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## THE ROLE OF THE MOLECULAR WEIGHT OF POLYVINYLPIRROLIDONE IN THE FORMATION OF TWO-LAYER POLYAMIDE/HYDROGEL MEMBRANES OF INCREASED STRENGTH

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The article presents the results of a study of the influence of the molecular weight of polyvinylpyrrolidone on the properties of two-layer hydrogel/polycapraamide membranes. Composite membranes are obtained by the developed method, which consists in the formation of hydrogel membranes with subsequent deposition from a solution into their outer surface of a reinforcing layer based on polyamide modified with polyvinylpyrrolidone. It was established that the molecular weight of polyvinylpyrrolidone, both in the composition of the hydrogel membrane and in the modifying solution, has a significant effect on the interaction between the layers of composite membranes and their characteristics, such as water content, bursting strength, and osmotic salt permeability.

**Key words:** two-layer membranes; molecular weight; hydrogel; 2-hydroxyethyl methacrylate; polyvinylpyrrolidone; polyamide.

### Introduction

Due to the three-dimensional network structure and unique properties, polymer hydrogels are currently the subject of extensive research and have revealed high potential in the field of medicine, therapy and diagnostics [1]. Hydrogels are promising materials that play an important role in the biomedical industry [2–9]. Hydrogels are materials that consist of a three-dimensional network of hydrophilic homopolymers or copolymers. These polymers interact with each other and form an internally insoluble polymer matrix. Hydrogels have the ability to absorb a significant amount of water or biological fluids [1]. However, along with their advantages, polymer hydrogels also have their limitations in use and disadvantages that require further attention and study. One of the main disadvantages of hydrogel membranes is their low mechanical strength. In order to improve the strength characteristics, polymer hydrogels are modified by creating composite materials based on them [10].

The authors [11] developed polymer composite membranes by forming a thin reinforcing layer on a hydrogel membrane-substrate by deposition of thermoplastic polymers from a solution, followed by evaporation of the solvent. Hydrogels based on copolymers of 2-hydroxyethyl methacrylate (HEMA) with polyvinylpyrrolidone (PVP) were used as polymeric substrate membranes. Aliphatic polyamide (PA-6) and polyvinylpyrrolidone dissolved in a mixture of formic acid and water were used to form a thin reinforcing layer [12]. The formation of composite membranes with optimal characteristics requires the establishment and study of factors affecting the structure and properties of composites. The influence of the composition of the initial polymer-monomer composition and the modifying solution, the thickness of the hydrogel substrate and the reinforcing layer, and technological parameters on the strength characteristics of two-layer membranes has been studied. At the same time, it is known [13] that the physicomaterial, thermophysical, and

chemical characteristics of polymers are greatly influenced by their molecular weight. In particular, the mechanical strength depends on the bond breaking energy and the degree of intermacromolecular interactions, which mainly depend on the molecular weight of the polymer.

**The aim of the study** was to study the influence of the molecular weight of polyvinylpyrrolidone on the properties of two-layer polyamide/hydrogel membranes.

### Materials and research methods

To obtain two-layer composite membranes, we used: 2-hydroxyethyl methacrylate (Sigma Chemical Co), purified and distilled in a vacuum (residual pressure 130 N/m<sup>2</sup>, T<sub>boil</sub>=351K), polyvinylpyrrolidone (PVP) with MM 12·10<sup>3</sup> g/mol (medical, of high purity) and 360·10<sup>3</sup> g/mol ("Pharm" qualification) before use, dried at 338 K in a vacuum for 2–3 hours, potassium persulfate, distilled water, polyamide (PA-6), formic acid (marking "h", C<sub>HCOOH</sub> = 80 wt.%.)

The formation of two-layer composite membranes was carried out according to the developed two-stage method [14], which consists in obtaining a hydrogel membrane-substrate based on HEMA and PVP copolymers, followed by its modification with an ultra-thin layer of PA-6/PVP mixture.

The amount of surface adsorption (A, kg/m<sup>2</sup>) and physical and mechanical properties (bursting strength (σ, MPa) and percentage elongation at

bursting (ε, %)) of the synthesized membranes were determined according to the methods [15]. To determine the water content (W, %), the weight method [16] was used, which consists in measuring the difference in the mass of dry and final samples. Membrane permeability was measured using sodium chloride as an example using the osmosis method [17].

### Results and discussion

In order to obtain composite membranes with improved properties, the influence of the molecular weight of PVP, both in the hydrogel substrate and in the modifying solution, on the amount of surface adsorption, strength characteristics, water content, and osmotic permeability of two-layer film products was studied.

In the Table 1 presents the results of the study of the amount of surface adsorption of hydrogel films from the time of modification. It was established that an increase in the exposure time of the hydrogel film in the modification solution leads to an increase in adsorption. At the same time, with an increase in the thickness of the hydrogel layer, a certain increase in the amount of surface adsorption is observed. This is explained by the fact that PVP macromolecules loosen the polymer network, occupying a larger volume of free space, which is filled with a modifying solution of the polymer mixture with PA-6/PVP.

Table 1

#### Dependence of the amount of adsorption of modified hydrogel films on the time of modification

HEMA:PVP:H<sub>2</sub>O = 48:12:40 wt.%; (PA-6/PVP): HCOOH = 7:93 wt.%;

PA-6:PVP = 95:5 wt%; MM PVP = 12·10<sup>3</sup> g/mol

No.	δ*, mm	Adsorption, A·10 <sup>3</sup> , kg/m <sup>2</sup>				
		Time of modification, min.				
		1	3	5	7	10
1	0,35	95	136	134	140	146
2	0,5	130	150	155	157	179

δ\* – hydrogel substrate thickness.

As the research results showed, the molecular weight of PVP in the initial polymer-monomer composition has a significant effect on the amount of adsorption of composite membranes. The results of the study of the amount of adsorption in the case of

using PVP with a molecular weight of 12·10<sup>3</sup> and 360·10<sup>3</sup> g/mol are presented in Fig. 1. As we can see, increasing the length of time the hydrogel film remains in the modifying solution leads to an increase in the amount of adsorption of the polycapromide

layer with a hydrogel substrate, which, at the same time, depends on the molecular weight of the PVP. It should be noted that the introduction of PVP with a molecular weight of  $360 \cdot 10^3$  g/mol into the hydrogel substrate leads to an increase in the amount of adsorption (Fig. 1, sample 3). Probably, this may be the result of the loosening of the PVP macromolecules of the polymer network, which have enough free space to be filled with the modifying solution of the PA-6/PVP-based polymer mixture. At the same time, the use of low-molecular-weight PVP for obtaining a hydrogel substrate is the reason for a lower adsorption value (Fig. 1, samples 1, 2). This can be explained by the fact that the modifying solution based on PA-6/PVP penetrates the surface layer in a smaller amount, forming a dense thin film on the surface. A similar dependence is observed in the case of use for the modification of PVP with a molecular weight of  $360 \cdot 10^3$  g/mol (Fig. 1, sample 1). It was established that the use of PVP with a molecular weight of  $12 \cdot 10^3$  g/mol in the modifying solution leads to a greater adsorption of two-layer polyamide hydrogel membranes, compared to the use of a solution with PVP of a molecular weight of  $360 \cdot 10^3$  g/mol. The modifying solution with a PVP molecular weight of  $12 \cdot 10^3$  g/mol penetrates the hydrogel faster, forming a dense film of a mixture of polyamide-6 and PVP on its surface, which actually stops adsorption (Fig. 1, sample 2). The reason for this is the smaller free volume in the structure of the hydrogel matrix formed in the presence of PVP with a molecular weight of  $12 \cdot 10^3$  g/mol. In this way, the modifying solution with lower viscosity penetrates more easily into the pores of the surface layer of the hydrogel substrate. It should also be noted that during the diffusion of the solution, two processes occur: 1) the mixture based on PA-6 and PVP settles in the water contained in the hydrogel; 2) the formation of physical intermolecular bonds between the chains of the HEMA-PVP network of the hydrogel matrix and the polymers of the precipitating mixture.

The influence of the duration of contact of the hydrogel substrate with the modifying solution and its concentration on the strength of the composite two-layer membranes was studied (Fig. 2). From the obtained results, it can be seen that with an increase in the holding time of the hydrogel in the modifying solution, the tension during the bursting increases. At the same time, the strength of composite membranes depends on the concentration of PA-6/PVP in the modifying solution.

With an increase in the concentration of PA-6/PVP, a significant increase in stress during bursting is observed (Fig. 2, curves 1–3). It was established that the minimum value of stress during bursting is observed at a concentration of PA-6/PVP of 3 wt.% in the solution (Fig. 2, curve 1), and the maximum is at a concentration of 7 wt. % (Fig. 2, curve 3).

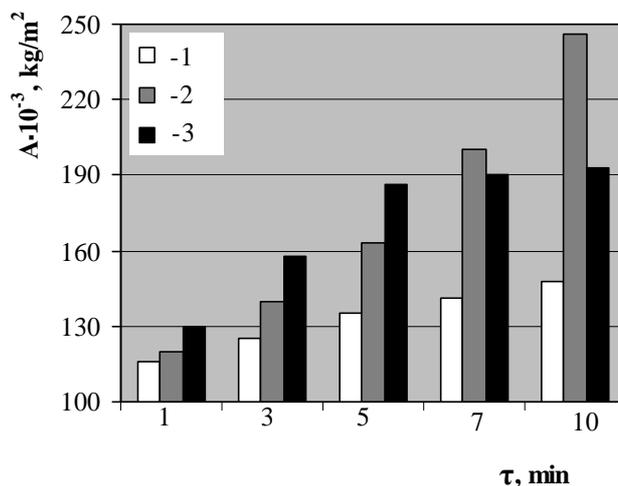


Fig. 1. Dependence of the value of surface adsorption (*A*) of the PA-6/PVP complex on the modification time of hydrogel films: Hydrogel: HEMA:PVP:H<sub>2</sub>O = 48:12:40 wt. % MM<sub>PVP</sub>: 1, 2 – 12·10<sup>3</sup> g/mol, 3 – 360·10<sup>3</sup> g/mol. Solution: (PA-6/PVP): HCOOH = 7:93 wt. %; PA-6:PVP = 95:5 wt. %, MM<sub>PVP</sub>: 1 – 360·10<sup>3</sup> g/mol, 2,3 – 12·10<sup>3</sup> g/mol, δ = 0.5 mm

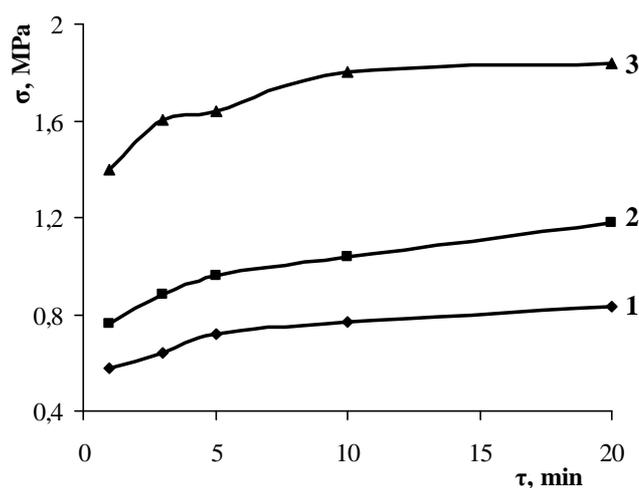


Fig. 2. Dependence of stress during bursting (*σ*, MPa) of composite membranes on the duration of stay of the hydrogel substrate in the modifying solution: MM<sub>PVP</sub> = 12·10<sup>3</sup> g/mol, δ = 0.5 mm. Hydrogel: HEMA:PVP:H<sub>2</sub>O = 48:12:40 wt. %. Solution: C<sub>PA-6/PVP</sub>, wt. %: 1 – 3; 2 – 5; 3 – 7; PA-6: PVP = 95:5 wt. %

The results of the study of the physical and mechanical properties of two-layer membranes with different MM PVP are shown in Fig. 3 and Table 2. As can be seen from the obtained results, the strength of the composite films increases with an increase in the exposure time of the hydrogel substrate in the modifying solution. At the same time, there is a decrease in the elongation rate during bursting (Fig. 3). This regularity is explained by the increase in the amount of adsorption in the near-surface layer of the hydrogel, which causes the formation of a deposited film of greater thickness.

It was established that in the case of using PVP with  $MM = 360 \cdot 10^3$  g/mol for the synthesis of a hydrogel substrate and PVP with  $MM = 12 \cdot 10^3$  g/mol for obtaining a modifying solution, the strength of the synthesized two-layer membranes is the highest. At the same time, in the case of using PVP with  $MM = 12 \cdot 10^3$  g/mol in the hydrogel substrate and PVP with  $MM = 360 \cdot 10^3$  g/mol in the modifying solution, the strength is somewhat lower. The use of high molecular weight PVP to obtain a hydrogel substrate helps to loosen the polymer matrix. This free volume is filled with an interpolymer material based on PVP with a low molecular weight ( $12 \cdot 10^3$  g/mol), forming a reinforcing layer. In the case of using PVP with a low molecular weight

during the synthesis of the polymer matrix, the modifying solution penetrates into the hydrogel in a limited amount, forming a film on the surface as much as possible. The connection between this film and the hydrogel substrate is weak, so its influence on the overall strength of the composite film is significantly less.

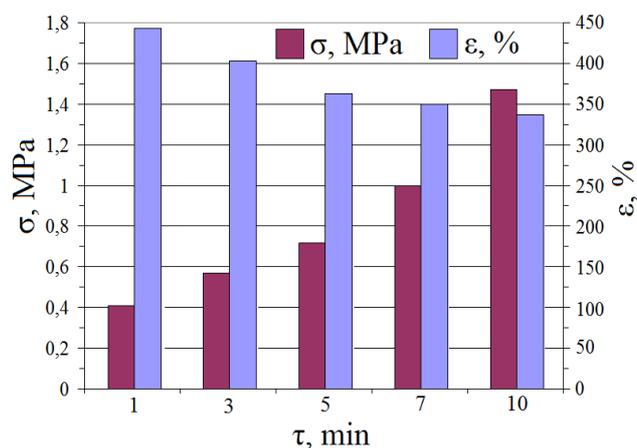


Fig. 3. The influence of the time of formation of composite films on stress ( $\sigma$ , MPa) and elongation ( $\epsilon$ , %) during the bursting of the obtained membranes: Hydrogel: HEMA:PVP:H<sub>2</sub>O=48:12:40 wt. %,  $MM_{PVP} = 12 \cdot 10^3$  g/mol. Solution: (PA-6/PVP):HCOOH = 7:93 wt. %, PA-6:PVP= 95:5 wt. %,  $MM_{PVP} = 360 \cdot 10^3$  g/mol,  $\delta = 0.5$  mm

Table 2

### Influence of the molecular weight of polyvinylpyrrolidone on the strength of two-layer membranes during bursting

(Hydrogel, wt. %: HEMA:PVP:H<sub>2</sub>O= 48:12:40. Solution, wt. %: (PA-6/PVP):HCOOH = 7:93, PA-6:PVP, wt. % = 95:5,  $\delta = 0.5$  mm)

No.	MM PVP in hydrogel	MM PVP in a modifying solution	Bursting strength, MPa
1	$12 \cdot 10^3$	$360 \cdot 10^3$	0.57
2	$360 \cdot 10^3$	$360 \cdot 10^3$	0.64
3	$360 \cdot 10^3$	$12 \cdot 10^3$	0.74

We also added the amount of hydrogel ball and PVP molecular weight to the water content composite membranes. It has been established that the membranes, which can be found in hydrogel pads PVP with  $MM 360 \cdot 10^3$  g/mol, are characterized by higher water content, lower membranes, which contain low molecular weight PVP. It is also possible to respect that a change in the composition of the hydrogel ball leads to a change in the water content of the composite membranes (Fig. 4).

In addition to the ability to absorb water, the ability of membranes to diffuse medicinal substances and salt solutions is an important characteristic of them, especially for medical applications. According to the method proposed by Karelin [17], the permeability of double-layer membranes for salt solutions was investigated using the osmosis method without applying external pressure. The osmotic permeability of the synthesized membranes was studied depending on the exposure time of the

hydrogel film in the modifying solution and the molecular weight of PVP. The results of measuring the osmotic salt permeability of composite two-layer membranes are presented in Figs. 5 and 6. According to the research results, it was found that with the increase in the duration of the osmotic process, an increase in the osmotic salt permeability is observed in all cases.

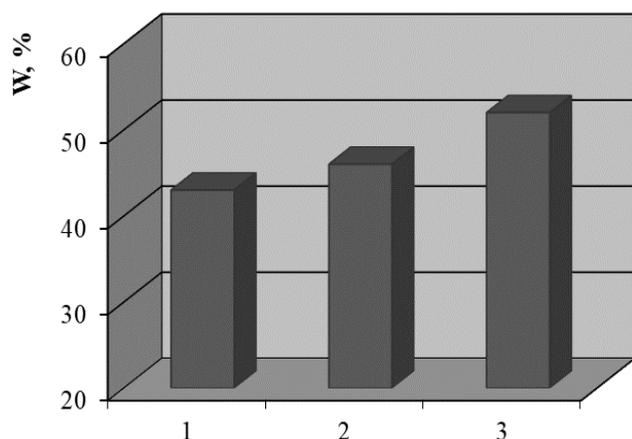


Fig. 4. Influence of the thickness of hydrogel films ( $\delta$ , mm) on the water content (W, %) composite membranes:

Hydrogel: HEMA:PVP:H<sub>2</sub>O = 48:12:40 wt. %;  $\delta$ , mm: 1 – 0.25; 2, 3 – 0.5;

MM PVP, g/mol: 1, 3 –  $360 \cdot 10^3$ , 2 –  $12 \cdot 10^3$ .

Solution: (PA-6/PVP): HCOOH = 7:93 wt. %, PA-6:PVP = 95:5 wt. %,

MM<sub>PVP</sub>, g/mol: 1, 3 –  $12 \cdot 10^3$ ; 2 –  $360 \cdot 10^3$ ,  $\tau_{mod.} = 3$  min

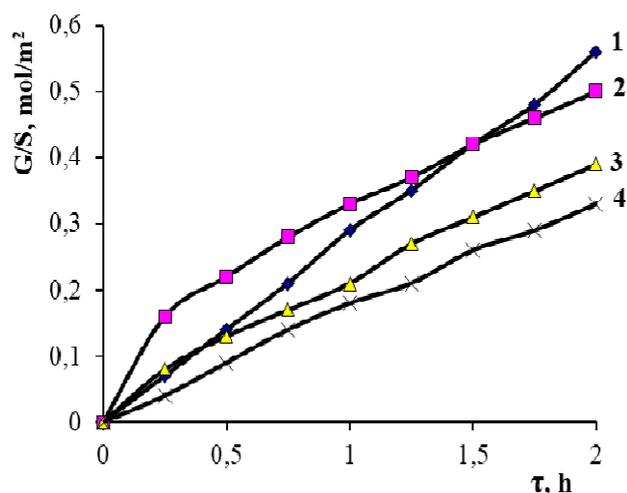


Fig. 5. Kinetics of osmotic salt permeability (G/S, mol/m<sup>2</sup>) of composite hydrogel membranes for sodium chloride: (MM<sub>PVP</sub> =  $12 \cdot 10^3$  g/mol; C<sub>NaCl</sub> = 4 wt. %;  $\delta = 0.5$  mm)

Hydrogel: HEMA:PVP:H<sub>2</sub>O = 48:12:40 wt. %.

Solution: (PA-6/PVP): HCOOH, wt. %: 1 – hydrogel film unmodified, 2 – 3:97; 3 – 5:95; 4 – 7:93.

PA-6:PVP = 95:5 wt. %.

Research has established that increasing the concentration of PA-6/PVP in the modifying solution leads to a slight decrease in osmotic salt permeability (Fig. 5). The formation of a denser film based on the PA-6/PVP complex slightly reduces the salt permeability, but this does not limit the possibilities of using the synthesized membranes.

The results of studies of the influence of MM PVP on the osmotic permeability of synthesized two-layer membranes (Fig. 6) showed that the highest values of salt permeability are observed for composite films obtained on the basis of hydrogel substrates synthesized in the presence of high molecular weight PVP and a modifying solution containing PVP with MM  $12 \cdot 10^3$  g/mol (Fig. 6, curve 1).

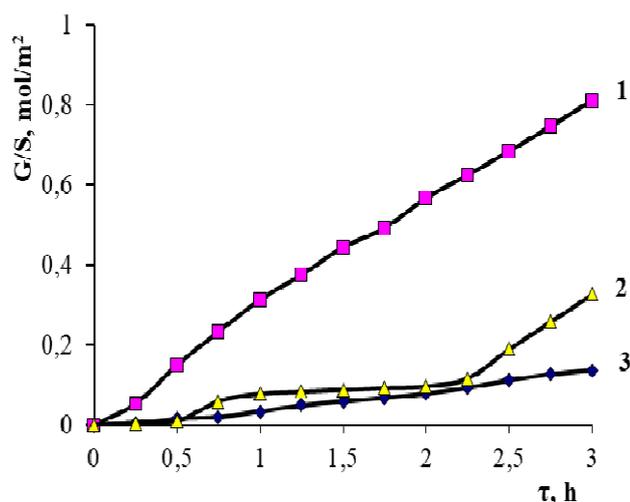


Fig. 6. The effect of MM<sub>PVP</sub> on the kinetics of osmotic salt permeability (G/S, mol/m<sup>2</sup>) of composite hydrogel-polycapraamide membranes:

Hydrogel: HEMA: PVP: H<sub>2</sub>O=48:12:40 wt. %, MM<sub>PVP</sub>, g/mol: 1,2 –  $360 \cdot 10^3$ ; 3 –  $12 \cdot 10^3$ .

Solution: (PA-6/PVP):HCOOH = 7:93 wt. %, PA-6:PVP=95:5 wt. %, MM<sub>PVP</sub>, g/mol: 1 –  $12 \cdot 10^3$ ;

2, 3 –  $360 \cdot 10^3$ ,  $\tau_{mod.} = 5$  min

The lowest values of salt permeability of composite films are observed in the case of using low molecular weight PVP for the synthesis of the hydrogel substrate, and PVP with MM  $360 \cdot 10^3$  g/mol for the preparation of the modifying solution (Fig. 6, curve 3).

## Conclusions

The influence of the molecular weight of polyvinylpyrrolidone on the properties of two-layer hydrogel/polycaproyamide membranes was investigated. As a result of research, it was established that the molecular weight of PVP, both in the original polymer-monomer composition and in the modifying PA-6/PVP solution, has a significant effect on the interaction between the layers of composite membranes and their characteristics, such as water content, bursting strength, osmotic salt permeability. It has been confirmed that the obtained composite two-layer membranes using PVP with a molecular weight of  $360 \cdot 10^3$  g/mol in the hydrogel substrate and PVP with a MM of  $12 \cdot 10^3$  g/mol in the reinforcing layer with PA-6/PVP have better strength and sorption properties and possess sufficiently high osmotic permeability.

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## **РОЛЬ МОЛЕКУЛЯРНОЇ МАСИ ПОЛІВІНІЛПІРОЛІДОНУ У ФОРМУВАННІ ДВОШАРОВИХ ПОЛІАМІД/ГІДРОГЕЛЕВИХ МЕМБРАН ПІДВИЩЕНОЇ МІЦНОСТІ**

Наведено результати дослідження впливу молекулярної маси полівінілпіролідону на властивості двошарових гідрогель/полікапроамідних мембран. Композиційні мембрани одержано розробленим методом, який полягає у формуванні гідрогелевих мембран з подальшим осадженням з розчину в їх зовнішню поверхню зміцнювального шару на основі поліаміду, модифікованого полівінілпіролідом. Встановлено, що молекулярна маса полівінілпіролідону, як у складі гідрогелевої мембрани, так і в модифікувальному розчині, істотно впливає на взаємодію між шарами композиційних мембран та їх характеристики, такі як водовміст, міцність під час проривання, осмотичну солепроникність.

**Ключові слова:** двошарові мембрани; молекулярна маса; гідрогель; 2-гідроксіетилметакрилат; полівінілпіролідон; поліамід.