

FORMATION AND PROPERTIES OF HYDROGEL MEMBRANES BASED ON CROSS-LINKED COPOLYMERS OF METHACRYLATES AND WATER-SOLUBLE POLYMERS

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Abstract

Experimental results concerning the effect of composition, nature of polymeric matrix, monomer and solvent on the structure, physico-mechanical and selective-transport characteristics of hydrogel membranes based on cross-linked grafted copolymers of methacrylates and water-soluble polymers (polyvinylpyrrolidone, polyvinyl alcohol) have been presented. Methods of high-penetrating hydrogel membranes formation have been developed and capability of directional control of their structure and operational characteristics has been determined.

Keywords: hydrogels, methacrylates, polyvinylpyrrolidone, polyvinyl alcohol, permeability

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Introduction

Cross-linked grafted copolymers of methacrylates and functionally active polymers, polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA) in particular, are widely used in medicine due to their valuable properties. The main area of application is production of contact lenses, biologically compatible implants, membranous drugs, membranes for biological compounds concentration and purification, systems of drug release, etc. [1,2]. Such materials form polymeric hydrogels after water sorption. It is well-known that hydrogel properties are determined by the chemical structure and structural parameters of their net. Therefore, in this paper we have investigated the effect of composition and formation conditions on the structure and properties of cross-linked hydrogel membranes based on PVP and PVA copolymers with methacrylates.

Materials and methods

Synthesis of hydrogel membranes and study of their compositions were carried out in accordance with previously developed procedure [3]. 2-Hydroxyethyl methacrylate (HEMA; Bisomer) and glycidyl methacrylate (GMA; Mitsubishi Rayon Co. Ltd) were used as monomers. Both HEMA and GMA were purified and distilled under vacuum: residual pressures were 130 and 520 N/m² and boiling temperatures were 78 and 69°C, respectively. High-purified PVP (AppliChem GmbH) with molecular weight of 10 · 10³ and PVA (Gohsenol) with acetate groups content 0.8-2.0% were used as polymeric matrices. Polymerization was initiated by potassium persulphate and isopropylbenzene hydroperoxide.

Hydrogel membranes were obtained by combining the membrane formation stage and composition polymerization stage in the solution of one or more solvents (mostly in water) or by hardening the composition in the formed membranous net after solvent evaporation. Before the experiments membranes were hydrated in water until the equilibrium state was achieved.

Structural parameters of the polymeric net in hydrated state were estimated by means of the molecular weight of macrochain section (M_n) between neighboring cross-linking nodes determined using module of high elasticity.

The molecular weight of chain section between neighboring cross-linking nodes was calculated by the following formula [4]:

$$M_n = \frac{L^5 \rho_p v_s}{0,5 - \mu}$$

where:

L – coefficient of linear swelling;

ρ_p – polymer density, kg/m³;

v_s – molar volume of the solvent, m³·kg⁻¹·mol⁻¹;

μ – parameter of polymer-liquid interaction

$$\mu = 0,5 - \frac{v_s \sigma_\infty L^4}{RT(\lambda^2 - \lambda^{-1})}$$

σ_∞ – equilibrium tension, kgf/m²

$$\lambda = 1 + \varepsilon, \quad 0 < \varepsilon < 0,3,$$

ε – equilibrium tension strain.

Sorption characteristics of obtained hydrogel membranes were determined using a gravimetric method. Mechanical properties were determined using a break method, by means of specially constructed device “Kimura Machinery” of 050/RT-6010 type, according to the procedure presented in [5]. This device allows to carry out investigations in aqueous medium. Diffusive permeability of synthesized membranes for water and model substance soluble in it (sodium chloride) without external pressure is determined using laboratory osmometer according to the procedure suggested by Karelin [6]. Effectiveness and inhibitory action for salt aqueous solutions at ultrafiltration were determined using FM-02 laboratory plant, being pressurized by air supplied from a compressor. The change of salt concentration in the solution was estimated by filtrate conductivity using P577 measuring bridge with platinum reference electrodes.

Membrane effectiveness by filtrate (J , m³·m⁻²·h⁻¹) at ultrafiltration is determined by the following formula [7]:

$$J = \frac{\Delta Q}{S \cdot \Delta \tau}$$

where ΔQ is volume (m³) of filtrate penetrating through the membrane with area S (m²) for time τ (h).

Inhibitory action for salts (R_z) is calculated by the following formula:

$$R_z = \frac{C_0 - C_f}{C_0} \cdot 100\%$$

where C_0 , C_f are salt concentrations in the initial solution and filtrate, respectively, mol/l.

Results and discussion

Investigations of physico-mechanical properties of synthesized hydrogel membranes show that the presence of PVA in their structure, when copolymer (PVA-HEMA) contains regularly allocated hydroxyl groups of high-molecular fragments and alkoxy branching, considerably improves deformation-strength characteristics (strength and elasticity increase, TABLE 1) compared with membranes, where hydroxyl groups of high-molecular fragments are changed

for pyrrolidone cycles with ionogenic groups ($-NCO$) of PVP macromolecules, as well as with known polyHEMA membranes [8] only with alkyl branching. The high mechanical strength of membranes based on PVA is caused, to our mind, by intermolecular interaction inside polymeric matrix due to hydrogen bonds between regularly allocated hydroxyl groups [9].

During membranes synthesis the change of water part for dimethylsulphoxide (DMSO) increases internodal molecular weight of hydrogel net which should increase their permeability. At the same time hydrogels' mechanical properties do not change (0.45 and 0.49 MPa, TABLE 1). Thus, introducing aprotic DMSO into the initial composition we can directionally regulate the structural parameters of hydrogel net and change penetrability of the membrane on its basis in the necessary direction.

Membranes based on PVA-PVP-HEMA combined polymeric matrix are characterized by less net density (higher M_n) compared with those based on polyHEMA [8] and PVA-HEMA (TABLE 1). However, mechanical strength of these membranes is relatively low (0.4-0.5 MPa), which essentially constricts possibilities of their application in baromembrane processes. The increase of PVP content, as well as the decrease of HEMA concentration in membranes based on PVA-PVP-HEMA combined polymeric matrix, result in the decrease of their mechanical strength (TABLE 1, pos. 2, 4) though the molecular weight of internodal fragment is the same.

In order to increase the mechanical strength of hydrogel membranes we investigated the possibility of introducing GMA, soluble in DMSO, into the initial composition. It has been established that GMA introduction (TABLE 1, pos. 6) slightly decreases the net density and increases mechanical characteristics twice.

Investigations confirm that the nature of polymeric matrix and initial monomer have an essential effect on the structural parameters of hydrogel net (M_n) (TABLE 1). However, for all PVA-containing membranes water content is approximately the same (TABLE 2).

We have established that permeability of synthesized hydrogel membranes during the processes without external pressure (osmosis) does not depend directly upon material water content and net structural parameters, i.e. the increase of water content and internodal molecular weight do not cause the identical increase of coefficients of water- (K) and salt-osmotic (α) permeability (TABLE 2). Apparently, in such a case conformational transformations and polarization of copolymer functional groups with appearance of a surface charge play the important role. The membranes based on PVA-PVP-HEMA combined polymeric matrix are characterized by higher osmotic water permeability compared with those based on PVA-HEMA and especially with membranes based on polyHEMA (TABLE 2).

It is known that in membranous processes the factors favorable to hydrogel polymeric net opening stimulate the decrease of strength on the one hand and the increase of water content with corresponding increase of hydrogel membranes effectiveness on the other hand [9]. We have established that in filtration processes synthesized membranes effectiveness increases with the increase of applied external pressure. Therefore for investigations of transport-selective characteristics in ultrafiltration processes we have chosen membranes with the structure ensuring regular and gradual change of effectiveness upon the pressure within the range from 0 to 2 kgf/cm².

The effect of pressure on the hydrogel membranes effectiveness by distilled water has been examined. For all membranes based on PVA and PVP the increase of applied pressure causes the increase of effectiveness by water.

TABLE 1. Physico-mechanical properties of hydrogel membranes in hydrated state.

No	Composition of forming solution, wt. parts				M_n , kg/mol	Tensile strength, σ_t , MPa	Relative elongation at rupture, ϵ_r , %
			HEMA	H ₂ O			
1.	–	30	30	200	15	10,5	500
2.	25	5	30	200	175	0,29	281
3.	25	10	30	200	180	0,45	390
4.	30	15	15	200	185	0,21	260
5.	25	10	30	200 DMSO	195	0,49	295
6.	25	10	15+15 GMA	100 + 100 DMSO	146	0,87	510

M_n is molecular weight of net internodal fragment

TABLE 2. Sorption-diffusive characteristics of hydrogel membranes (thickness 30 μ m).

No	Composition of forming solution, wt. parts				Water content, W, %	Coefficient of permeability	
	PVA	PVP	HEMA	H ₂ O		by water $K \cdot 10^4$, m ³ ·m ⁻² ·h ⁻¹	by NaCl α , mol·m ⁻² ·h ⁻¹
1.	30	–	30	200	84	52	404
2.	5	25	30	200	75	150	320
3.	10	25	30	200	80	280	320
4.	15	30	15	200	81	280	437
5.	–	–	100	100	40	5	80

Moreover, if under small pressures (0.2-0.6 kgf/cm²) there is minimum dependence of effectiveness upon pressure, the pressure differential more than 0.6 kgf/cm² leads to the exponential increase of effectiveness (FIG. 1). Apparently, the optimum orientation of polymeric chains in the direction of pressure effect with the formation of a channel type structure with a minimum resistance to a liquid flow takes place.

The effect of mixture structure on the membranes permeability has been established. In particular, at ultrafiltration processes the change of water part for DMSO under low pressures (till 1 kgf/cm²) also increases the effectiveness of synthesized hydrogel membranes (FIG. 1).

The results of investigations concerning the effect of the mixture structure upon hydrogel membranes effectiveness by water confirm the possibility of their application as ultrafiltration membranes. Moreover, the change of a solvent composition allows to change their effectiveness under ultrafiltration pressures higher than 0.6 kgf/cm². We may conclude that membranes based on combined matrix PVA and PVP are sufficiently strong, they can withstand the pressure differential till 2 kgf/cm² and may be used in baromembranous separation processes from aqueous solutions.

The transport-selective characteristics of synthesized hydrogel membranes have been investigated in ultrafiltration processes of model substances – electrolytes of different nature: NaCl, CaCl₂ and Na₂SO₄. Transport properties of synthesized hydrogel membranes have a complicated character. Their high elasticity does not prevent ultrafiltration: at the pressure differential prior to 0.2 kgf/cm², the process is not accompanied by deformation of membranes porous structure and their effectiveness by water increases with the increase of applied pressure (FIG. 2).

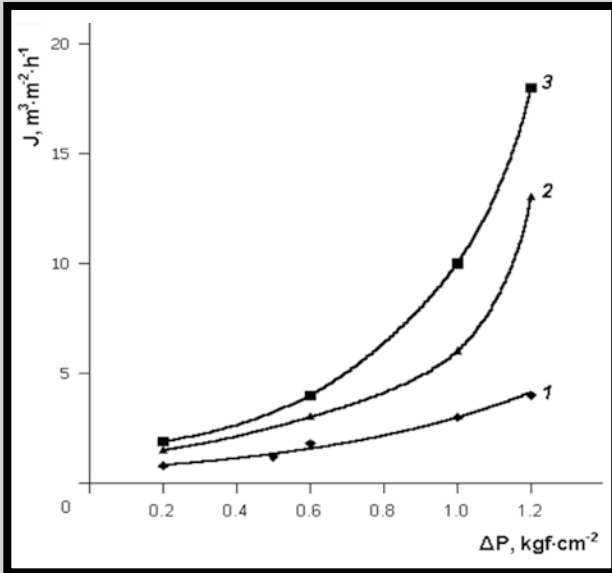


FIG. 1. Dependence of hydrogel membranes effectiveness by water (J) upon pressure differential (ΔP) ($\delta = 30 \mu\text{m}$).
 Composition of forming solution, wt. parts:
 1 – PVA:PVP:HEMA:H₂O = 10:25:30:200;
 2 – PVA:PVP:HEMA:GMA:H₂O:DMSO = 10:25:15:15:100:100;
 3 – PVA:PVP:HEMA:DMSO = 10:25:30:200.

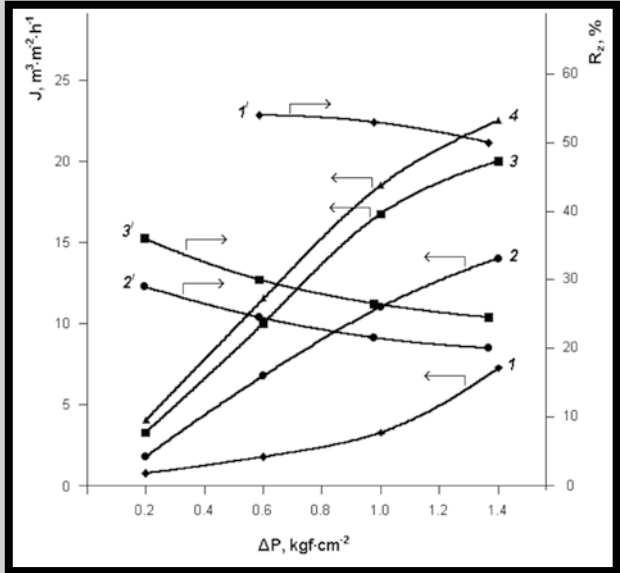


FIG. 2. Dependence of effectiveness by filtrate (J) and inhibitory action (R_z) upon pressure differential (ΔP) at ultrafiltration of salt solutions for hydrogel membranes based on PVA-HEMA ($\delta = 30 \mu\text{m}$).
 $C_{\text{salt}} = 0,1 \text{ mol/l}$; 1, 1' – Na₂SO₄; 2, 2' – NaCl; 3, 3' – CaCl₂; 4 – H₂O.

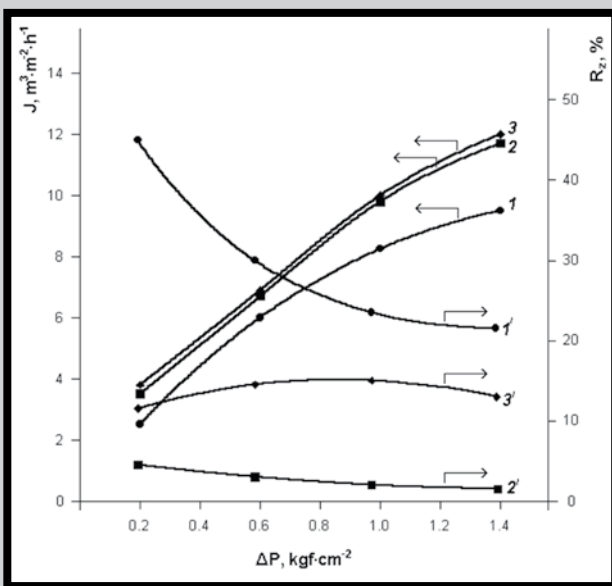


FIG. 3. Dependence of effectiveness by filtrate (J) and inhibitory action (R_z) upon pressure differential (ΔP) at ultrafiltration of salt solutions for hydrogel membranes based on PVA-PVP-HEMA ($\delta = 30 \mu\text{m}$).
 $C_{\text{salt}} = 0,1 \text{ mol/l}$; 1, 1' – NaCl; 2, 2' – CaCl₂; 3, 3' – Na₂SO₄.

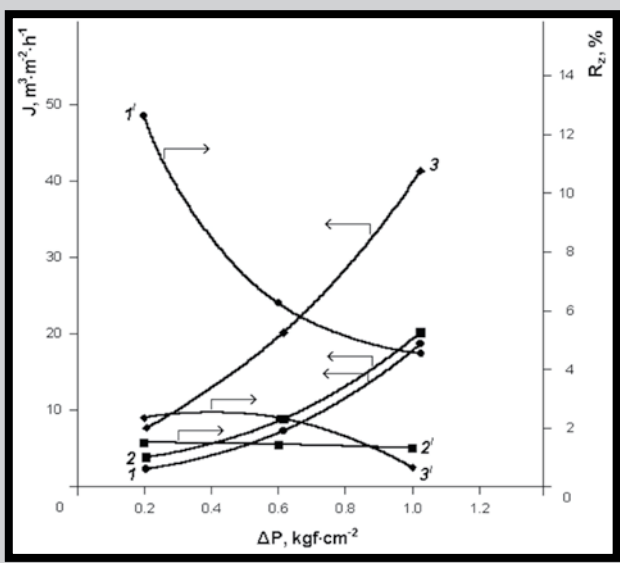


FIG. 4. Dependence of effectiveness by filtrate (J) and inhibitory action (R_z) upon pressure differential (ΔP) at ultrafiltration of salt solutions for hydrogel membranes based on PVA-PVP-HEMA-GMA ($\delta = 30 \mu\text{m}$).
 $C_{\text{salt}} = 0,1 \text{ mol/l}$; 1, 1' – NaCl; 2, 2' – CaCl₂; 3, 3' – Na₂SO₄.

At the same time there is a specific property of synthesized hydrogel membranes - the inhibitory action takes place at ultrafiltration of low-molecular substance solutions (FIG. 2). This fact contradicts to some extent with structural-steric concepts taking into account the ratio between ion and molecule sizes and structural parameters of polymeric matrix net (M_n), as well as high values of water content of synthesized hydrogels.

Transport and inhibit mechanisms depend upon hydrogel chemical nature. Thus, effectiveness of hydroxyl-containing hydrogel membrane based on PVA-HEMA at ultrafiltration of sodium sulphate decreases in 2-3 times compared with the transport of calcium and sodium chlorides. Such membrane has a higher inhibitory action for sodium sulphate and less selectivity for chlorides. Moreover, the selectivity is approximately the same for all chlorides, regardless of cation size (FIG. 2). We may assume that in such a case the values of ion charge and ion polarization activity are of great importance. At the same time, at ultrafiltration the effectiveness of both chlorides is practically the same.

Ultrafiltration characteristics of hydrogel membranes with a combined polymeric matrix, when PVP macromolecules containing –NCO group were introduced into a hydroxyl-containing matrix, differ from membranes characteristics based on PVA-HEMA. The effectiveness of membranes based on PVA-PVP-HEMA decreases compared with that of PVA-HEMA membranes. Moreover, the effectiveness is practically the same within the range of pressure differential prior to 1.5 kgf/cm² (FIG. 3). On the contrary, the inhibitory action of such membranes considerably increases. With the following increase of pressure differential it decreases from 40 to 20% (FIG. 3). Obviously, it is connected with a gel compacting due to the chains conformational changes under pressure.

The introduction of GMA hydrophobic fragments into the copolymer with the combined polymeric matrix (PVA-PVP-HEMA-GMA) (FIG. 4) determines the essential decrease of effectiveness for both chlorides. Moreover, the effectiveness related to sodium sulphate is the same as that for membranes based on PVA-PVP-HEMA. Selectivity related to sodium chloride at small pressure differential ($R_z = 50\%$ at 0.2 kgf/cm²) slightly increases and inhibitory action by sodium sulphate decreases, especially with the increase of pressure ($R_z = 2.5\%$ at 1 kgf/cm²).

Conclusions

It has been established that nature of polymeric matrix (PVP, PVA or their mixture), which is a structural element of hydrogel and which ensures mechanical properties of the obtained material, is the determinative factor affecting the diffusive characteristics of hydrogel membranes. Macromolecule segments in the internodal space of three-dimensional net possess active functional groups (–OH, –AlkOH, –NCO), which surely affect the diffusion of polar compounds through them.

The obtained results show that diffusive-transport characteristics of investigated hydrogel membranes are defined not only by their water content but by the structure of polymeric matrix (first of all by the chemical structure of polymeric net fragments) as well. This fact offers the challenge for controlled synthesis of biologically compatible hydrogel membranes with high permeability depending upon their practical application.

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