

# Flat ultrafiltration PAN/BNE membranes with temperature-responsive performance obtained by modification with “smart” PVA copolymer

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**Abstract.** The ultrafiltration (UF) composite polyacrylonitrile (PAN)/ butadiene–acrylonitrile elastomer (BNE) membrane obtained by the phase inversion method was modified with temperature sensitivity by physicochemical immobilization of hydrophobically modified poly(vinyl alcohol) (HMPVA). HMPVA was prepared by partial acetalization of poly(vinyl alcohol) (PVA) with a molar mass of 75000 g/mol, resulting in a temperature-sensitive copolymer with a phase transition temperature ( $T_H$ ) of 40.2°C. Modification of the membranes was performed by introducing aqueous HMPVA solutions of different concentrations into the membrane structure, followed by its immobilization by cross-linking with glutaraldehyde. The composition, technological and structural characteristics of the membranes before and after the modification were investigated. Scanning electron microscopy (SEM) and barodynamic determinations were used in the typical UF operating pressure range (0–0.5 MPa), evaluating permeability ( $J$ , l/m<sup>2</sup>.h) and rejection ( $R$ , %) of water and albumin as a calibrant (molecular mass ~76 kDa). Temperature-sensitive HMPVA in the membrane structure optimizes the energy and material efficiency of the membrane process, including membrane service life and maintenance.

## 1 Introduction

Membrane technology is based on separation processes of gas and/or liquid mixtures and constituent components. Membrane technology began its development in the 70s of the 20th century and until now has established itself on an industrial scale in various fields - pharmacy, food and beverage, pulp and paper, etc. The competitiveness of this technology is due to the low capital costs, high technological and environmental efficiency, affordable organization and management of the processes [1]. This makes it adaptable to the principles of the circular economy and sustainable growth and to the trends of Industry 4.0 [2-4].

At the basis of the activity of all membrane processes is the most important element – the semipermeable membrane. The classification of processes and membranes is determined by different signs - structural, morphological, physicochemical, technological, etc. The possibilities for obtaining them are also diverse. This allows different materials to be used alone and as composites, or combining material and membrane synthesis. In addition to the capabilities of modeling the membrane characteristics, a variety of methods and means can be used to modify the forming conditions and/or the materials [5].

Polymers are a conventional material for forming semi-permeable membranes operating under elevated pressure conditions, such as microfiltration (MF),

ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO). Polyacrylonitrile (PAN) and its copolymers are preferred because of its functionality due to qualities such as relative hydrophilicity, chemical, mechanical and thermal resistance under the operational conditions of membrane filtration and the possibilities of preparation and modification. The quality of PAN membranes obtained by the phase inversion method is determined by the homogeneity, respectively, the composition of the polymer solutions and the conditions under which the coagulation of the polymer takes place during the inversion from liquid to solid state. These are also the main factors on which the structural and morphological realization of the pore distribution in the membranes depends, as a consequence of which are their main technological parameters - permeability and selectivity [6-9].

The membrane structure can be modified in different ways, for example by different additives in the polymer solution or by their incorporation into the finished structure. Modified or not, depending on the technological characteristics and structural specificity of the membranes, they are used in water purification, separation, isolation and fractionation of microorganisms, proteins, etc. [10-12]. Membrane modification can be done with hydrophobically modified poly(vinyl alcohol) (HMPVA), a representative of so-called "smart" materials with temperature-stimulated

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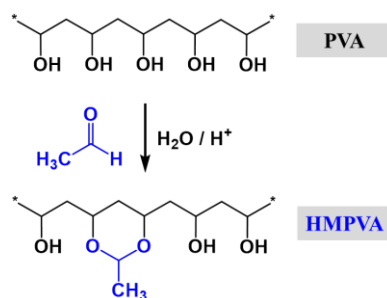
sensitivity, by being introduced and retained in a macroporous membrane structure by cross-linking.

The presented research aims to investigate the possibility of manipulating the performance characteristics of a UF PAN/BNE membrane by introducing and retaining by cross-linking a thermosensitive "smart" HMPVA into the membrane structure. Temperature sensitive polymers have a phase transition temperature ( $T_{tr}$ ), according to which the conformational state of the macromolecules changes. This is expressed as the collapse of the polymer chains from elongated helices to collapsed globules and vice versa. The ability for HMPVA to be located in the membrane structure will expand the membrane's performance capabilities related to its permeability and selectivity according to temperature conditions and within the limits critical for stimulating the sensitivity of the "smart" polymer. The choice of the receiving pure (unmodified) membrane and its qualities are of great importance for the result [13-17].

## 2 Experimental

Polyacrylonitrile fibers obtained from the ternary copolymer poly(acrylonitrile-methylacrylate-2-acryloamide-2-methylpropanesulphonic acid) (PAN) produced in Bulgaria from LUKOIL Neftochim Bourgas Co. and butadiene-acrylonitrile elastomer (SKN-40) (BNE) produced by Omskyi Kautchuk, Russia, were used.

Hydrophobically modified poly(vinyl alcohol) was synthesized according to the method already reported in the literature [18]. Briefly, a solution of PVA in deionized water (2.5 %) was prepared and cooled to 15 °C. Then the corresponding amount of acetaldehyde was added dropwise to the aqueous PVA solution at vigorous stirring while maintaining this temperature with thermostat. The temperature was raised to 30 °C and the the reaction was let to proceed at this temperature under vigorous stirring for four hours. The obtained modified PVA was isolated from the solution by precipitation when raising the temperature to 60 °C, purified by repeated dissolution in deionized water and followed precipitation by raising the temperature, and finally lyophilized.



**Fig. 1** Synthesis of HMPVA in aqueous solution

Reaction scheme of the hydrophobic modification of PVA is presented in Fig.1. The extend of PVA modification, i.e. the content of introduced acetal groups was determined by NMR spectroscopy and confirmed by Fourier transform infrared spectroscopy (FTIR) analysis

and measurement of the temperature of phase transition - cloud point ( $T_{CP}$ ) measurement of HMPVA aqueous solution. Characterization of the synthesized HMPVA: substituted -OH groups 17.8 mol % (NMR); acetal content 8.9 mol %; phase transition temperature (cloud point) in aqueous solution 40.2 °C.

NMR analysis was performed on a Bruker Avance DRX 250 spectrometer (Bruker) in DMSO-d<sub>6</sub> as solvent. Phase transition temperature ( $T_{tr}$ ), also known as cloud points was evaluated by means of UV-Vis spectroscopy by measuring the transmittance of HMPVA aqueous solution at a wavelength of 500 nm as a function of temperature.

The membranes are formed by a dry-wet phase reversal technique from polymer solutions in an aqueous coagulation bath. The polymer solutions were composed of 16.2 wt.% PAN or 16.2 wt.% PAN and 1 wt.% BNE and solvent N,N-dimethylformamide (DMF) product of "Fluka", Germany. The fibers and elastomer are dissolved in DMF when heated to about 70°C and stirred until the solutions are completely homogenized. After filtration and deaeration, a film was drawn from the polymer solutions onto a calendered polyester mat attached to a glass plate. The polyester mat brand FO-2403, a product of "Velidon Filtren", Germany has a density of 100 ± 5 g/m<sup>2</sup> and a thickness of 2 ± 0.1 nm. Up to 15 sec. after casting the solution, the plate is immersed in a bath of distilled water at a temperature of 25 ± 1°C to carry out the phase inversion process and form the membrane structure. The membranes are left for half an hour in the coagulation bath, after which they are washed intensively with water to completely remove the solvent.

The modification of the formed ultrafiltration PAN/BNE membrane was carried out by introducing the thermosensitive polymer into the pore structure of the membrane and immobilized by cross-linking. From each membrane, pieces with an area of 100 cm<sup>2</sup> were prepared and treated on the side of the selective layer or on the side of the polyester support with a liquid mixture with the following composition: impregnating solution - (1.25g HMPVA in 50ml H<sub>2</sub>O), pH corrector (0.1 ml 10% HCl) and cross-linking agent - (0.1 ml 50% glutaraldehyde). For more effective cross-linking, the membranes were first left in a dryer for 30 min at T=40°C and 24 h at room temperature.

Membrane morphology was analyzed from images taken with scanning electron microscope JSM-5510 ("JEOL", Japan). All samples were sputter-coated with gold before analysis. For cross-section analysis, the membrane samples were freeze fractured in liquid nitrogen.

IRAffinity-1 Shimadzu FTIR spectrophotometer equipped with reflectance measuring appliance (MIRacle Attenuated Total Reflectance Attachment) was used to study solid samples of PAN/ HMPVA membranes.

The permeability and rejection of the membranes to water and albumin as calibrant were performed with an ultrafiltration laboratory cell SM 165-26 ("Sartorius", England). The experiments were carried out at different temperatures of 22, 32 and 42°C which are below and above the  $T_{tr}$  of 40.2°C characteristic for HMPVA. The

permeability for water was studied as function of the pressure ( $J=f(P)$ ). The time for which 10 ml of distilled water passed through the membrane was determined. The time measured at certain pressure was used to calculate membrane permeability by the formula:

$$J = \frac{V}{S \cdot \tau}, \text{ l/m}^2 \cdot \text{h} \quad (1)$$

where:  $J$  – flux permeate through the membrane,  $\text{l/m}^2 \cdot \text{h}$ ;  $V$  – volume of permeated flux, l;  $S$  – effective area of tested samples,  $\text{m}^2$ ;  $\tau$  – record time, h;

The rejection of the membranes were determined at pressure of 0.3 MPa by measuring the time for which 10 ml of permeate of calibrant solution pass through the membrane and calculating by the formula:

$$R = \frac{C_2 - C_1}{C_2} \cdot 100, \% \quad (2)$$

where:  $R$ – rejection of the membrane, %;  $C_2$ – concentration of calibrant in the feed, g/l;  $C_1$ – concentration of calibrant in the permeate, g/l;

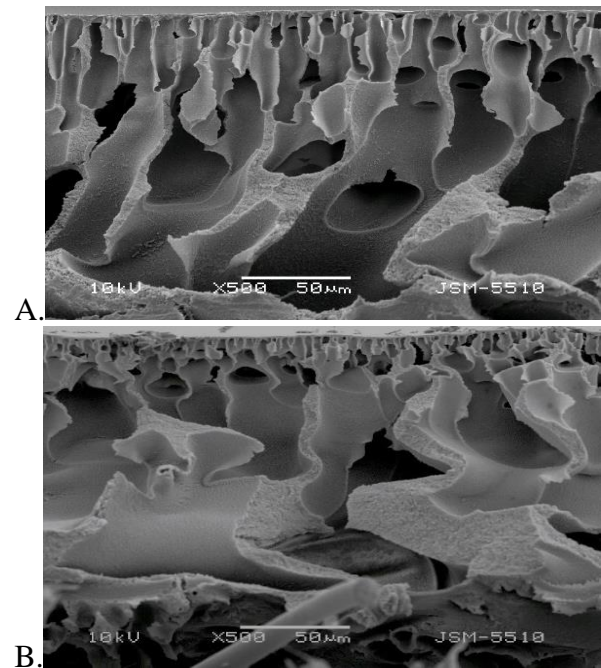
The concentration of porcine serum albumin with molecular weight 76 kDa („Merck”, Germany) was determined applying the calibration curve method. UNICA 8625 UV-Vis spectrometer (France) was used and absorption of albumin solutions at the wavelength  $\lambda=280$  nm was measured against 0.9 wt.% NaCl solution (blank test)

### 3 Results and discussion

The leading conditions in choosing a suitable membrane for modification by physicochemical immobilization of the thermosensitive polymer is that it has a structure with volume pores and mechanical stability. Such a membrane was selected from PAN/BNE membranes developed in other studies [19,20]. It has been proven that, depending on the amount used as an additive in PAN polymer solutions, BNE structurally modifies the membranes in the desired direction. The selected membrane with the relevant qualities for the purpose of the study was formed from a solution with a composition of 16.2 wt.% PAN, 1.0 wt.% BNE in DMF solvent. To visualize the morphological differences of the asymmetric structures of PAN and PAN/BNE membranes, scanned images are presented in Fig. 2. From the cross-sectional image of the PAN/BNE membrane, it is evident that the pores in the drainage sublayer are more voluminous compared to the PAN membrane with the same polymer concentration. This layer primarily provides the amount of flux passed through the membrane per unit time.

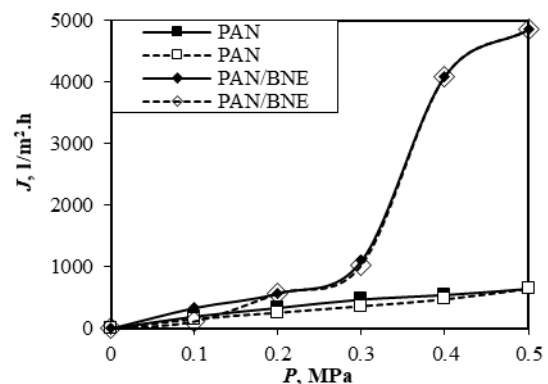
The morphological differences in the structure of the membranes (Fig. 2) are reflected in the water permeability values, which are represented by the hysteresis curves in Fig. 3. They are constructed as  $J=f(P)$  when increasing and decreasing the pressure by 0.1 MPa in the range of 0 to 0.5 MPa and applied perpendicular to the water flow and the membrane. The change in pressure ensures the inclusion and exclusion of pores of different sizes in the membrane filtration process. From the course of the

curves, the change in permeability depending on the pressure is followed, and from the size of the hysteresis area limited between them, the mechanical stability of the membrane structure under the operating conditions can be judged.



**Fig. 2.** SEM images of a cross-section of PAN (A) and PAN/BNE (B) membranes.

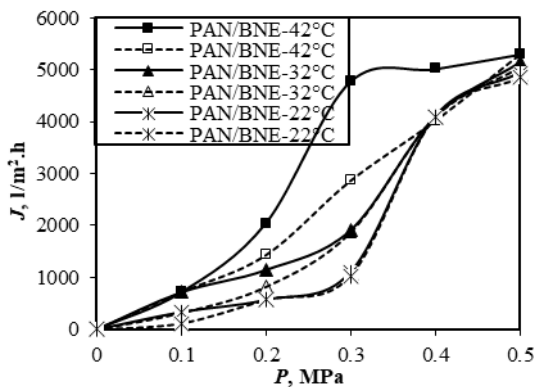
According to the presented results (Fig. 3), both membranes have an optimal ratio of hysteresis area, but the one chosen as the object of the target modification has a much higher water permeability up to 4 850  $\text{l/m}^2 \cdot \text{h}$  at maximum pressure. Undoubtedly, these values are determined by the morphological differences (Fig. 2) caused by the different polymer composition, as all other conditions related to the preparation are identical.



**Fig. 3.** Hysteresis curves of water flux permeability of PAN and PAN/BNE membranes.

The technological characteristics of the membrane were measured at different temperatures - 22, 32 and 42 °C, in order to pre-test its behavior according to the temperature conditions stimulating the sensitivity of the modifying HMPVA. The results for the receiving (base-

line) membrane specified for the modification are reflected in Fig. 4 and Table 1.



**Fig. 4.** Hysteresis curves of water flux permeability of PAN/BNE membranes at different operating temperatures.

The structure is affected by temperature and pressure. The membrane exhibits water permeability and hysteresis area that increase proportionally with increasing temperature. According to this, at  $T=42\text{ }^{\circ}\text{C}$  the structure has the lower mechanical stability compared to the lower temperatures. Selectivity and permeability to albumin under the same conditions follow the same dependence on the influence of temperature. It should be noted that, in principle for a UF process, selectivity and permeability are inversely related [21-23].

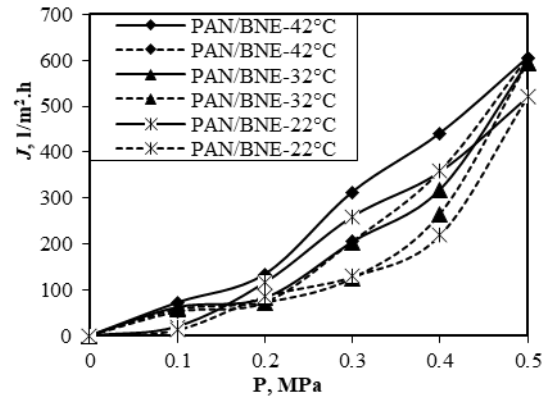
**Table 1.** Technological characteristics of the membranes determined toward albumin at different temperatures (working pressure 0.3 MPa).

Temperature (°C)	Membrane characteristics	
	$J_{\text{alb}}$ (l/m <sup>2</sup> .h)	$R_{\text{alb}}$ (%)
22	101	25
32	143	20
42	184	18

After impregnation of the membranes on the side of the selective layer and on the side of the polyester macroporous support with a temperature-sensitive polymer, it was found that a positive result was obtained only in the second variant of treatment. This reinforces the assumption that the macroporous structure enables easier access of polymer into it.

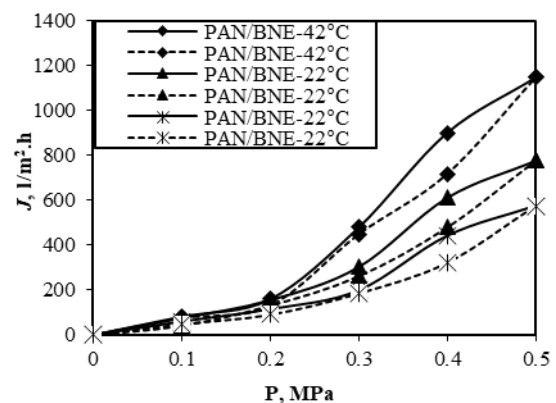
The modification of the membranes with HMPVA polymer is carried out with different volumes of impregnating liquid mixture with concentrations of HMPVA, respectively: 10 ml - 0.25 wt.%, 2.5 ml - 0.06 wt.%, 1 ml - 0.03 wt.%. When cross-linking with the solution with the highest concentration, the membrane structure is compacted and the water permeability is significantly reduced (Fig. 5).

A cross-linked HMPVA polymer film was also observed on the side of the selective surface opposite to the treated substrate. This is indicative of an excess of impregnating mixture and the cause of drastically reduced water permeability compared to the unmodified membrane (Fig.4 and 5).



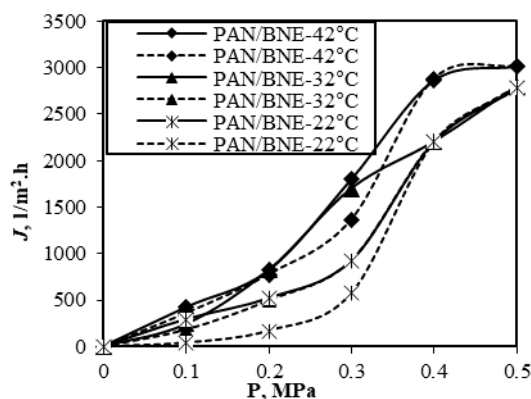
**Fig. 5.** Hysteresis curves of water flux permeability of a membrane modified with 0.25 wt.% HMPVA at different operating temperatures.

Subsequently, smaller amounts of the cross-linking mixture were used, which made the penetration and distribution of HMPVA in the structure of the membranes more efficient. From the hysteresis curves for the respective membranes in Figs. 6 and 7, an increase in the water permeability values is observed, and at 0.06 wt.%, an optimal compaction of the pore structure was also achieved. The same membrane has smaller hysteresis areas at all three temperature regimes (Fig.6), compared to the unmodified (Fig.4) and modified with 0.25 wt.% (Fig.5) and 0.03 wt.% HMPVA. The modifying temperature-sensitive effect of HMPVA regarding the permeability and selectivity of the membrane structure is also very well expressed. The water permeability of the membrane remarkably changes according to the conformational change of HMPVA in accordance with the change of temperature relative to the  $T_{tr}$  and applied pressure. At the highest pressure, the water permeability of 573 l/m<sup>2</sup>.h at a temperature below the  $T_{tr}$  increases to 1147 l/m<sup>2</sup>.h at a temperature above the  $T_{tr}$ . The changes are the result of the reaction of HMPVA as a result of its physicochemical binding to the membrane structure and evidence of its effective retention according to the methodology carried out.



**Fig. 6.** Hysteresis curves of water flux permeability of a membrane modified with 0.06 mass% HMPVA at different operating temperatures.





**Fig. 7.** Hysteresis curves of water flux permeability of a membrane modified with 0.03 mass% HMPVA at different operating temperatures.

Confirmation of the modifying importance of HMPVA, expressed in sharing its temperature sensitivity with the structure of the PAN/BNE membrane, are the permeability and selectivity values of the membranes reflected in table 2. Regarding the selectivity of the membranes, the results also change in proportion to the temperature change when using 2.5 ml and 1.0 ml of HMPVA impregnating solution. The difference in selectivity values below and above  $T_{tr}$  is more significant with the smallest immobilized amount of HMPVA. This explains the possibility of the polymer penetrating the finer membrane structure of the selective layer. The configuration of HMPVA in the membrane matrix shows stability in the temperature range where the differences in the permeabilities and selectivities of the membranes are probably due to the change in the behavior of the polymer membrane matrix. At temperatures above  $40.2^{\circ}\text{C}$  ( $T_{tr}$  of the polymer), the collapse of the HMPVA polymer creates conditions for high permeability but low selectivity.

**Table 2.** Technological characteristics of the modified membranes determined toward albumin at different temperatures (working pressure 0.3MPa).

HMPVA content	Membrane characteristics			
	at 22°C		at 42°C	
	$J_{alb}$ (l/m <sup>2</sup> .h)	$R_{alb}$ (%)	$J_{alb}$ (l/m <sup>2</sup> .h)	$R_{alb}$ (%)
10 ml 0.25 wt.%	25	65	76	24
2.5 ml 0.06 wt.%	34	57	56	23
1ml 0.03 wt.%	57	49	717	3

The modification with 2.5 ml of impregnating solution with a HMPVA concentration of 0.06 wt.% is optimal. The imputed temperature intelligence in the PAN/BNE membrane, by immobilizing HMPVA in its structure, makes it technologically attractive for UF application. It could be successfully applied to separate

liquid mixtures under temperature conditions with and without the stimulation of temperature "intelligence". Depending on these conditions, the membrane will exhibit the corresponding performance characteristics. This will optimize the energy and material efficiency of the membrane process regardless of the purpose - purification, separation, concentration or others, including the operational life and maintenance of the membrane.

## 4 Conclusions

It was found that UF composite PAN/BNE membrane can be modified with temperature sensitivity by physico-chemical immobilization of HMPVA introduced as an impregnating solution on the side of the membrane polyester support. An optimal temperature-stimulated reaction, according to the  $T_{tr}$  of HMPVA ( $40.2^{\circ}\text{C}$ ), definitely exhibits the membrane modified with 0.06 wt.% HMPVA. It has been proven to change according to the  $T_{tr}$  its technological characteristics - for the permeability to water from 573 l/m<sup>2</sup>.h to 1147 l/m<sup>2</sup>.h and to the calibrant from 34 l/m<sup>2</sup>.h to 56 l/m<sup>2</sup>.h at the selectivity of 57% of 23%. The most effective structure-modifying amount of HMPVA also improves and the mechanical resistance of the membrane.

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