Development of the Forming Technology of Combined Membranes Based on Hydrogel and Polycaproamide

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Abstract – The technology of forming of composite polymer membranes by modifying the surface of hydrogels thru thin layer of polymer has been developed. The physical, mechanical properties and surface adsorption of composite membranes are determined. It was established that via variation of composite structures of hydrogel and modifying layers of composite membranes can be directed regulating of their physical and mechanical properties and surface adsorption of the obtained composite membranes.

Keywords – combined membranes, hydrogels, polycaproamide, polyvinylpyrrolidone, 2-hydroxyethylmethacrylate, modification solution.

I. Introduction

The modern research and development in field of polymer and membrane technologies are focused on innovations making it possible to improve properties of known synthetic membranes. The leading place in the above mentioned studies belong to the production of the latest composite or hybrid membranes wich contain functional polymer hydrogels. Polymer hydrogels are three-dimensionally crosslinked polymer systems that, due to its porous structure possess selective permeability for various chemical and biological molecules. Also described polymer hydrogels have good sorption properties, biocompatibility and are capable for biodegradation [1]. Besides numerous advantages the polymer hydrogels also have disadvantages. Their porous structure makes it possible to absob solutions, while at the same time making them vulnerable to mechanical stress [2]. Insufficient strength of hydrogels caused insecurity in their use at high pressures and loads, and therefore narrowed the fields of their application.

There are various methods of membranes modification with organic and inorganic fillers [3] which are directed to increase the strength of existing membranes based on polymer hydrogels [4], etc. A successful combination of various materials makes it possible to create composite materials with unique properties. Therefore, it is advisable to create composite polymer materials by modifying them with compatible polymers to improve their working characteristics.

Currently, the search for strengthening material and its bonding with hydrogel is an actual as well as the development of an effective method for the modification of polymer hydrogels and membranes with strengthening material, which would retain the selectively permeable characteristics of the hydrogel.

Formation of composite polymer membranes is associated with two technological processes: the creating of a porous base and the application of thin fine-porous selective layer on it [5, 6].

One of the most productive directions in the development of polymer membranes is the creation of composite membranes of a heterogeneous structure. In such membranes, porous substrates can be considered as modified ones by thin and ultra-thin layers of porous synthetic material. The laying on of thin polymer films by precipitation from solutions is an effective method for modifying the surface of polymer membranes, which makes it possible to consider this technology as promising for the creation of specially designed membranes.

For surface modification of membranes with thin hetero-layers the multicomponent polymer solutions are applied.[5, 7]. The method of film deposition from solutions makes it possible to form thin films of definite structure, uniform in thickness and distribution of functional groups. Also it allows in wide ranges to vary both qualitative and quantitative composition of the modifying layer, while giving for the composition membranes additional special properties.

II. Formation of combined membranes

In order to develop a technology for the formation of composite polymer membranes of high strength the films based on aqueous solutions of hydrogels from copolymers of polyvinylpyrrolidone (PVP) and 2-hydroxyethyl methacrylate (HEMA) [8] were synthesized and applied on their surface microporous films based on the interpolymer complex of polycaproamide (PA-6)/PVP. The thin strengthening modifying layer was applied by precipitation diffusion of PA-6/PVP polymer blend from the formiate solution due to the contact of the hydrogel sample surface with the solution surface.

The working out the technology of obtaining of composite polymer membranes was conducted by research the influence of the concentration of PA-6/PVP in formic acid, the concentration of formic acid, the time of laying on of the film, the temperature and time of evaporation of the acid from the composite film on the amount of surface adsorption and, consequently, on the physical and chemical properties of the obtained membranes.

The influence of combined membranes on the adsorption properties of hydrogel has been investigated. Simultaneously the conditions for the formation of the hydrogel substrate were studied, namely the ratio of the polymer aqueous phase, the replacement of part of the water phase with water soluble additives, in particular glycerol, formic acid, as well as the temperature mode of the matrices hardening (three stages of temperature increase) and the stage of hydration of the obtained hydrogel films of thickness 0,35 mm and 0,5 mm.

The dependence of the amount of the obtained hardened layer on the researched conditions was studied. It was determined that the optimum concentration of formiate

solution is 7 % by weight, the time of its laying on to the hydrogel (modification time) is 5 minutes, the evaporation temperature is 75...80 °C and the time of solvent evaporation is 30 min. Hydration of the obtained combined membranes was carried out in three stages: 1,5% aqueous solution of sodium bicarbonate (50 °C), distilled water (50 °C), distilled water (25 °C) – 2 hours.

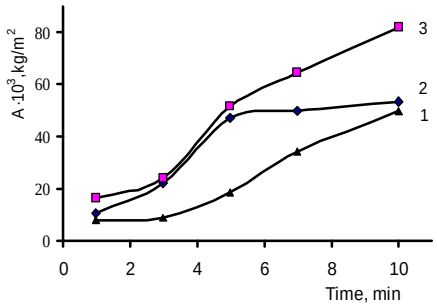

Fig. 1 Dependence of surface adsorption (A, kg/m^2) of combined membranes on time of modification. HEMA : PVP: H_2O = 48 : 12 : 40 wt. h., HEMA : PVP = 8 : 2 wt. h., PA-6 : PVP = 95 : 5 % by weight, PA-6/PVP : HCOOH, mass %: 1,2 – 7 : 93, 3-10 : 90, Initial concentration [HCOOH] = 80 % by weight, δ, mm: 1 – 0,35 mm, 2 – 0,5 mm.

The ressearch have determined that surface adsorption increases with the modification time of the combined membranes increase and also with the increase of the formiate solution concentration (Fig. 1). It is shown that while increasing the thickness of the hydrogel layer the surface adsorption is slightly higher (Fig. 1)

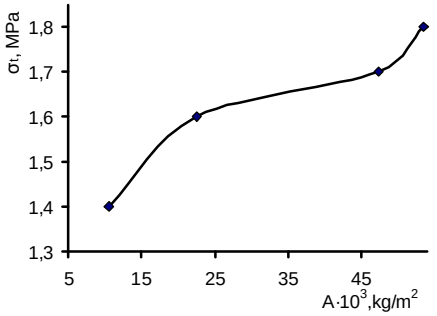

Fig. 2 Dependence of the strength (σt, MPa) of the combined membranes on the surface adsorption. HEMA : PVP : H_2O = 48 : 12 : 40 wt. h., HEMA : PVP = 8 : 2 wt. h., PA-6/PVP : HCOOH = 7 : 93,% by mass, Initial concentration [HCOOH] = 80% by weight, PA-6 : PVP = 95 : 5 % by mass, δ = 0,5 mm.

As we can see from Fig. 2 with increasing of modification time of hydrogel membranes, the strength increases with an increase of the adsorption of polymer layer based on PA-6/PVP.

The influence of the additives on the structure of hydrogel is determined. The conformation of chains of mentioned hydrogel substantially changes (rectified in glycerine and twisted and packed in formiate acid). An increase in the amount of water in the initial composition causes the formation of diluted hydrogel with reduced strength and deteriorated optical properties.

Conclusion

Consequently, we developed the technology of forming of combined hydrogel membranes based on 2-hydroxyethylmethacrylate copolymers with polyvinylpyrrolidone, which were strengthened with nano-layer made of PA-6/PVP polymer blends, and the dependence of their physical and mechanical properties on the surface adsorption was studied.

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