formic acid (Figure 7).

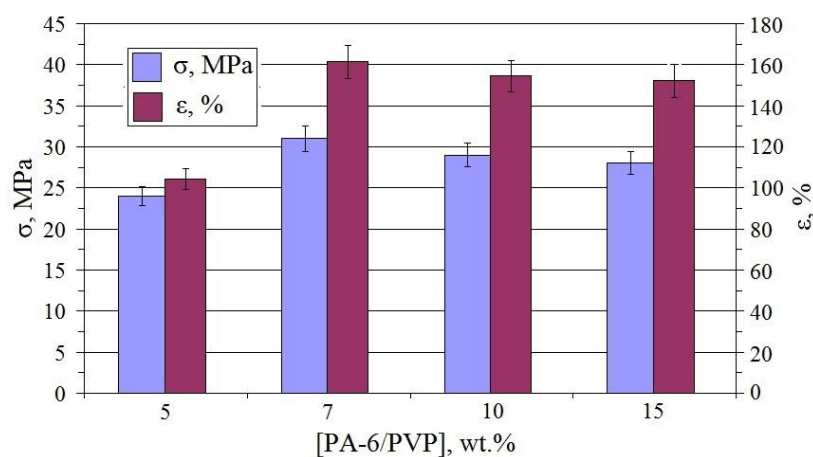


Figure 7. The effect of the concentration of PA-6/PVP mixture in formic acid on the physico-mechanical characteristics of PA-6/PVP films (PA-6:PVP = 95:5 wt.%; $MM_{PVP} = 12 \times 10^3$ g/mol; [FA] = 80 wt.%).

It was found that the properties of films based on the mixture of polyamide with PVP change in an extreme dependence depending on the content of the PA-6 mixture and PVP in the modifying solution. The maximum values of ultimate stress and relative elongation during break are characteristic of films obtained with a concentration of the polymer mixture [PA-6/PVP] = 7 wt.%. From the given composition of the modifying solution, the influence of the PMC formulation and the duration of modification on the strength characteristics of two-layer membranes was investigated (Figure 8).

The results presented in Figure 2 indicate a decrease in the strength of hydrogel films with an increase in the concentration of polyvinylpyrrolidone in the original composition. In the case of composite two-layer films, the influence of PVP content in the hydrogel substrate has an extreme character—the two-layer membranes with the formulation of PMC in the hydrogel substrate HEMA:PVP:H₂O = 48:12:40 wt.% are characterized by the highest break strength (Figure 8, curve 2). The strength of composite films increases with an increase in the contact time of the membrane substrate with the PA-6/PVP solution. These changes are associated with an increase in the value of the specific amount of modifying film on the surface layer of the hydrogel substrate (Figure 4) and an increase in the thickness of the reinforcing layer of higher strength due to the formation of intermolecular physical bonds.

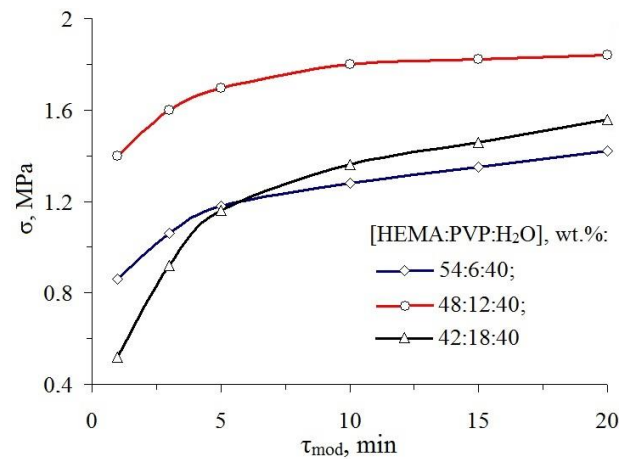


Figure 8. Dependence of the break stress (σ , MPa) of composite membranes on the PMC formulation and the exposure time (τ_{mod}) of the hydrogel in the modifying solution. Hydrogel substrate: $\text{MM}_{\text{PVP}} = 12 \times 10^3$ g/mol, $\delta = 0.5$ mm. Modifying solution: (PA-6/PVP):FA = 7:93 wt.%; PA-6:PVP = 95:5 wt.%; [FA] = 80 wt.%.

The dependence of the strength characteristics of two-layer films on the MM_{PVP} and the thickness of the membrane substrate was established.

As the results show (Figure 9), in the case of using PVP with $\text{MM} = 360 \times 10^3$ g/mol (sample 2) for the synthesis of a hydrogel substrate, the strength of two-layer films is higher, compared to films whose hydrogel substrate was obtained in the presence of PVP with $\text{MM} = 12 \times 10^3$ g/mol (sample 1). At the same time, the strength characteristics of composite membranes are affected by the different molecular weight of PVP, which is present in the modifying solution (samples 1 and 3).

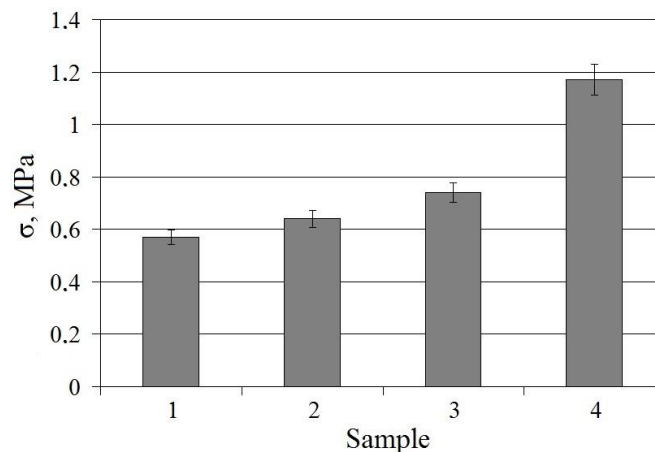


Figure 9. The effect of the molecular weight of PVP and the thickness of the hydrogel substrate on the strength of composite membranes. Hydrogel substrate: HEMA:PVP:H₂O = 48:12:40 wt.%; MM_{PVP} : 1— 12×10^3 , 2— 360×10^3 ; δ , mm: 1—0.5, 4—0.3. Modifying solution: (PA-6/PVP):FA = 7:93 wt.%; PA-6:PVP = 95:5 wt.%; MM_{PVP} , g/mol: 1, 2— 360×10^3 , 3, 4— 12×10^3 .

This can be explained by the fact that PVP with $\text{MM} = 360 \times 10^3$ g/mol in the hydrogel film contributes, as noted above, to the loosening of the polymer network, the free volume of which is filled with an interpolymer based on PVP with $\text{MM} = 12 \times 10^3$ g/mol with the formation of a rigid layer. With the use of PVP with $\text{MM} = 12 \times 10^3$ g/mol during the synthesis of the polymer matrix, the modifying solution penetrates into the volume of the hydrogel in a much smaller amount, forming, mainly, a film on the surface, the connection of which with the hydrogel substrate is much weaker, and therefore, its influence on the overall strength of the composite film is smaller. It was found that the strength of the

composite membranes during the same time of exposure to the hydrogel substrate in the modifying solution increases with a decrease in its thickness (Figure 9, samples 2 and 4), which indicates a greater contribution of the reinforcing layer to the overall strength of the composite membranes, especially when this layer is commensurate with the thickness of the hydrogel substrate.

3.2.2. Swelling Capacity and Osmotic Permeability of Composite Membranes

Important operational characteristics of hydrogel materials are their swelling in solvents. Copolymers pHEMA-gr-PVP are characterized by a relatively high ability to adsorb water and other solvents and high osmotic permeability for dissolved low molecular weight substances [31]. Therefore, an important task was to investigate how the presence of a reinforced layer on the surface of hydrogel films will affect these characteristics.

The swelling capacity of the obtained materials was characterized by their water content (W , %) (Figure 10). For research, composite membranes were used, which consist of a hydrogel substrate based on the original composition HEMA:PVP:H₂O = 48:12:40 wt.% and a reinforcing layer, for the formation of which a modifying solution was used with the ratio (PA-6/PVP):FA = 7:93 wt.% and PA-6:PVP = 95:5 wt.%. The research shows that an increase in the exposure time of hydrogel films in a modifying solution (Figure 10a) leads to a decrease in the water content of composite membranes. This occurs naturally since the sorption capacity of membranes depends on the volume of their pores. In this case, with an increase in the modification time of the hydrogel substrate, the amount of polyamide in the pores of the substrate layer, which is in contact with the modifying solution, proportionally increases.

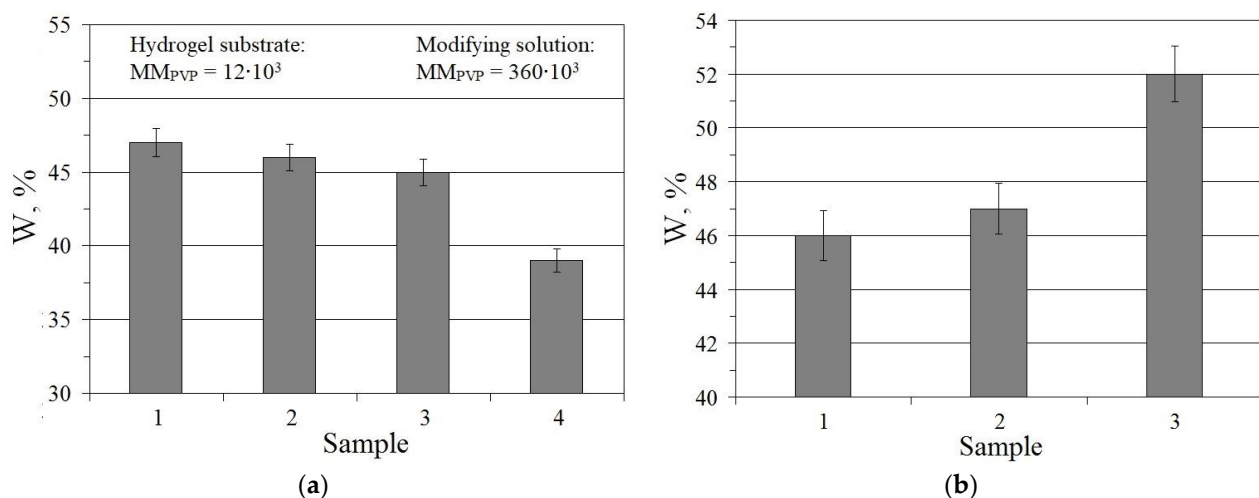


Figure 10. Dependence of water content (W , %) of composite membranes on modification time (a) and molecular weight of PVP (b). (a)— τ_{mod} , min: 1—1; 2—3; 3—5; 4—7; (b)— MM_{PVP} , g/mol: hydrogel substrate: 1— 12×10^3 , 2, 3— 360×10^3 ; modifying solution: 1, 2— 360×10^3 , 3— 12×10^3 .

Previous studies have established that together with an increase in the molecular weight of PVP, the swelling capacity of hydrogels based on pHEMA-gr-PVP copolymers increases as well [31]. This regularity is also characteristic of the obtained composite materials. As can be seen (Figure 10b), the composite films, the hydrogel substrate of which was obtained using PVP with $MM_{PVP} = 360 \times 10^3$ g/mol, are characterized by higher water content compared to the substrates obtained in the presence of PVP with $MM_{PVP} = 12 \times 10^3$ g/mol.

The permeability of the obtained two-layer films was characterized by the results of the study of the process of osmosis of a model substance (sodium chloride) from an aqueous solution. It was found that the osmotic permeability of the composite membranes deteriorates compared to the unmodified hydrogel substrate (Figure 11a). It happens

naturally that the decrease in osmotic permeability occurs with an increase in the content of the polyamide/PVP mixture in the modifying solution.

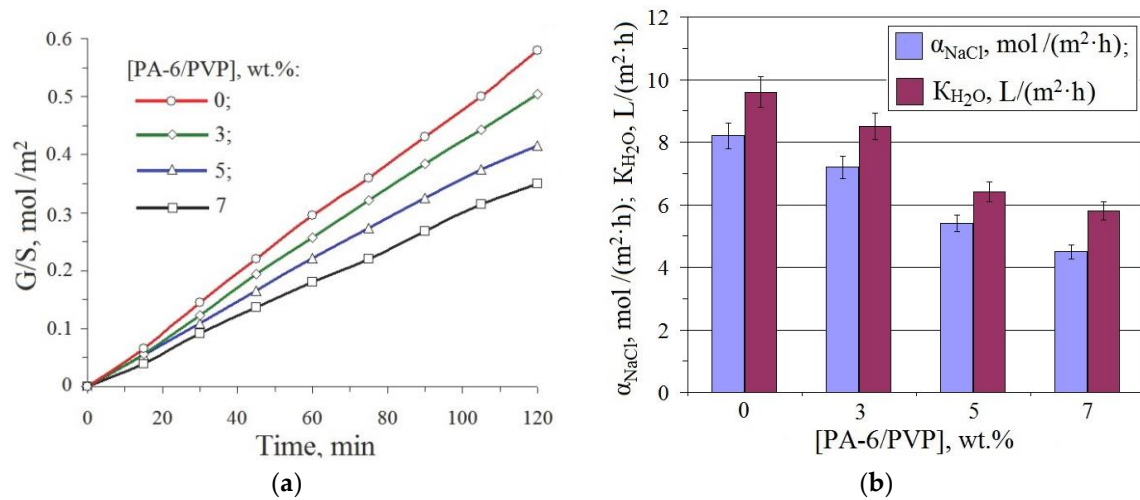


Figure 11. Dependence of osmotic salt permeability, G/S (a), salt permeability α_{NaCl} , and water permeability K_{H_2O} coefficients (b) of composite membranes on the concentrations of PA-6/PVP in the composition of the modifying solution. Hydrogel substrate: HEMA:PVP:H₂O = 48:12:40 wt.%; $MM_{PVP} = 360 \times 10^3$ g/mol; modifying solution: PA-6:PVP = 95:5 wt.%; [FA] = 80 wt.%; $MM_{PVP} = 12 \times 10^3$ g/mol; $\tau_{mod} = 5$ min.

This is a result of the fact that as the content of PA-6/PVP in the modifying solution increases, as mentioned in Section 3.1, a denser PA-6/PVP layer is formed on the hydrogel substrate. Naturally, with an increase in the content of polyvinylpyrrolidone in the composition of the hydrogel substrate, the osmotic salt permeability increases (Figure 11b).

As in the case of the effect on adhesion strength and physico-mechanical characteristics, the osmotic permeability of composite membranes is also affected by the molecular weight of PVP (Figure 12).

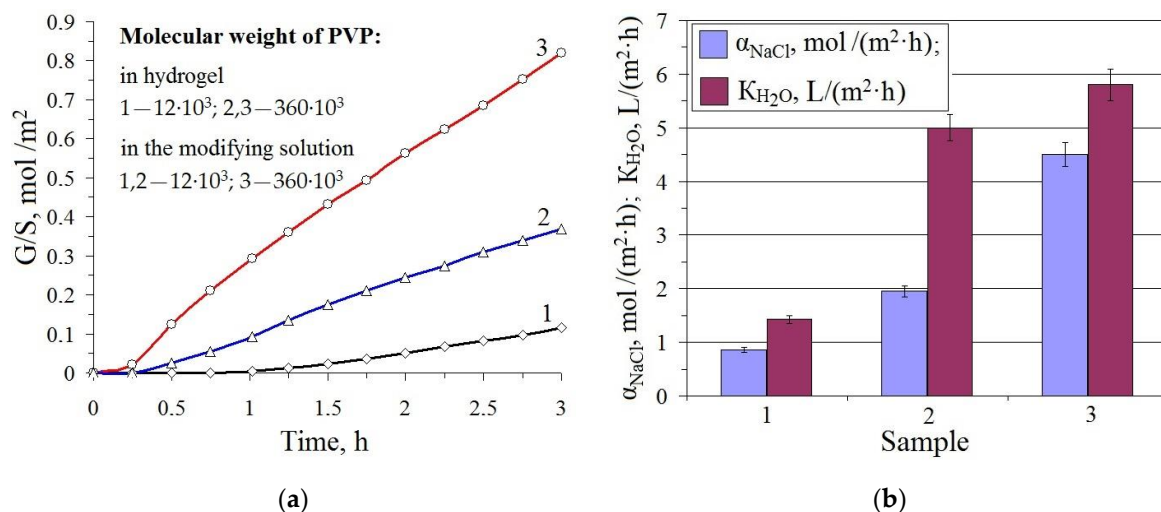


Figure 12. Dependence of osmotic salt permeability, G/S (a), salt permeability α_{NaCl} , and water permeability K_{H_2O} coefficients (b) of composite membranes on the molecular weight of PVP. Hydrogel substrate: HEMA:PVP:H₂O = 48:12:40 wt.%; modifying solution: (PA-6/PVP):FA = 7:93 wt.%; PA-6:PVP = 95:5 wt.%; [FA] = 80 wt.%; $\tau_{mod} = 5$ min.

It was found that the highest osmotic permeability and coefficients of salt and water permeability (Figure 12a) are characteristic of composite films when in a modifying solution PVP with $MM = 12 \times 10^3$ g/mol is used and in a hydrogel substrate PVP with $MM = 360 \times 10^3$ g/mol during the exposure time of the hydrogel substrate in the modifying solution $\tau_{\text{mod}} = 5$ min.

4. Conclusions

The regularities of the reinforcement of hydrogel films based on HEMA with PVP copolymers using the formation of a reinforcing layer on the basis of polyamide/PVP mixture on the surface of a swollen hydrogel film have been established.

The strength characteristics of composite two-layer membranes directly depend on the value of a specific amount of modifying film on the surface of hydrogel substrate, which mainly depends on the concentration and ratio of PA-6:PVP in the modifying solution, the concentration of HCOOH as a solvent, MM_{PVP} , both in the hydrogel substrate and in the modifying solution. The value of the specific amount of modifying film increases with an increase in the concentration of PA-6/PVP and the exposure time of the hydrogel substrate in the modifying solution in the instance of introducing into composition a polyvinylpyrrolidone with $MM = 360 \times 10^3$ g/mol.

It was established that the strength of composite membranes can be adjusted within wide limits by using polyvinylpyrrolidone with different molecular weights. The use of PVP with $MM_{\text{PVP}} = 12 \times 10^3$ g/mol in the modifying solution and PVP with a molecular weight of $MM_{\text{PVP}} = 360 \times 10^3$ g/mol in the membrane substrate ensures improvement of the sorption of the modifying solution by the hydrogel membrane substrate, the formation of a dense surface strengthening layer on it, and formation of a composite membrane with increased strength, water content, and salt permeability.

The dependences of the osmotic salt and water permeability of the obtained composite membranes on their formulation and conditions of formation were established, and it was shown that the osmotic salt and water permeability slightly decrease compared to the original hydrogels.

The obtained results indicate that the formation of a PA-6/PVP reinforcing layer on the surface of hydrogel films by the deposition method from solutions is an effective method of creating composite hydrogel materials, which allows us to consider this technology as promising for the creation of special-purpose membranes.

Author Contributions: Conceptualization, N.B., O.G., E.S. and L.D.; methodology, N.B., O.G. and L.D.; software, O.G.; validation, N.B., O.G., E.S. and L.D.; formal analysis, O.G., L.D. and E.S.; investigation, N.B. and L.D.; resources, O.G. and L.D.; data curation, O.G. and E.S.; writing—original draft preparation, N.B., O.G., E.S. and L.D.; writing—review and editing, N.B., O.G., E.S. and L.D.; visualization, O.G. and L.D.; supervision, O.G., L.D. and E.S.; project administration, O.G., L.D. and E.S.; funding acquisition, E.S. and L.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by project APVV-21-0418 granted by The Ministry of Education, Science, Research and Sport of the Slovak Republic.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to privacy.

Acknowledgments: The emergence of this article was supported by the project APVV-21-0418.

Conflicts of Interest: The authors declare no conflicts of interest.

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