PVA-based Pervaporation Membranes for Separation of Water-Alcohol Solutions: A Review

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Dehydration of alcohols has attracted a great deal of attention owing to its wide application in several medical, pharmaceutical and chemical industries. High separation efficiency, low energy consumption, simplicity and minimum contamination are the main characteristics making pervaporation (PV) a promising method in the area of alcohol dehydration to provide extremely pure alcohols. Due to their high selectivity and processability, polymers are the main materials for PV membranes. Poly(vinyl alcohol) (PVA) is the most commonly used polymer because of its desired hydrophilicity, flexibility, good film-forming ability and low cost. However, excessive swelling is the main challenge in fabrication of PVA membranes for dehydration application; to overcome this disadvantage, various attempts have been made to modify PVA membranes for separation of water and alcohols. In this paper, various modifications and developments performed to improve the PV performance of PVA-based membranes for separation of water and alcohols are reviewed.

Keywords: Separation, Alcohols, Poly(vinyl alcohol), Membrane, Dehydration

INTRODUCTION

Alcohols are among the most commonly used materials in the pharmaceutical, medical and chemical industries. However, one of their impurities is water, which makes azeotrope mixtures or mixtures with close boiling points. At present, the most common method for separation of water from alcohols is distillation. Although distillation is a successful technology in separation of a wide range of mixtures, this approach has its own challenges for separation of azeotrope/close boiling point mixtures since it is based on the volatility and boiling point differences of feed components. Moreover, distillation is a costly and highly energy consumption process [1]. Therefore, alternative processes such as pervaporation (PV) have been introduced for separation of not only azeotrope or close boiling point mixtures, but also thermal sensitive feeds [2]. PV is a membrane-based process. The key part of the PV set-up is membrane which can be considered as a physical barrier between feed and product sections, called the permeate side. In this process, the liquid feed is in contact with the membrane upstream, and the vapor product is gathered at downstream side using an external force such as vacuum or sweeping an inert purge gas [3]. Figure 1 represents a schematic of PV cell and PV set-up. First, the feed cell is filled with an aqueous alcohol mixture, while a mechanical stirrer keeps the feed solution homogeneous. Different temperatures can be chosen to investigate the effect of feed temperature. While the pressure at feed side was kept atmospheric, a vacuum pump is usually applied to adjust the downstream pressure to near 5-10 mm Hg. The product at permeate side is gathered in a glass U-tube while a cold trap is used to keep the temperature low enough to collect the product in liquid or solid form. Two identical routes are used for collecting the product; the first route is designed to collect the product for the first 2-6 h to let the system reach the steady state point. Interestingly, the membrane is selective towards one or more special feed
components, which results in reduction of their fractions in the feed stream. Moreover, the PV process does not require any third additive, so there is no contamination in either the permeated product or the feed. Accordingly, PV is assumed to be an environmentally-friendly technique. As the main objective in PV technique is the separation of the component with the lower fraction in the feed mixture, with only the separated components in their vapor state, this alternate method would consume less energy [4]. Therefore, PV is of great interest for alcohol dehydration applications.

**PV History**

“Pervaporation” technique was firstly introduced by Kober [5] in 1917, when he paid attention to the evaporation of water through a tightly closed bag. In the case of alcohol dehydration via PV process, Heisler et al. [6] studied the effect of solute and temperature in ethanol dehydration. For many years, although alcohol dehydration was widely investigated via the PV process, low permeation flux was the main challenge for commercial application of PV membranes. Finally, in 1982, a Germany company, Gesellschaft für Trenntechnik (GFT) Co., developed a thin layer of poly(vinyl alcohol) (PVA) supported by a porous, thick layer of poly(acrylonitrile) (PAN) for ethanol dehydration through PV technique. Successful application of GFT in alcohol dehydration has encouraged many researchers to study different ways for modification of PVA-based membranes for separation of water and alcohols.
PVA IN FABRICATION OF PV MEMBRANES FOR ALCOHOL DEHYDRATION

PV membranes can be classified into three main types: polymeric/organic membranes, ceramic/inorganic membranes and mixed matrix membranes (MMMs). In this regard, simple preparation and application, good flexibility as well as low total costs are amongst the promising features for polymeric membranes to be the most widely used material to separate water from alcohols via the PV process. The performance of polymeric membranes during the PV process extremely depends to the characteristics of the selected polymer, which has an enormous impact on the membrane resistance, its flux and also the selectivity [7]. Three main factors, including adequate chemical resistance, adsorption capacity and suitable mechanical strength, are essential to choose a suitable type of polymer. In addition, to reach a desirable separation, a suitable molecular interaction should be established between the polymer film and feed components.

For dehydration of organic solvents, hydrophilic polymers are required. In fact, their hydrophilic power is defined on the basis of their functional groups and their interactions with water molecules through hydrogen or dipole-dipole bonds. Alginates, chitosan and poly(vinyl alcohol) are all hydrophilic polymers that are frequently studied for fabrication of PV membranes [8]. Poly(vinyl alcohol) is a semi-crystalline polymer with many hydroxyl groups which can make strong bonds between not only the polymer chains, but also the polymer chains and the water molecules. Consequently, this polymer has a strong affinity towards water. In fact, suitable elongation ability, tensile strength, hydrophilicity, thermal resistance and good film-forming ability have made PVA the most widely studied polymer in the field of PV [9-13].

In recent years, the preparation of PVA membrane has become common due to its promising chemical properties and reasonable price [14]. Unfortunately, PVA membranes experience excessive swelling when they are in contact with aqueous solutions, resulting in unstable structure without long-term stability. Moreover, the swollen PVA membranes transport both water and alcohol molecules, which is why these membranes show low water selectivity [8]. Therefore, some modifications have to be made on PVA membranes for their successful application in the PV process [9]. Polymer crosslinking and grafting, blending, incorporation of fillers, decreasing the thickness of PVA membranes and fabrication of hollow fiber of PVA membranes have been sought to modify the PV performance of PVA membranes in alcohol dehydration. As discussed earlier, the first industrial sample of PVA-based pervaporation membranes for dehydration of ethanol, called GFT, consisted of a crosslinked layer of this polymer, supported by a porous poly(acrylonitrile) layer [8,10].

One of the effective parameters on the separation performance of membranes is the thickness of the membranes. In fact, based on Fick’s First Law, the flux of a membrane can be increased by decreasing the thickness, which means higher flux can be achieved through decreasing the thickness of membranes. Accordingly, preparation of supported membranes has been a subject of interest [14]. Preparation of supported membranes is a suitable method for membranes modification, in which a thin selective layer is supported by a porous layer which requires the mechanical stability of the structure while the top layer is responsible for the separation phenomenon [15,16].

Membrane geometry is another parameter that can make a big difference to achieve a better separation result. Among membranes with different geometries, hollow fibers have been more suitable candidates owing to their high ratio of surface area to volume, high packing density, their self-supporting structure, and low investment cost [17-25]. The aforementioned positive advantages of hollow fiber membranes have encouraged researchers to investigate the performance of hydrophilic PVA hollow fiber membranes.

**Membrane Performance Parameters in PV Process**

For quantitative evaluation of PV experiments, flux (J) and separation factor (SF) are two frequently-used parameters. The permeation flux (J) can be described by Eq. (1) as the mass of collected product (W) on the permeate side with respect to the effective area (A) over time of the PV cycle (t):

\[ J = \frac{W}{A \cdot t} \]  

(1)
From Eq. (1), the preferred unit for reporting of flux is kg/(m² h); however, there are some reports in which the volume of the collected product was used instead of W for calculation of flux. As dehydration of alcohols is of interest in this review, the separation factor (SF) is calculated for water with respect to the alcohol, as below:

\[ SF = \frac{Y_{\text{water}} / X_{\text{water}}}{Y_{\text{alcohol}} / X_{\text{alcohol}}} \]  

(2)

where \( Y_i \) and \( X_i \) correspond to weight fraction of \( i \) component in permeated permeate and feed, respectively. To evaluate the separation ability of a membrane in one parameter, PSI index is defined by Eq. (3):

\[ \text{PSI} = J \times (SF - 1) \]  

(3)

Herein, we use kg/(m² h) to report \( J \) and PSI.

**MODIFICATION OF PVA-BASED PV MEMBRANES FOR ALCOHOL DEHYDRATION**

There are some review papers about PV membranes [4,26-32]; however, in this paper for the first time, the main objective is to focus on PVA membranes in dehydration of aqueous mixtures of alcohols via the PV process.

**The Effects of PVA Structure and Properties**

PVA was crosslinked by amic acid for PV dehydration of isopropanol/water solutions, and the influence of different variables such as degree of hydrolysis of PVA, feed temperature and concentration were investigated [33]. It was claimed that the crystallinity of the crosslinked membranes was enhanced for PVA with higher degree of hydrolysis. As mass transport occurs through amorphous regions, higher selectivity and lower flux were observed when PVA with a higher degree of hydrolysis was used.

The effects of PVA concentration and molecular weight on PV performance of PVA membranes crosslinked with glutaraldehyde were examined by Yu et al. [34]. The reported results illustrate that when PVA molecular weight increased, the longer polymer chains were more entangled with decreased free volume. As a result, the higher molecular weight of PVA led to decreasing the flux and increasing the separation factor. As for the effect of PVA concentration, it was observed that increasing polymer concentration has the same influence on the flux and separation factor. As a matter of fact, higher PVA concentration resulted in formation of thicker membranes with lower diffusion rates for water and isopropanol molecules. Since the decreasing rate of the water molecules’ diffusion was lower than that of isopropanol, the separation factor increased at the expense of flux.

**Crosslinking and Grafting**

Severe swelling of PVA films in aqueous environments is responsible for increased free volumes and chain mobility of PVA-based membranes and their decreased selectivity. In consequence, crosslinking is considered not only among one of the modification treatments, but also an obligatory modification strategy when PVA membranes are used in PV separation of aqueous alcohol solutions. The stability of the membranes made of crosslinked PVA has been proven in strong acidic or basic environments [35]. Due to the high thermal and chemical stability of crosslinked PVA membranes, they have been successfully used in various categories of membrane separation processes such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis. In addition, crosslinked PVA membranes have been applied in PV separation of organic/organic and water/organic mixtures.

Although PVA can be crosslinked by non-chemical methods such as freeze-thaw inducement of crystallization, thermal modification (heat treatment) and irradiation, the stability and strength of these modifications are not sufficient for long-term application of PVA [36]. The most typical method for PVA crosslinking is the chemical technique in which the chains of the polymer are attached to each other using a chemical agent. Glutaraldehyde [11], carboxylic acids [36], maleic acid [37], malic acid [38], citric acid [39], amic acid [40], sulfur succinic acid [41], formaldehyde [36], etc., are the examples of crosslinking agents used for modification of PVA membranes.

Kim et al. [42] investigated the impacts of various crosslinking conditions of PVA in dehydration of 95 wt% ethanol. They reported that despite improving the stability
of PVA membranes in aqueous feed, their selectivity and flux decreased with increasing the crosslinking degree of polymer. Although the authors did not give any explanation for their findings, it was concluded that determination of the optimum value of crosslinking degree is necessary.

The effect of modification of PVA membranes by crosslinking with two different agents including citric acid and malic acid was studied by Burshe et al. [43]. They prepared membranes crosslinked at 150 °C for an hour by 5, 10 and 14% wt of any two of the mentioned crosslinkers for dehydration of aqueous solutions of several alcohols (methanol, ethanol, isopropanol, n-propanol, iso-butanol and n-butanol). The XRD analysis showed that membranes modified with citric acid were less crystalline in comparison with those crosslinked by malic acid [39]. Thus, PVA membranes treated with citric acid showed higher water selectivity at the same experimental conditions. Also, higher selectivity and lower flux were obtained when PVA chains were crosslinked by increasing the concentration of the crosslinkers. Furthermore, it was observed that alcohols with more carbons could be separated from water molecules with higher selectivity despite lower flux. The larger molecules of alcohols need more energy and free volumes for diffusion across crosslinked PVA membranes. Interestingly, alcohols with the same number of carbons but different arrangements diffused differently through the same PVA membrane in a way that the selectivity of the crosslinked PVA membranes increased when alcohol structure changed from normal butanol to iso-butanol. Table 1 summarizes the reported PV results for PVA membranes crosslinked with 10 wt% citric acid in dehydration of feed mixtures containing 10 wt% of different alcohols at 30 °C.

In 1995-1996, a group of researchers investigated the PV performance of PVA membranes crosslinked by poly (acrylic acid) (PAA) in dehydration of methanol and ethanol [44,45]. In addition, the effects of different parameters including feed concentration and temperature and the amount of crosslinking were studied. The results indicated that the greater the amount of the crosslinker (PAA) used, the less mobility of PVA chains was achieved; the best separation performance was obtained when the weight ratio of PVA/PAA was 80/20. The PVA/PAA: 80/20 membranes could dehydrate the 90 wt% methanol aqueous mixture at 70 °C with the separation factor of 465 and flux of 0.109 kg/(m² h), while for the 95 wt% methanol mixture a better separation factor (2650) and lower flux (0.033 kg/(m² h)) were reported.

Asymmetric membranes of PVA crosslinked with different amounts of glutaraldehyde were used in PV separation of water and isopropanol mixtures [34]. It was observed that increasing the glutaraldehyde content resulted in decreasing the chain mobility of PVA, so both alcohol flux and water flux decreased. However, the water flux dropped by lower rate indicated an improvement in the separation factor of membranes.

Sulfur succinic acid (SSA) contains hydrophilic functional groups of carboxylic acid (C=O) and sulfuric acid groups (SO₂H). It can make hydrogen bonds with OH groups of PVA. The existence of OH and SO₂H moieties can increase the water affinity of PVA membranes. The positive potentials of SSA encouraged Rhim et al. [46] to prepare PVA membranes which were thermally modified with SSA as the crosslinking agent for dehydration of various aqueous binary mixtures of methanol, ethanol and isopropanol at two different temperatures, 60 and 70 °C. As expected, more PVA chains went through chemical interactions when a higher weight percent of SSA (7 wt%) was used. According to Table 2, for dehydration of alcohols with greater numbers of carbon atoms, membranes with 7 wt% of SSA have a lower flux and a higher separation factor. In summary, owing to the smaller size of methanol molecules compared to ethanol and isopropanol, modified PVA membranes could allow more methanol molecules to transfer towards the permeate side. Hence, the maximum flux and the minimum separation factor were recorded in the case of methanol dehydration.

In 2002, Chiang et al. [47] used poly (sodium styrene sulfonic acid-co-maleic acid) (PSSA-co-MA) including both hydrophilic and hydrophobic functional groups to crosslink PVA for preparation of new membranes. The prepared membranes were tested for PV dehydration of different alcohols. The experiments revealed that increasing the amount of crosslinking agent results in more hydrophilic groups. So, water molecules could make stronger hydrogen bonds with sulfonic acid groups of the membranes and the selectivity of the membranes was enhanced, while formation of water clusters led to decreased flux.
The influence of four different crosslinking agents including glutaraldehyde (GA), oxalic acid (OA), dimethyl urea (DMU) or tetra ethyl ortho silicate (TEOS) for modification of PVA membranes in separation of water from azeotrope mixture of isopropanol was also studied [48]. The results indicate that the membranes modified with GA were more efficient in the dehydration process. Furthermore, the structure of PVA membrane changed into a much more compact state when the crosslinker with shorter length (OA) was used, so the permeation flux was lower than that in membranes modified by GA. As for membranes modified by DMU/TEOS, the PVA structure became tighter and denser, so the selectivity of these membranes was higher than those crosslinked by GA/OA. However, when PVA went through crosslinking by GA/OA, enhanced hydrophilicity of the membranes corresponded to higher flux compared to those modified by DMU/TEOS.

The effect of time dependence of the esterification reaction between fumaric acid and PVA membranes for dehydration of isopropanol mixtures was studied by Heydari et al. [49]. Reported results indicated that the esterification reaction between hydroxyl groups of PVA and fumaric acid functional groups was intensified by increased crosslinking time. The best PV performance was reported when PVA was crosslinked by fumaric acid for 60 min in dehydration of 90 wt% isopropanol at 60 °C. The separation factor and flux were 1492 and 0.082 kg/(m² h), respectively.

To gather information on the effect of the type of PVA crosslinking, Huang et al. [50] prepared thermally and chemically crosslinked PVA membranes in ethanol dehydration. Thermal modification was done at 125 °C, while esterification reaction between PVA chains and

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**Table 1. PV Results for Dehydration of Different Alcohols for PVA Membranes Crosslinked by Citric Acid (10 wt%)**

<table>
<thead>
<tr>
<th>Alcohol in feed</th>
<th>Flux (kg/(m² h))</th>
<th>Separation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.202</td>
<td>8.6</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.084</td>
<td>91</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>0.078</td>
<td>141</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>0.053</td>
<td>291</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>0.082</td>
<td>171</td>
</tr>
<tr>
<td>Iso-butanol</td>
<td>0.052</td>
<td>351</td>
</tr>
</tbody>
</table>

**Table 2. Summary of PV Results for PVA Membranes Cross-linked by SSA**

<table>
<thead>
<tr>
<th>Alcohol in feed</th>
<th>Flux (kg/(m² h))</th>
<th>Separation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.8</td>
<td>24</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.291</td>
<td>171</td>
</tr>
<tr>
<td>Iso-propanol</td>
<td>0.206</td>
<td>1969</td>
</tr>
</tbody>
</table>
glutaraldehyde under ambient temperature was chosen as chemical crosslinking. Compared to thermal treatment, PVA chains experienced more crosslinking reactions through esterification by glutaraldehyde. As a result, chemically-modified PVA chains were more rigid, so there was less free volume for molecules to pass through across the membranes, which favors water selectivity.

Parallels to crosslinking, surface modification or grafting have been of interest in studying the effects of the wettability and surface properties of PVA membranes. There are some reports in separation of water-alcohol mixtures via the PV process by crosslinked PVA membranes where PVA surface was modified. For example, Nam et al. [51] used different contents of carboxymethyl group to prepare surface-modified PVA membranes for isopropanol dehydration. Separation factor of 362 and permeation flux of 0.831 kg/(m² h) were reported for PV separation of mixtures with 15 wt% of water at 80 °C.

In 2011, 4-sulfophthalic acid (SPTA) was used to prepare sulfonated PVA membranes to separate water and isopropanol at different temperatures [52]. SPTA could crosslink PVA chains, and the affinity of PVA membrane towards water molecules could develop because of the hydrophilic sulfonic acid groups of SPTA. The separation factor and flux of PVA membranes with 15 wt% of SPTA were found to be about 3452 and 0.0351 kg/(m² h) for 90 wt% isopropanol aqueous solution at 40 °C.

Rafik et al. [53] deposited an allyl alcohol or acrylic acid plasma-polymerized layer on PVA membranes for PV separation of water/ethanol azeotropic mixture. However, plasma-treated PVA membranes were not as efficient as GFT ones in ethanol dehydration.

Zhang et al. [54] studied the effect of introduction of hydrophilic ammonium groups on PVA surface, so the modified PVA is known as quaternized poly(vinyl alcohol) (q-PVA). Then q-PVA was used for preparation of PV membranes crosslinked by glutaraldehyde to dehydrate the 85 wt% ethanol solution. It was found that increasing the degree of quaternization resulted in reduction of crystallinity and improving the hydrophilicity of membranes. Hence, both permselectivity and permeability of PVA membranes increased.

In 2019, chemical grafting of PVA membrane was investigated by Kulkarni et al. [55]. They tried to study the effect of grafting different amounts of benzaldehyde-2-sulfonic acid (B2-SA) onto PVA chains. Meanwhile, tetraethyorthosilicate (TEOS) was incorporated into PVA to crosslink the polymer chains. Hence, the PVA-based membranes with chemical structure shown in Fig. 2 were prepared to dehydrate 90 wt% isopropanol mixtures. Interestingly, sulfonated phenyl groups of B2-SA could interact strongly with PVA, so hydrophilicity of the B2-SA-grafted PVA membranes was increased. Moreover, PVA chains were disordered due to the existence of sulfonate phenyl groups of B2-SA, which was the reason for decreasing the crystallinity of the B2-SA-grafted membranes. Based on the results, the best separation properties were obtained when PVA was grafted by 7.5 wt% B2-SA and the separation factor and flux were 6420 and 0.02 kg/(m² h), respectively.

In general, it can be concluded that the structure of PVA membranes would be more compact and denser by a higher degree of PVA crosslinking, accompanied with lower mobility and flexibility of chains. Subsequently, free volume of membranes and swelling in aqueous feeds would decrease, leading to reduction of permeation flux. Moreover, crosslinking agents with longer chains could provide more free volumes among PVA chains. In addition, if the crosslinking agent introduces new hydrophilic groups such as sulfonic acid moieties to the membrane structure, it may improve either the rigidity or hydrophilicity of the membrane. So, the separation factor would be improved by making more and stronger hydrogen bonds.

To sum up, it is important to notice that although crosslinking of PVA membranes has been considered a modification strategy, it is a necessary step in the preparation of PVA membranes for PV dehydration purposes. Otherwise, the membrane’s chemical stability in aqueous solutions is insufficient, so dissolution of polymer chains in the feed may occur. Meanwhile, suitable surface modification of PVA could effectively alter the separation ability of PVA-based membranes in the PV process.

Blending

Blending is one of the available methods to modify membranes. In fact, blending is the process of combination of at least two polymers to use the advantages of two or more polymers in one structure. In this regard, several
blends of PVA and other polymers such as chitosan (CS), poly(acrylic acid) (PAA), poly(vinyl pyrrolidone) (PVP) and sodium alginate (SA) were prepared.

In order to control the excessive swelling of PVA membranes, Ping et al. [56] mixed PVA with PVP to separate water and ethanol. In fact, establishing hydrogen bonds between the chains of two distinct polymers led to their miscibility in every fraction, which is responsible for enhanced selectivity of PVA membranes.

Chitosan (CS), sodium alginate (SA) and PVA are the most widely used materials in the area of preparation of hydrophilic PV membranes for dehydration purposes. As the chemical structures and properties of the three mentioned polymers are different, some efforts have been made to develop binary blends of CS, SA and PVA.

Sodium alginate (SA) and PVA are very hydrophilic polymers which have been blended in preparation of PV membranes for dehydration of different alcohol solutions [57,58]. PVA is a flexible polymer with suitable flux but low water selectivity while sodium alginate is a rigid polymer with high glassy temperature that has significant relaxation at temperatures below its glassy temperature [57].
Both PVA and SA membranes are hydrophilic in nature and their PV performance was studied separately. As a result, blended membranes of these polymers have been tested in dehydration of ethanol and isopropanol mixtures [57,58]. Increasing flux of the blended membranes was observed due to their improved hydrophilicity, while the reverse was recorded for separation factor.

In 1992, Lee et al. [59] studied the dehydration ability of blend membranes of PVA and CS to investigate the effects of various parameters including feed concentration and weight ratio of two polymers. A separation factor and flux of 450 and 0.47 kg/(m² h) were reported, respectively, when the blend membrane composed of 60 wt% of PVA and 40 wt% of CS dehydrated a mixture of 90 wt% ethanol. Other blend membranes including 25 wt% of PVA and 75 wt% of CS were used to separate water from isopropanol aqueous mixtures [60]. The flux of 0.644 kg/(m² h) was reported while the percentage of water in the permeate side was about 100 wt%.

Chitosan-PVA blend membranes with different PVA weight percent (20, 40 and 60 wt%) were tested for separation of water from 90 wt% isopropanol aqueous mixtures at 30 °C [61]. To hinder the excessive swelling of the membranes, urea formaldehyde/sulfuric acid (UFS) mixture was used to crosslink polymer chains. The FTIR analysis indicated a successful crosslinking between NH₂ groups of chitosan and UFS, and OH groups of PVA and the crosslinking agent. Actually, blend membranes containing 20 wt% PVA could successfully dehydrate isopropanol with the separation factor and permeation flux of 17991 and 0.1133 kg/(m² h), respectively.

Poly(vinyl amine) (PVAm) with high number of hydrophilic NH₂ groups was blended with PVA at three different weight ratios for preparation of PVAm-based membranes for isopropanol dehydration [62]. The results indicated that when the PVA:PVAm weight ratio was 100:30, the separation factor of 2085 and the flux of 0.16 kg/(m² h) were observed for dehydration of a mixture containing 85 wt% isopropanol at 60 °C. Based on this paper, increasing PVAm in PVA membrane resulted in increasing the intramolecular hydrogen bonding between two polymers. As a result, the crystallinity of PVA membranes decreased by an increase in the number of PVAm membranes. As mass transport can occur through amorphous regions, membranes with higher amount of PVAm showed higher flux without significant decrease in separation factor.

To separate water from alcohols via blended PVA-based membranes, mixing PVA with another polymer which can crosslink PVA chains at the same time can be a good alternative. Therefore, blended membranes of PVA/poly (acrylic acid-co-maleic acid) with weight ratio of 60/40 were prepared to study the PV performance for dehydration of ethanol and iso-butanol [63]. It was reported that maleic groups could increase water selectivity of PVA membrane. Adoor et al. [64] proposed to control the undesired swelling of PVA membranes via providing an appropriate balance between the hydrophilicity and hydrophobicity of the membranes. So, hydrophobic poly(methyl methacrylate) (PMMA) was used to modify the PV ability of PVA membranes for isopropanol dehydration. In this regard, hydrophobic poly(ether sulfone) (PES) was chosen to be blended with PVA at several ratios to dehydrate ethanol aqueous solution via PV technique [65]. For an aqueous mixture of 90 wt% isopropanol at 80 °C, the separation factor and flux were 86.1 and 0.298 kg/(m² h), respectively. Owing to its nontoxic and environmentally-friendly nature, carboxymethylcellulose was blended with PVA for PV separation of alcohol and water solutions [66]. The most notable membrane performance was observed when the PVA/carboxymethylcellulose weight ratio was 1:1; the selectivity was 4000 and the flux of 0.29 kg/(m² h) were obtained for dehydration of the azeotrope isopropanol mixture.

To fabricate a suitable hydrophilic membrane for alcohol dehydration by blending technique, Ruckenstein et al. [67] chose polyacrylamide (PAAM), which is somewhat brittle but more highly selective towards water. So, the interpenetrating network membranes of PVA and PAAM were prepared. Glutaraldehyde and N,N'-methylenebisacrylamide (BisAAM) were used as crosslinking agents for PVA and PAAM, respectively. According to their study, the greater the amount of PAAM used, the greater the water selectivity of the membranes obtained. However, when the content of PAAM was over 16 wt%, the membranes were too brittle to use in PV, which means the optimum weight ratio of PAAM in PVA blend membrane was 16%. The blended membranes could
dehydrate 15 wt% of ethanol mixture with the separation factor of 600 and the permeation flux of 0.32 kg/(m^2 h).

Thin layer blend membranes of PVA and PSSA were prepared to separate different binary mixtures of alcohols and water via PV process [68]. Also, the effects of application of different metal salts of PSSA on PV results were investigated. The best results of their experiments corresponded to blend membranes with the PVA:PSSA ratio of 3:2, while SO_3H groups of PSSA changed into Ba^{2+} metal salt. Owing to lower diffusion ability of alcohols with larger molecular size, higher separation factors were reported in case of dehydration of isopropanol and butanol. Table 3 summarizes the obtained results for this study.

Beta-cyclodextrin (CD) oligomer was used to fabricate PVA membranes for ethanol dehydration by Yamasaki et al. [69]. In order to avoid CD dissolution from the membranes, PVA was crosslinked by glutaraldehyde. Membranes’ selectivity increased by addition of 33 wt% CD, provided that the ethanol content of the feed was more than 90 wt% or lower than 40 wt%. As for permeation rate, membranes’ behavior was different based on ethanol concentration of the feed. For mixtures with low alcohol content, blend membranes resulted in enhancing the water permeation flux of membranes. This might due to an increase in water diffusion coefficient that is accompanied by a decrease in diffusion coefficient of ethanol. For concentrated alcohol feeds, even though the presence of CD favors increasing the water diffusion coefficient, water solubility of membranes dropped and the water permeation rate decreased.

As a polar polymer groups, Nylon 66 was evaluated in fabricating PVA-based membranes for 2-butanol dehydration [70]. Unfortunately, blended membranes of PVA-Nylon 66 crosslinked by glutaraldehyde showed poor selectivity for azeotrope mixture of water and 2-butanol solutions. Due to hydroxyl groups of polyelectrolyte (PEC) surface and their success in preparation of PV membranes, blend membranes of PEC and PVA were studied in alcohol dehydration via the PV process [71,72]. Zhao et al. [72] found that the blend membranes of PEC and PVA were successful in separation of water from feed containing 90 wt% isopropanol. As a matter of fact, the crystallinity and swelling of PVA membranes decreased through formation of hydrogen bonds between hydroxyl groups of both PVA and PEC chains. The separation factor and flux were about 1002 and 1.35 kg/(m^2 h) when PVA:PEC weight ratio of 1:1 membrane was used in dehydration of 90 wt% isopropanol mixture at 70 °C. The performance of PVA blend membranes with different compounds such as sericin [73] was also investigated for separation of water from various alcohols.

In conclusion, two distinct perspectives can be sought in modification of PVA membranes by polymer blending for PV dehydration application: (i) increasing the hydrophilicity

**Table 3. PV Results for Dehydration of 95 wt% Alcohol Mixtures for Membranes with Ba^{2+}**

<table>
<thead>
<tr>
<th>Alcohol in feed</th>
<th>J (kg/(m^2 h))</th>
<th>Separation factor</th>
</tr>
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<tbody>
<tr>
<td>Methanol</td>
<td>0.17</td>
<td>43</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.15</td>
<td>1570</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>0.15</td>
<td>13900</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>0.23</td>
<td>18600</td>
</tr>
<tr>
<td>Isobutanol</td>
<td>0.20</td>
<td>32800</td>
</tr>
<tr>
<td>t-Butanol</td>
<td>0.21</td>
<td>17900</td>
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</tbody>
</table>
property of PVA membranes by addition of hydrophilic polymers with suitable ability for separation of organic aqueous solutions, (ii) balancing the hydrophilicity and hydrophobicity of membranes by introducing hydrophobic polymers into the PVA matrix in order to decrease the effects of excessive swelling of PVA-based membranes.

**Supported PVA Membranes**

Decreasing the membranes’ thickness is among the promising modification methods. In fact, based on Fick’s First Law, the flux of a membrane can increase with decreasing the thickness, which means the higher flux would be obtained through decreasing the membranes’ thickness. Consequently, preparation of supported membranes has been of interest [14]. Unfortunately, decreasing the thickness of membranes results in fabrication of unstable membranes, especially for dehydration purposes with low mechanical strength. As a result, as shown in Fig. 3, supported membranes have been developed in a way that a thin non-porous layer is supported by a thick porous layer; the support layer mainly provides the mechanical stability of the structure while the top layer is responsible for the separation phenomenon [15,16]. In this regard, various attempts have been made to improve the permeation flux of PVA membranes [74-76]. In addition, as discussed earlier, the first commercial grade of PVA-based membranes, made up of a thin layer of PVA on a poly(acrylonitrile) (PAN) support, for ethanol dehydration via PV process was introduced by GFT [10]. The thick support layer can be made up of polymers or ceramic materials as described below:

Although there are some reports on fabrication of polymer supported PVA membranes for the dehydration process, their objective was not to study the effect of the thickness of PVA-based membranes and application of the support layer. Herein, we review only those reports focused on the influence of the support layer.

**Polymer-supported PVA membranes.** In 1992 [76], for dehydration of aqueous ethanol solution, PVA membranes supported with poly(acrylonitrile) (PAN) were prepared. To address the effect of the support layer on PV performance, the effect of the PAN dope composition was investigated. Findings indicated that the supported PVA membranes experienced lower swelling compared to unsupported PVA membranes with improved selectivity. Furthermore, it was reported that the porosity and molecular weight cut-off of the PAN layer could influence the PV dehydration results.

Blended membranes of PVA and chitosan which were supported on a polysulfone sub-layer were used to dehydrate water/ethanol feed with concentration close to azeotrope mixture. Compared to thick blended membranes
of PVA and chitosan, better chemical and mechanical stability against water were reported [77].

Poly(acrylonitrile) (PAN) was used as a support layer for fabrication of blended membranes of PVA and chitosan (CS) for ethanol dehydration in different publications [68,69]. The results indicated a higher hydrophilicity and enhanced flux for PVA-CS/PAN membranes compared to those for PVA/PAN, although with lower separation factor [69].

Morris et al. [78] designed a set of experiments using a blend of sodium alginate (SA) and PVA with weight ratio of 4:1. Next, the blend was cast onto a PAN layer. It was observed that when the thickness of the membranes increased, the required time for the evaporation of solvent increased, allowing more intensive crosslinking among the blended polymer chains. As a result, an unusual decrease of flux and increase in selectivity were reported for thicker membranes. In 2020, Li et al. [79] tried to improve the PV performance of PVA membranes supported by PAN. First, self-aggregation crosslinking of PVA was initiated with ammonium persulfate (APS). Next, to regulate the interface properties between PVA and the support layers, PAN was modified by tannic acid (TA). Thus, the phenolic OH groups of TA could make hydrogen bonds with OH groups of PVA to improve the interfacial properties of PVA/PAN membranes. The flux of the permeated product containing 99.99 wt% water was about 0.118 kg/(m² h) when 8 g of PVA and 12.5 g of APS were used.

Ruckenstein et al. [67] studied the effect of reducing the thickness of the interpenetrating polymer network of PVA-polyacrylamide (PAAM) for dehydration of ethanol solution by fabrication of supported and unsupported membranes. The thickness of unsupported PVA-PAAM membranes decreased from 40 μm to 4 μm when polyethersulfone (PES) was used as the support layer. As expected, the thinner the top layer was, the higher the flux observed, while a common trade-off trend was observed for separation factor.

Ceramic-supported PVA membranes. As discussed, inserting a thin selective layer on a porous supporting layer is an effective method to modify PV membranes [80]. On the other hand, rising pressure gradient across membranes is followed by increasing mass transport driving force, so preparation of membranes with enough mechanical stability is required [81]. Ceramic supports with high surface porosity offer special advantages including chemical, thermal and mechanical stabilities over the polymer supports [81].

2006, Peters et al. [80] cast an ultra-thin layer of PVA with thickness of 0.3-0.8 μm on a two-layer ceramic support. In order to prepare a defect-free support surface, a thin layer of γ-alumina with a thickness between 3 and 4 μm was applied on the surface of α-alumina layer. After PV dehydration of aqueous solutions of 1-propanol, 2-propanol and 1-butanol, the obtained separation factor was in the range of 500-10000 while the corresponding flux was in the range of 0.8-2.6 kg/(m² h). Hence, it seems ceramic-supported PVA membranes were more efficient in alcohol dehydration compared to polymer-supported PVA membranes.

In 2010, Zhu et al. [82] evaluated the performance of the blended membranes of PVA and chitosan supported by ZrO$_2$/Al$_2$O$_3$ with different pore sizes. The selective layer was crosslinked by mixtures of sulfuric acid and maleic anhydride to separate water from ethanol and tert-Butanol. Moreover, it was asserted that the pore size of the ceramic support could significantly influence the dehydration ability of the membranes. Also, the results indicated that introducing chitosan into the PVA matrix leads to a decrease in crystallinity and hydrophilicity of the top layer. Surprisingly, enhancing of flux was reported without a remarkable drop of separation factor for the ceramic-supported PVA-CS membranes.

To sum up, in the field of fabrication of a thin layer of a selective polymeric layer on a ceramic support, different parameters such as porosity, roughness and pore size of the ceramic support have profound impacts on the thickness of the selective layer, affecting the morphology of the whole membrane and its performance [83].

Hollow Fibers

Another important parameter with an enormous impact on performance of membranes is the geometry and the modulus design of the membrane. Owing to their high surface-to-volume ratios, hollow fibers seem to be more proper candidates for fabrication of commercial membranes [24,25]. High packing density, self-supporting structure, low capital cost, the possibility of reverse washing and high
ratio of surface-to-volume are some special characteristics of hollow fibers as suitable modulus for preparation of membranes [17-23].

Polysulfone (PSF) hollow covered by a PVA layer were used in separation of water from ethanol aqueous solutions via the PV process [84], while maleic acid was used to crosslink PVA chains thermally. To improve the dehydration ability of PVA/PSF hollow fiber membranes, Dong et al. [85] added sodium alginate to PVA before coating the top layer on the PSF hollow fibers. The PV results indicated that increasing the PVA content up to 80 wt% results in an extreme rise of flux, whereas the separation factor decreased. If the weight percentage of PVA was over 80 in the selective top layer, there would be a sharper decline of separation factor due to the high flexibility of PVA chains in an aqueous environment. Furthermore, as stated before, sodium alginate is a rigid polymer, which means it could balance the mobility of PVA chains. Table 4 summarizes the obtained results for dehydration of several 90/10 wt% alcohol/water mixtures. It is worthy to notice that as the solubility parameter of ethanol was close to the membrane, ethanol showed stronger affinity towards membranes as compared to other alcohols. Thus, the lower separation factor was observed for ethanol dehydration.

Perfluorosulfonic acid (PFSA) with pendant side chains terminated by sulfonate acid was used to prepare PV membranes [86]. Even though PFSA was used previously in PV investigations, it did not show the desired separation factor; contrary to PVA membranes with better separation factor but lower flux. Considering the positive potential of these two polymers, hollow fibers of polysulfone (PSF) were covered by blends of PFSA and PVA for isopropanol dehydration. All prepared PVA-based membranes were crosslinked thermally; the effect of chemical crosslinking of PVA chains via post-treatment in maleic acid solution was also studied. The best separation performance for isopropanol dehydration was reported when PVA:PFSA ratio was 3:5 and the membranes were thermally treated at 160 °C for an hour, followed by 3 h of chemical crosslinking in 4 wt% maleic acid solution at 40 °C.

**Mixed Matrix Membranes**

Incorporation of fillers into polymers that results in fabrication of mixed matrix membranes (MMMs) can improve the permeation performance of membranes. In mixed matrix membranes, particles or fillers should be dispersed in the polymer while the fillers are surrounded by polymer chains. Thus, MMMs take advantages of both organic and inorganic moieties. Although it is usual to observe a trade-off trend between flux and separation factor. There are some reports indicating that scattering fillers such as zeolites could increase either the separation factor or the permeation flux [87,88]. In fact, fillers have an enormous impact on separation ability of polymeric membranes through different ways: (i) in case of hydrophilic additives, the overall affinity of the membrane towards water increases, indicating that the structure can adsorb more

<table>
<thead>
<tr>
<th>Alcohol in feed</th>
<th>Flux (kg/(m² h))</th>
<th>Separation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>0.375</td>
<td>400</td>
</tr>
<tr>
<td>Iso-propanol</td>
<td>0.42</td>
<td>1750</td>
</tr>
<tr>
<td>Normal-butanol</td>
<td>0.56</td>
<td>700</td>
</tr>
<tr>
<td>Tert-butanol</td>
<td>0.36</td>
<td>720</td>
</tr>
</tbody>
</table>
water resulting in improving the permeation rate by sacrificing the selectivity; (ii) as for hydrophobic fillers, the undesired swelling of the PVA membranes may be limited. Thus, it is possible to balance the hydrophilicity/hydrophobicity of the whole selective layer; (iii) it is asserted that some of the fillers would increase the selectivity of the membranes via their molecular sieving ability; it means water molecules can pass through the membrane due to specific pore diameter and molecular sieving feature of fillers that can hinder the passage of alcohol molecules. For example, there are some additives such as 4A zeolite that their pore diameters (4 Å) are less than the kinetic diameter of ethanol, whereas water molecules with kinetic diameter of about 0.264 nm are capable to pass through these particles [89]. Zeolites, nanotubes (NTs), metal oxides, nanoclays and heteropolyacids (HPA) are the most widely used fillers incorporated into the PVA matrix for alcohol dehydration purpose, so we classified this section based on the type of the fillers. Finally, a review of PVA MMMs with fillers that do not belong to the aforementioned commonly-used categories will be presented.

Zeolites. One of the most typical particles for fabrication of MMMs is zeolites. On the plus side of zeolite membranes, they do not suffer from excessive swelling, leading to low water selectivity of PVA membranes [89]. Moreover, both thermal and chemical stability of zeolite membranes are higher than those of polymeric ones. Unfortunately, fabrication of zeolite membranes is not only more expensive, but also more complicated. Besides, zeolite membranes are brittle [89]. It seems that MMMs can make use of both polymeric and un-polymeric materials. It is worth mentioning that the separation performance of mixed matrix membranes extremely depends on the type of both the dispersed and continuous (matrix) phases as well as the morphology of their interface. Huang et al. [89] investigated the PV separation of water and ethanol by using MMMs made up of PVA and zeolite 4A while fumaric acid was used to decrease the swelling of PVA membranes. The results showed that the higher permeation flux was observed for higher zeolite loading due to hydrophilicity of the dispersed phase. Surprisingly, contrary to the ubiquitous trade-off trend between separation factor and flux, when the number of particles increased to 20 wt%, both flux and separation factor were enhanced. Zeolite particles could not be dispersed effectively in further increase in zeolite content, resulting in reduction of the separation factor.

In another attempt [90], PVA membranes were modified by incorporating KA zeolite particles for separating water from 80 wt% ethanol mixtures. Next, a thin layer of crosslinked PVA and KA zeolites was cast on a poly(acrylonitrile-co-methyl acrylate) [poly(AN-co-MA)] porous layer that was cast on poly (phenylene sulfide) (PPS) nonwoven fibers. It was reported that the separation factor increased from 511 to 1276 when PVA membrane was filled with 20 wt% zeolite.

In 2007, a group of researchers investigated the effects of incorporation of a distinct type of zeolites named 1-silicate into PVA membranes to separate water from isopropanol [91]. They observed that the separation factor of the pristine PVA membrane was increased from 77 to 2241 by addition of 10 wt% of 1-silicate. Meanwhile, the flux dropped from 0.095 kg/(m² h) for unfilled PVA membrane to 0.069 kg/(m² h). It was claimed that different factors such as hydrophobicity of particles, pore dimension, three-dimensional sinusoidal channels and electrostatic forces between the positively charged cations and the negatively charged zeolite framework were all responsible for the observed alcohol dehydration performance.

Mixed matrix membranes of PVA and four different types of zeolites including KA, NaA, Ca and NaX were prepared to separate water from various aqueous alcohol solutions [92]. According to the results, A-type zeolites could effectively increase the passage of both water and small molecular size alcohols such as methanol due to their smaller pore size. Meanwhile, the NaX type hindered the diffusion of larger size alcohols. On the other hand, in the case of methanol dehydration, there was a decline in separation factor for the filled membranes except for KA zeolites. Generally, addition of zeolites could increase the flux of PVA membranes. The summarized results of the obtained flux and separation factor of zeolite filled membranes at 50 °C are presented in Table 5.

Decreasing thickness, polymer blending, and incorporation of inorganic fillers are amongst the promising strategies to modify the dehydration ability of PV membranes. In this regard, Amnuaypanich et al. [93] tried to take the benefits of all three mentioned strategies. They
developed PVA membranes through incorporation of zeolite 4A particles into a blend of natural rubber (NR) and PVA which was supported by a thick, porous nylon layer to dehydrate water-ethanol mixtures. Comparing the performance of the unfilled PVA-NR blend membranes and PVA-NR mixed matrix membranes shows that physical crosslinking of PVA by zeolites, chemical crosslinking of PVA with sulfosuccinic acid as well as balancing the

<table>
<thead>
<tr>
<th>Zeolite type in PVA matrix</th>
<th>Flux (ml m⁻² h⁻¹)</th>
<th>Separation factor</th>
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</thead>
<tbody>
<tr>
<td>Methanol/water solution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>183</td>
<td>15.5</td>
</tr>
<tr>
<td>KA</td>
<td>235</td>
<td>15.5</td>
</tr>
<tr>
<td>NaA</td>
<td>258</td>
<td>13.8</td>
</tr>
<tr>
<td>CaA</td>
<td>323</td>
<td>10.4</td>
</tr>
<tr>
<td>NaX</td>
<td>376</td>
<td>8.5</td>
</tr>
<tr>
<td>Ethanol/water solution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>140</td>
<td>40</td>
</tr>
<tr>
<td>KA</td>
<td>164</td>
<td>40</td>
</tr>
<tr>
<td>NaA</td>
<td>172</td>
<td>36.6</td>
</tr>
<tr>
<td>CaA</td>
<td>194</td>
<td>22.3</td>
</tr>
<tr>
<td>NaX</td>
<td>214</td>
<td>19.4</td>
</tr>
<tr>
<td>Iso-propanol/water solution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>146</td>
<td>233</td>
</tr>
<tr>
<td>KA</td>
<td>179</td>
<td>410</td>
</tr>
<tr>
<td>NaA</td>
<td>183</td>
<td>328</td>
</tr>
<tr>
<td>CaA</td>
<td>190</td>
<td>233</td>
</tr>
<tr>
<td>NaX</td>
<td>216</td>
<td>233</td>
</tr>
<tr>
<td>t-Butanol/water solution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>118</td>
<td>516</td>
</tr>
<tr>
<td>KA</td>
<td>135</td>
<td>1170</td>
</tr>
<tr>
<td>NaA</td>
<td>140</td>
<td>1170</td>
</tr>
<tr>
<td>CaA</td>
<td>157</td>
<td>1170</td>
</tr>
<tr>
<td>NaX</td>
<td>170</td>
<td>516</td>
</tr>
</tbody>
</table>
hydrophilicity of PVA through blending with hydrophobic NR all suppressed the excessive swelling of PVA membranes. Moreover, it was observed that 4A zeolites with pore size smaller than the kinetic diameter of ethanol molecules and larger than that of water could improve the selectivity toward water as well as their positive effect on flux. Accordingly, introducing alternative paths via zeolite pores was accountable for improving the flux.

The pervaporation separation of water-ethanol mixtures was investigated using mixed matrix membranes of different types of zeolites including 3A, 4A, 5A, NaX, NaY, 1-silicalite and beta [94]. According to the results, PV performance of the membranes depends on the pore structure of the zeolites and their hydrophilic/hydrophobic nature. For NaX and NaY zeolites with same pore size, the NaX-filled membranes showed higher selectivity than MMMs containing NaY since the former was more hydrophilic than the latter. On the other hand, MMMs with either NaX or NaY could improve the permeation rate of PVA membranes. As for application of hydrophobic zeolites such as 1-silicate and beta into PVA membranes, the lower hydrophobicity and larger pore size of beta particles led to increase of both flux and separation factor. Meanwhile, a decreasing trend was observed for the flux in the case of 1-silicalite, and the permeation flux decreased because the filler decreased the hydrophilicity of PVA membranes.

High surface area, homogenous distribution of pore size and high cavity volume of NaY zeolite were the promising properties for preparation of PVA-NaY mixed matrix membranes for isopropyl alcohol dehydration by Kursun et al. [95]. An increase in zeolite content led to restriction of chain mobility of PVA and increasing rigidity of the membranes that are all in favor of selective transport of water molecules; however, decreased free volumes resulted in reduction of flux. The best dehydration performance for azeotrope mixture at 35 °C was reported for incorporation of 0.5 wt% of NaY nanoparticles with separation factor of 2690 and flux of 0.005 kg/(m²h).

To investigate the effects of balancing between hydrophilicity and hydrophobicity of PVA membranes for selective dehydration of 90 wt% isopropanol solution, Kittuar et al. [96] fabricated MMMs of PVA by incorporating ZSM-5 particles. Owing to hydrophobicity of the dispersed phase, the hydrophilicity and swelling behavior of MMMs were reduced by increasing the amount of ZSM-5 in membranes. Increasing the amount of hydrophobic fillers led to enhancing water selectivity without significant drop in their flux. Anyway, the separation performance of the prepared membranes was not of interest in terms of selectivity (<1000) and flux (<0.1 kg/(m²h)). In 2019, Huang et al. [97] reported that dispersion of ZSM-5 particles could be effective for improving the water selectivity of PVA membranes without significant decrease of flux for isopropanol dehydration.

Suhas et al. [98] studied the effect of the silica/alumina ratio in H-ZSM-5 zeolites in fabrication of PVA MMMs for PV dehydration of ethanol and isopropanol. Their observations indicated that nanoparticles with higher alumina content could make better interactions with PVA matrix, resulting in higher separation factor and flux. For example, the separation factor and flux were, respectively, about 568 and 0.144 kg/(m²h) when the silica-to-alumina ratio of H-ZSM-5 was 38 in dehydration of 90 wt% isopropanol at 30 °C, while the separation factor and flux were about 334 and 0.138 kg/(m²h) for H-ZSM-5 with the silica/alumina ratio of 408 in the same experimental conditions.

Samei et al. [81] cast a thin layer of PVA containing different amounts of fumed silica onto a homemade tubular ceramic support. The membranes were evaluated for separation of water from ethanol. Higher PVA concentration in the coating solution resulted in the formation of thicker selective layers that led to fabrication of a smoother surface. Hence, membranes with a thicker active layer had a better separation factor as a result of the decrease in permeation flux. The greater the amount of fumed silica dispersed, the more hydrophilicity achieved. Therefore, an excessive swelling of the selective layer occurred corresponding to improvement of flux and decreasing the separation factor.

**Metal oxides.** Aminabahavi et al. [7] used titanium oxide (TiO₂) nanoparticles to improve the hydrophilicity of PVA membranes crosslinked by glutaraldehyde for isopropanol dehydration at 30 °C. Polyaniline (PANI) was used to make TiO₂ particles much more compatible with the matrix. From the results, the addition of low quantities of TiO₂ fillers resulted in infinite separation factors by sacrificing the
permeation flux. However, surface modification of nanoparticles with PANI could improve the permeated flux. For example, the flux was 0.180 kg/(m² h) for incorporation of 0.5 wt% TiO₂ into PVA matrix in dehydration of 90 wt% isopropanol that increased to 0.256 kg/(m² h) when TiO₂ was coated by PANI.

Iron oxide was in-situ synthesized to be dispersed homogeneously into PVA membranes [90]. Based on the reported results, thermal, mechanical and barrier properties of the MMMs were improved. The three different weight ratios of Fe(II):Fe(III) were also evaluated to remove water from aqueous isopropanol mixtures, however, the permeation ability of MMMs was unsatisfactory. The flux of all mixed matrix membranes was lower than that of pristine PVA membrane.

**Nanotubes (NTs).** A novel class of fillers with brilliant features is hydrophobic carbon nanotubes (CNTs). Their open-ended structure and tubular shape as well as their significant mechanical strength and chemical stability make CNTs promising candidates for preparing mixed matrix membranes [99,100]. The special physical structure of this new generation of fillers may end in rapid mass transport. However, CNTs tend to agglomerate due to Van der Waals forces among the tubes, making their pretreatments necessary. In this regard, Shirazi et al. [99] studied the permeation performance of PVA membranes modified with acid-treated CNTs. Chain rigidification of PVA membranes was reported by incorporation of 2 wt% of the oxidized CNTs due to good interactions between both phases. The selectivity of MMMs with 2 wt% of the modified CNTs was 1794 while it was 119 for unfilled PVA membranes.

Multi-walled CNTs (MWCNTs) were pretreated by an acidic mixture of concentrated HNO₃: H₂SO₄ in a volume ratio of 1:3 to attach COOH groups onto CNTs’ walls [101]. For a mixture of ethanol with 10 wt% water, the permeation flux of the membranes is enhanced by increasing the amount of fillers. The best separation performance for 90 wt% ethanol dehydration was obtained when 3 wt% of the modified nanotubes were used with the separation factor and permeation flux of about 1300 and 1.3 kg/(m² h), respectively.

Isopropanol aqueous solutions were dehydrated over PVA-based MMMs of poly(allylamine hydrochloride)-wrapped-CNTs (PAH-W-CNTs) [102]. The separation factor of pristine PVA membranes increased from 141 to 948 by incorporation of 1 wt% of the modified CNTs without significant changes in the flux.

Panahian et al. [103] studied the effects of modification of supported PVA membranes containing unmodified-MWCNTs (PVA-CNTs), carboxyl-functionalized-MWCNTs (PVA-modified CNTs), and TiO₂-carboxyl functionalized-MWCNTs (PVA-TiO₂-CNTs) for ethanol dehydration. To prepare carboxyl-functionalized-CNTs, first CNTs were treated by H₂SO₄:HNO₃ mixture, then the oxidized CNTs were treated by monohydrate citric acid known as carboxyl-functionalized-MWCNTs. The functionalized CNTs coated by TiO₂ nanoparticles were called TiO₂-carboxyl functionalized-MWCNTs. They claimed that although addition of all nanotubes (with/without modification) resulted in lower permeations compared to the neat PVA membrane, functionalization of CNTs by COOH groups favored the separation factor. In addition, coating of TiO₂ on surface of carboxyl functionalized-MWCNTs led to increasing the separation factor from 662 for MMMs with functionalized-MWCNTs to 805 without a significant decrease in flux from 0.395 kg/(m² h) to 0.388 kg/(m² h) for MMMs with functionalized-MWCNTs.

Incorporation of CNTs into PVA matrix is challenging owing to strong hydrophobicity and Van der Waals interactions among the walls of CNTs. Preparation of hydrophilic nanotubes with the unique structural features of CNTs and hydrophilic fillers was carried out by Raeesi et al. [100]. They studied the effectiveness of thermally-synthesized TNTs in modification of PVA membranes for isopropanol dehydration. Based on the reported results, PVA membranes with 2 wt% of TNTs could separate water from isopropanol with separation factor and flux of 4291 and 0.062 kg/(m² h), respectively. Interestingly, contrary to CNTs, TNTs could be dispersed into PVA matrix up to 10 wt% without modifications.

Halloysite nanotubes (HNTs) are aluminosilicate nanotubes with the molecular formula Al₂SiO₅(OH)₄·nH₂O that can be well-dispersed in water. Chaudhari et al. [104] studied the PV performance of PVA blends and poly(vinyl amine) (PVAm) incorporated with modified-HNTs. First, dried HNTs were pretreated by piranha solution containing sulfuric acid/hydrogen peroxide (3:1 v/v). Next, surface-
modified HNTs were used for fabrication of MMMs for the purpose of isopropanol dehydration. The experiments showed that the best PV performance was obtained when 5 wt% of the modified HNTs was dispersed into a blend of PVA/PVAm (100:30 g g⁻¹). For example, in dehydration of 90 wt% isopropanol mixture at 40 °C, the separation factor and flux were 93313 and 0.031 kg/(m² h), respectively.

**Heteropolyacids (HPAs).** Heteropolyacids (HPAs) are polyoxometalate inorganic fillers with suitable hydrophilicity that contain tungsten, molybdenum or vanadium. Teli et al. [105] studied the effect of adding 1 to 7 wt% phosphomolybdic heteropolyacids particles into PVA matrix. They placed the HPA inorganic fillers in a free volume of polymer chains. So, water molecules could interact more with membranes, resulted in increased hydrophilicity. In fact, the higher the filler content, the more water selectivity was observed, while an opposite trend was recorded for the flux of the membranes.

In 2010, Magalad et al. [106] mixed the aqueous solutions of PVP 6 wt% and PVA 6 wt% with PVP:PVA volume ratio of 1:9. PVA chains crosslinked by glutaraldehyde, and then the effect of dispersion of three different weight ratios (4, 8 and 12 wt%) of phosphomolybdic acid (PMA) were studied in PV dehydration of ethanol solution. In general, addition of 4 wt% of PMA particles led to formation of hydrates and hydrogen bonding between PMA groups and either polymers or water molecules, all of which were in favor of water selectivity. The contact angle of MMMs was dropped by incorporation of higher amount of PMA, corresponding to increasing the hydrophilicity and swelling of the membranes. Consequently, increasing flux and decreasing selectivity were reported.

The influence of the type of alcohol and feed on the performance of mixed matrix membranes containing PVA, poly(vinyl pyrrolidone) (PVP) and phosphomolybdic acid (PMA) was studied by Magalad et al. [106,107]. As shown in Fig. 4, OH groups of PMA could interact with hydroxyl groups of PVA while C=O groups of PVP might also interact with hydroxyl groups of PVA. For dehydration of 10 wt% ethanol mixture at 27 °C, when 4 wt% of PMA was incorporated into PVA-PVP blend, the separation factor and flux were 3324 and 0.046 kg/(m² h), respectively. It was concluded that by using the same membranes in the same conditions, all prepared MMMs showed better separation factors for isopropanol dehydration compared to those for ethanol. For example, the separation factor of membranes with 4 wt% PMA was about 29991 for aqueous feed mixture containing 90 wt% isopropanol that was around 9 times more than that for the 90 wt% ethanol solution.

Silicotungstic acid (STA), a member of HPA family, was modified by melamine to prepare PVA membranes for isopropanol dehydration [108]. As a water soluble filler, STA could be well dispersed in PVA but PVA-STA membranes suffered from leaching of STA during PV cycles. To overcome this challenge, Chaudhari et al. [108] tried to modify the STA particles with melamine and prepared mixed matrix membranes of PVA and melamine-modified-STA. Long-time stability of MMMs was observed with constant PV performance when STA was treated by 8 wt% melamine.

**Nanoclays.** Montmorillonite (MMT) is a common clay mineral that can make good interactions with various polymers due to its intercalation chemistry. Adoor et al. [109] evaluated the ability of hydrophilic sodium montmorillonite (Na’MMT) clay for preparation of MMMs of crosslinked PVA membranes for isopropanol dehydration. They reported that although clay particles were hydrophilic, their MMMs had lower sorption uptake compared to pristine crosslinked PVA membranes because the hydrophilicity of Na’MMT was lower than that of PVA chains. As a result, the solvent uptake of the filled membranes decreased, which caused an increase in the separation factor of the MMMs. Also, the higher separation factors were related to the greater water adsorption ability of the clay layers compared to that of alcohol, due to stronger electrostatic interaction of water molecules with sodium ions of MMMs. Consequently, the separation factor of pristine PVA membrane, MMMs with 5 and 10 wt% of MMT, were 77, 1116 and 2241, respectively. However, pristine PVA membrane showed higher hydrophilicity with the highest flux for the dehydration of aqueous 90 wt% isopropanol solution. Bentonite nanoclay was also incorporated into crosslinked PVA matrix for isopropanol dehydration [110]. Halloysite nanoclay (HNC) is a tubular hydrophilic clay that can be easily dispersed in water. Rao et al. [111] studied the isopropanol dehydration by preparation of PVA-HNC MMMs. It was reported that
water molecules could transport across the MMMs easier and faster than isopropanol due to the crystalline and hydrophilic nature of nanoclay particles.

**Other types of fillers.** In addition to zeolites, metal oxide particles, nanotubes and hetero-polyacids, as the most typical fillers, there are other types of filler that are presented below.

There are other types of inorganic fillers which can act as filler and crosslinking agent, for example, aminopropyltriethoxysilane (APTEOS) [112]. APTEOS could limit the excessive swelling of PVA membranes through its hydrophobic amid groups. On the other hand, APTEOS could decrease the crystallinity of PVA membrane by its larger aminopropyl groups. Therefore, membranes made up of this class of nanofillers showed higher flux. As a matter of fact, APTEOS could interact well with PVA chains by formation of both hydrogen and siloxane bonds; therefore, the membranes’ structure was much amorphous and resulted in facilitated transport of molecules. Besides, there was a sharp rise in separation factor for MMMs containing APTEOS when the filler loading was under 5. By addition of more than 5 wt% of APTEOS, the hydrophobicity of the membranes had a negative impact on the water selectivity. Surprisingly, the modified PVA MMMs could successfully break the trade-off between separation factor and flux for separation of
water-ethanol mixtures.

Dehydration of isopropanol aqueous solutions was investigated by preparing PVA MMMs via reaction of polymer chains with aminopropyltriethoxysilane (APTEOS) and tetraethoxysilane (TEOS) [113]. Covalent bonds between silane groups and hydroxyl groups of polymer chains were known as responsible for undesired swelling of PVA membranes. Unlike the typical reverse trend between separation factor and flux, the covalent bonds increased for higher ratios of APTEOS/(APTEOS + TEOS).

Glycidyl trimethyl ammonium chloride (GTMAC) with four different mass contents was chosen to prepare PVA-based hydrophilic membranes since its N(CH₃)₃ groups are highly hydrophilic in nature [114]. In addition, tetraethoxysilane (TEOS) was used to crosslink PVA chains. The results show that the higher concentrations of GTMAC led to greater swelling of membranes, which can be related to the presence of more N(CH₃)₃ groups that interact with water molecules to be adsorbed easily on the membrane surface. Thus, membranes with 30 wt% of GTMAC could separate water from isopropanol at 30 °C with the separation factor of 1570 and flux of 0.019 kg/(m² h).

Fullerene can be used as a filler in the fabrication of hydrophilic PVA membranes as fullerene hydroxyl groups can interact well with hydroxyl groups of PVA. Further, fullerene can act as a crosslinking agent for PVA. Fullerol C₆₀(OH)₁₂ is one of the derivatives of fullerene C₆₀ nanoparticles used for fabrication of MMMs of PVA for dehydration of different alcohols [115,116]. Penkova et al. [115] studied n-butanol dehydration via PV process and compared the effectiveness of incorporation of fullerol nanoparticles on separation performance of PVA membranes. Meanwhile, mixed matrix membranes of PVA and fullerol were crosslinked physically (thermally) or chemically (with maleic acid). An opposite behavior was reported for PV ability of thermally-modified MMMs and chemically-modified MMMs in terms of both separation factor and flux. Physical crosslinking of PVA-fullerol MMMs might change the morphology of the membranes into a rigidified structure with low flux and high separation factor. In fact, hydrogen bonds could be converted to strong covalent bonds during the evaporation step in physical crosslinking, resulting in intense rigidification of PVA chains. On the other hand, chemical treatment of PVA-fullerol MMMs led to increasing the flux with decreasing the separation factor because of enhanced hydrophilicity of the membranes as well as formation of hydrophilic channels. The best results were observed when PVA was treated by 35 wt% maleic acid and 5 wt% fullerol. Carboxyfullerene is also a member of the fullerene family that was used by Penkova et al. [117] for modification of PVA membrane as both crosslinking agent and filler. The authors reported that when the water content of ethanol aqueous mixture increased from 4.4 to 30 wt%, the separation factor decreased sharply from 217251 to 775 while the flux increased from 0.026 to 0.046 kg/(m² h).

Nanocomposite membranes of polyaniline (PANI) were synthesized by in situ polymerization of PANI in PVA which was crosslinked through post-treatment by glutaraldehyde. In order to assess the effects of PANI content, 3 different amounts of this filler were scattered in PVA [118].

In 2005, Upadhay et al. [119] studied the effects of addition of lithium chloride (LiCl), as an organic salt, on PVA membranes for dehydration of isopropanol. They showed that the membranes became amorphous after using the salt that influenced the separation factor. It was found that the selectivity of water towards isopropanol was increased by adding LiCl. Ebrahimian et al. [120] studied the dehydration of azeotrope isopropanol mixture by addition of lithium bromide (LiBr) to the PVA matrix, and their observations indicated that LiBr could influence the separation behavior through increasing hydrophilicity and crystallinity of the PVA membrane. Graphitic carbon nitride (g-C₃N₄) is a 2D lamellar sheet structure similar to graphene oxide (GO) that may interact with hydroxyl groups of PVA. Interestingly, g-C₃N₄ lattice is composed of hole defects smaller than methanol and ethanol molecules but larger than water molecules. Consequently, g-C₃N₄ were incorporated into PVA membranes for ethanol (90 wt%) dehydration and both the separation factor and the flux were enhanced almost three times compared to pristine PVA membrane [121].

A layer of poly (acrylic acid)-co-acrylonitrile (PAA-co-AN) with/without different contents of SiO₂ was sandwiched between 2 layers of PVA acetal to prepare PVA-based membranes for PV application [122].
presence of SiO$_2$ effectively increased both the separation factor up to 10 times compared to membranes without particles as well as enhanced the permeation rate of 0.325 kg/(m$^2$ h) for PV dehydration of 95 wt% methanol mixture at 60 °C.

Silver nanoparticles were dispersed into the PVA matrix via an in-situ generation method [123]. The authors tried to improve the hydrophilicity of PVA membranes for ethanol dehydration through addition of hydrophilic silver nanoparticles. Although significant improvement was not achieved in terms of flux and separation factor, it was declared that ethanol could dissipate agglomerated silver nanoparticles at higher temperature.

**Combinations**

Although there are some publications focusing on more than one modification strategy (e.g., crosslinked/grafted membranes, blended membranes, supported membranes and mixed matrix membranes) to study the PV performance of PVA membranes in alcohol dehydration, the authors devoted their study only to the effects of one of their modifications. For example, the effect of incorporation of different contents of one filler on the PVA matrix has been discussed in an article, while all of the prepared PVA membranes were supported by a fixed support. We refer to this publication in mixed matrix membrane (MMMs) section. However, in 2018, Dmitrenko et al. [124] made a valuable effort to modify PVA membrane for isopropanol dehydration through two different types of modifications: a) bulk modification including blending of PVA with poly(allylamine hydrochloride) (PAH) and incorporation of fullerene nanoparticles, and b) surface modification of PVA by deposition of thin layers of two different polyelectrolytes. All prepared membranes were supported by commercial ultrafiltration UPM-20 porous supports. The authors investigated the effects of blending, incorporation of nanofillers, crosslinking and surface modification (grafting) of supported PVA membranes.

Poly(allylamine hydrochloride) (PAH) is a cationic hydrophilic polyelectrolyte, chosen to prepare blends membranes of PVA. The H-bonding organization of PVA was disrupted by PAH chains. So, the flux increased about two times compared to pristine PVA membrane, while there was a remarkable decrease in separation factor.

As for introduction of nanofillers into the polymer matrix, fullerene nanoparticles could crosslink PVA chains in PVA-PAH blends, resulting in increases of both separation factor and flux of PVA-PAH membranes.

Layer-by-layer deposition of two different polyelectrolyte, poly(allylamine hydrochloride) (PAH) as a polycation and poly(sodium-4-styrenesulfonate) (PSSA) as the polyanion, was also suggested for surface modification of PVA-fullerenol-PAH membranes. It was found that 10 bilayers of PAH and PSSA could successfully improve the separation performance of supported PVA-fullerenol-PAH mixed matrix membranes.

It is worthy to mention that when the thickness of the deposited bilayers increased from 10 to 20, the flux and selectivity of the membrane decreased. It was asserted that increasing the number of bilayers led to increasing PEC, which could be crosslinked, and used to fabricate thicker membranes. So, lower diffusion passes would exist. As a result, there was a reduction trend for permeation rate. Formation of polar meshes in PEC layers and enhanced hydrophilicity of the top bilayers led to increasing their water sorption. Hence, isopropanol molecules could penetrate more easily, leading to a decreased separation factor.

To sum up, the preferred membrane was 10 bilayers-deposited PVA membranes filled with 5 wt% fullerene-4.7 wt% PAH and crosslinked with 35 wt% maleic acid supported by commercial ultrafiltration UPM-20 support. The flux was about 8.5 times greater than commercial PERVAPTM 1201 (Sulzer) for isopropanol dehydration.

**CONCLUSIONS**

Owing to the importance of alcohols in the medical, pharmaceutical and chemical industries, many efforts have been undertaken to separate water from the aqueous solutions of these solvents. As a membrane-based process, pervaporation is undoubtedly one of promising alternatives to the traditional separation process. As PVA-based membranes have been successful at both the commercial and research levels, several studies have been devoted to come up with different ideas and methods to improve the separation performance of these membranes for alcohol dehydration purposes. In general, it can be concluded that
various parameters could affect the alcohol dehydration ability of PVA membranes including operating conditions (i.e., feed concentration, temperature, downstream pressure), geometry and thickness of membrane, morphological structure and the physiochemical properties and compatibility of the modifier agent. In general, increases in free volume or the mobility of PVA chains could result in flux enhancement while rigidification of PVA structure, formation of denser membranes and reduction of swelling would improve the selectivity of PVA membranes. Considering the results, the reviewed studies indicate that:

By increasing PVA molecular weight, the length of polymer chains and the interaction between chains increase. The chains are more entangled. Therefore, the resulting free volume between molecules reduces. As the free volume decreases, the sorption and diffusion rate of water and IPA decrease, and thus the permeation flux decreases.

PVA concentration also has a remarkable impact on membrane performance; increasing PVA concentration causes thicker membranes that will decrease the diffusion rate of water and alcohol. Thus, the permeation rate of PVA membranes will drop.

According to Fick’s First Law of Diffusion, decreasing the membranes’ thickness leads to better separation performance; i.e., fabrication of thin layer or supported membranes is indicated by the discussion.

Preparation of hollow fiber membranes would be much more challenging, and their pristine features could provide better pervaporation performance.

The idea of fabrication of MMMs could successfully gather the advantages of polymeric and inorganic membranes that require more efforts to achieve PVA membranes with outstanding separation behavior. To sum up, each type of modification method has its cons and pros; the alcohol dehydration of PVA membranes can be remarkably enhanced by providing an optimum value resulting from different modification strategies merged into one strategy.

REFERENCES

