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Development of Novel Membranes Based on Polyvinyl Alcohol Modified by Pluronic F127 for Pervaporation Dehydration of Isopropanol

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Abstract: Membrane methods are environmentally friendly and can significantly improve the design and development of new energy consumption processes that are very important nowadays. However, their effective use requires advanced membrane materials. This study aims to improve the performance of pervaporation polyvinyl alcohol (PVA)-based membrane for isopropanol dehydration. To achieve this goal, two methods were applied: (1) bulk modification of PVA by Pluronic F127 and (2) development of supported PVA-based membrane using polyphenylene isophthalamide (PA) as a substrate with a various porosity. Developed membranes were characterized by Fourier-transform infrared spectroscopy, scanning electron microscopy (SEM), contact angle measurement, and swelling experiments. The concentration influence of PA casting solution (12–20 wt.%) on the performance of porous PA membranes (substrates) was investigated in ultrafiltration of pure water and bovine serum albumin (BSA) solution as well as by microscopic methods (SEM and atomic force microscopy). The developed dense and supported PVA-based membranes were tested in the pervaporation dehydration of isopropanol. Optimal transport characteristics were obtained for a supported membrane with a PVA-based selective layer containing 3 wt.% Pluronic F127 onto an ultrafiltration PA (17 wt.%) substrate: improved permeation flux 0.100–1.164 kg/(m² h) and 98.8–84.6 wt.% water content in the permeate in pervaporation dehydration of isopropanol (12–80 wt.% water).

Keywords: polyvinyl alcohol; composite membrane; Pluronic F127; pervaporation; isopropanol dehydration



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1. Introduction

Membrane separation methods have found many applications in various industrial processes during the past few decades, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), electrodialysis (ED), reverse osmosis (RO), gas separation (GS), etc. Pervaporation (PV) is one of the membrane separation technologies that has attracted widespread attention in the last century. It is also related to sustainable processes due to its potential advantages such as its eco-friendly nature; its low-energy requirements; its ease of operation; and its ability to separate close-boiling components, and isomeric and azeotropic mixtures [1,2]. The pervaporation separation depends on the diffusion behavior and the difference in the component solubility through the membrane [3]. In recent years, pervaporation has been used in a variety of applications such as the separation of organic mixtures [4,5], the dehydration of aqueous–organic mixtures [6–9], and the purification of an aqueous solution by removing dilute organic compounds [10,11]. Pervaporation has many advantages over conventional processes for liquid mixture separation, especially for the separation of azeotropic mixtures. Although pervaporation has been known for over 70 years, this technique was used commercially after installing a commercial pervaporation

plant (Gesellschaft für Trenntechnik GFT mbH, Hameln, Germany) (GFT) in 1982 and innovating a new supported membrane [12].

Since the 1980s, commercial applications have been established for alcohol dehydration systems and other solutions. For isopropanol (IPA) dehydration, Mitsui Zosen of Tokyo, Japan, at Ohgaki designed and built a plant to dehydrate isopropanol from 87 to 99.7 wt.% with a capacity of 500 kg/h using GFT PVA-supported membrane. The dehydration of isopropanol is important because it is needed as a cleaning agent in pharmaceuticals, semi-conductors, and electronic applications and as an industrial solvent for various cosmetics, waxes, gums, and oils. However, IPA forms an azeotropic mixture with water (12 wt.% water and 88 wt.% IPA) at 80.4 °C under atmospheric pressure, 101.3 KPa (760 mmHg) [13,14]. The separation of an azeotropic water–IPA mixture by the conventional method is energy-consuming and needs additional chemicals that can cause contamination in the final output. Pervaporation is a useful technique with strategic and environmental advantages over the traditional way of separating azeotropic water–IPA mixture [15–20]. It can separate water through a membrane without adding other reagents.

Polymeric membranes are widely used materials for the pervaporation dehydration of alcohols [21,22] due to their flexibility, easy film-forming ability, and cost-effectiveness. The well-known membrane materials used for alcohol dehydration in pervaporation are water-soluble polymers such as polyvinyl alcohol (PVA) [23], chitosan (CS) [24], and alginate (Alg) [25] due to their environmental safety and high water selectivity. However, these membranes swell in an aqueous solution, resulting in a decrease in their mechanical and thermal stability. Thus, the additional cross-linking of these polymers is required to suppress membrane swelling. The pervaporation performance of alcohol dehydration is governed by the physical structure and chemical nature of the membrane. For the use of membranes in pervaporation dehydration, the existence of a significant number of sorption centers is crucial [21]. Water-selective sorption on the membrane surface happens due to a functional polar group, leading to dipole–dipole, ion–dipole, and hydrogen bonding interactions between the membrane surface and water molecules. In addition, the water selectivity can be enhanced by changing the free volume of the membrane. Thus, a membrane with the tailored properties improves the pervaporation dehydration performance.

The PVA-based membrane is attractive for the pervaporation dehydration of organic mixtures since it shows high selectivity to water, anti-fouling potential, good mechanical properties, film-forming ability, and chemical and thermal resistance [26,27]. PVA is also a biodegradable non-toxic polymer [28], which makes it possible to develop membranes based on it that do not affect the environment. However, PVA membranes typically have low mechanical strength and poor stability in aqueous solution due to immoderate swelling [21]. As a result, separation performance is significantly decreased, and low stability during long-term operation occurs. Therefore, some studies were devoted to suppressing membrane swelling and improving the thermal and chemical stability of the membrane in aqueous solutions, including grafting [29], cross-linking [26,30], and heat treatment [24,31]. Hybrid membranes based on PVA are widely used for the pervaporation of water–IPA mixtures. PVA grafted with 30 wt.% of glycidyltrimethylammonium chloride (GTMAC) was used to separate 10 wt.% water–90 wt.% IPA mixtures by pervaporation at 30 °C. The permeation flux of 0.0192 kg/(m²h) with a separation factor of 1570 was obtained [32]. The pervaporation PVA membrane blended with CS was cross-linked by glutaraldehyde. The membrane was examined for dehydration of IPA, and the membrane containing 75 wt.% CS had a good mechanical strength and the best transport characteristics: a permeation flux of 0.644 kg/(m²h) with 100% water in the permeate in pervaporation dehydration of a 90% isopropanol mixture at 60 °C [33]. Suhas et al. developed a PVA membrane modified by zeolite particles [34]. It was demonstrated that separation factors of membranes with zeolite with lower alumina and with higher alumina content were 334 and 568, respectively, for the separation of an IPA–water mixture (10 wt.% water) at 30 °C. B.V.K. Naidu et al. improved the PVA membrane selectivity in the separation of a water–IPA mixture by dispersing nanosized polyaniline (PANI) particles in the membrane matrix [35].

The PVA–PANI nanocomposite membrane successfully separated the azeotropic water–IPA mixture compared with simple distillation, demonstrating the following transport characteristics in the pervaporation dehydration of IPA (10 wt.% water) at 30 °C: a permeation flux of 0.069 kg/(m²h) and a separation factor of 564. Another attractive method used to improve the membrane properties and to obtain better permeability is blending different compatible polymers in various concentrations [36–40] or introducing modifiers to polymer matrix such as zeolites [41], hetero-polyacids (HPA) [42], titanium dioxide (TiO₂) [19], zeolite imidazolate framework (ZIF) [43], carbon nanoparticles (fullerene and its derivatives) [31,44,45] and nanotubes (CNTs) [46], graphene oxide (GO) [3], etc.

Pluronic F127 (PL) is an amphiphilic synthetic tri-block copolymer of polyethylene oxide–polypropylene oxide–polyethylene oxide (PEO–PPO–PEO). It is actively used as a pore-forming agent and for increasing the hydrophilicity of the membrane surface. Pluronic F127 solubility in cold water is more significant than in hot water due to the increased solvation energy and hydrogen bonds at lower temperatures [47]. Pluronic F127 is considered one of the best additives for polymer membrane matrices due to its amphiphilic structure. It has good dispersion in both hydrophobic and hydrophilic polymers due to the different affinity of PEO (hydrophilic) and PPO (hydrophobic) blocks for solvents [48,49]. The addition of Pluronic F127 into polymer membrane matrices controls the hydrophilicity, roughness of the membrane surface, pore size, porosity, and size of macrovoids in the membrane substructure [44,50]. Pluronic F127 has been used to improve pervaporation membrane characteristics in several studies [50–54]. Polysulfone (PSF) dense membrane was modified by Pluronic F127 and used to separate water–ethyl acetate mixtures [50]. The addition of 3 wt.% Pluronic F127 into the PSF membrane matrix led to an increase in the permeation flux by 1.7 and 2.7 times, respectively, with 100% water in the permeate in the pervaporation of 98 wt.% water–2 wt.% ethyl acetate and 96 wt.% water–4 wt.% ethyl acetate mixtures. Polystyrene (PS) membranes were developed for the pervaporation of 10 wt.% aqueous ethanol solution [51]. The pervaporation results obtained demonstrated that PS modified by 1.5 wt.% Pluronic F127 improved the membrane performance (permeation flux of 140 g/(m² h) and separation factor of 39). Pluronic F127 was used as a surface modifier to prepare polyethersulfone (PES) dense membranes using the surface segregation method for the pervaporation separation of a thiophene–n-octane mixture. At 30 °C and 500 mg/L sulfur in the feed mixture, the permeability was 3.10 kg/(m²h), with a separation factor of 3.50 [53]. The pervaporation polyphenylene isophthalamide (PA) membranes were developed by Pluronic F127 modification and tested to separate an azeotropic methanol/toluene mixture [54]. The results obtained demonstrated that the addition of 10 wt.% Pluronic F127 into the PA membrane matrix increased the permeability of the PA dense membrane by two times and that the methanol content in the permeate increased by 5 wt.% compared with the pristine PA membrane. Within the framework of the literature review, it has been found that the Pluronic F127 effect on the performance of PVA-based membranes is understudied.

Thus, for the first time, PVA was modified by Pluronic F127 for the separation of an azeotropic water–IPA mixture. This study aims to improve the pervaporation dehydration performance of PVA membranes by adding Pluronic F127, cross-linking by maleic acid, and using developed ultrafiltration PA membranes of different porosity as a substrate for the development of highly efficient supported PVA-based membranes.

2. Materials and Methods

2.1. Materials

Polyvinyl alcohol (PVA, 141 kDa, analysis certificate No 553041-3013) obtained from ZAO LenReaktiv (St. Petersburg, Russia) was used as a membrane material for the preparation of dense membranes and a thin selective layer of supported membranes. Polyphenylene isophthalamide (PA, Fenylon C2, lot. 12/2018) was obtained from UNIPLAST Ltd. (Vladimir, Russia) and used to prepare a substrate for the supported PVA membranes. Maleic acid (MA); isopropanol (IPA); N, N-dimethylacetamide (DMA); and LiCl were

obtained from Vecton (Saint Petersburg, Russia) and used without additional treatment. Amphiphilic copolymer polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO) (PL, Pluronic F127, 12.6 kDa) was obtained from Sigma-Aldrich (St. Louis, MI, USA) and used as a modifier. Bovine serum albumin (BSA, 67 kDa, No A2244, 0050: Albumin fraction V (pH 5.2)) was purchased from PanReac AppliChem (Moscow, Russia) and used for fouling experiments in ultrafiltration. Lavsan (polyester non-woven fabric) was obtained from ZAO LenReaktiv (St. Petersburg, Russia) and used as mechanical support to prepare porous PA membranes (substrates).

2.2. Membrane Preparation

2.2.1. Dense Membranes

Dense PVA and PVA-PL membranes (thickness $40 \pm 2 \mu\text{m}$) were prepared by casting the 2 wt.% PVA aqueous solution with/without 35 wt.% MA (with respect to the PVA weight) and Pluronic F127 (0, 1, 2 and 3 wt.% with respect to the PVA weight) into a Petri dish and dried at 40°C for 24 h. The obtained membranes with MA were cross-linked by the following heat treatment at 110°C for 120 min. The optimal concentration of Pluronic F127 was limited to 3 wt.%, since the higher concentration of Pluronic F127 led to a deterioration in mechanical properties of membranes and poor dispersion in polymer solution.

2.2.2. Porous Membranes

The porous PA membranes were prepared via non-solvent induced phase separation (NIPS) (by immersion in a precipitation bath with distilled water at 25°C) using lavsan as a mechanical support. PA solutions of different concentrations (12, 15, 17, and 20 wt.%) in DMA containing ~ 0.7 wt.% LiCl (for solution stabilization) were kept for 4 days at -5°C . Then, the solution was casted onto a glass plate with fixed lavsan. Then, the glass plate was submerged in a water bath and the DMA extracted from PA. After the film formation, the membranes were left for 12 h in distilled water for complete DMA extraction.

2.2.3. Supported Membranes

The supported membranes with a thin selective layer were prepared by casting 2 wt.% PVA aqueous solution with/without 35 wt.% MA and Pluronic F127 (3 wt.% with respect to PVA weight) onto the surface of the ultrafiltration PA membrane prepared from the different concentrations of the casting solution (12, 15, 17, and 20 wt.%). The supported membranes were then dried at $22 \pm 2^\circ\text{C}$ (room temperature) to form a selective layer with a thickness of $1.5 \pm 0.3 \mu\text{m}$, as determined by scanning electron microscopy. Cross-linking of the selective PVA layer was also obtained by thermal treatment at 110°C for 120 min. PA was chosen as a substrate due to several reasons: (i) the good adhesion to PVA when forming a stable selective layer for the pervaporation application, (ii) good membrane forming properties and the ease of variation in the membrane porous structure, (iii) mechanical and chemical stability, and (iiii) economic accessibility.

The abbreviations used in this work to describe PVA-based membranes are presented in Table 1. For ease of membrane designation, the substrate is indicated after the slash (/) sign.

2.3. Membrane Investigation Methods

2.3.1. Scanning Electron Microscopy (SEM)

The morphology of both the cross-section and the surface of membranes were obtained by Zeiss Merlin SEM (Carl Zeiss SMT, Oberkochen, Germany) operating at an accelerating voltage of 1 kV and a beam current 100 pA. The membranes were fractured perpendicular to the surface after five minutes of immersion in liquid nitrogen. There was no conductive coating to avoid the modification of morphology by a deposited layer.

Table 1. The PVA-based membrane samples.

Membrane	Type	Cross-Linker		Modifier		Casting Solution Concentration (wt.%)
		Type	Content (wt.%)	Type	Content (wt.%)	
PVA	Dense	-	-	-	-	2
PVA-PL (1 wt.%)	Dense	-	-	PL F127	1	2
PVA-PL (2 wt.%)	Dense	-	-	PL F127	2	2
PVA-PL (3 wt.%)	Dense	-	-	PL F127	3	2
PVA-MA	Dense	MA	35	-	-	2
PVA-MA-PL (1 wt.%)	Dense	MA	35	PL F127	1	2
PVA-MA-PL (2 wt.%)	Dense	MA	35	PL F127	2	2
PVA-MA-PL (3 wt.%)	Dense	MA	35	PL F127	3	2
PA-12	Porous	-	-	-	-	12
PA-15	Porous	-	-	-	-	15
PA-17	Porous	-	-	-	-	17
PA-20	Porous	-	-	-	-	20
PVA/PA-12	Supported	-	-	-	-	2/12
PVA/PA-15	Supported	-	-	-	-	2/15
PVA/PA-17	Supported	-	-	-	-	2/17
PVA/PA-20	Supported	-	-	-	-	2/20
PVA-MA/PA-17	Supported	MA	35	-	-	2/17
PVA-MA-PL (3 wt.%) / PA-17	Supported	MA	35	PL F127	3	2/17

2.3.2. Atomic Force Microscopy (AFM)

The atomic force microscopy (NT-MDT NTegra Maximus atomic force microscope with standard silicon cantilevers with the rigidity of 15 Nm^{-1} , NT-MDT Spectrum Instruments, Moscow, Russia) was applied to analyze the surface roughness of the selective layer of the fabricated membranes.

2.3.3. FTIR Spectroscopy (FTIR)

The Fourier transform infrared (FTIR) spectra of the dense membranes based on PVA and its composite with Pluronic F127 was obtained with a resolution of 0.5 cm^{-1} at $22 \pm 2 \text{ }^{\circ}\text{C}$ in the spectral range $4000\text{--}500 \text{ cm}^{-1}$ on an FTIR spectrometer (BRUKER-TENSOR 27, Bremen, Germany).

2.3.4. Ultrafiltration

The permeability of the porous PA membranes was estimated during the ultrafiltration using a dead-end ultrafiltration cell (scientific and production cooperative "BIOTEST", Kirishi, Russia) with an effective surface area of 28.26 cm^2 , as shown in Figure 1.

All ultrafiltration experiments were performed at ambient temperature ($22 \pm 2 \text{ }^{\circ}\text{C}$) with a stirrer velocity of 500 rpm and a transmembrane pressure of 1 bar. The membranes were initially pressurized at 1 bar for 1 h before ultrafiltration to obtain a steady water flux during the ultrafiltration. The pure water flux (J_W) was calculated from the following Equation (1):

$$J = \frac{V}{A * \Delta t}, \quad (1)$$

where V indicates the permeate volume (L), A is the effective membrane area (m^2), and Δt is the ultrafiltration time (h).

Bovine serum albumin (BSA) 0.5 wt.% solution in a phosphate buffer ($\text{pH} = 7.0\text{--}7.2$) was used to determine the membrane rejection efficiency. The concentration of BSA in the permeate and feed was estimated by spectrophotometry at a wavelength of 280 nm, corresponding to the BSA solution's maximum absorbance using a Spectrophotometer

PE-5400 UV (“ECROCHEM”, Moscow, Russia). The rejection coefficient (R) of BSA was calculated from the following Equation (2):

$$R = \left(1 - \frac{C_p}{C_f}\right) * 100\%, \quad (2)$$

where C_p and C_f (g/L) are permeate and feed concentrations.

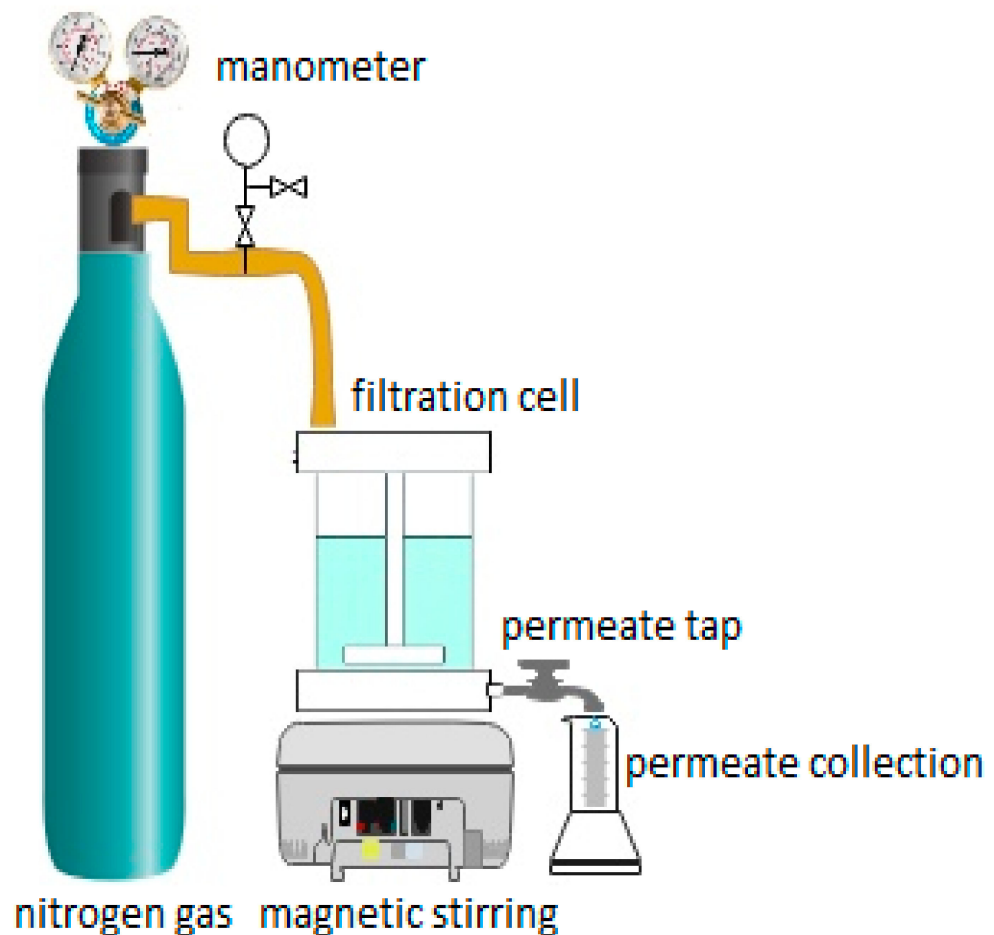


Figure 1. The scheme of the filtration setup.

The antifouling performance of porous PA membranes was established using BSA solution. The fouling experiments were characterized by the flux recovery ratio (FRR) to investigate the membrane antifouling performance and their efficiencies after washing by distilled water using the following Equation (3):

$$FRR = \frac{J_{w2}}{J_{w1}} * 100\%, \quad (3)$$

where J_{w1} and J_{w2} are the flux of pure water before and after the membranes fouling with BSA solution, respectively.

2.3.5. Pervaporation

The pervaporation experiments were operated using a laboratory cell with the effective membrane area of 9.6 cm^2 at $22 \pm 2^\circ \text{C}$ in a steady-state regime (Figure 2). The permeate was collected in a glass trap cooled by liquid nitrogen.

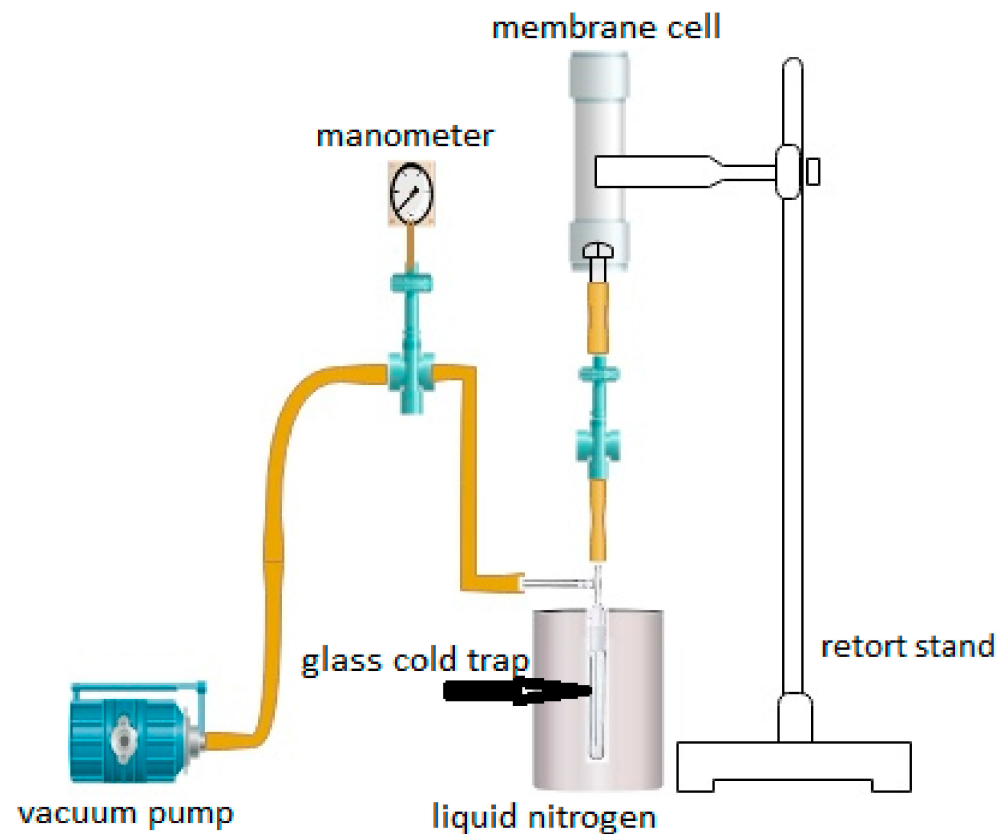


Figure 2. The scheme of the pervaporation setup.

The pervaporation performance was mainly assessed by two parameters: the permeation flux (J) and the separation factor (β). The permeation flux (J) was determined using the following Equation (4):

$$J = \frac{\Delta g}{S * \Delta t}, \quad (4)$$

where Δg represents the permeate weight (kg) collected in a glass trap during the operating time Δt (h) and S is the effective membrane area (m^2).

The separation factor (β) was defined using the following Equation (5):

$$\beta = \frac{\frac{P_w}{P_{IPA}}}{\frac{F_w}{F_{IPA}}}, \quad (5)$$

where P_W and P_{IPA} are the weight fractions of water and isopropanol in the permeate, respectively, and where F_W and F_{IPA} are the weight fractions of water and isopropanol in the feed, respectively.

Finally, the pervaporation data were recorded after reaching a stable state of mass transfer, which means that the equilibrium membrane swelling was achieved. The pervaporation data were steady under stable operating conditions. In addition, pervaporation experiments under the same operating conditions were repeated three times and averaged.

2.3.6. Contact Angle Determination

The contact angle values were obtained by the sessile drop method using a contact angle meter (OCA 20, DataPhysics instruments GmbH, Filderstadt, Germany) at 22 ± 2 °C to evaluate the hydrophilic–hydrophobic balance of the membrane surface.

2.3.7. Swelling Experiment

The sorption of penetrating substances occurs due to the activity gradient, when the liquid mixtures encounter the membrane surface. Sorption is a thermodynamic phenomenon in which equilibrium is reached when the chemical potential of substances are sorbed by the polymer matrix and becomes equal to the chemical potential of those substances in the bulk solution. The sorption of penetrating substances depends on the solubility of these substances into the membrane matrix.

To determine the equilibrium swelling degree (sorption) of polymer membranes, films of known weight were immersed into a liquid (IPA–water mixture 88/12 wt.%) at 22 ± 2 °C. After 24 h, the membrane films were weighed after removing excess liquid with the filter paper. The previous procedure was repeated until the swollen films remained steady in weight. The swelling degree (S) (g of liquid/100 g of dry polymer) was calculated using the following Equation (6):

$$S = \frac{S_m - S_0}{S_0} * 100\%, \quad (6)$$

where S_m is the weight of the swollen membrane and S_0 is the weight of the dry membrane. The sorption experiment was repeated three times for each membrane.

3. Results and Discussion

3.1. Development and Study of Dense PVA Membranes

Pluronic F127 was added into dense PVA membranes cross-linked by MA or without additional treatment to improve the membrane's transport properties for pervaporation dehydration of isopropanol. The pervaporation separation of components using dense membranes can be explained by the solubility-diffusion mechanism, where structure, morphology, swelling characteristics, and free volume of the membranes are essential factors. To evaluate the effect of Pluronic F127 addition and chemical cross-linking by MA on the membrane properties, various analysis methods (FTIR, SEM, swelling experiments, and contact angle measurement) were applied.

3.1.1. Transport Properties of Dense PVA Membranes Modified by Pluronic F127

The transport properties of dense PVA membranes with/without chemical cross-linking by MA and modified by Pluronic F127 were tested in the pervaporation of the azeotropic water–IPA (12/88 wt.%) mixture (Figure 3).

As shown in Figure 3, the permeation flux of PVA-based membranes increases with the rise in Pluronic F127 content in the membrane matrix. The addition of Pluronic F127 to the membrane increased the membrane surface's hydrophilicity (confirmed by water contact angle data below). Additionally, it acts as a pore-forming agent (shown by SEM data below), which leads to an increase in membrane permeability. All membranes were 99.9 wt.% water selective due to the high affinity of PVA for water because of its hydrophilic functional –OH groups [55]. It should be noted that the PVA membrane containing 3 wt.% Pluronic F127 possessed optimal transport characteristics: a permeation flux of 0.017 kg/(m²h) and a high water concentration in the permeate (99.9 wt.%).

Chemically cross-linked by MA PVA-PL (3 wt.%) membrane was obtained to improve the stability and for the promising industrial use of this membrane for separation of dilute mixtures [56]. The cross-linking of pure PVA was also carried out to compare the transport properties with the modified membrane. Chemically cross-linked PVA and PVA-PL (3 wt.%) membranes were also tested in pervaporation of the azeotropic water–IPA (12/88 wt.%) mixture (Figure 3). It was demonstrated that cross-linking of dense PVA and PVA-PL (3 wt.%) membranes by MA slightly reduces the permeability from 0.008 to 0.007 kg/(m² h) for a membrane based on pristine PVA and from 0.017 to 0.015 kg/(m² h) for a membrane based on PVA-PL (3 wt.%) composite. The cross-linking of PVA by MA results in converting the extensive hydrogen bonding in PVA to a covalent bond. The covalent bond structure changes the inner structure (free volume) of the membrane [57]. The chemical cross-linking of PVA membranes also led to a decrease in the size and number of cavities in the

membrane cross-sectional morphology (confirmed by SEM data below) and an increase in the membrane resistance to water (confirmed by contact angle measurements below).

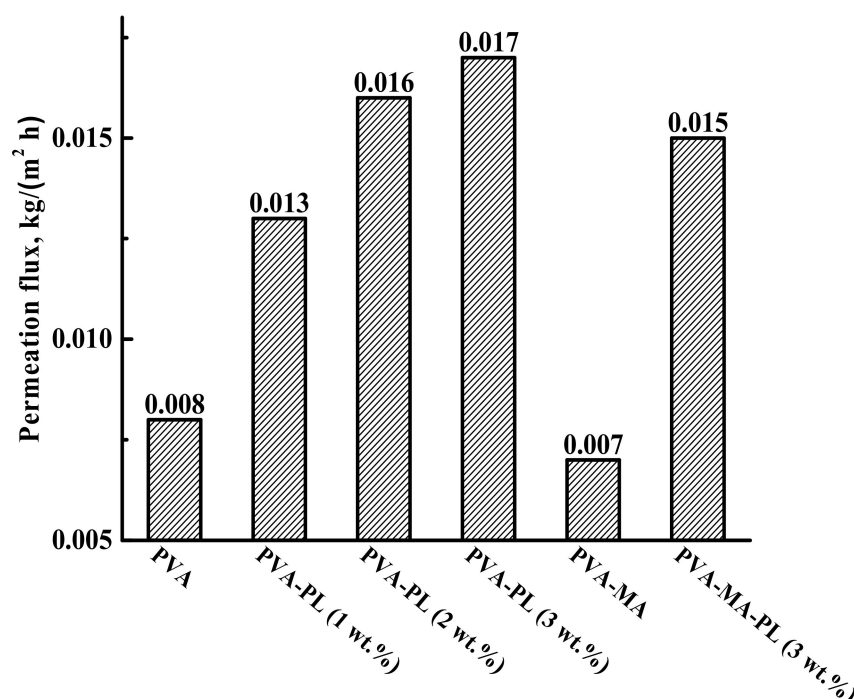


Figure 3. The permeation flux of dense PVA-based membranes in pervaporation separation of the azeotropic water–IPA (12/88 wt.%) mixture. The water content in the permeate for all membranes was 99.9 wt.%.

Thus, the chemically cross-linked PVA-MA-PL (3 wt.%) membrane had optimal transport characteristics for the pervaporation dehydration of the azeotropic water–IPA (12/88 wt.%) mixture, despite a slight decrease in permeability (from 0.017 to 0.015 kg/(m² h)). To use it efficiently in the industry, it is necessary to develop a supported membrane with a thin selective layer based on the PVA-MA-PL (3 wt.%) composite on a porous substrate. Porous PA substrate was developed separately and optimized (Section 3.2) to improve the separation process efficiency.

3.1.2. Structure Characteristics of Dense PVA Membranes Modified by Pluronic F127

The structure and morphology of the dense membrane play essential roles in the pervaporation separation. The dense PVA membranes with/without chemical treatment and modified by Pluronic F127 have been studied by various analysis methods such as FTIR, SEM, swelling experiments, and contact angle measurement to investigate the changes in structural characteristics. The FTIR spectra of Pluronic F127, PVA, PVA-PL (3 wt.%), PVA-MA, and PVA-MA-PL (3 wt.%) membranes are presented in Figure 4.

In the spectrum of pure PVA, the broadband at 3278 cm^{−1} is attributed to the hydroxyl groups (OH) and the stretching band at 2911 cm^{−1} refers to the CH₂ stretching [58,59]. The peaks at 1710 cm^{−1} have been ascribed to the stretching vibration of C=O of the residual acetate groups [59–61]. The absorption band at 1413 cm^{−1} ascertained the existence of symmetric bending of CH₂. Additionally, the peak at 1324 cm^{−1} corresponds to vibrations for the CH and OH modes [59]. The peak at 916 cm^{−1} was assigned to CH₂ rocking, while the peak at 843 cm^{−1} was assigned to C–C stretching vibrations of the planar zigzag carbon backbone.

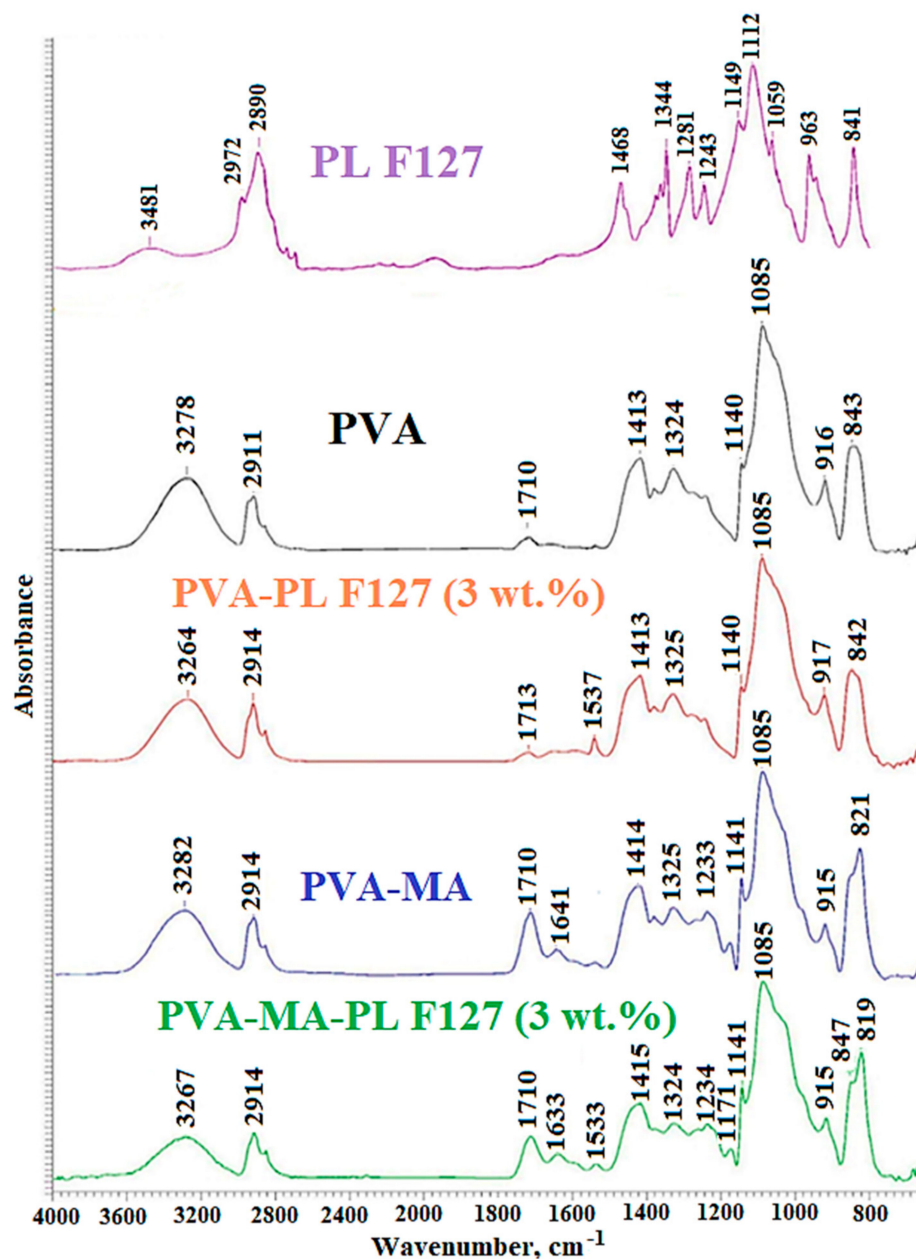


Figure 4. FTIR spectra of Pluronic F127, PVA, PVA-PL (3 wt.%), PVA-MA, and PVA-MA-PL (3 wt.%) membranes.

When the Pluronic F127 was added to the PVA membrane matrix, the peaks at 3278, 2911, 1710, 1324, 916, and 843 cm^{-1} were slightly shifted. It was also noted that the peak intensity at 1537 cm^{-1} increased with the addition of Pluronic F127. These slight changes may be due to the superimposition of PVA and modifier peaks as well as the low content of Pluronic F127 in the membrane matrix.

In the spectrum of PVA-MA membranes, there are changes in the peaks in the spectral range 800–2000 cm^{-1} . The intensive stretching band at 1710 cm^{-1} indicates the existence of an ester carbonyl group [56,62]. The absorption peak at 1641 cm^{-1} is a clear indication of the presence of $-\text{CO}-\text{CH}=\text{CH}-$ stretching, which confirms the interaction of PVA with unsaturated MA, causing the formation of an unsaturated ester due to cross-linking of polymer chains [56]. The modification with 3 wt.% Pluronic F127 of PVA-MA membrane led to less intensity and the shift in peak at 3282 to 3267 cm^{-1} , indicating the cross-linking of polymer chains. Peaks at 1710 and 1633 cm^{-1} corresponding to an ester carbonyl group

and $-\text{CO}-\text{CH}=\text{CH}-$ stretching, respectively, are also observed for the PVA-MA-PL (3 wt.%) membrane. FTIR spectra of PVA-MA and PVA-MA-PL hybrid membranes confirmed the formation a cross-linking network. The changes in PVA FTIR spectra obtained by adding Pluronic F127 or/and MA significantly affected the membrane performance.

The morphology of dense PVA and PVA-MA membranes modified by Pluronic F127 was investigated using SEM (Figure 5).

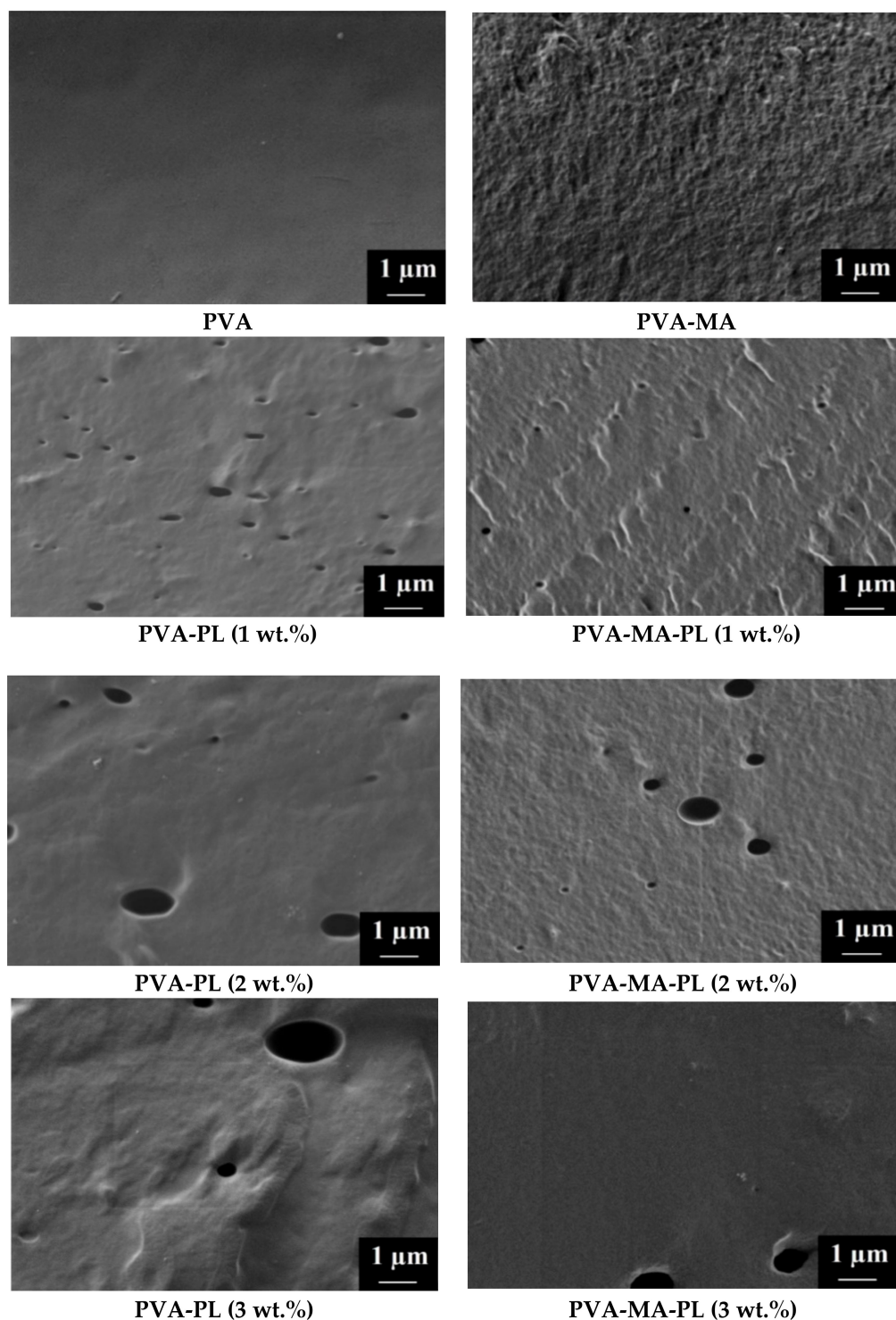


Figure 5. SEM cross-sectional micrographs of dense PVA and PVA-MA membranes modified by different contents of Pluronic F127 (0–3 wt.%).

Figure 5 demonstrates that the morphology of the pristine PVA membrane without any modification is smooth and flat. The addition of 1 wt.% Pluronic F127 into the PVA membrane matrix led to some cavities forming. With increasing Pluronic F127 content in the PVA matrix, the number of cavities decreased but their size became larger. The chemically cross-linked by MA PVA membrane (PVA-MA) had a rough cross-sectional structure compared with the untreated PVA membrane (Figure 5). The chemical cross-linking of PVA-PL (1, 2, 3 wt.%) membranes by MA decreased the number and the size of the formed cavities. MA acts as a cross-linking agent, leveling the effect of Pluronic F127. This may be why the cross-linked PVA membranes by MA have slightly lower permeation flux than uncross-linked PVA membranes (Figure 3).

The surface properties of PVA membranes (with/without the chemical cross-linking) were investigated by measuring the water contact angle to estimate the changes due to the addition of Pluronic F127. The water contact angles of PVA and PVA-MA membranes modified by Pluronic F127 (1, 2, and 3 wt.%) are presented in Figure 6.

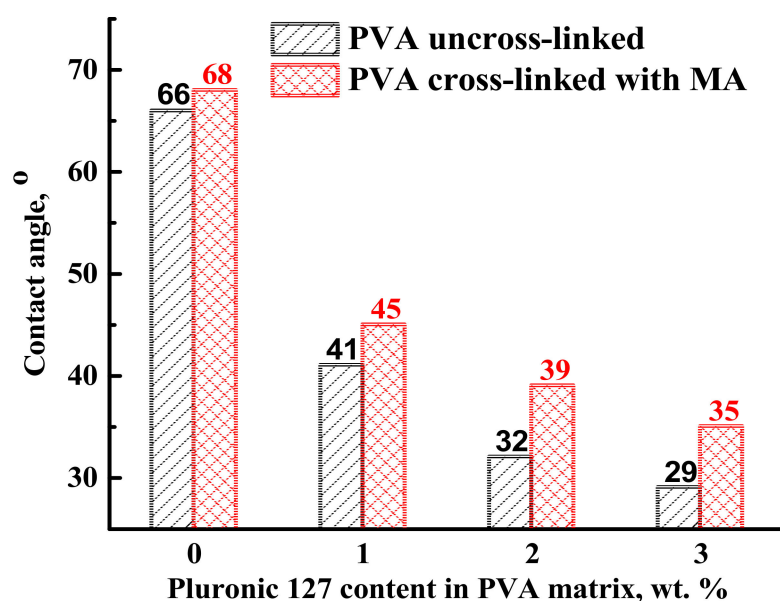


Figure 6. The dependence of the water contact angle value on the Pluronic F127 content in the PVA membrane.

The data in Figure 6 demonstrate that the contact angle remarkably decreases with the increase in Pluronic F127 content in PVA and PVA-MA matrices. This indicates a practical enhancement in the membrane surface hydrophilicity due to the addition of Pluronic F127. Pluronic F127 consists of hydrophilic polyethylene glycol (PEG) blocks and hydrophobic polypropylene glycol (PPG) blocks. The hydrophobic PPG groups are embedded in the PVA chains and stay fixed in the membrane matrix, while the hydrophilic PEG groups are released on the membrane surface. Thus, the surface of PVA membranes becomes more hydrophilic due to an increase in the number of hydrophilic blocks of PEG of Pluronic F127 on the membrane surface. Additionally, it should be noted that chemically cross-linked membranes have slightly higher contact angle values compared with the uncross-linked membranes. This may be due to the levelling effect of MA on Pluronic F127, resulting in lower surface hydrophilicity.

The solubility-diffusion mechanism is used to explain the transport of components through the dense membranes during the pervaporation process. In this mechanism, three main stages of the process can be distinguished: (1) component sorption on the membrane surface, (2) component diffusion through the membrane, and (3) component desorption from the opposite membrane side. Since the first stage of the solubility-diffusion mechanism is component sorption, the equilibrium swelling of membranes based on PVA

and its composites with Pluronic F127 (with/without chemical cross-linking) was estimated to evaluate the penetration of components (water and IPA) through the membrane during the pervaporation. The degree of swelling for PVA-based membranes in an IPA–water mixture (12 wt.% water) is presented in Figure 7.

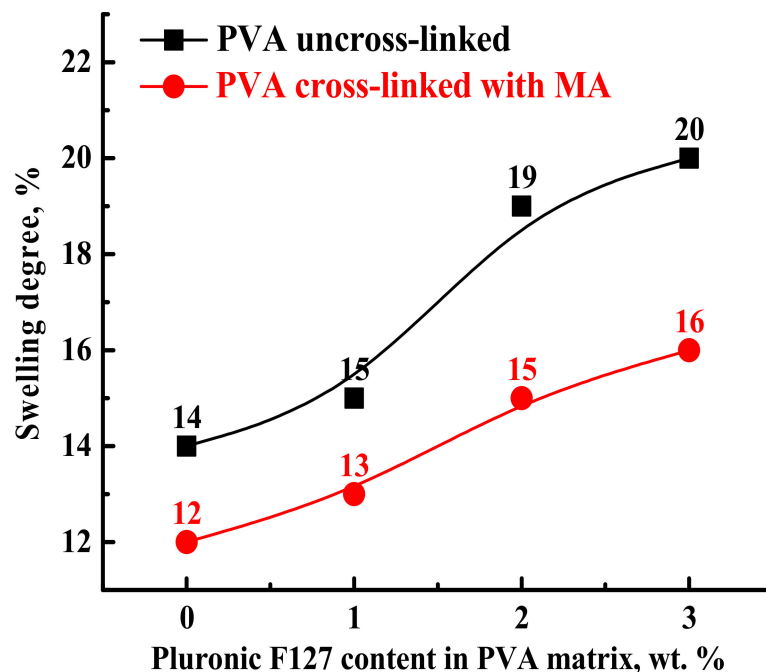


Figure 7. Degree of swelling for PVA-based membranes in the azeotropic water–IPA (12/88 wt.%) mixture.

The data presented demonstrate that the addition of Pluronic F127 into the PVA and PVA-MA matrices increases the degree of swelling. This may be due to the amphiphilic nature of Pluronic F127, which contains hydrophobic PPG parts and hydrophilic PEG parts. Additionally, it can be seen that the degree of swelling of cross-linked PVA by MA membranes is slightly lower than that of uncross-linked ones. This is because the cross-linking of PVA by MA suppresses the swelling of PVA in water and due to the leveling effect of MA on Pluronic F127. These results are consistent with the contact angle data (Figure 6).

For the industrial application of dense PVA membranes, it is necessary to create a supported membrane with a thin selective layer based on PVA deposited on a porous substrate, improving the membrane performance. A thin selective layer based on PVA-MA-PL-F127 (3 wt.%) was chosen due to its optimal characteristics (as obtained in Section 3.1). The PA porous membrane was used as a substrate. In order to obtain supported membranes with increased productivity, it was very important to optimize the porous membrane (substrate) separately by choosing the right material, concentration, and conditions of its preparation and by optimizing its properties. The next section describes a new porous PA-based substrate that has been developed and optimized for supported PVA membranes modified by Pluronic F127.

3.2. Development and Study of Porous PA Membranes (Substrates)

A porous PA substrate was prepared from a PA solution of different concentrations (12–20 wt.%) to select the optimal porosity and surface properties and to obtain a defect-free thin PVA layer. The structural characteristics of the prepared PA membranes (substrates) were studied by SEM and AFM methods. The transport properties of porous PA substrates were evaluated by ultrafiltration of pure water and the bovine serum albumin (BSA) solution to estimate its productivity.

3.2.1. Structure of PA membranes (substrates)

The inner morphology of porous PA membranes was analyzed by SEM. The SEM cross-sectional micrographs of porous membranes (substrates) obtained from a PA solution of various concentrations (12, 15, 17, and 20 wt.%) are presented in Figure 8.

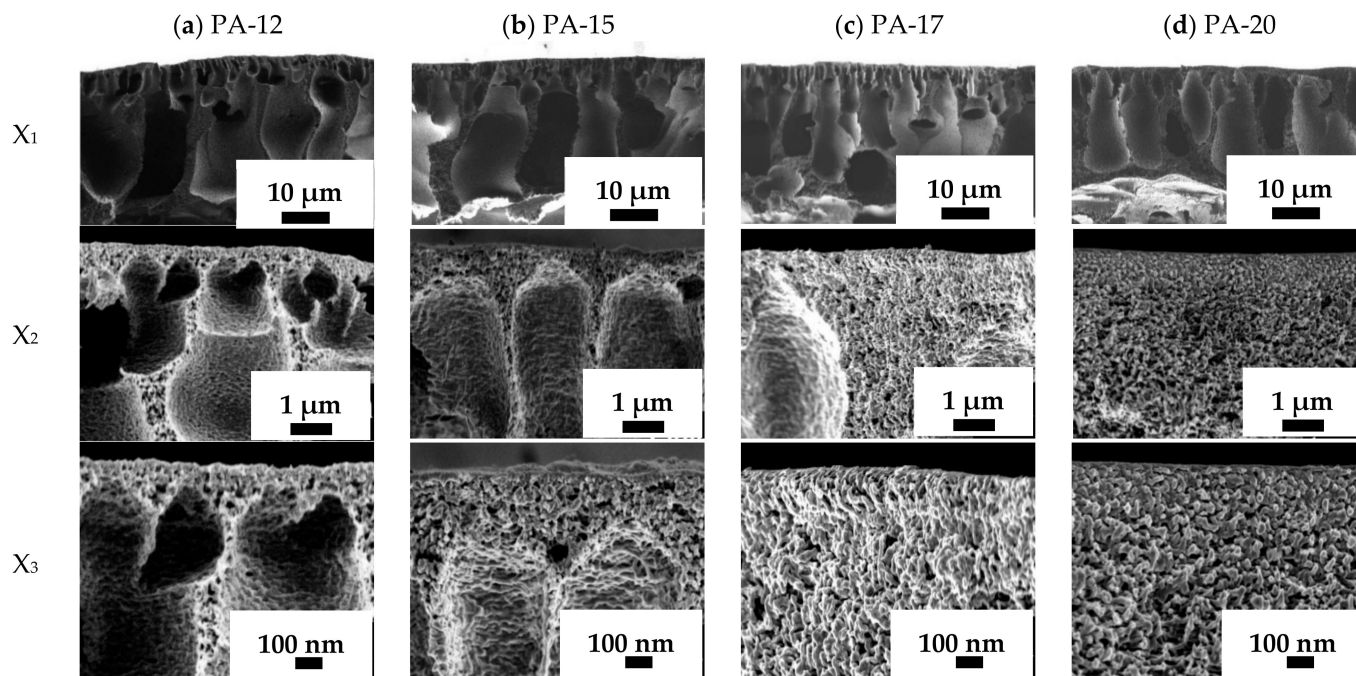


Figure 8. The SEM cross-sectional micrographs of porous PA membranes (substrates) prepared from a PA solution of various concentrations (a) 12 wt.%, (b) 15 wt.%, (c) 17 wt., and (d) 20 wt.% at different magnification ($X_1 = 1.00$ K, $X_2 = 25.00$ K, and $X_3 = 50.00$ K).

Figure 8 demonstrates that the macrovoids of the PA membrane decrease significantly with increasing concentration of the casting PA solution from 12 to 20 wt.%. In addition, the upper layer of the membrane (selective layer) becomes denser and thicker as the concentration of PA in the casting solution increases. The following steps can explain the mechanism of pore formation on the surface of the membrane: upon immersing the support with the casting polymer solution in the coagulation bath with non-solvent (water), the solvent in the casting solution spreads out into the coagulation bath while the non-solvent spreads into the PA casting solution. This process continues until the non-solvent has wholly replaced the solvent in the casting solution [63]. An increase in the concentration of the PA solution leads to an increase in the polymer solution viscosity; consequently, the exchange rate of non-solvent (water)–solvent (DMA) decreases during phase inversion, which leads to slower precipitation of the PA on mechanical support lavsan [64].

The surface characteristics of the PA membranes (substrates) were detected by AFM. AFM images with a scan size of $15 \times 15 \mu\text{m}$ of PA membranes (substrates) prepared from PA solution of various concentrations (12, 15, 17, and 20 wt.%) are presented in Figure 9.

Based on AFM images, the roughness characteristics of the surfaces of PA membranes (substrates) were calculated in terms of the root-mean-squared roughness (R_q) and average roughness (R_a) (Table 2).

As can be observed from the data in Table 2, the average surface roughness and the root-mean-squared roughness decrease with an increase in the PA casting solution concentration from 12 to 20 wt.%. These surface changes can contribute to a more uniform deposition of a thin dense layer based on PVA and its composites with Pluronic F127.

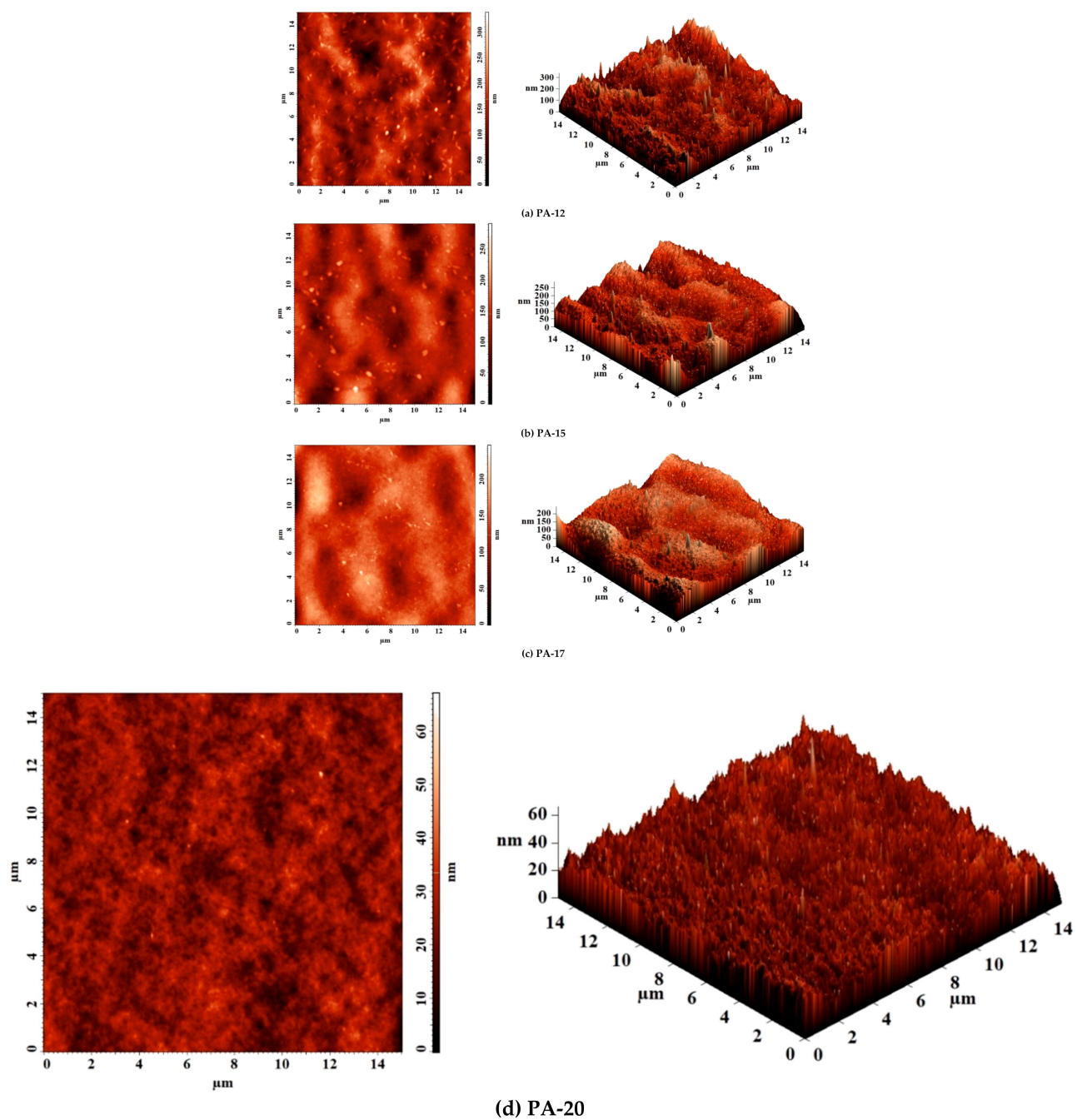


Figure 9. AFM images of the porous PA membranes (substrates) prepared from a PA solution of different concentrations: (a) 12 wt.%, (b) 15 wt.%, (c) 17 wt.%, and (d) 20 wt.%.

Table 2. Surface parameters of PA substrates.

Membrane	Surface Parameters	
	Average Roughness, Ra (nm)	Root-Mean-Squared Roughness, Rq (nm)
PA-12	30.3	37.9
PA-15	24.0	30.2
PA-17	18.7	24.0
PA-20	4.20	5.30

3.2.2. Transport Properties of PA Membranes (Substrates)

The influence of the concentration of the PA casting solution (12, 15, 17, and 20 wt.%) on the performance of porous PA membranes (substrates) was investigated in ultrafiltration of pure water and bovine serum albumin (BSA) solution (Table 3).

Table 3. Transport properties of porous PA membranes (substrates) in ultrafiltration.

Membrane (Substrate)	Pure Water Flux (J_W), l/(m ² h)	Flux of BSA (J), l/(m ² h)	R, %	FRR, %
PA-12	580	276	33	58
PA-15	392	123	82	70
PA-17	233	76	99	76
PA-20	63	59	99	87

The data demonstrate that the pure water flux (J_W) and flux of BSA (J) of the PA membranes (substrates) decrease with increasing polymer concentration (from 12 to 20 wt.%) in the casting solution, but the rejection coefficient and flux recovery ratio increase. The membrane permeability and rejection are associated with membrane porosity [65]. Thus, increasing the concentration of the casting solution leads to a decrease in the macrovoids and porosity and to the formation of a thicker and denser skin layer (confirmed by SEM, Figure 8), resulting in a less permeable but more selective (with higher rejection coefficient) asymmetric porous membrane [66].

The flux recovery ratio (FRR) of PA membranes (substrates) increases with the increase in PA casting solution concentration (Table 3). This can be explained by the fact that PA membranes (substrates) with smaller pore sizes are less prone to protein contamination during the ultrafiltration and usually have higher FRR values. In addition, a decrease in the surface roughness of PA membranes (substrates) (shown by AFM images, Figure 9) also contributes to less contamination of the PA membrane surface and to an easier ability to wash off proteins from the membrane surface.

During the ultrafiltration, optimal transport properties were obtained using the PA porous membrane (substrate) prepared from the 17 wt.% PA casting solution on lavsan. This PA membrane (substrate) has sufficiently high permeability for water and BSA as well as rejects BSA (99 %) and FRR (76 %).

3.3. Development and Study of Supported PVA Membranes

3.3.1. Transport Properties of Supported PVA/PA Membranes

The transport properties of supported PVA membranes using porous PA membranes prepared from different concentrations (12, 15, 17, and 20 wt.%) as a substrate during the pervaporation of the azeotropic water–IPA (12/88 wt.%) mixture are presented in Figure 10.

The data in Figure 10 demonstrate that the use of the PA-12 ultrafiltration membrane as a substrate results in an increase in PVA/PA-12 permeability but a decrease in selectivity. On the other hand, an increase in the PA concentration in the casting solution leads to an increase in water content in the permeate but a decrease in membrane permeability. The best transport properties are demonstrated by a supported PVA membrane on the PA-17 substrate with a permeation flux of 0.04 kg/(m² h) and water content in a permeate of 96.9 wt.%. Thus, the PA-17 ultrafiltration membrane was chosen as a substrate for the development of a supported PVA-based membrane.

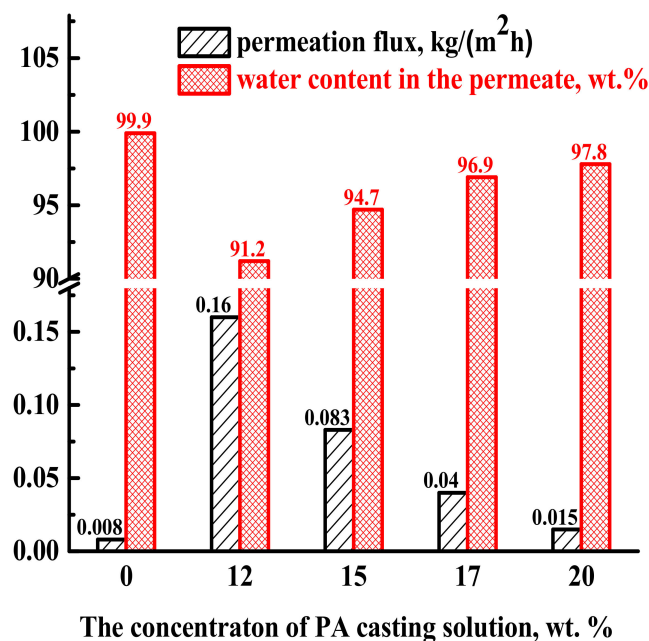


Figure 10. The permeation flux and water content in the permeate of supported PVA/PA membranes using PA membranes prepared from solutions of various concentrations (12, 15, 17, and 20 wt.%) as the substrate.

3.3.2. Transport Properties of Supported PVA-MA-PL (3 wt. %)/PA-17 Membrane

The supported PVA-MA-PL (3 wt.%) membrane on a porous PA-17 membrane was prepared to achieve high permeability for the industry potential. The choice of PVA-MA-PL (3 wt.%) as a thin layer and porous PA-17 membrane as a substrate depends on the study of structure, physicochemical properties, and transport properties of both membranes (Section 3.1, Section 3.2, and Section 3.3.1). The supported membrane based on PVA-MA was also developed for a comparison with the modified PVA-MA-PL (3 wt.%) membrane. The resulting membranes were tested in pervaporation separation of the azeotropic mixture of water–IPA (12/88 wt.%) (Figure 11).

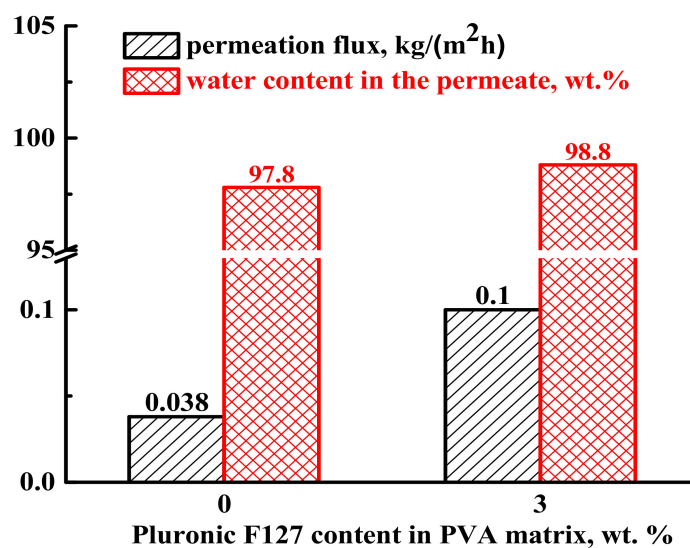


Figure 11. The dependence of permeation flux and water content in the permeate on Pluronic F127 content of PVA-MA/PA-17 membranes in pervaporation separation of an isopropanol–water (12/88 wt.%) mixture.

The use of a PA-17 substrate for the development of supported membranes led to an increase in the membrane permeation flux maintaining a high water content in the permeate compared with dense membranes. This is because the thickness of the supported membrane's selective layer is skinny compared with a dense membrane. Using the PA-17 membrane as a substrate increased the permeability from 0.007 kg/(m² h) for a dense PVA-MA membrane (Figure 3) to 0.038 kg/(m² h) for the supported PVA-MA/PA-17 membrane (Figure 11). Moreover, the addition of 3 wt.% Pluronic F127 increased the permeability to 0.1 kg/(m² h) and water content in the permeate to 98.8 wt.%. This is because Pluronic F127 increases the membrane surface hydrophilicity (Figure 6).

3.3.3. Study the Stability of the Supported PVA-MA-PL (3 wt.%)/PA-17 Membrane

The stability of the PVA-MA-PL (3 wt.%)/PA-17 membrane was studied because it exhibited high permeation flux and high water content in the permeate (Figure 11). The transport properties of this membrane were studied in the separation of water–IPA mixtures up to 80 wt.% water in the feed (Figure 12).

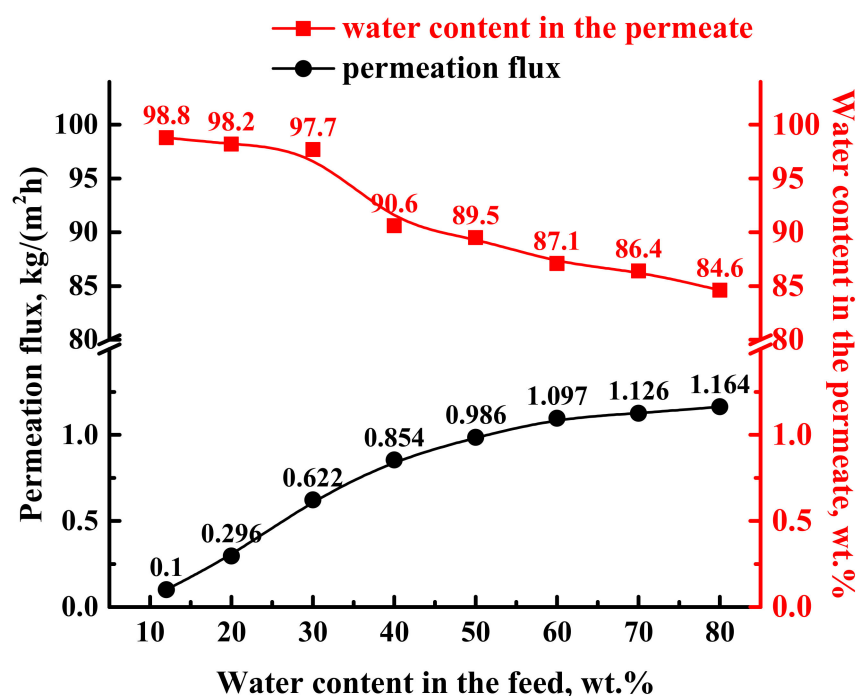


Figure 12. The dependence of the permeation flux and water content in the permeate on the water content in the feed (12–80 wt.%) during pervaporation separation of the water–IPA mixture using PVA-MA-PL (3 wt.%)/PA-17 membrane.

The permeability of the membrane and the permeate's water content vary depending on the feed composition. With high water content, the membrane tends to swell, increasing the membrane free volume. Therefore, the membrane permeability increases with the rise in water content in the feed mixture, but the permeate's water content decreases. However, the membrane still has high selectivity: the water content in the permeate decreased from 98.8 to 84.6 wt.% with increasing water concentration in the feed mixture from 12 to 80 wt.%.

The membrane stability was also investigated during the pervaporation separation of the azeotropic mixture of water–IPA (12/88 wt.%) for five days (Figure 13).

The permeation flux of membrane slightly changed from 0.1 to 0.158 kg/(m²h) and the water content in the permeate changed from 98.8 to 94.1 wt.%. However, the membrane was found to have a high degree of stability over time, and membrane swelling could explain the slight changes.

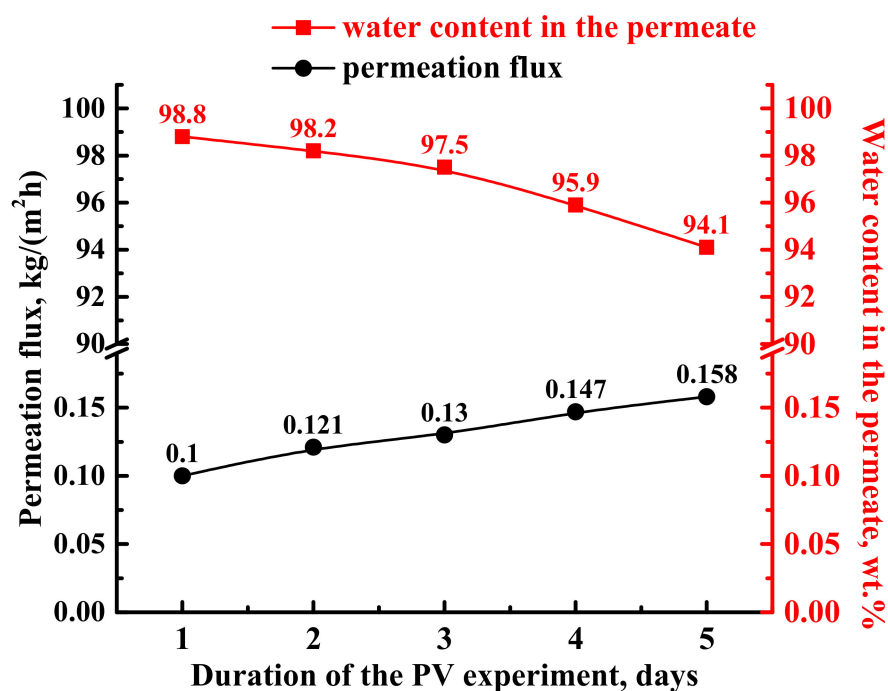


Figure 13. The dependence of permeation flux and water content in the permeate of PVA-MA-PL (3 wt. %)/PA-17 membrane on time during pervaporation separation of the azeotropic mixture of water–IPA (12/88 wt. %) for five days.

3.4. Comparison of Supported PVA-MA-PL (3 wt. %)/PA-17 Membrane Performance with Other Studies

The comparison of a supported PVA-MA-PL (3 wt. %)/PA-17 membrane in pervaporation dehydration of isopropanol with developed PVA-based membranes in other studies was carried out under close conditions to the present work (Table 4).

Table 4. Comparison of PVA-based membranes in pervaporation dehydration of isopropanol.

Membrane	Cross-Linker	Modifier	Support	Water in Feed, wt. %	T, °C	Permeation Flux, kg/(m²h)	Separation Factor (β)	Reference
PVA-MA-PL (3 wt. %)/PA-17	MA	PL F127	PA	12	22	0.100	589	This work
CS-PVA/PVDF	GA	CS	PVDF	10	30	0.070	683	[67]
PVA/PVP-PMA	GA	PMA	-	10	30	0.036	29,991	[68]
PVA-CA	CA	-	-	10	30	0.053	291	[69]
PVA-USF	USF	-	-	10	30	0.095	77	[70]
PVA/GA	GA	-	-	10	30	0.040	21	[71]
PVA-NaAlg (75:25)/GA	GA	-	-	10	30	0.039	91	
PVA-MA-PL (3 wt. %)/PA-17	MA	PL F127	PA	20	22	0.296	218	This work
PVA-CS	MA	CS	UPM-20	20	22	0.233	69	[17]
PVA-fullerenol (5 wt. %)-CS (20 wt. %)	MA	CS/Fullerenol	UPM-20	20	22	0.241	121	
PVA-fullerenol (5 wt. %)-CS (20 wt. %)/LbL-5 ^{PSS} , CS	MA	CS/Fullerenol	UPM-20	20	22	0.340	101	

PVDF—polyvinylidene fluoride, PVP—polyvinyl pyrrolidone, PMA—phosphomolybdic acid, GA—glutaraldehyde, CA—citric acid, USF—urea formaldehyde/sulfuric acid, PSS—poly(sodium 4-styrenesulfonate), UPM-20—substrate based on aromatic polysulfone amide.

It was found that the supported PVA-MA-PL (3 wt.%)/PA-17 membrane exhibited a relatively higher permeation flux and separation factor in the pervaporation separation of a water–IPA mixture (12 and 10 wt.% water) compared with the membranes described in [69–71]. However, the developed membrane has a lower separation factor with higher permeability even at 22 °C compared with CS-PVA/PVDF and PVA/PVP-PMA membranes [67,68]. According to our knowledge, there is no reported PVA membranes for isopropanol dehydration at 22 °C and 12 wt.% water content in the feed to make a full and clear comparison. However, at 22 °C and 20 wt.% water content in the feed, the PVA-MA-PL (3 wt.%)/PA-17 membrane has a higher permeation flux and/or separation factor compared with the PVA-based membranes described [17]. However, this membrane had a lower permeation flux than the reported PVA-fullerenol (5 wt.%)-CS (20 wt.%)/LbL-5^{PSS}, CS membrane in [17], but this membrane had higher selectivity. Thus, in this work, a supported PVA-MA-PL (3 wt.%)/PA-17 membrane with improved transport properties and stability for pervaporation dehydration of IPA was successfully developed.

4. Conclusions

In this study, dense and supported PVA membranes with improved transport properties were developed in order to increase the efficiency of the pervaporation process for waste water application, which belongs to the sustainable processes and is an excellent alternative to the traditional processes of separating liquid mixtures of low molecular weight substances. The introduction of Pluronic F127 into the PVA membrane led to a change in the membrane properties: the formation of rougher inner structure with cavities, surface hydrophilization, and increased swelling in water–IPA mixture. All of these changes led to improved transport properties of modified membranes for isopropanol dehydration by pervaporation. The addition of 3 wt.% Pluronic F127 into dense PVA membrane increased the permeation flux from 0.008 to 0.017 kg/(m²h), maintaining 99.9 wt.% water in the permeate. The cross-linking of the PVA-PL (3 wt.%) membrane by MA increased the membrane stability in an aqueous solution but slightly decreased the membrane permeability (0.015 kg/(m²h)).

The productivity of the developed cross-linked dense PVA membranes was further improved using a created porous PA membrane as a substrate. The membrane performance was influenced by the PA membrane's porosity (the concentration of the PA casting solution). The application of an ultrafiltration PA-17 membrane as a substrate increased permeation flux of the supported PVA-MA membrane to 0.04 kg/(m²h). Further improvement in the performance of the supported PVA membrane was obtained by adding 3 wt.% Pluronic F127. The optimal transport characteristics were obtained for a supported membrane with a PVA-MA-PL (3 wt.%) selective layer onto an ultrafiltration PA (17 wt.%) substrate: 0.1–1.164 kg/(m²h) permeation flux and 98.8–84.6 wt.% water content in the permeate in the pervaporation dehydration of isopropanol (12–80 wt.% water). This developed membrane exhibited a higher permeation flux and/or separation factor in the pervaporation dehydration of IPA (12 and 20 wt.% water) even at ambient temperature (22 °C) compared with the PVA-based membranes described in the literature [17,67–71].

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References

1. Kuzminova, A.; Dmitrenko, M.; Mazur, A.; Ermakov, S.; Penkova, A. Novel Pervaporation Membranes Based on Biopolymer Sodium Alginate Modified by FeBTC for Isopropanol Dehydration. *Sustainability* **2021**, *13*, 6092. [\[CrossRef\]](#)
2. Zereshki, S.; Figoli, A.; Madaeni, S.S.; Simone, S.; Esmailinezhad, M.; Drioli, E. Effect of polymer composition in PEEKWC/PVP blends on pervaporation separation of ethanol/cyclohexane mixture. *Sep. Purif. Technol.* **2010**, *75*, 257–265. [\[CrossRef\]](#)
3. Dmitrenko, M.; Chepeleva, A.; Ljamin, V.; Mazur, A.; Semenov, K.; Solovyev, N.; Penkova, A. Novel Mixed Matrix Membranes Based on Polyphenylene Oxide Modified with Graphene Oxide for Enhanced Pervaporation Dehydration of Ethylene Glycol. *Polymers* **2022**, *14*, 691. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Lu, L.; Sun, H.; Peng, F.; Jiang, Z. Novel graphite-filled PVA/CS hybrid membrane for pervaporation of benzene/cyclohexane mixtures. *J. Memb. Sci.* **2006**, *281*, 245–252. [\[CrossRef\]](#)
5. Smitha, B. Separation of organic–organic mixtures by pervaporation? A review. *J. Memb. Sci.* **2004**, *241*, 1–21. [\[CrossRef\]](#)
6. Ortiz, I.; Urtiaga, A.; Ibáñez, R.; Gómez, P.; Gorri, D. Laboratory and pilot plant-scale study on the dehydration of cyclohexane by pervaporation. *J. Chem. Technol. Biotechnol.* **2006**, *81*, 48–57. [\[CrossRef\]](#)
7. Li, J. Laboratory and pilot-scale study on dehydration of benzene by pervaporation. *J. Memb. Sci.* **2002**, *203*, 127–136. [\[CrossRef\]](#)
8. Chapman, P.D.; Oliveira, T.; Livingston, A.G.; Li, K. Membranes for the dehydration of solvents by pervaporation. *J. Memb. Sci.* **2008**, *318*, 5–37. [\[CrossRef\]](#)
9. Hu, C.; Li, B.; Guo, R.; Wu, H.; Jiang, Z. Pervaporation performance of chitosan–poly(acrylic acid) polyelectrolyte complex membranes for dehydration of ethylene glycol aqueous solution. *Sep. Purif. Technol.* **2007**, *55*, 327–334. [\[CrossRef\]](#)
10. Peng, M.; Vane, L.M.; Liu, S.X. Recent advances in VOCs removal from water by pervaporation. *J. Hazard. Mater.* **2003**, *98*, 69–90. [\[CrossRef\]](#)
11. Liu, L.; Jiang, Z.; Pan, F.; Peng, F.; Wu, H. The unusual change of permeation rate in PDMS membranes filled with crystalline calixarene and its derivative. *J. Memb. Sci.* **2006**, *279*, 111–119. [\[CrossRef\]](#)
12. Wilson, I.D. *Encyclopedia of Separation Science*, 1st ed.; Elsevier Science Ltd.: Amsterdam, The Netherlands, 2000; ISBN 978-0-12-226770-3.
13. Lide David, R. *CRC Handbook of Chemistry and Physics: A Ready-Reference Book of Chemical and Physical Data*, 79th ed.; CRC Press: Boca Raton, FL, USA, 1999; ISBN 978-0-8493-0468-2.
14. Othmer, K. *Encyclopedia of Chemical Technology, Volumes 1-26*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2007; ISBN 0471484962.
15. Dmitrenko, M.E.; Penkova, A.V.; Kuzminova, A.I.; Morshed, M.; Larionov, M.I.; Alem, H.; Zolotarev, A.A.; Ermakov, S.S.; Roizard, D. Investigation of new modification strategies for PVA membranes to improve their dehydration properties by pervaporation. *Appl. Surf. Sci.* **2018**, *450*, 527–537. [\[CrossRef\]](#)
16. Adoor, S.G.; Sairam, M.; Manjeshwar, L.S.; Raju, K.V.S.N.; Aminabhavi, T.M. Sodium montmorillonite clay loaded novel mixed matrix membranes of poly (vinyl alcohol) for pervaporation dehydration of aqueous mixtures of isopropanol and 1,4-dioxane. *J. Membr. Sci.* **2006**, *285*, 182–195. [\[CrossRef\]](#)
17. Dmitrenko, M.; Penkova, A.; Kuzminova, A.; Missyul, A.; Ermakov, S.; Roizard, D. Development and characterization of new pervaporation PVA membranes for the dehydration using bulk and surface modifications. *Polymers* **2018**, *10*, 571. [\[CrossRef\]](#) [\[PubMed\]](#)
18. Sairam, M.; Naidu, B.V.K.; Nataraj, S.K.; Sreedhar, B.; Aminabhavi, T.M. Poly(vinyl alcohol)-iron oxide nanocomposite membranes for pervaporation dehydration of isopropanol, 1,4-dioxane and tetrahydrofuran. *J. Memb. Sci.* **2006**, *283*, 65–73. [\[CrossRef\]](#)
19. Sairam, M.; Patil, M.; Veerapur, R.; Patil, S.; Aminabhavi, T. Novel dense poly(vinyl alcohol)–TiO₂ mixed matrix membranes for pervaporation separation of water–isopropanol mixtures at 30 °C. *J. Memb. Sci.* **2006**, *281*, 95–102. [\[CrossRef\]](#)
20. Mosleh, S.; Khosravi, T.; Bakhtiari, O.; Mohammadi, T. Zeolite filled polyimide membranes for dehydration of isopropanol through pervaporation process. *Chem. Eng. Res. Des.* **2012**, *90*, 433–441. [\[CrossRef\]](#)
21. Jyothi, M.S.; Reddy, K.R.; Soontarapa, K.; Naveen, S.; Raghu, A.V.; Kulkarni, R.V.; Suhas, D.P.; Shetti, N.P.; Nadagouda, M.N.; Aminabhavi, T.M. Membranes for dehydration of alcohols via pervaporation. *J. Environ. Manag.* **2019**, *242*, 415–429. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Castro-Muñoz, R.; Galiano, F.; Fila, V.; Drioli, E.; Figoli, A. Mixed matrix membranes (MMMs) for ethanol purification through pervaporation: Current state of the art. *Rev. Chem. Eng.* **2019**, *35*, 565–590. [\[CrossRef\]](#)
23. Wang, J.; Li, M.; Zhou, S.; Xue, A.; Zhang, Y.; Zhao, Y.; Zhong, J.; Zhang, Q. Graphitic carbon nitride nanosheets embedded in poly(vinyl alcohol) nanocomposite membranes for ethanol dehydration via pervaporation. *Sep. Purif. Technol.* **2017**, *188*, 24–37. [\[CrossRef\]](#)

24. Ghobadi, N.; Mohammadi, T.; Kasiri, N.; Kazemimoghadam, M. Modified poly(vinyl alcohol)/chitosan blended membranes for isopropanol dehydration via pervaporation: Synthesis optimization and modeling by response surface methodology. *J. Appl. Polym. Sci.* **2017**, *134*, 44587. [\[CrossRef\]](#)
25. Yeom, C.K.; Jegal, J.G.; Lee, K.H. Characterization of relaxation phenomena and permeation behaviors in sodium alginate membrane during pervaporation separation of ethanol-water mixture. *J. Appl. Polym. Sci.* **1996**, *62*, 1561–1576. [\[CrossRef\]](#)
26. Gautam, L.; Warkar, S.G.; Ahmad, S.I.; Kant, R.; Jain, M. A review on carboxylic acid cross-linked polyvinyl alcohol: Properties and applications. *Polym. Eng. Sci.* **2022**, *62*, 225–246. [\[CrossRef\]](#)
27. Razmgar, K.; Nasiraei, M. Polyvinyl alcohol-based membranes for filtration of aqueous solutions: A comprehensive review. *Polym. Eng. Sci.* **2022**, *62*, 25–43. [\[CrossRef\]](#)
28. Shiue, A.; Yin, M.-J.; Tsai, M.-H.; Chang, S.-M.; Leggett, G. Carbon Dioxide Separation by Polyethylene Glycol and Glutamic Acid/Polyvinyl Alcohol Composite Membrane. *Sustainability* **2021**, *13*, 13367. [\[CrossRef\]](#)
29. Kırşun, F.; Işıklan, N. Development of thermo-responsive poly(vinyl alcohol)-g-poly(N-isopropylacrylamide) copolymeric membranes for separation of isopropyl alcohol/water mixtures via pervaporation. *J. Ind. Eng. Chem.* **2016**, *41*, 91–104. [\[CrossRef\]](#)
30. Dave, H.K.; Nath, K. Synthesis, Characterization and Application of Disodium Tetraborate Cross-Linked Polyvinyl Alcohol Membranes for Pervaporation Dehydration of Ethylene Glycol. *Acta Chim. Slov.* **2018**, *65*, 902–918. [\[CrossRef\]](#)
31. Dmitrenko, M.E.; Penkova, A.V.; Missyul, A.B.; Kuzminova, A.I.; Markelov, D.A.; Ermakov, S.S.; Roizard, D. Development and investigation of mixed-matrix PVA-fullerenol membranes for acetic acid dehydration by pervaporation. *Sep. Purif. Technol.* **2017**, *187*, 285–293. [\[CrossRef\]](#)
32. Sajjan, A.M.; Jeevan Kumar, B.K.; Kittur, A.A.; Kariduraganavar, M.Y. Development of novel grafted hybrid PVA membranes using glycidyltrimethylammonium chloride for pervaporation separation of water–isopropanol mixtures. *J. Ind. Eng. Chem.* **2013**, *19*, 427–437. [\[CrossRef\]](#)
33. Svang-Ariyaskul, A.; Huang, R.Y.M.; Douglas, P.L.; Pal, R.; Feng, X.; Chen, P.; Liu, L. Blended chitosan and polyvinyl alcohol membranes for the pervaporation dehydration of isopropanol. *J. Memb. Sci.* **2006**, *280*, 815–823. [\[CrossRef\]](#)
34. Suhas, D.P.; Aminabhavi, T.M.; Raghu, A.V. Mixed matrix membranes of H-ZSM5-loaded poly(vinyl alcohol) used in pervaporation dehydration of alcohols: Influence of silica/alumina ratio. *Polym. Eng. Sci.* **2014**, *54*, 1774–1782. [\[CrossRef\]](#)
35. Naidu, B.V.K.; Sairam, M.; Raju, K.V.S.N.; Aminabhavi, T.M. Pervaporation separation of water + isopropanol mixtures using novel nanocomposite membranes of poly(vinyl alcohol) and polyaniline. *J. Memb. Sci.* **2005**. [\[CrossRef\]](#)
36. Zhou, K.; Zhang, Q.G.; Han, G.L.; Zhu, A.M.; Liu, Q.L. Pervaporation of water–ethanol and methanol–MTBE mixtures using poly(vinyl alcohol)/cellulose acetate blended membranes. *J. Memb. Sci.* **2013**, *448*, 93–101. [\[CrossRef\]](#)
37. Zereszki, S.; Figoli, A.; Madaeni, S.S.; Galiano, F.; Drioli, E. Pervaporation separation of ethanol/ETBE mixture using poly(lactic acid)/poly(vinyl pyrrolidone) blend membranes. *J. Memb. Sci.* **2011**, *373*, 29–35. [\[CrossRef\]](#)
38. Otvagina, K.; Penkova, A.; Dmitrenko, M.; Kuzminova, A.; Sazanova, T.; Vorotyntsev, A.; Vorotyntsev, I. Novel Composite Membranes Based on Chitosan Copolymers with Polyacrylonitrile and Polystyrene: Physicochemical Properties and Application for Pervaporation Dehydration of Tetrahydrofuran. *Membranes* **2019**, *9*, 38. [\[CrossRef\]](#)
39. Garg, P.; Singh, R.P.; Choudhary, V. Selective polydimethylsiloxane/polyimide blended IPN pervaporation membrane for methanol/toluene azeotrope separation. *Sep. Purif. Technol.* **2011**, *76*, 407–418. [\[CrossRef\]](#)
40. Chaudhari, S.; Kwon, Y.; Moon, M.; Shon, M.; Nam, S.; Park, Y. Poly(vinyl alcohol) and poly(vinyl amine) blend membranes for isopropanol dehydration. *J. Appl. Polym. Sci.* **2017**, *134*, 45572. [\[CrossRef\]](#)
41. Golemme, G.; Bruno, A.; Manes, R.; Muoio, D. Preparation and properties of superglassy polymers—zeolite mixed matrix membranes. *Desalination* **2006**, *200*, 440–442. [\[CrossRef\]](#)
42. Teli, S.B.; Gokavi, G.S.; Sairam, M.; Aminabhavi, T.M. Mixed matrix membranes of poly(vinyl alcohol) loaded with phosphomolybdic heteropolyacid for the pervaporation separation of water–isopropanol mixtures. *Colloids Surfaces A Physicochem. Eng. Asp.* **2007**, *301*, 55–62. [\[CrossRef\]](#)
43. Benzaqui, M.; Semino, R.; Carn, F.; Tavares, S.R.; Menguy, N.; Giménez-Marqués, M.; Bellido, E.; Horcajada, P.; Berthelot, T.; Kuzminova, A.I.; et al. Covalent and Selective Grafting of Polyethylene Glycol Brushes at the Surface of ZIF-8 for the Processing of Membranes for Pervaporation. *ACS Sustain. Chem. Eng.* **2019**, *7*, 6629–6639. [\[CrossRef\]](#)
44. Penkova, A.V.; Dmitrenko, M.E.; Sokolova, M.P.; Chen, B.; Plisko, T.V.; Markelov, D.A.; Ermakov, S.S. Impact of fullerene loading on the structure and transport properties of polysulfone mixed-matrix membranes. *J. Mater. Sci.* **2016**, *51*, 7652–7659. [\[CrossRef\]](#)
45. Dmitrenko, M.E.; Penkova, A.V.; Kuzminova, A.I.; Atta, R.R.; Zolotarev, A.A.; Mazur, A.S.; Vezo, O.S.; Lahderanta, E.; Markelov, D.A.; Ermakov, S.S. Development and investigation of novel polyphenylene isophthalamide pervaporation membranes modified with various fullerene derivatives. *Sep. Purif. Technol.* **2019**, *226*, 241–251. [\[CrossRef\]](#)
46. Kim, S.; Pechar, T.W.; Marand, E. Poly(imide siloxane) and carbon nanotube mixed matrix membranes for gas separation. *Desalination* **2006**, *192*, 330–339. [\[CrossRef\]](#)
47. Escobar-Chávez, J.J.; López-Cervantes, M.; Naik, A.; Kalia, Y.N.; Quintanar-Guerrero, D.; Ganem-Quintanar, A. Applications of thermo-reversible pluronic F-127 gels in pharmaceutical formulations. *J. Pharm. Pharm. Sci.* **2006**, *9*, 339–358.
48. Burts, K.S.; Plisko, T.V.; Bilyukovich, A.V.; Penkova, A.V.; Pratsenko, S.A. Modification of polysulfone ultrafiltration membranes using block copolymer Pluronic F127. *Polym. Bull.* **2021**, *78*, 6549–6576. [\[CrossRef\]](#)
49. Polak, D.; Sułkowska, J.; Szwast, M. The influence of surfactant Pluronic P123 addition on the mixed matrix membrane PEBAX 2533—ZIF-8 separation properties. *Desalin. WATER Treat.* **2021**, *214*, 64–73. [\[CrossRef\]](#)

50. Plisko, T.V.; Penkova, A.V.; Burts, K.S.; Bildyukevich, A.V.; Dmitrenko, M.E.; Melnikova, G.B.; Atta, R.R.; Mazur, A.S.; Zolotarev, A.A.; Missyul, A.B. Effect of Pluronic F127 on porous and dense membrane structure formation via non-solvent induced and evaporation induced phase separation. *J. Memb. Sci.* **2019**, *580*, 336–349. [\[CrossRef\]](#)
51. Mulijani, S.; Mulanawati, A. Enhanced Performance of Asymmetric Polystyrene Membrane by Incorporation of Pluronic F127 and Its Application for Pervaporation Separation. *Procedia Chem.* **2012**, *4*, 360–366. [\[CrossRef\]](#)
52. Semsarzadeh, M.A.; Ghalei, B. Characterization and gas permeability of polyurethane and polyvinyl acetate blend membranes with polyethylene oxide–polypropylene oxide block copolymer. *J. Memb. Sci.* **2012**, *401–402*, 97–108. [\[CrossRef\]](#)
53. Li, B.; Zhao, W.; Su, Y.; Jiang, Z.; Dong, X.; Liu, W. Enhanced desulfurization performance and swelling resistance of asymmetric hydrophilic pervaporation membrane prepared through surface segregation technique. *J. Memb. Sci.* **2009**, *326*, 556–563. [\[CrossRef\]](#)
54. Dmitrenko, M.E.; Penkova, A.V.; Atta, R.R.; Zolotarev, A.A.; Plisko, T.V.; Mazur, A.S.; Solovyev, N.D.; Ermakov, S.S. The development and study of novel membrane materials based on polyphenylene isophthalamide—Pluronic F127 composite. *Mater. Des.* **2019**, *165*, 107596. [\[CrossRef\]](#)
55. Schildknecht, C.E. Polyvinyl alcohol, properties and applications, C.A. Finch, Wiley, New York, 1973. 622 pp. \$37.50. *J. Polym. Sci. Polym. Lett. Ed.* **1974**, *12*, 105–106. [\[CrossRef\]](#)
56. Gohil, J.M.; Bhattacharya, A.; Ray, P. Studies on the Crosslinking of Poly (Vinyl Alcohol). *J. Polym. Res.* **2006**, *13*, 161–169. [\[CrossRef\]](#)
57. Penkova, A.V.; Acquah, S.F.A.; Dmitrenko, M.E.; Chen, B.; Semenov, K.N.; Kroto, H.W. Transport properties of cross-linked fullereneol–PVA membranes. *Carbon N. Y.* **2014**, *76*, 446–450. [\[CrossRef\]](#)
58. Abdelrazek, E.M.; El Damrawi, G.; Al-Shahawy, A. Some studies on calcium phosphate embedded in polyvinyl alcohol matrix before and after γ -irradiation. *Phys. B Condens. Matter.* **2010**, *405*, 808–816. [\[CrossRef\]](#)
59. Omkaram, I.; Sreekanth Chakradhar, R.P.; Lakshmana Rao, J. EPR, optical, infrared and Raman studies of VO₂⁺ ions in polyvinylalcohol films. *Phys. B Condens. Matter.* **2007**, *388*, 318–325. [\[CrossRef\]](#)
60. Pirzada, T.; Arvidson, S.A.; Saquing, C.D.; Shah, S.S.; Khan, S.A. Hybrid silica-PVA nanofibers via sol-gel electrospinning. *Langmuir* **2012**, *28*, 5834–5844. [\[CrossRef\]](#)
61. Abdelghany, A.M.; Abdelrazek, E.M.; Tarabiah, A.E. Modeling and Physical Properties of Lead Sulphide/Polyvinyl Alcohol Nano-Composite. *Quantum Matter.* **2016**, *5*, 257–262. [\[CrossRef\]](#)
62. Xie, Z.; Hoang, M.; Duong, T.; Ng, D.; Dao, B.; Gray, S. Sol–gel derived poly(vinyl alcohol)/maleic acid/silica hybrid membrane for desalination by pervaporation. *J. Memb. Sci.* **2011**, *383*, 96–103. [\[CrossRef\]](#)
63. Young, T.-H.; Chen, L.-W. Pore formation mechanism of membranes from phase inversion process. *Desalination* **1995**, *103*, 233–247. [\[CrossRef\]](#)
64. McKelvey, S. Phase separation, vitrification, and the manifestation of macrovoids in polymeric asymmetric membranes. *J. Memb. Sci.* **1996**, *112*, 29–39. [\[CrossRef\]](#)
65. Liu, R.; Liu, H.; Sha, F.; Yang, H.; Zhang, Q.; Shi, S.; Zheng, Z. Investigation of the Porosity Distribution, Permeability, and Mechanical Performance of Pervious Concretes. *Processes* **2018**, *6*, 78. [\[CrossRef\]](#)
66. Elahi, S.H.; Escobar, I.C. Investigation of the Effects of Thickness and Presence of Pore Formers on Tailor-Made Ultrafiltration Polysulfone Membranes. In *ACS Symposium Series*; American Chemical Society: Washington, DC, USA, 2011; pp. 271–283. ISBN 9780841226180.
67. Wang, J.; Zhang, W.; Li, W.; Xing, W. Preparation and characterization of chitosan-poly (vinyl alcohol)/polyvinylidene fluoride hollow fiber composite membranes for pervaporation dehydration of isopropanol. *Korean J. Chem. Eng.* **2015**, *32*, 1369–1376. [\[CrossRef\]](#)
68. Mali, M.G.; Magalad, V.T.; Gokavi, G.S.; Aminabhavi, T.M.; Raju, K.V.S.N. Pervaporation separation of isopropanol–water mixtures using mixed matrix blend membranes of poly(vinyl alcohol)/poly(vinyl pyrrolidone) loaded with phosphomolybdic acid. *J. Appl. Polym. Sci.* **2011**, *121*, 711–719. [\[CrossRef\]](#)
69. Burshe, M.C.; Sawant, S.B.; Joshi, J.B.; Pangarkar, V.G. Separation Sorption and permeation of binary water–alcohol systems through PVA membranes crosslinked with multifunctional crosslinking agents. *Sep. Purif. Technol.* **1997**, *12*, 145–156. [\[CrossRef\]](#)
70. Rao, K.S.V.K.; Subha, M.C.S.; Sairam, M.; Mallikarjuna, N.N.; Aminabhavi, T.M. Blend membranes of chitosan and poly(vinyl alcohol) in pervaporation dehydration of isopropanol and tetrahydrofuran. *J. Appl. Polym. Sci.* **2007**, *103*, 1918–1926. [\[CrossRef\]](#)
71. Kurkuri, M.D.; Toti, U.S.; Aminabhavi, T.M. Syntheses and characterization of blend membranes of sodium alginate and poly(vinyl alcohol) for the pervaporation separation of water + isopropanol mixtures. *J. Appl. Polym. Sci.* **2002**, *86*, 3642–3651. [\[CrossRef\]](#)