

Nanocomposite Membranes with pH- and Thermo-sensitive Function

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Recent researches and development in the field of membrane science are focused on improvement of synthetic membranes' functionality. Combination of soft polymer pH- and temperature-sensitive hydrogels with rigid ultrafiltration membrane attracts much interest as a new class of smart functional systems. In this research we develop pH- and temperature-sensitive composite membranes using radical copolymerization method and study their properties depending on hydrogel composition, nature of synthetic membranes, temperature and pH of external medium.

Keywords: Membrane, Hydrogel, Swelling, pH-, Thermo-sensitivity, Phase transition.

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1. INTRODUCTION

The so-called "smart" systems that tend to copy functioning of living organisms and natural formations responding to environmental factors by changing their physico-chemical surface characteristics, i.e. sorbability, swelling ability, permeability, surface activity and selectivity, optical characteristics are in the focus of attention of investigators. Ionic strength, illumination ability, change of electrical and magnetic fields are outer factors that experimentally influence the above-mentioned systems [1]. Nevertheless, the most common living nature factors, environmental pH and temperature changes in particular, play leading role in engineering and study of "smart" polymer systems.

Polymer hydrogels with pH- and thermo-responsive functions are of primary importance in biomedical investigations connected with the development of pharmaceuticals characterized by prolonged action and targeted delivery for molecular separation (cut-off), controlling enzyme activity and development of materials for biocompatibility improvement [2-3]. Application of such hydrogels in physico-chemical processes associated with pressure and other thermodynamic parameters changes is restricted by the gel structure instability. Transport through swollen hydrogels by means of convective flow becomes possible only when the gel is stabilized in nanoporous substrate and retains its integrity [4]. Therefore, combination of pH- and thermo-responsive hydrogel properties with structural and mechanical merits of polymer membranes opens unique ways for the development of stable "smart" polymer systems with numerous promising fields of application.

The aim of the present work is to study combination of the functions of manufactured ultra-filtration membranes with pH- and thermo-responsive hydrogels, as well as study of working parameters of the obtained nanocomposite systems.

2. MATERIALS AND METHODS

Manufactured ultrafiltration polyvinylidene fluoride (PVF) (UV 150-T) membranes with cut-off 150 kDa of Microdyn Nadir production (Germany) were used for

modification.

Since PVF membranes are chemically stable, the modification was carried out by accomplished hydrogel formation in membrane pores using radical polymerization. N-isopropylacrylamide (NiPAA) and allylaminehydrochloride (AAM) were chosen for this process. N,N-methylenebisacrylamide (MBA) as a cross-linking agent and components of the redox initiating system of ammonium persulphate (PSA) and tetramethylenediamine (TMED) were used without prior purification.

Components of gel-forming composition were homogenized on the ultrasound bath for 2 min, cooled to 0°C followed by 2 min argon bubbling through the specified composition. Then the composition was triply passed in vacuum through manufactured ultrafiltration membranes and placed in gauge between two flat-parallel glass plates for 1 hour to accomplish polymerization. Prepared composite membranes were multiply washed in excess of distilled water. Concentration of cross-linked polymer in hydrogel was 21% (mass), concentration of a cross-linking agent constituted 0.13% (mass) and the ratio of NiPAA and AAM in the composition was equal to 9:1 (mass).

Equilibrium swelling ratio was found by the following formula: $Q = (m_s - m_d) / m_d$, where m_s and m_d is mass of an equally swollen and dried sample, respectively. Results of 10 parallel measurements were averaged in the process of calculation. Study of the swelling degree of copolymer hydrogels was carried out at pH 1.69; 6.86; and 9.18 in the temperature range from 5 to 54°C.

Membrane separation characteristics were studied by dead-end ultra-filtration stirred cell Amicon 8050 (Millipore, USA)

0.01% water solution bull insulin with molecular mass of 6.0 kDa were used in order to find retention coefficient (R%) of the prepared membranes.

3. RESULTS AND DISCUSSION

Sensitive properties of specific components of pH- and thermo-sensitive hydrogels are due to informational restructuring of macromolecular chains resulted from changes in the ratios of hydrophilic – hydrophobic interactions both of polymer chains themselves and

those of solvent molecules.

Synthetic weak acidic or weak basic polyelectrolytes are widely used for this purpose, whose chain conformation depends on dissociation degree of ionogenic groups [5].

Poly-N-isopropylacrylamide (PiPAA) is one of the most wide-spread thermo-sensitive polymers. Slight temperature changes at about critical value (32°C for PiPAA) result in reverse phase transition due to folding and unfolding of polymer macromolecules. At temperatures higher than critical, part of hydrophobic interactions of chains increases and polymer solubility decreases. If temperature is lower than critical polymer-solvent interactions are prevailing leading to polymer hydrophilization and its transition in a soluble form [6].

Hydrogel swelling coefficient is an important parameter determining quantity of a solvent in hydrogelequilibrium state and is the function of polymer network structure, cross-linking degree, hydrophily and functional group dissociation degree, that, in turn, depends on temperature, ionic strength and media pH.

NiPAA-based homopolymers swelling coefficient is almost non-dependent on media pH. NiPAA copolymerization with various monomers allows purposefully change swelling curves character and phase transition temperature (T_p) of polymer hydrogels. Thus, addition of hydrophilic chains results in T_p growth, while that of hydrophobic ones in its decrease [7].

As is seen from Fig.1, phase transition temperature for the polymer containing 10% of allylaminehydrochloride constitutes 35-37°C, a little bit higher value than that for PiPAA homopolymer. Allylamine is a monomer containing hydrophilic amino-groups, therefore its introduction into the synthesized mixture in the quantity of 10% (mass) causes rise in phase transition temperature. Nevertheless, as it can see from differential swelling curves, pH influence on the speed of the system response to temperature changes is considerable, thus it can be stated that hydrogel structure depends both on temperature and pH of the environment.

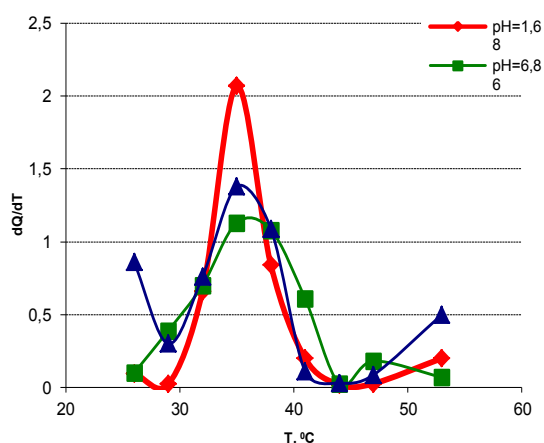


Fig. 1 – Differential temperature dependence of hydrogel swelling degree based on NiPAAm (9:1);

Among membrane main transport characteristics are their productivity and selectivity. As is known from Gagen-Pausel equation, voluminous flow through membrane is inversely proportional to solution viscosi-

ty, hence with the rise of temperature the membrane productivity grows linearly, while its selectivity remains almost unchanged. Separation (cut-off) and transportation characteristics of the obtained PVF-PiPAA-AAm membranes are given in Fig.2 and Fig 3.

Obtained membranes also demonstrate thermo- and pH-sensitivity, but pH- and temperature dependences of voluminous flow values and retention coefficient differ substantially. Changes of differential and integral curves of the voluminous flow at various pH (Fig.2) show that the membranes demonstrate phase transition at 35°C. Here pH influences both speed of the system response on temperature change and temperature interval itself. In acidic and neutral pH, differential curves peaks are at 35° C and 37° C, respectively.

The prepared membranes show the quickest response to temperature changes in acidic medium, while the slowest response is observed in neutral one due to the decrease of swelling degree of amino-containing hydrogels at pH increase.

Fig.2 shows that at temperature lower than that of phase transition, voluminous flow does not practically depend on temperature in neutral and acidic pH contradicting Gagen-Pausel equation. The above-mentioned fact means that in this case membrane transport properties are determined by hydrogel structure and are not influenced by the morphology of PVF membrane. Classical increase of the voluminous flow value with the temperature growth is observed at pH 9.5 when hydrogel has the lowest swelling degree.

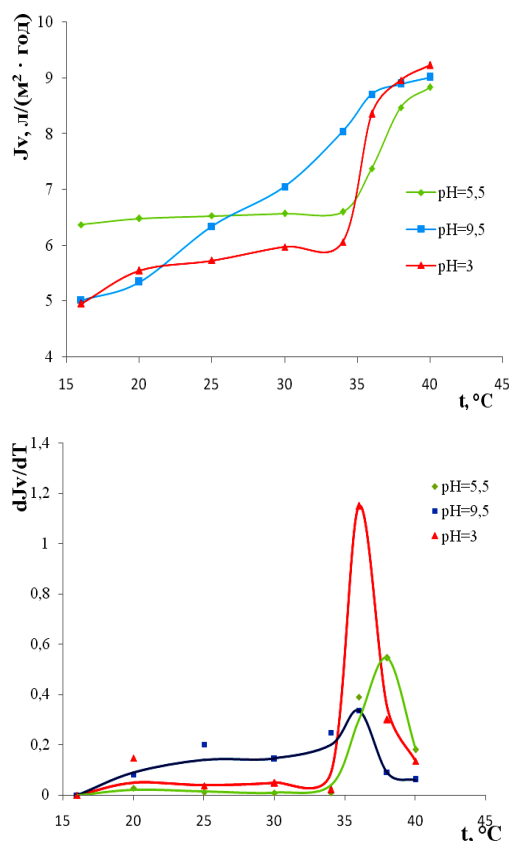


Fig. 2 – Integral (1) and differential (2) dependences on water flux (J_v) of PVF-nanocomposite membrane versus temperature and pH

The obtained membranes are characterized by high retention coefficient that is pH- and temperature function, as well (fig3).

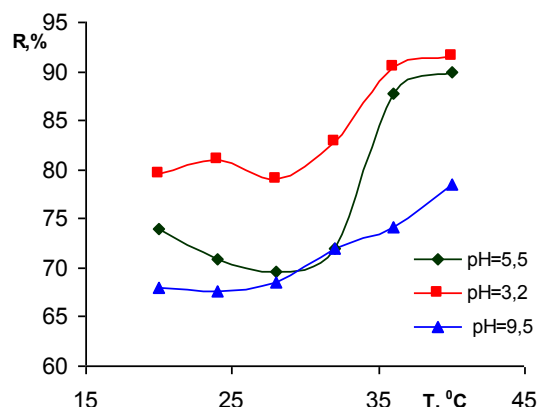


Fig. 3 – Retention coefficient of insulin for PVF-nanocomposite membrane versus temperature and pH.

The highest retention coefficient is characteristic for the membrane at acidic pH due to ionization of hydrogel amino groups. When pH value changes from 3.0 to 9.5, retention coefficient decreases by 25-40% depending on temperature. It is worth mentioning that insulin retention coefficient increases with the increase of temperature and growth of voluminous flow at temperatures higher than that of phase transition. At neutral pH, retention coefficient increase at the expense of phase transition is from 70 to 87%, while for acidic pH this value constitutes from 80 to 95%. This can be explained by the peculiarities of the formation of compo-

site hydrogel polymer membranes with different surface nature initiating mixture of monomers does not get in the membrane porous space and hydrogel is formed on its surface in the process of hydrogel formation on hydrophobic polyvinylidene fluoride membranes. Hydrogel membrane formed in this case is a prototype of dynamic membrane, with its own structure and does not depend on porous structure of carrier membrane. Thus, hydrogel structure is thickened due to phase transition resulting on retention coefficient increase.

4. CONCLUSIONS

Nanocomposite membranes were formed with the help of hydrogel immobilization in polyvinylidene fluoride manufactured ultra-filtration membranes

PiPAA and AAm (9:1)-based hydrogels have been synthesized using radically initiated copolymerization. Hydrogel temperature dependence of hydrogel swelling degree in pH range of 1.68 to 9.18 was studied, and temperature of phase transitions found to be equal to 35-37°C.

The membrane transport characteristic has been investigated. It was found that at neutral and acidic pH up to T_p , transport properties of modified membrane are determined by hydrogel structure and do not depend on membrane morphology. Membrane productivity and retention coefficient increase by 15-20% presumably due to thickening of hydrogel membrane porous structure.

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