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Review

Porous Polyvinyl Alcohol Membranes: Preparation Methods and Applications

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Abstract: Polymeric membrane technology is a constantly developing field in both the research and industrial sector, with many applications considered nowadays as mature such as desalination, wastewater treatment, and hemodialysis. A variety of polymers have been used for the development of porous membranes by implementing numerous approaches such as phase inversion, electrospinning, sintering, melt-spinning and cold-stretching, 3D printing, and others. Depending on the application, certain polymer characteristics such as solubility to non-toxic solvents, mechanical and thermal stability, non-toxicity, resistance to solvents, and separation capabilities are highly desired. Poly (vinyl alcohol) (PVA) is a polymer that combines the above-mentioned properties with great film forming capabilities, good chemical and mechanical stability, and tuned hydrophilicity, rendering it a prominent candidate for membrane preparation since the 1970s. Since then, great progress has been made both in preparation methods and possible unique applications. In this review, the main preparation methods and applications of porous PVA based membranes, along with introductory material are presented.

Keywords: poly (vinyl alcohol); polymeric membranes; porous materials; separation applications

1. Introduction

Polymeric membranes are used in a vast array of applications; predominantly in water treatment, gas separations, medical, industrial, fuel cells, and others [1–10].

The membrane's purpose is to act as a selective barrier for species of interest. In order for that to be achieved, a membrane must have a certain structure. Typically, these can be either porous, having openings of a desired diameter acting as a sieve, or non-porous, where the chemical nature of the polymeric matrix dominates molecular diffusion, favoring the passage of a certain component against other(s). Membrane performance typically is a trade-off between permeability, which is the normalized flux of the desired component and the selectivity, which is defined as the ratio of the compositions of the species of interest in the permeate side. This means that it is challenging to achieve both high fluxes accompanied with high selectivity. Membrane structure plays a vital role in controlling these factors; dense structures exhibit high selectivity but low permeability (disproportional to the membrane's thickness) while porous structures are characterized by high fluxes and lower selectivity. The combination of these two cases is considered as the ideal scenario: an asymmetric structure comprising of a highly porous substrate, providing flux and mechanical strength, and a thin dense layer providing the desired selectivity. This asymmetry is highly desirable but many challenges remain still on how to achieve controlled structures with desired properties and up-scalable capabilities. Common polymers used for the membrane preparation include cellulose acetate (CA), polyethersulfone (PES), polysulfone (PSf), poly(vinylidene fluoride) (PVDF), polyacrylonitrile (PAN), polytetrafluoroethylene (PTFE), poly-(1,4-phenylene ether), ether sulfone (PPEES), sulfonated poly(ether ether ketone) (SPEEK), poly(p-phenylene sulfide) (PPS), polypropylene (PP), polycarbonate (PC), poly(dimethyl siloxane) (PDMS), polyether block amide (PEBAX), polyimides (PI), ultra-high molecular weight polyethylene (UHMWPE), and others. Several polymer characteristics are taken into consideration in regard to specific membrane applications [11–15] such as thermal, chemical, and mechanical stability as well as hydrophobicity/hydrophilicity. For example, hydrophilic polymers such as poly (vinyl alcohol) (PVA) are the choice of preference when it comes to pervaporation [16] or treating oil containing wastewater [17].

Properties of Poly(Vinyl Alcohol)

Synthetic routes for the preparation of poly (vinyl alcohol) have been reported since the 1920s from Herrmann and Haehnel [18] by saponifying poly (vinyl esters) and in the 1930s by Herrmann, Haehnel, and Berg [19] by transesterification. Since then, various preparation routes have been proposed, while in the industrial scale, the majority of PVA is produced via the polymerization of vinyl esters or ethers (usually vinyl acetate), with subsequent saponification or transesterification. Hydrolysis of poly (vinyl acetate), (PVAc) to PVA can be performed in solution, suspension, or emulsion with alkaline or acidic catalysts. The preferred process is transesterification in methanol in the presence of catalytic amounts of sodium methoxide [20]. In reality, PVA is a copolymer consisting of hydroxyl and acetyl units remaining from the incomplete hydrolysis of the parent poly (vinyl acetate). Therefore, polymers with greater than 50% hydroxyl groups are considered as poly (vinyl alcohols) while the ones with more than 50% acetyl groups are poly (vinyl acetates). The percentage of OH– (%mol) groups in the final product is also called degree of hydrolysis (DH) and the properties of PVA are greatly dependent on that. Typical commercial degrees of hydrolysis are 70–72%mol, 87–89%mol and 99+%mol (fully hydrolyzed). Solubility of PVA is greatly dependent on the DH with the fully hydrolyzed grades being more difficult to dissolve, typically in hot water, than the lower hydrolysis grades producing more viscous aqueous solutions. This phenomenon is attributed to the strong hydrogen intramolecular bonds that form in the fully hydrolyzed grades than the lower ones [21]. PVA is also soluble in polar solvents like N-methyl-2-pyrrolidone [22], dimethyl sulfoxide, diethylenetriamine, formamide, N,N-dimethylformamide, and hexamethylphosphoric triamide, glycerol (hot), and piperazine while it is not soluble in lower alcohols, tetrahydrofuran, dioxane, ethylene glycol formal, ketones, esters, carboxylic acids, and concentrated aqueous solutions [23].

PVA's melting point is approximately 220–230 °C for fully hydrolyzed grades and 180–190 °C for partially hydrolyzed ones. A similar effect is observed in glass transition temperature, which ranges from 65–85 °C while the decomposition temperature is 220–250 °C.

The crystal structure of PVA was first reported by Bunn [24] in 1948 and confirmed by studies conducted by Assender and Windle [25,26] using x-ray, and Takahashi [27] neutron diffraction. The crystal cell is monoclinic (a = 7.81 Å, b = 2.52 Å, c = 5.51 Å, $\alpha = \gamma = 90^o$, $\beta = 91.7°$) [25] with the intramolecular hydrogen bonds responsible for the chain arrangements as can be seen in Figure 1.

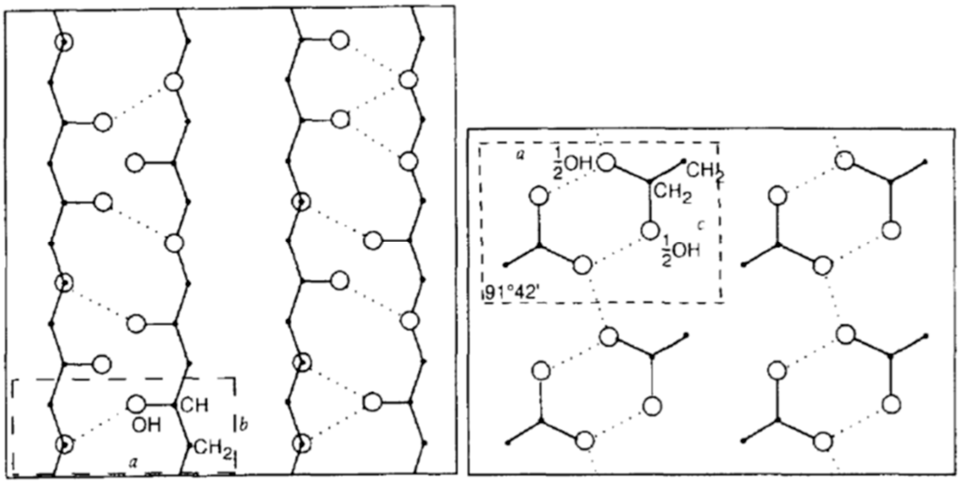

Figure 1. The crystal structure of poly (vinyl alcohol) as proposed by Bunn. Reprinted with permission from [25]. Copyright 1998 Elsevier B.V.

Annealing affects the crystal structure and crystallinity, resulting in increased levels of the latter, as can been seen in Figure 2 Crystal formation is also altered in the presence of nanoparticles [28], especially with hydrophilic ones like clays [29,30], as seen in Figure 3, where the addition of bentonite clay induced an additional crystal formation.

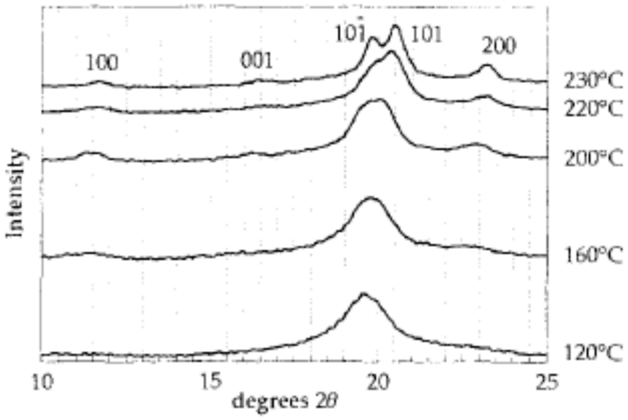

Figure 2. X-ray powder diffraction traces from films annealed at different temperatures. Reprinted with permission from [25]. Copyright 1998 Elsevier B.V.

The reported density for the amorphous part of PVA is $p_a = 1.269$ g/cc, while for the crystalline part it is $p_c = 1.345$ g/cc [31,32].

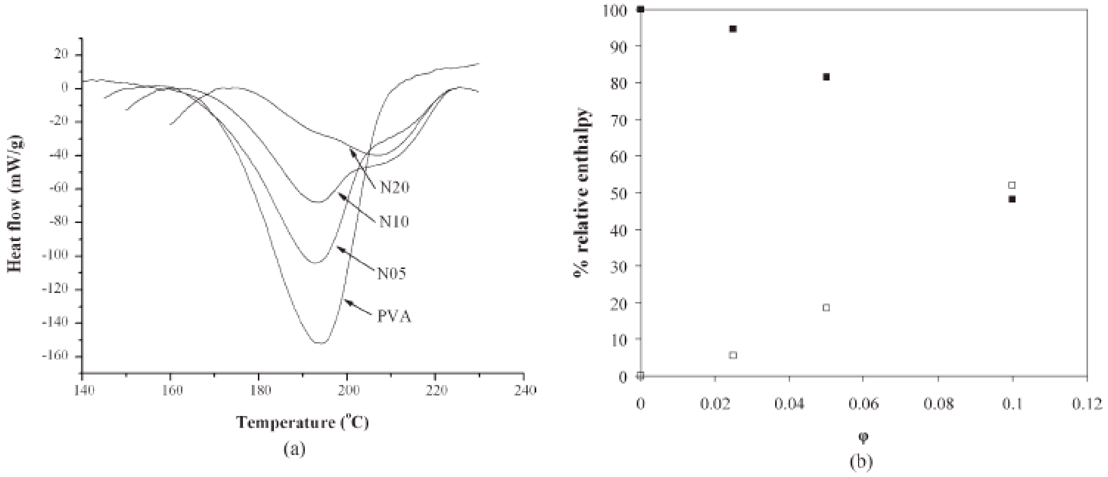

Figure 3. (**a**) Differential scanning callorimetry curves in the melting region. (**b**) Fraction of the heats of fusion for the two phases (closed symbols: bulklike phase, open symbols: clay induced phase). Reproduced by permission from [33]. Copyright 2011 Wiley Periodicals, Inc.

Additionally, the great film forming, adhesion, good mechanical and optical properties, O_2 barrier capability in low humidity [33–35], non-toxicity [36,37], biocompatibility and partial biodegradability [38,39], and relatively easy nanocomposite preparation capabilities [40] render PVA a valuable candidate material in diverse and demanding applications.

Due to these properties, PVA has found its way in a wide spectrum of technological fields ranging from biomedical to construction. Indicative applications include fibers, water soluble packaging, protective colloid in emulsion and suspension polymerization, adhesives, sizing, paper industry, tissue engineering [41], wound dressing [42] contact lenses, drug delivery systems [43–46], and orthopedics [47].

Practical applications of poly(vinyl alcohol) based membranes require that it should be crosslinked prior to use in order to retain the structure and mechanical properties, especially in water related processes;

studies have also shown that crosslinking can induce minimum effects on the thermal and mechanical properties, or even their deterioration [48]. Crosslinking can be performed via various chemical or physical paths [49–51]. Chemical crosslinking requires di-functional crosslinking reagents [49] that typically include glutaraldehyde [52,53], as can be seen in Figure 4a,b, acetaldehyde, formaldehyde, and other monoaldehydes. The crosslinking reaction takes place in an acidic environment with sulfuric and hydrochloric acids being the common chemicals used. A list of common crosslinkers used on PVA can be seen in

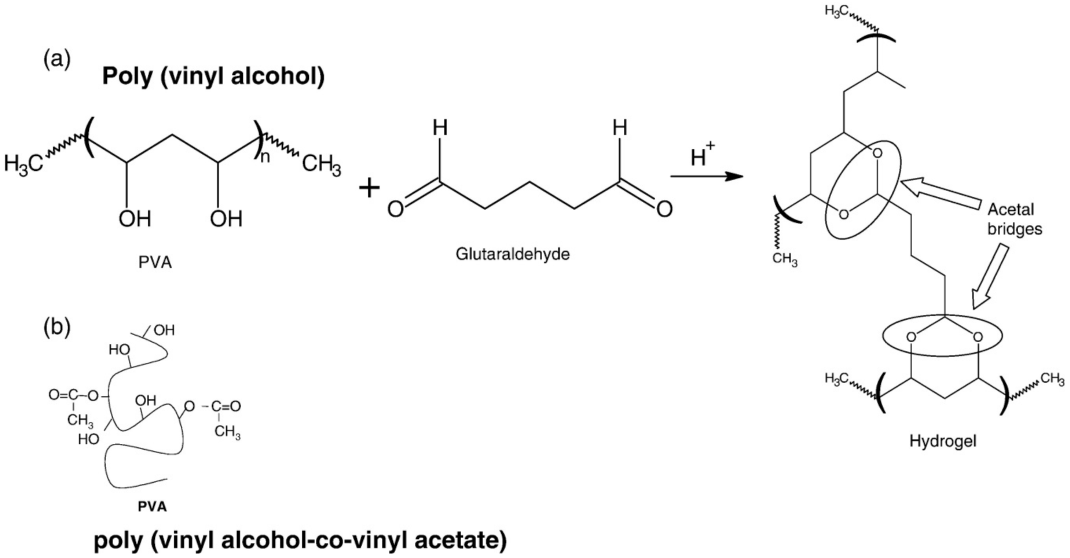

Figure 4. Crosslinking reaction between (**a**) poly (vinyl alcohol) and (**b**) glutaraldehyde. Reproduced with permission from [53]. Copyright 2007 Elsevier B.V.

Table 1. Crosslinkers used on poly (vinyl alcohol) (PVA), adapted from [49]. Since some of these crosslinking agents are considered toxic, proper actions should be taken in order that no residues exist in the final material. Crosslinking reactions of PVA with some commonly used acids [54] can be seen in Figure 5. Other crosslinking methods include freeze/thaw method [16], heat treatment [55], and γ-irradiation [56].

Table 1. Crosslinkers used on poly (vinyl alcohol) (PVA), adapted from [49].

Glutaraldehyde	Formaldehyde
Citric acid	Boric acid
Tetraethoxysilane	Malic acid
Poly(acrylic acid)	Glyoxal
Genipin	PEG diacylchloride
Terephthaldegyde	Malonic acid
Sulfur -succinic acid	Acetaldehyde
Acrolein and methacrolein	Fumaric acid
Urea formaldehyde/H_2SO_4	1,2-Dibromoethane
Divinyl sulfone	γ-Glycidoxypropyltrimethoxysilane
Maleic acid and anhydride	Trimesoyl chloride
Toluene diisocyanate	Glycidyl acrylate

As a membrane material, PVA is considered attractive due to the following advantages: hydrophilicity, water permeability, good mechanical properties, thermal and chemicals resistance, anti-fouling potential, and film forming ability. On the negative side, PVA is permeable to ions, has a high degree of swelling, compacts under pressure, and shows low flux when it is highly crosslinked [40].

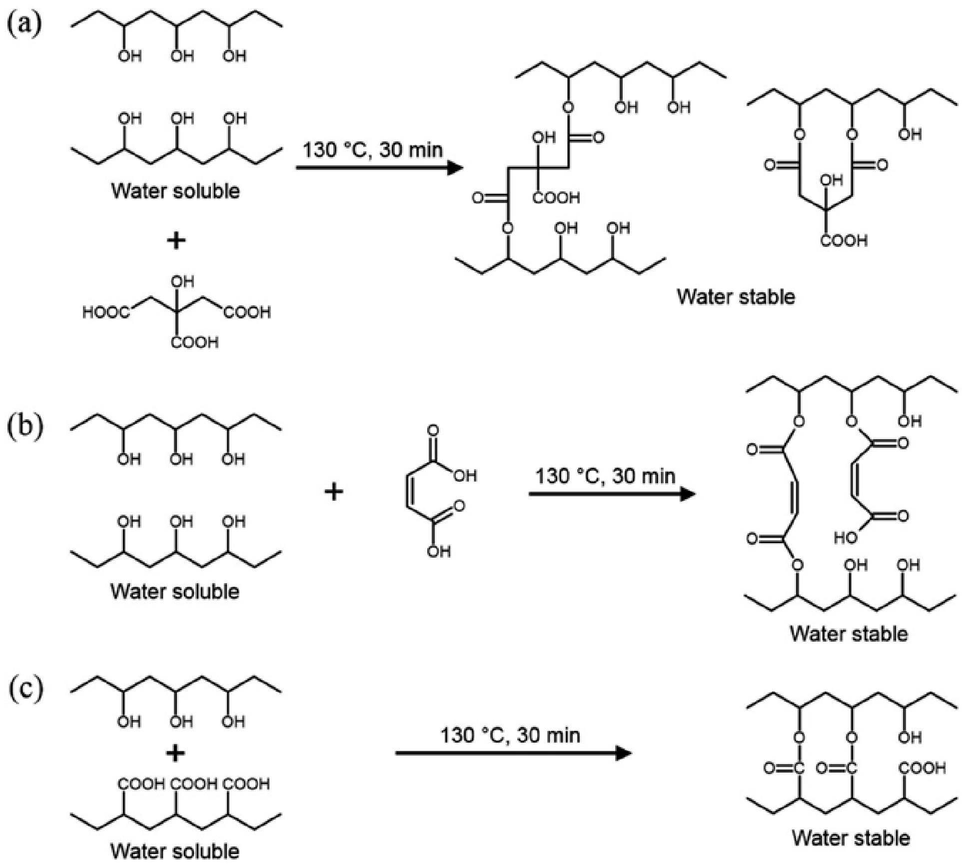

Figure 5. Cross-linking reactions between (**a**) citric acid, (**b**) maleic acid and (**c**) poly (acrylic acid) and PVA. Reproduced with permission from [54]. Copyright 2017 WILEY-VCH Verlag GmbH & Co.

In this context, dense (non-porous) PVA has been used in various membrane preparations for many years. The main applications include the implementation of PVA based membranes in pervaporation [57] for the dehydration of ethanol [58–63], isopropanol [64], acetic acid [65], ethylene glycol mixtures [66], direct methanol fuel cells [67], reverse osmosis desalination [68], CO_2 separation [69], as a polymer electrolyte membrane [70,71], biodiesel synthesis [72], ion exchange [73], and others.

Furthermore, poly (vinyl alcohol) has attracted a lot of research interest as a membrane for separations, especially in water treatment due to its low biofouling tendency [74], a known issue that affects various membrane processes [75].

2. Polymeric Porous Structures

Over the last 60 years or so, there has been great progress in several techniques that have been developed for the preparation of porous polymeric membranes both on industrial and lab scale [76–79] including (a) phase inversion also called phase separation (PS), (b) track-etching, (c) stretching, (d) sintering, (e) electrospinning, and interfacial polymerization [80]. In parallel, the effects of nanoparticle incorporation during membrane preparation have also been extensively studied for both performance and structure control [81,82].

In the following paragraphs, the main techniques for obtaining porous structures and how they were applied for the case of PVA will be described.

2.1. Phase Inversion Method

Phase inversion can be generally described as the process by which a homogeneous polymer solution becomes separated in a polymer rich and in a polymer lean phase in a controlled manner [83]. The polymer rich phase will eventually become the membrane's solid skeleton, while from the residual lean phase, the pores will be created. Structures obtained by this method typically result in a sponge or finger-like macropores (i.e., pore diameter > 50 nm) [84].

Phase inversion, also called demixing or precipitation, is the general term of the process and can be divided in the following sub categories [85,86]:

Non solvent induced phase separation (NIPS), also referred to as immersion precipitation, in which the addition of a non-solvent in the polymer solution results in a miscibility gap, according to the ternary diagram of the system as shown in Figure 6 [87]. NIPS is the primary technique for the production of asymmetric structures and polymeric membranes on an industrial scale, resulting in pore size diameters ranging from hundreds of nanometers to 10+ µm. Typically, the polymeric solution is casted in the appropriate support (e.g., a non-woven fabric [88]) and is afterward dipped in a non-solvent bath, resulting in the immediate solid membrane formation.

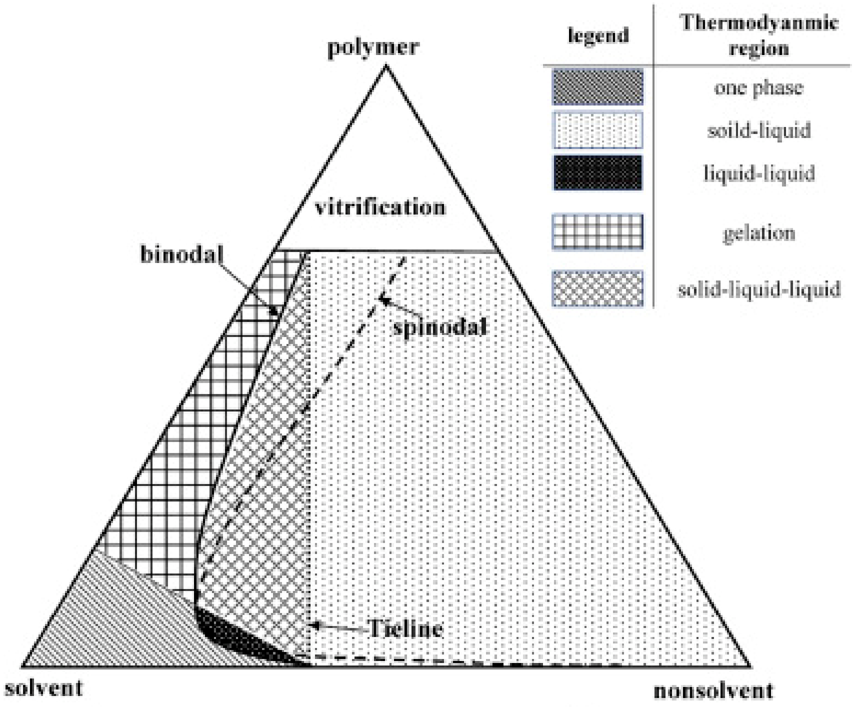

Figure 6. Schematic representation of different possible thermodynamic regions for a ternary semicrystalline polymeric system. Reproduced with permission from [87]. Copyright Elsevier B.V. 2015.

Evaporation induced PS (EIPS), in which the polymer is dissolved in a mixture of a volatile solvent and a less volatile non-solvent. As solvent evaporation starts, the composition of the solution is changing in favor of the non-solvent and eventually results in polymer precipitation, forming an asymmetric skinned membrane.

Vapor-induced PS (VIPS) was first introduced by Zsigmondy and Bachmann [89] in 1918 and then developed further by Elford in 1937 [90]. In the VIPS process, the casted membrane is placed in a controlled environment chamber containing non-solvent vapors, which penetrate from the vapor phase to the polymer solution and induce phase inversion [91–93]. In general, VIPS is regarded as a more controllable technique with the tradeoff of longer production time requirements.

Temperature induced PS (TIPS), in which the temperature of the polymer solution is changed so that the polymer solubility in a solvent changes, eventually leading to precipitation.

2.2. Electrospinning

Electrospinning (electrostatic + spinning) is a technique used to create polymer nanofibers from polymeric solutions ranging in diameter from less than 3 nm to 1 µm with the aid of an electrostatic force (Figure 7) [94,95]. Although not the most popular porous material manufacturing process, electrospinning has evolved, especially in the last few years, into a promising manufacturing process of membrane technology called electrospun nanofibrous membranes (ENMs). By carefully selecting the proper fiber diameter, consecutive layering and packing density, a porous asymmetric structure can be therefore shaped with membrane characteristics such as high air permeability and targeted liquid entry and bubble point pressure. Electrospinning was introduced as a mean of processing textile yarns in the 1930s [96], though it originates in the studies of Lord Rayleigh, and since then it was used in a variety of material preparation [97] including among others, medical applications [98], protective textiles, [99,100], and filtration membranes [101]. The main advantages of ENMs is their high surface area and porosity, open structure, controllable manufacturing, and nanocomposite capability. Typically ENMs are produced as thin layers, which depending on the transmembrane pressure of the intended application can require the need of a support (usually a non-woven fabric) in order to provide mechanical stability.

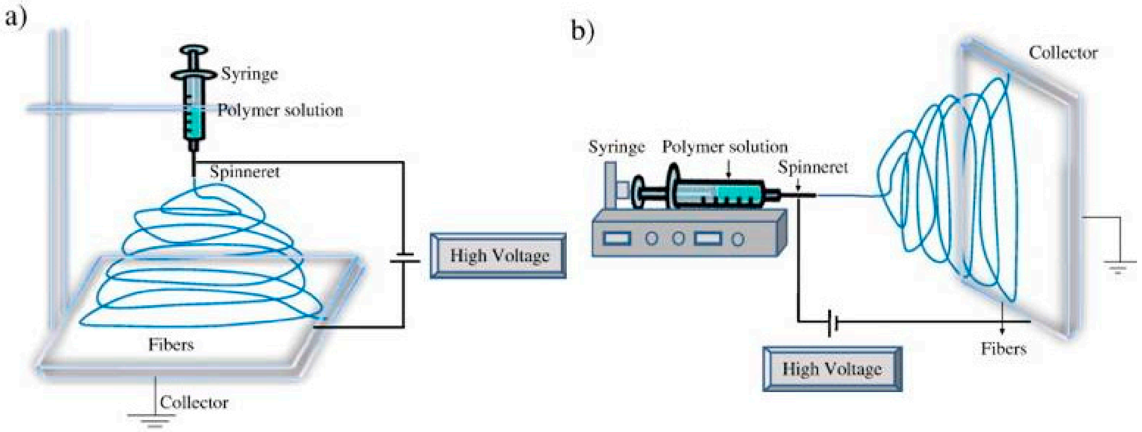

Figure 7. Schematic diagram of setup of electrospinning apparatus. (**a**) Typical vertical setup and (**b**) horizontal setup of electrospinning apparatus. Reproduced with permission from [94]. Copyright 2010 Elsevier Inc.

A special category of PVA based porous materials is the development of hydrogels that have been studied for many years, mainly for biomedical applications [39]. Although not intended to function as membranes, their preparation routes can be adapted to obtain porous polymeric structures as supports and separating elements [102].

3. Porous Poly(Vinyl Alcohol) Preparation Methods

Chae et al. [103] reported a phase inversion method to prepare porous PVA membranes using water as the solvent and isopropyl alcohol as the non-solvent. The membrane was composed of packed microspheres as a result of crystallization with its degree depending on the solvent/nonsolvent ratio. The preparation route was as follows: 1 mL of the PVA aqueous solution (with concentration of 2, 4, 6, 8, or 10% PVA) was poured into a polystyrene (PS) Petri dish filled with 20 mL isopropanol. To perform the crosslinking of the formed structure, 3 mL of gludaraldehyde (4 wt%) and 0.5 mL of hydrochloric acid (35–37%) was added in the Petri dish and left for 12 h. The scanning electron microscopy (SEM) images of the prepared samples can be seen in Figure 8.

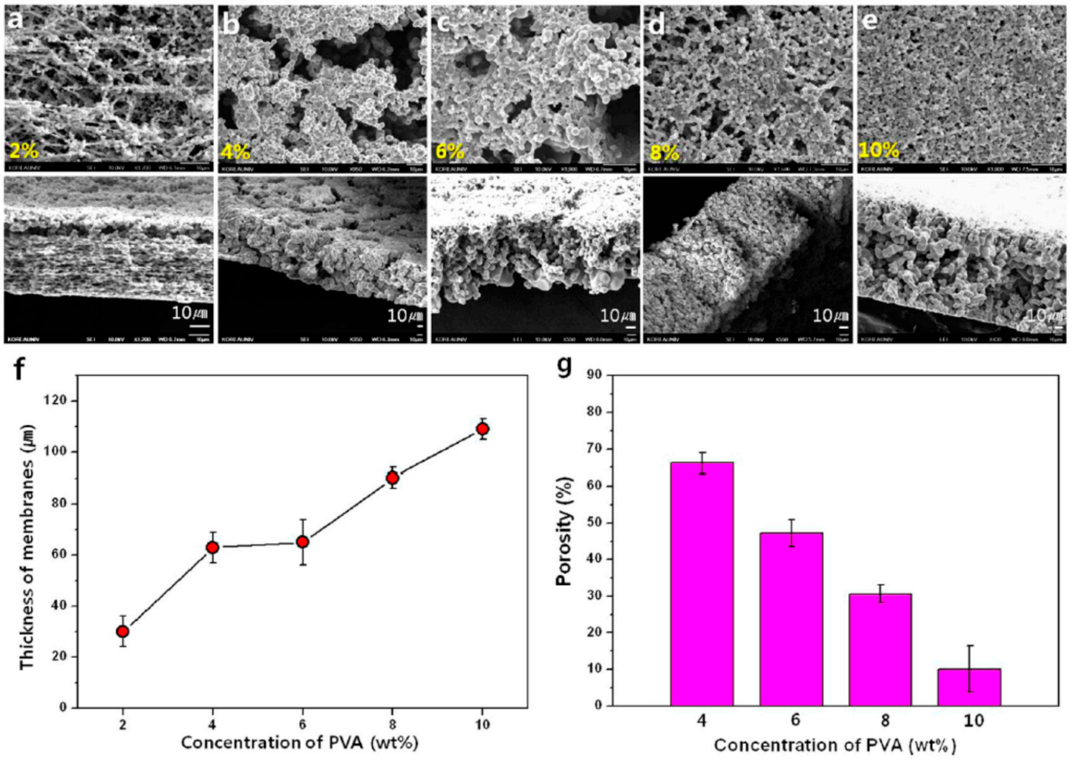

Figure 8. Surface and cross-sectional scanning electron microscopy (SEM) images of the matrix as a function of the PVA solution concentration: (**a**) 2, (**b**) 4, (**c**) 6, (**d**) 8, and (**e**) 10% PVA solutions. (**f**) The thickness of the matrix as a function of the PVA solution concentration. (**g**) Graph showing the porosity as a function of the PVA solution concentration. Reproduced with permission from [64]. Copyright 2014 ACS publications.

The PVA chains were found to be self-aggregated into a porous structure under the influence of dipole−dipole interactions in a low-polarity solvent (Figure 9), while the porosities of the matrices prepared using 4−10% PVA solutions were estimated at 67.6−14.9%

Kim and Lee [104] reported the preparation of integrally skinned asymmetric PVA (99+% hydrolyzed, Mw. 31,000–51,000) membrane structures by using 2-propanol as the non-solvent and a mixture of N-methyl-2-pyrrolidone and water as a cosolvent membrane structure from asymmetric having a dense layer to uniform porous was found to be dependent on the ratio between NMP and water. As the NMP ratio increased, the structure was driven toward the asymmetric structures. The preparation route that followed was: 100 g of 10 wt% PVA solution in the cosolvent mixture was prepared by mixing at 80 °C for 12 h. The resulting solutions were cast on a glass plate at 25 °C with a casting knife and submerged into an isopropanol bath for 20 min at 25 °C.

Ahmad et al. [105] prepared PVA (88% hydrolyzed, 88,000 Mw) asymmetric membranes using deionized water as the solvent and a mixture of sodium hydroxide (4.0 wt%) and sodium sulfate (8.0 wt%) as a coagulant in similar way with previous studies [106]. The prepared membrane was then crosslinked using glutaraldehyde (10 g/L), sodium sulfate (45 g/L), and sulfuric acid (5 g/L) for 0.5, 1.0, 1.5, and 2 h of reaction time. Although not clear from the electron microscopy observation, by increasing the crosslinking reaction time, the pore size distribution became narrower while the average pore size was also reduced, as depicted in Figures 10 and 11. The membranes were evaluated for their pure water flux with the results indicating that there is no clear relationship between pore size and water permeability, rather, a relationship between the hydrophilicity and the water flux.

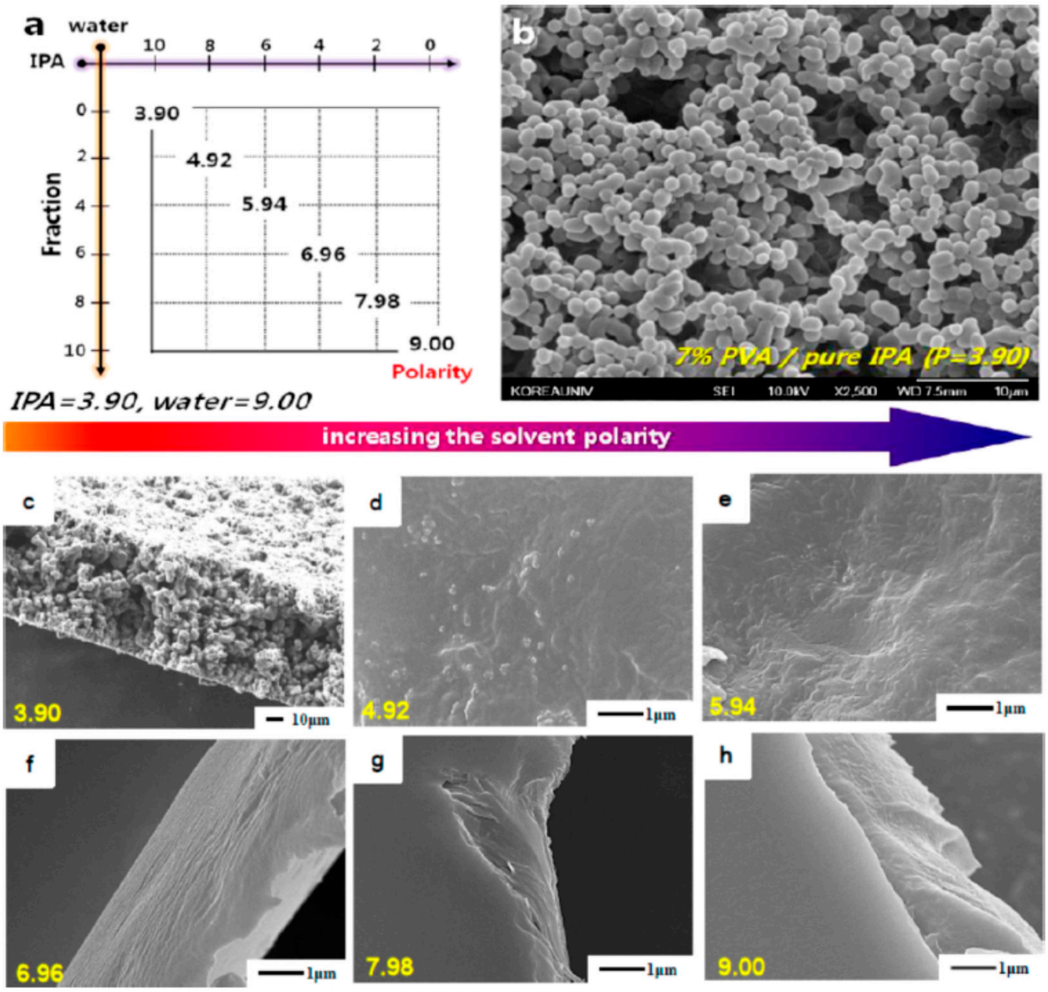

Figure 9. Polarity of the binary solvent mixtures and morphology of the PVA matrix prepared at each solvent polarity. Reproduced with permission from [64]. Copyright 2014 ACS publications.

Wang et al. [107] studied the influence of (a) chemical crosslinking with glutaraldehyde and sulfuric acid, and (b) heating, as post treatment methods in porous PVA membranes. The casting solution was a 10 wt% PVA (99% hydrolysis, polymerization degree, 1750) and 0.5 wt% poly(ethylene glycol) (Mw. 10,000). After degassing (50 °C for 12 h), the solution was cast onto a glass plate, and immediately immersed in acetone, where it remained for 30 min. A crosslinking solution comprised with glutaraldehyde (3 wt%) and sulfuric acid (5 wt%) in a saturated sodium sulfate solution (27.5%, 1 g/100 g) was used. PVA membranes were immersed into the crosslinking solution at 25 °C for different times (5, 10, and 30 min), washed with deionized water, and dried with acetone. For the heat-treatment, it was performed at 120 °C for different durations (one, two, and three hours). The membranes were evaluated on their water permeation flux, morphology, and mechanical properties. Chemical crosslinking did not have any major effect on the membrane's structure, whereas heat treatments increased crystallinity and thus changed their morphology.

Chuang et al. [108] prepared asymmetric PVA (Mw 74,800) membranes (Figure 12) and studied the effect of including dextran (Mw 12,000) and poly (vinyl pyrrolidone) (Mw 10,000) in the membrane casting solution. Membranes were prepared using water as the solvent, and $Na_2SO_4/KOH/H_2O$ as the coagulant medium Findings indicate that when PVP was introduced in the solution, compact structures were favored, while the addition of dextran induced the pore formation on the membrane's top layer.

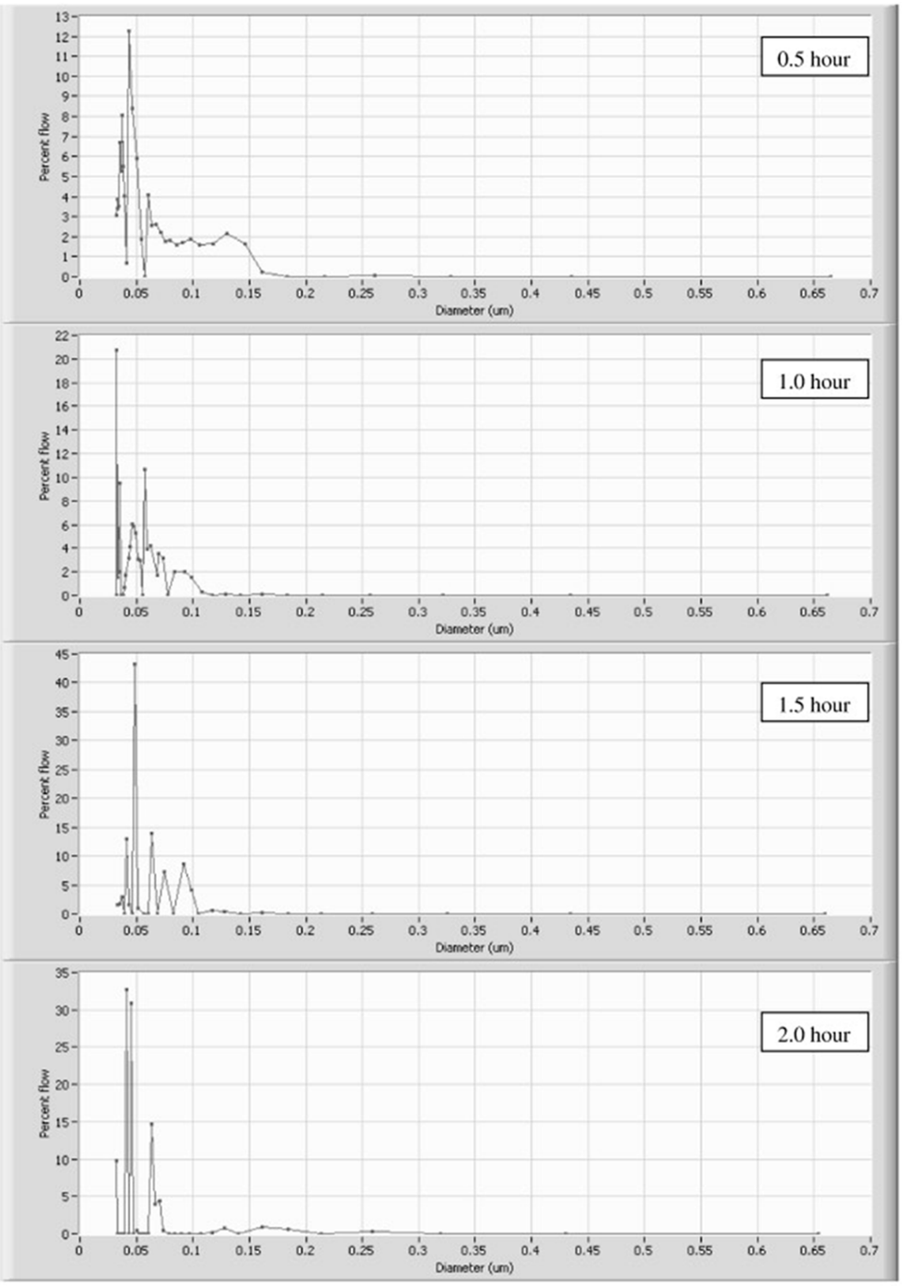

Figure 10. Pore size distribution of crosslinked PVA membranes at different crosslinking durations. Reproduced with permission from [78]. Copyright © 2011 Elsevier B.V.

The membranes were evaluated on their ultrafiltration capabilities with respect to the rejection of dextran and PVP.

The same group also studied the role of adding acetic acid in the structure of PVA membranes [109]. Acetic acid containing aqueous PVA solutions were immersed in a $Na_2SO_4/KOH/H_2O$ coagulation medium with the findings suggesting an apparent effect of the acidic acid in the overall morphology as a consequence of the filtration performance of the prepared membranes. The thickness of the dense layer was decreased by the increased acidic acid content. A reason for this observation can be found in the increased amount of H_3O^+, affecting the acid–base equilibrium during coagulation.

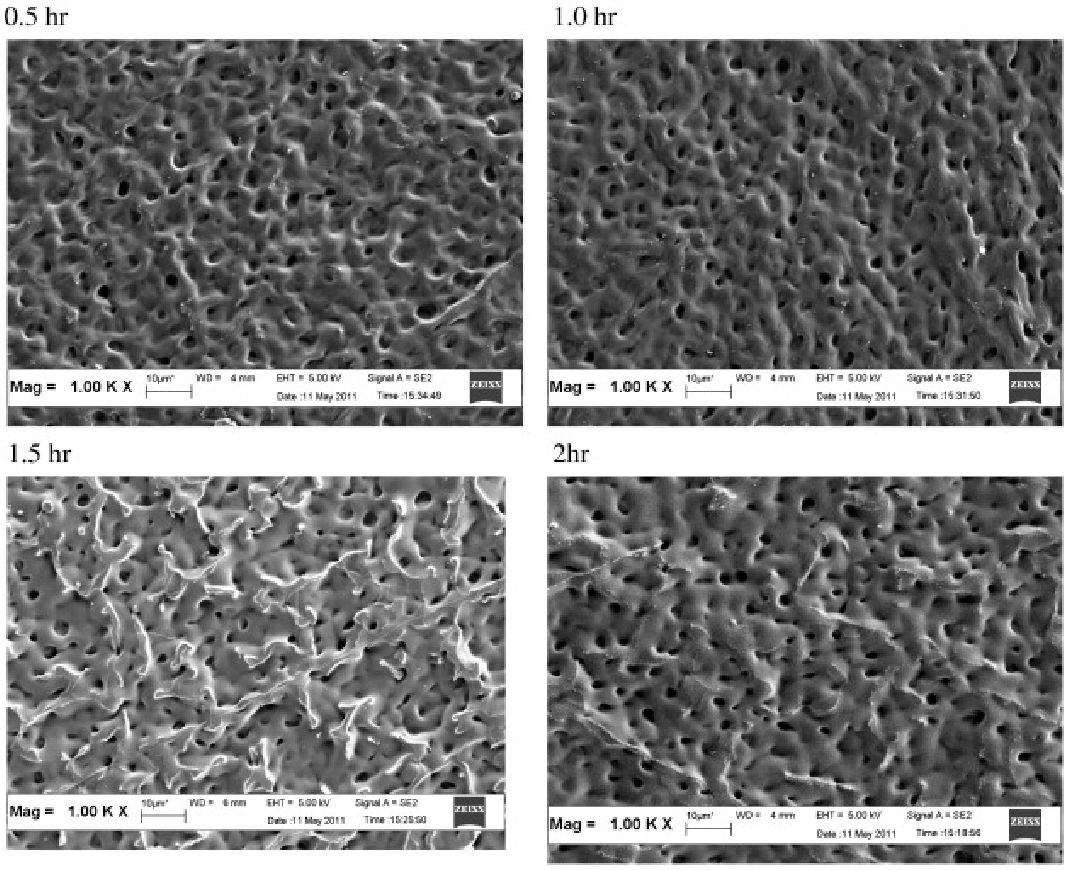

Figure 11. Effects of crosslinking time toward the PVA membrane surface. Reproduced with permission from [78]. Copyright © 2011 Elsevier B.V.

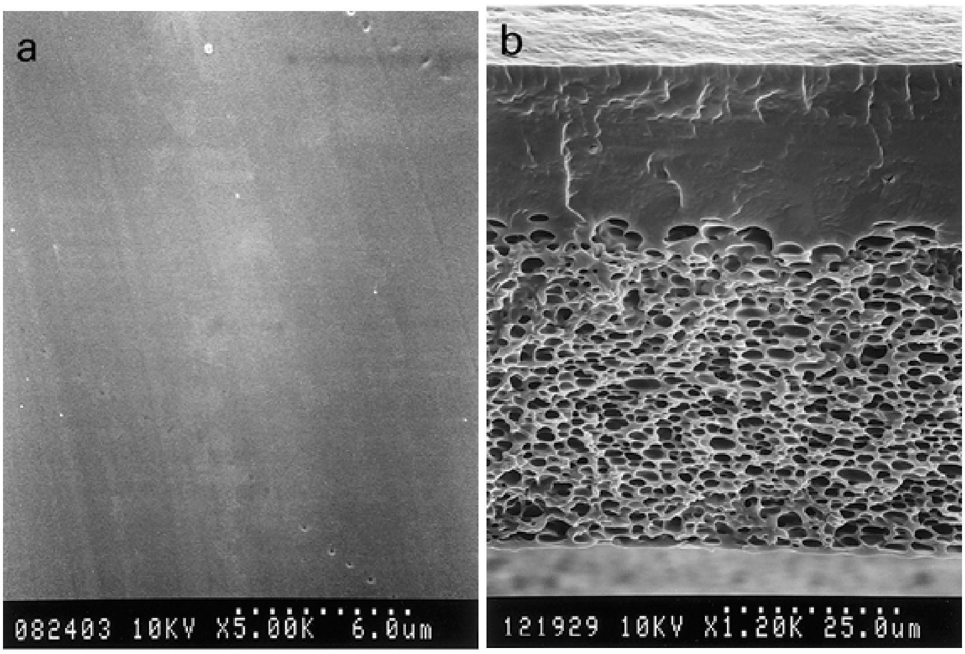

Figure 12. SEM images of a PVA membrane: (**a**) top layer and (**b**) cross-section. Reproduced with permission from [108]. Copyright 2000 Elsevier Science Ltd.

In a study by M'Barki et al. [110], porous membranes were prepared by temperature induced phase serration with a PVA of 72% DH selected due to its low cloud point temperature (Tcp, 47 °C for 10 wt% polymer). The membrane microstructure resulted from phase separation mechanisms occurring by spinodal decomposition. Authors studied the binary PVA/water phase diagram (Figure 13) as well as the crosslinking kinetics in order to determine the desired conditions for membrane preparation.

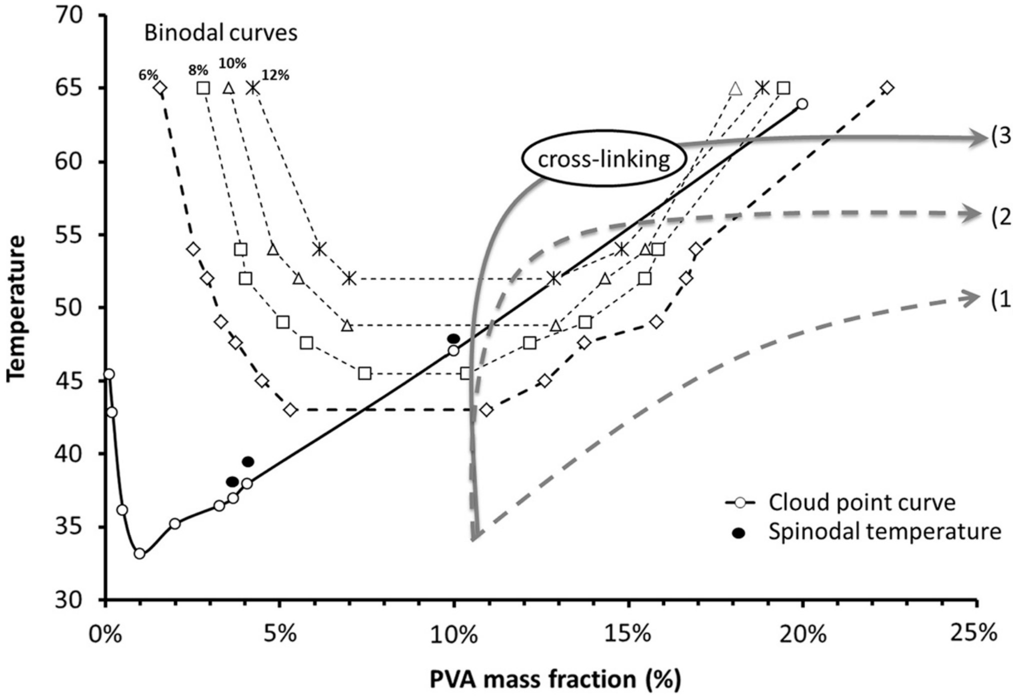

Figure 13. Experimental binary phase diagram of PVA72–water solution showing the cloud point curve, the spinodal temperatures and the binodals for several concentrations. Paths (1) and (2) lead to the formation of dense membranes. Path (3) induces the formation of porous membrane thanks to the crosslinking reaction in the diphasic region. Reproduced with permission from [110]. Copyright 2014 Elsevier B.V.

In order to produce the porous membranes, hydrocloric or sulfuric acid was added to the casting solution (PVA 10 wt% and gludaraldehyde 0.5 wt%) and after 1 min of stirring, it was cast onto a glass substrate that was placed in a heated support of the required temperature under a controlled relative humidity environment for 15 min. Afterward, the prepared membrane was removed and dried at 60 °C. Results indicated that the crosslinking control was the key step to obtaining porous membrane morphology (Figure 14).

Modeling studies of the PVA/water system that have also been performed by the same group [111] suggested that simulations showed that the initial solution thickness could have a significant influence on the membrane formation dynamics as well as volatile catalyzer components such as hydrochloric acid.

Additional thermodynamic analysis providing useful estimations for the membrane formation of the PVA/water/DMSO mixtures was performed by Young and Chuang [112] by using the Flory–Huggins ternary solution theory, indicating optimum ratios favoring system demixing.

Interesting approaches for creating porous structures are by utilizing microfluidics [113] or supercritical CO_2 as a component in polymeric solutions [114]. Studies conducted by Reverchon et al. [115,116] reported the preparation of PVA membranes by supercritical CO_2 assisted phase inversion. The authors reported their findings with respect to preparation conditions such as polymer concentration, ethanol to CO_2 ratio, temperature, and pressure. Several morphologies found to be achievable with macropores from 0.5–4 µm and a top layer that is either dense or porous, as can be seen in Figures 15 and 16.

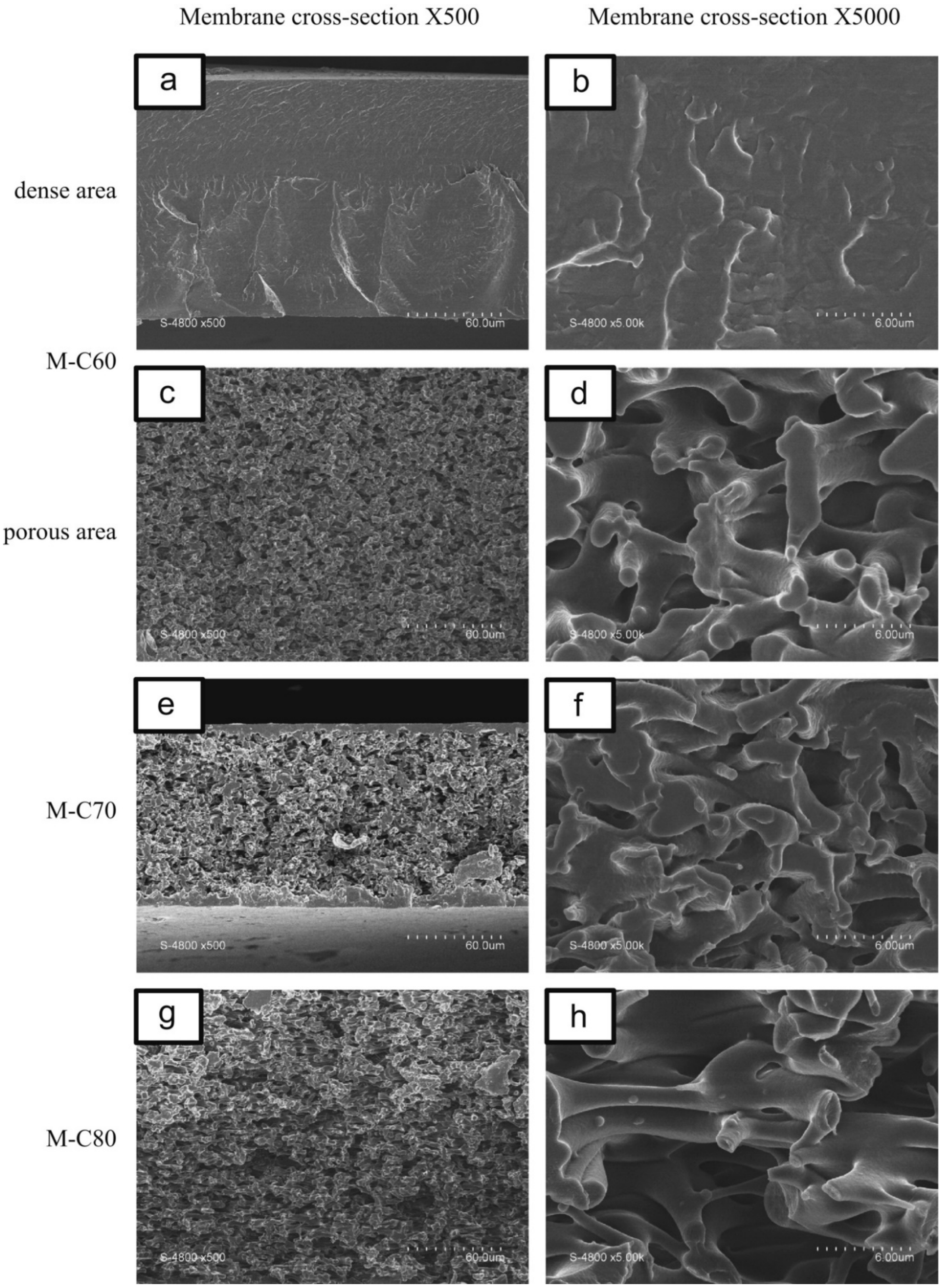

Figure 14. Effect of temperature on the membrane structure made with hydrochloric acid as the catalyst. Reproduced with permission from [110]. Copyright 2014 Elsevier B.V.

The gas foaming method was used by Narkkun et al. [117] to produce L-arginine functionalized PVA (average molecular weight 130,000 g mol^{-1} and 99% hydrolyzed) with CO_2 introduced from the thermal decomposition of sodium bicarbonate ($NaHCO_3$) at 130 °C. The membranes exhibited a structure with an average pore size of 32–56 μm depending on the amount of grafted L-arginine.

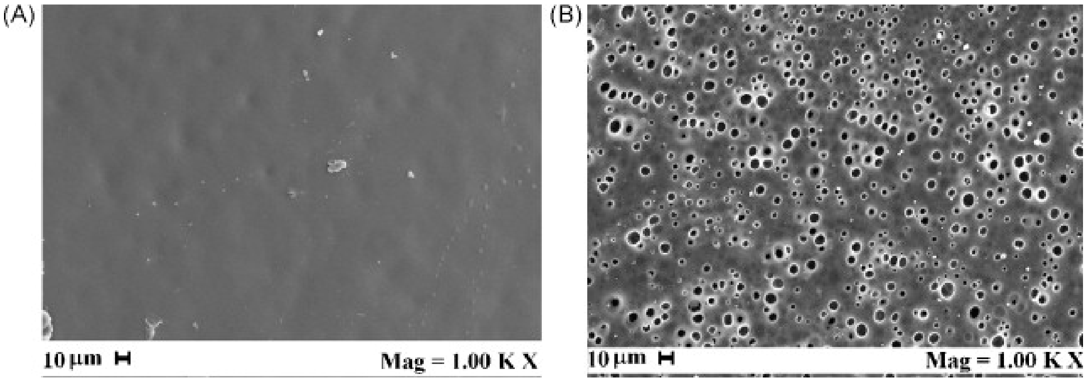

Figure 15. PVA membrane surface obtained at *P* = 200 bar, *T* = 45 °C and 10% (*w*/*w*), with an ethanol: CO_2 ratio of 40:60, *w*/*w* (**A**) and 60:40, *w*/*w* (**B**). Reproduced with permission from [115]. Copyright 2008 Elsevier.

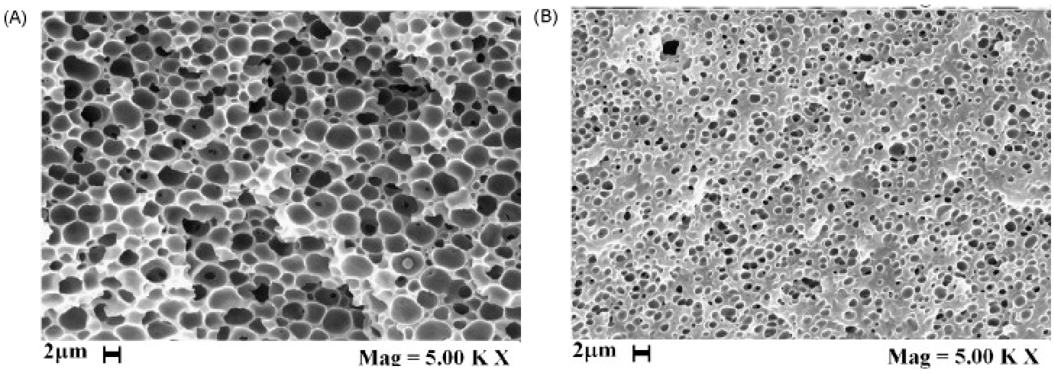

Figure 16. Effect of polymer concentration on the PVA membrane section at *P* = 250 bar, *T* = 55 °C and with an ethanol: CO_2 ratio of 60:40, *w*/*w*, (**A**) 10% (*w*/*w*) and (**B**) 20% (*w*/*w*). Reproduced with permission from [115]. Copyright 2008 Elsevier.

Wu et al. [118] reported the preparation of a composite PVA ultrafiltration membrane for the treatment of oily water by crosslinking PVA to a mixed cellulose ester microfiltration membrane and the results indicated that the prepared membrane had excellent antifouling properties against oil.

Treatment of oil/water emulsions was also studied by means of highly porous electrospun PVA membranes (crosslinking with GA in acetone) by Wang et al. [119] using a variety of PVA grades. The ultrafiltration experiments were performed in PVA coated scaffolds with a hydrogel layer of ~1.8 µm (Figure 17) and compared to a Pebax 1074 coating with the PVA water flux reaching 130 LMH and Pebax 57 LMH.

Citric acid crosslinking stability of electrospun PVA fibers have been proposed as a promising alternative to GA [120] while Truong et al. [54] reported a comparison of crosslinking stability by using citric acid (Figure 18), maleic acid, and PAA to PVA (Mw 100,000). The prepared membranes where evaluated in two potential applications: (a) for metal uptake in aqueous systems and (b) ammonia adsorption after decorating the membranes with a metal organic framework copper benzene-1,3,5-tricarboxylate (HKUST-1).

Preparation of PVA hydrogels by the freezing and thawing technique was first reported by Peppas [121,122] in the 1970s. Recently, Li and coworkers [123] reported a macroporous PVA hydrogel with improved mechanical properties due to the addition of Agarose (AG) as a pore forming agent. The study claims that the AG-interacting water hybrids can facilitate the formation of ice particles and thereby the macropores. By introducing AG, the crystallinity of macroporous PVA hydrogels is improved and the hydrogel network is enhanced by the hydrogen bonds, strengthening the mechanical stiffness.

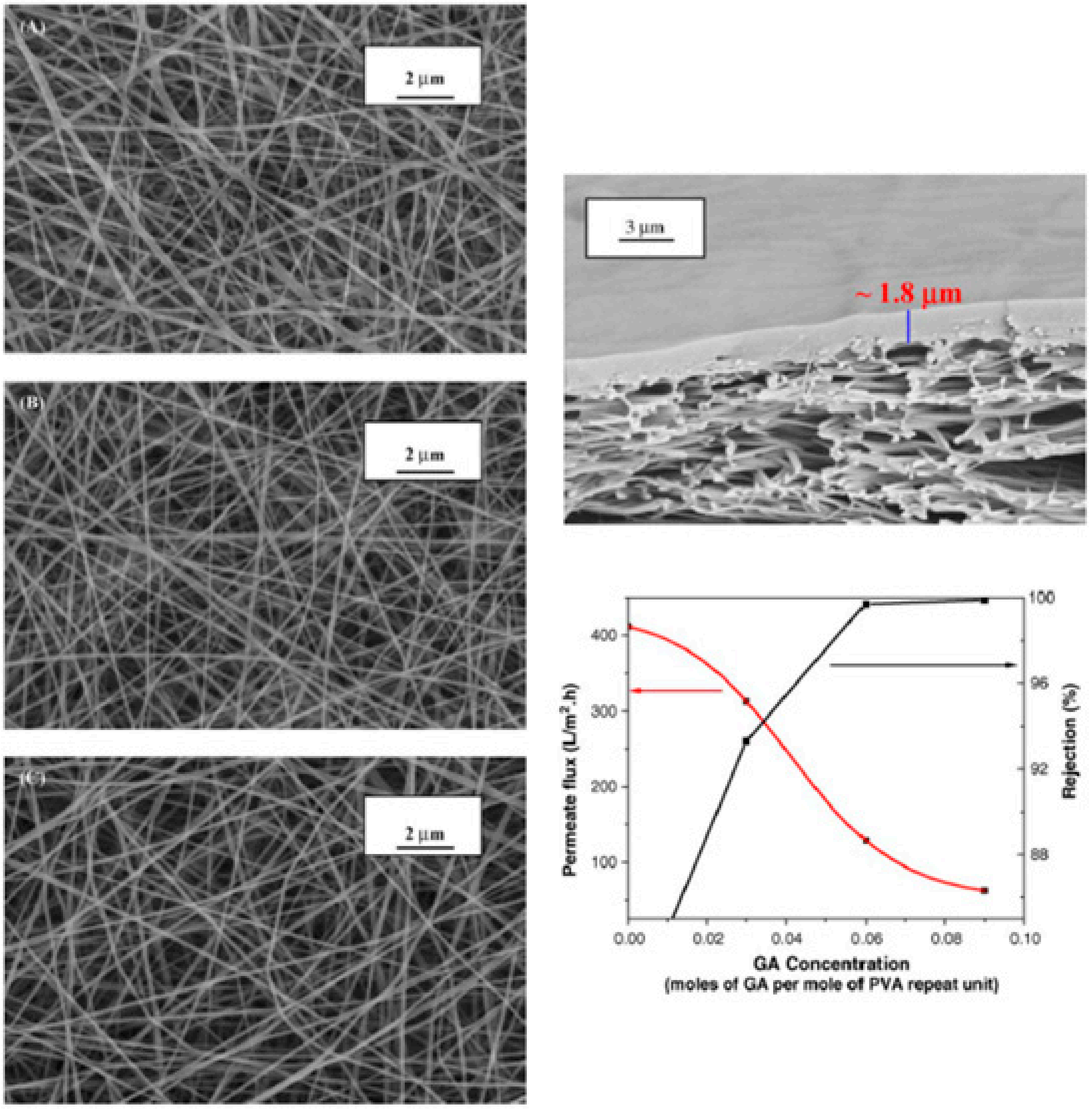

Figure 17. (**Left**) SEM images of electrospun PVA membranes with various molecular weights but similar degrees of hydrolysis: (**A**) 98% hydrolyzed, Mw 13,000–23,000 g/mol (electrospun from 24 wt% solution); (**B**) 98% hydrolyzed, Mw 78,000 g/mol (from 11 wt% solution); and (**C**) 98–99% hydrolyzed, Mw 85,000–124,000 g/mol (from 9 wt% solution). (**Upper right**) Typical SEM cross-sectional image of PVA nanofibrous composite membrane. (**Lower right**) Relations of permeate flux and solute rejection of the nanofibrous composite membranes with the degree of crosslinking in the PVA hydrogel coating for separation of oil/water emulsion (feed pressure: 100 psi; temperature: 30–35 °C). Reproduced with permission from [119]. Copyright 2006 Elsevier.

Porous films have been also reported to be produced by SiO_2 etching. According to Lee and Wey [124], they dispersed the nanoparticles in a PVA solution that were cast onto a glass with a 250 µm thickness overnight, and the next day, the dried membrane was peeled off and annealed for 2 h at 160 °C under vacuum. A 2 M NaOH solution was used to etch the SiO_2, resulting in adjustable pore size porous membranes.

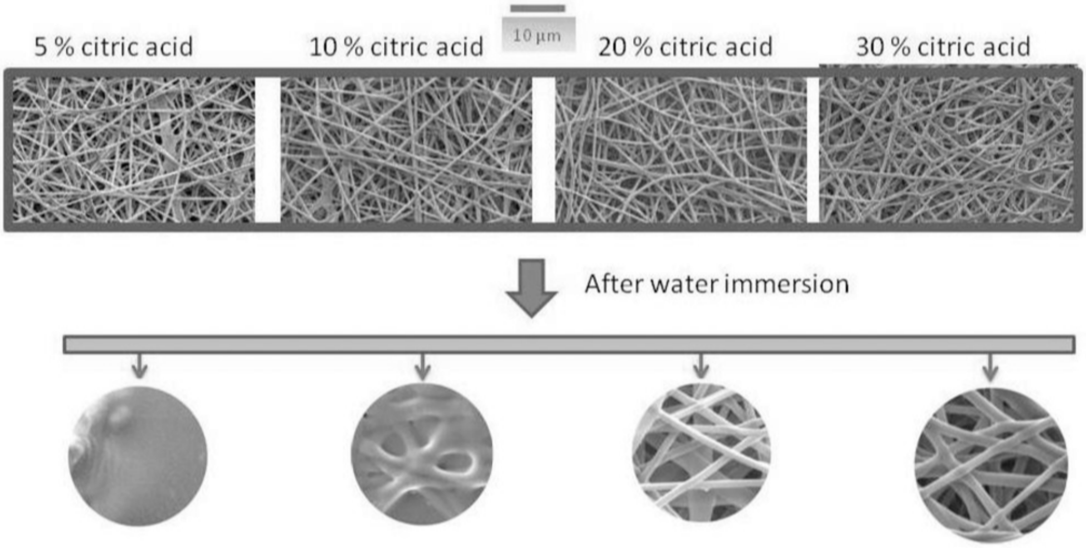

Figure 18. SEM images of citric acid–PVA membranes before and after water immersion. Reproduced with permission from [54]. Copyright 2017 WILEY-VCH Verlag GmbH & Co.

4. Conclusions and Future Prospective

Membranes, especially those developed for water treatment, are expected to be of research and industrial focus for many years to come due to factors like climate change, environmental pollution, and population growth. PVA based porous membranes will continue to be developed by incorporating functional nanomaterials and by finding innovative ways of pore structure control like microfluidics. Currently, PVA is one of the polymers of choice when it comes to dehydration via the pervaporation method. Various types of commercially available PVA membranes exist in the market with the aim to provide solutions for dehydration or methanol removal from mixtures of volatile organic compounds, a trend that is expected to continue. Crosslinking density as well as the crosslinkers will be in the forefront of pervaporation research, aiming eventually at increased process thermal efficiency. Hydrophilic membranes will also be the center of research attention for ultrafiltration applications, mainly due to their high achievable fluxes, low fouling, and oil rejection. Based on the above, PVA is currently used on a commercial scale as the selective layer-coating in various polymeric membranes based on polymers such as PVDF and PSf. Implementation of green preparation routes alongside the vast progress in the synthesis of water compatible and ecofriendly nanoparticles in the preparation of PVA based membranes can contribute to the ever growing concern of toxic solvent use by the industry. Nanoparticle addition, together with new preparation routes, can boost the properties and durability of PVA membranes, introducing them into new and exciting fields. In order for PVA to be a successful replacement material of the conventional used polymers, a series of improvements should be achieved including mechanical compression resistance, consistent selectivity under different operating environments, low fouling, and improved mechanical properties. Intensive research currently undertaken by groups around the world exploring the unique properties of PVA ensures successful solutions for the above-mentioned aspects.

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