

## Thin film nanocomposite (Tfnc) membranes: Future direction of Tfnc synthesis for alcohol dehydration

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### ABSTRACT

Polymeric membranes separation among the new and reliable separation and purification techniques in terms of energy consumption, ease of the process, and high selectivity due to polymer properties can be tailored to specific needs. This comprehensive review highlights polymeric membranes' current development, specifically on thin film nanocomposite membranes for alcohol dehydration via pervaporation (PV). Discussion on substrate choice and fillers incorporating in respective polymers and how significant both materials in PV application has been scrutinized. Recent works on Thin Film Nanocomposite (TFNC) membranes showed that there is still a gap in factors or parameters involved in TFNC synthesis, which the same old weakness of membrane swelling, flux loss, and selectivity deficit seem left to be discovered. A performance plot of IPA dehydration from recent works has been provided within this paper as a benchmark for researchers to compare their findings. This review emphasizes on finding a set of parameter and nanomaterial as a possible approach for future TFNC development.

### Abbreviations

AA	Acrylic acid
BTCH	tricarbohydrazide — 1,3,5-benzenetricarboxylic acid trihydrazide
CA	cellulose acetate
CaA	calcium alginate
CBT	Coagulation Bath Temperature
CHF	ceramic hollow fiber
CMS	carbon molecular sieve
CNC	cellulose nanocrystal
CNTs	Carbon nanotubes
CS	chitosan
DMAc	Dimethylacetamide
DMC	Dimethyl carbonate
EPMA	2,3-(epoxypropyl)-methacrylate
ETMS	Ethyltrimethoxysilane
Fe	Ferum
FESEM	Field Emission Scanning Electron Microscopy
FTM	Facilitated Transport Membrane
GA	Glutaraldehyde
GO	Graphene oxide

GTMAC	Glycidyltrimethylammonium chloride
HMDACS	hexamethylene 1, 6-di(aminocarboxysulfonate)
HPA-7	heteropolyacid
HPC	Hydroxypropyl cellulose
IPA	Isopropyl alcohol
KA	potassium exchanged zeolite A
MAT	Matrimid 5218
MMM	Mixed matrix membranes
MOF	Metal-organic framework
MPD	meta-phenylene diamine
MPI	Membrane Performance Index
NaA	sodium form of zeolite A
NaAlg	Sodium alginate
NaX	sodium X zeolite
NaY	Sodium Y zeolite
NH <sub>2</sub>	Ammonia (amino group)
NMP	N-Methyl-2-pyrrolidone
PA	Polyamide
PAI	Polyamide-imide
PAN	Polyacrylonitrile
PANI	Polyaniline
PBI	Polybenzimidazole

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PDMS	Polydimethylsiloxane
PE	Polyethylene
PEBA/PEBAX	Polyether Block Amide
PEEK	Polyether ether ketone
PEG	Polyethylene glycol
PEI	Polyethylenimine
PI	Polyimide
PMAA	Poly(methacrylic acid)
PMMA	Poly(methyl methacrylate)
POSS	polyhedral oligosilsesquioxane
PSF	Polysulfones
PTA	Purified Terephthalic Acid
PTFE	Polytetrafluoroethylene
PV	Pervaporation
PVA	Poly(vinyl alcohol)
PVP	Polyvinylpyrrolidone
SA	sodium alginate
SEM	Scanning Electron Microscopy
TEOS	Tetraethyl orthosilicate
TFNC	Thin film nanocomposite
TiO <sub>2</sub>	Titanium dioxide
TMC	trimesoyl chloride
TPU	Thermoplastic Polyurethane
ZIF 8	zeolitic imidazolate framework-8
ZnO	Zinc oxide
ZSM5	Zeolite Socony Mobil-5

## 1. Introduction

Traditional weakness in old fashioned liquid-liquid separation (distillation) is the tendency of azeotropic mixture formation – which requires a high amount of energy for such process to occur successfully. It is found that pervaporation processes are more reliable to break azeotropes directly. Pervaporation (PV) is a membrane separation technique that has a significant ability to remove water from liquid mixtures. The separation mechanism in the conventional distillation depends on the vapour-liquid equilibrium, while PV offers a diffusivity-based separation – as different component diffuses at different rates while some can selectively choose which liquid to be passed through. Each membrane can be specifically tailored to tackle the components via partial vaporization of a liquid mixture. Due to the vaporization of permeating components, PV is the most economical when feed mixture's concentration is low for the favourable permeating components. Fugacity differences between feed and permeate can be expressed as the driving forces for components transfer through the membrane matrix.

A PV system's main advantage is the ability to separate binary or ternary mixture at close boiling point, and azeotropic form besides its low energy consumption and high selectivity permeate. The simplicity of operation with no additional chemical needed to make PV an eco-friendly, economical, and safe separation method compared to others such as azeotropic distillation. For this solvent dehydration, the polymer-based membrane is the most widely explored due to the low-cost material and easily developed in combination with a different kind of polymer to enhance its capability and improve its weaknesses. The sorption-diffusion mechanism model based on Fick's law is commonly used to describe the transport mechanism in PV membranes. As the three steps transport mechanism is applied, surface adsorption/absorption, solution diffusion across membrane film, and desorption at permeate side, the membrane film's hydrophilicity plays a vital role in increasing the separation efficiency.

A hydrophilic membrane might be used to separate water from water/organic mixtures. Recent trends in membrane separation involve developing a composite or mixed matrix membrane by incorporating porous filler. A mixed-matrix membrane might be useful for water pervaporation since it shows molecular sieve effects and good thermal, chemical, and mechanical stabilities. The current situation of a

polymeric membrane in PV application is that the hydrophilic polymers tend to kill the separation performance over time- surface swelling due to high water contents in the feed solution. On the other hand, hydrophobic polymers provide minimum water contents in permeate solution due to its low permeability but are proven to be water selective. Hydrophilic modification of these polymers could be a turning point to cater to surface swelling in the PV membrane while maintaining an outstanding separation efficiency.

Pervaporation (PV) works by accepting liquid feed on a membrane surface, which preferentially allows one component to pass through. For the process to occur successfully, the membrane's underside is held at a vacuum while the feed temperature will be kept close to its saturation temperature. This condition will subsequently vaporize the passing liquid. While the pass through vapour condensed as a permeate component, the retentate is recycled back to the feed tank for further purification or separation process [2].

Different material will cater different liquid mixture, two main factors to be considered in choosing the membrane material is the mass flux,  $J$  ( $\text{kgm}^{-2} \text{h}^{-1}$ ), and the separation factor (Eq. 1) - the quality measure of the separation provided by the membrane.

$$\alpha = \frac{y_p/y_f}{x_p/x_f} \quad (1)$$

$x_f$  and  $y_f$  representing the weight fractions of water and organic compound of the feed components, while  $x_p$  and  $y_p$  representing the weight fractions of water and organic compound in permeate streams [3]. A higher value of  $\alpha$  is desirable for the membrane material as it indicates a greater separation degree. As  $\alpha \rightarrow \infty$ , the membrane was said to be super selective. The typical weakness in membranes separation is the existence of a performance trade-off between mass flux and separation factor, in which any modifications of one eventually will decrease the other and vice versa.

Hydrophilicity and hydrophobicity of membranes are often discussed as crucial factors in solvent dehydration. Hydrophilic membranes are favorable for a mixture with a low water concentration as they allow lower amount of water to permeate through easily, leaving the dehydrated components as retentate [4]. Hydrophilic membranes are intended to consolidate attractive interactions between water and the membrane material, such as dipole-dipole interactions, hydrogen bonding, and ion-dipole interactions [5]. Alternately, a feed comprising a large number of water contents needed hydrophobic membranes for the PV, leaving water as retentate instead of solvent.

The hydrophilicity of membranes film can be measured by determining the angle of a water droplet in contact with the membranes film. The angle describes the material-water affinity. The wider the drop spread, the lower the contact degree, and the higher the affinity between them. This is shown in Fig. 1 and is the wettability of the material with respect to water. This measurement can also be made for any solvent to be dehydrated to assess the material compatibility.

Ethanol and water forms an azeotrope at approximately 4 wt% water [6], and isopropanol (IPA)- water form an azeotrope at around 12 wt% water [6]. Usually, cyclohexane is introduced to the feed mixture before the distillation process occurs to dehydrate the mixture and completely break the water-ethanol azeotrope. In return, cyclohexane's addition

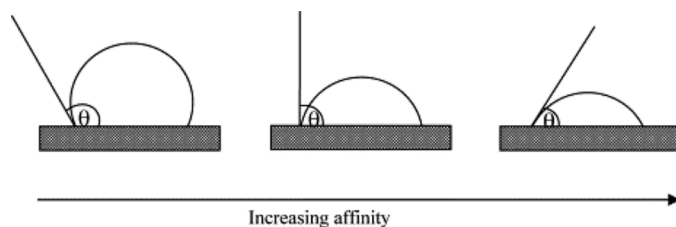


Fig. 1. Contact angle measurement on a non-porous surface [2].

added another impurity to the solvent, which makes the solvent incompatible with some process such as the one in pharmaceutical industries that need high purity solvents [7]. Thus, pervaporation has been turned to as an alternative method of alcohol dehydration as it's almost independent of the vapour-liquid equilibrium because the transport resistance depends on the sorption equilibrium and mobility of the permeate components in the membrane [8]. Thus, it can break these azeotropes without the need for additional chemicals.

Polymer based membranes are well known for its organic polymer chain that can be cross linked with other material to enhance the porous structure and molecule diffusivity. However, the recent trends showing that inorganic membranes consist of ceramics and zeolite being the centre focus of current research. Although these are harder to produce on large-scale industry and cost higher, they may offer several advantages over polymeric membranes, such as solvent resistance and the ability to operate at higher temperatures. Another membrane that showed significant progress in separation technology is mixed matrix membranes (MMM). This kind of membranes comprising of composite membranes based on organic polymeric with inorganic particles dispersed throughout the polymeric structure to modify its polymeric properties.

The material used in synthesized the polymeric membranes determine the separation performance as some are known to be very high selective sorption-diffusion, and some tend to have robust structure but low in term of separation capability. These all depends on the polymer's inter and intramolecular structure, which can form hydrogen bond with water.

Hydrophilic polymeric membranes function as molecular sieves that are durable to water and preferentially sorb the water molecules over other molecules in the process stream. The selective permeation of water needs to have high-sorption centres [5], and it should interact with water by dipole-dipole actions, ion-dipole actions (in the case of a polyelectrolyte), and/or hydrogen bonding in order to be a suitable polymer. Thus, it is desirable to select a membrane with one of these features incorporated in the polymer chain or modify an existing membrane to include such features.

A high-water perm-selectivity in a membrane can be achieved in two ways, either by increasing the diffusion ratio of water to the organic solvent or increasing the sorption ratio of water to the organic solvent. The overall performance of the membrane is affected by the ability of the membrane to swell during operation. During the swelling process, the polymer chains are stretched, and the pore size in the space between them increases. This affects the flux through the pores but, due to their increase in size, it decreases the membrane's selectivity as the larger molecules find it easier to pass through.

By reducing the hydrophilic ratio to hydrophobic moieties in a membrane, the swelling tendency can be reduced, increasing the separation factor and decreasing the flux. The reverse is also true, and the properties of a membrane are influenced by manipulating this ratio. Other than that, the degree of cross-linking also affects the membrane's selectivity. The higher the level of cross-linking between the polymer chains, the more compact the network structure becomes. This strengthens the membrane forming a rigid, stable membrane structure and reduces the degree that the membrane is able to swell when it is in operation. The glass transition temperature ( $T_g$ , below which a polymer is hard and brittle) of a polymer is also important to consider when selecting a polymer for use, as the properties of the polymer material are quite different above and below this temperature. Modifying the glass transition temperature of a material by blending is often used to improve the mechanical characteristics of a polymer, so they are more suitable for a particular process.

## 2. Recent progress of polymeric membranes in pervaporation

For the past 10 years, polymeric membrane in PV revolved around two configurations: the composite and mixed matrix. Both of these

membranes seem promising as its pervaporation's selectivity data scored higher as the research progress grows. A successful pervaporation process mainly governs by four criteria; (1) choice of polymeric material that suit the species to be separated to, like the use of PDMS for DMC-ethanol azeotrope so that coupling effect by the permeating components can be minimized [9], (2) chemical interaction between polymer and feed component which can cause swelling and plasticizing effect [10], (3) long term stability of membrane with good mechanical strength, and (4) better permeation flux and membrane selectivity.

PVA is the first membrane material used for pervaporation application and is most widely used to dehydration organics. Membranes made from only PVA have shown low separation selectivity and permeation flux. Therefore, to overcome this problem, PVA needs some modification to improve its hydrophilicity. However, when the membrane is operated under high fraction of water in feed mixtures, the -OH groups along PVA main-chains make the PVA-based membranes suffer from excessive swelling.

To answer the hydrophilic/hydrophobic arguments of material selection, which choosing one will sacrifice the other, researchers came out with multilayered membranes film. Wang et al. implemented Polybenzimidazole (PBI) as an active layer to the hydrophobic based film. By doing this kind of film, both properties are present in a single film configuration [11]. The outer PBI layer serves as the selective part of the membrane due to its hydrophilicity and chemical resistance ability, while the hydrophobic based layer provides a robust minimum swell structure. To further enhance the surface hydrophilicity, Han et al. successfully grafted Chitosan to PBI membranes. By doing so, more hydrophilic moieties are introduced to the PBI membrane surface to increase the surface hydrophilicity, water solubility, and permeation fluxes of the membrane [12]. Even though the selectivity and flux reading seem promising, PBI-CS membranes still suffer high swelling when facing impurities with high water content.

Some are addressing the weaknesses in polymeric membranes pervaporation due to weak intermolecular chain. This loose bonding was said to be unstable for certain permeating species and conditions. The introduction of crosslinker as a binding medium to hold together two different polymeric materials that possesses the excellent criteria for pervaporation is one step further in membrane synthesis. This unique material will strengthen the bonding of the long polymeric chain, not just that, some of the crosslinker contributing to hydrophilicity enhancement and film morphology. XU et al. in his work of network cross-linking of polyimide membranes for pervaporation dehydration, managed to synthesized a novel tricarbohydrazide — 1,3,5-benzenetri-carboxylic acid trihydrazide (BTCH) crosslinker for PI film [13]. The addition of BTCH to the PI polymer matrix disrupted the chain arrangement by introducing an active amine site, and as a result, a denser film is achieved. By having an amine group in a polymeric membrane chain, changes in physicochemical of the film that imparts not only the physical and chemical stability but also a better per-selectivity and comparable permeability are expected. This dense PI-BTCH film successfully increases the water selectivity from 2000 to 7000, but a gradual flux loss is observed as BTCH contents are increased, as shown in Fig. 2. We can say that presence of BTCH increases the water selectivity of the film by providing a better chemical affinity of water favourable as it is compared to isopropanol.

The presence of -NH<sub>2</sub> in recent research shows an improvement in either flux or water selectivity [4,13–18]. The addition of the amine group to polymeric membrane film also influences the molecular chain, thus resulting in increasing membrane free volume, surface roughness, and hydrophilicity. This compound functionalized the overall film performance as it showed a greater affinity towards water. These phenomena can be best ascribed by the interaction of hydrogen bonding of water molecules and imide/amide groups supported by the size of water molecules, which is smaller than IPA.

In another way, Amine has also been used as a carrier in a Facilitated Transport Membrane, FTM. This kind of membranes is terminally active

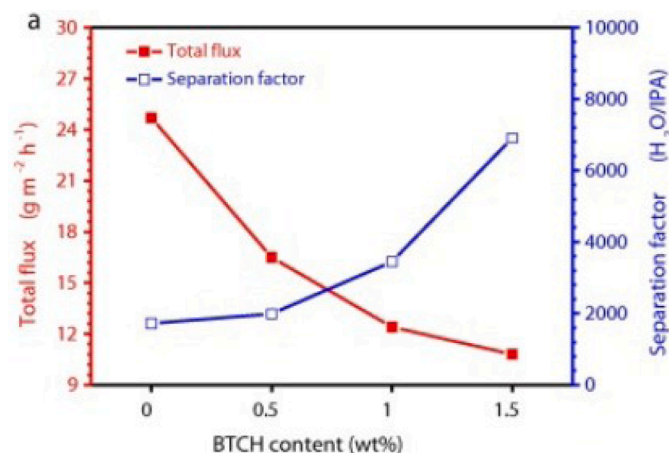


Fig. 2. Effect of BTCH content on the total flux and separation factor of PI-BTCH film [13].

due to the presence of a chemical agent. Most FTM works in liquid or supported liquid membranes, but recently, research on solid polymeric membranes reported a notable result in incorporating chemical carriers. Crosslinked poly(vinyl amine) and PVA for IPA dehydration by Chaudari et al., 2017 managed to increase permeant flux from 0.023 to 0.1  $\text{kg}/\text{m}^2 \cdot \text{h}$  by utilizing  $\text{NH}_2$  at its best within the amine carrier [19]. The so called 'fixed carrier' in polymeric membrane matrix acts by providing a flexible attraction, and the most crucial part is that it offers an equal magnitude of both association and dissociation rate for the separation process. In this case, the separation was said to be polymer polarity driven as described by the theory of which the transportation occurred from one polar site to another [20]. The film's hydrophilic nature has

been enhanced by introducing an immense amount of active  $\text{NH}_2$  polar site, which in return provides better water sorptivity. Referring to Fig. 3, the water molecule is in favour of the film pathway, the polar fixed carrier providing an alternative path avoiding the polymer chain clutter, applying the favority of polar-polar attraction between water molecule and the carrier from adsorption site to permeate side, as the relative polarity of water is 1 compared to IPA which is around 0.546.

One thing to be considered in applying fixed carrier is the method of film formation, some method leads to entanglement and compaction of a polymeric chain; forming a denser film. When we talk about polymer, chain arrangement will always be one factor for how efficient the species flow within. A slower flux rate should be expected from a dense film.

We already see how amine has been utilized in recent polymeric membrane development as a crosslinker and FTM. Having amine is an advantage for flux enhancement, but the way it was introduced to a polymeric film creates another gap to be filled in. Table 1 summarize the progress of recently developed material for IPA dehydration.

From the recent data, a plot of justification summarized how far the progress of membrane development, specifically for IPA dehydration, is constructed as in Fig. 4.

Most of the works marked a low flux rate ( $< 0.4 \text{ Kg}/\text{m}^2 \cdot \text{h}$ ) reading with improvement in selectivity. It showed how the progress of polymeric membrane development in alcohol dehydration should be focused on. This should be the direction of future research to surpass this plot. We all know there is only two way, which is by flux rate and selectivity, to indicate the progress of current research in membrane development for isopropanol dehydration. A greater value measures the selectivity itself towards infinity; it is still unclear how to relate and prove the progressive growth in membrane development. The inconsistency of the selectivity-flux relationship, which by increasing in one will suffer the other, still cannot be an absolute value to evaluate the membrane.

Even though some research managed to score more than 10k

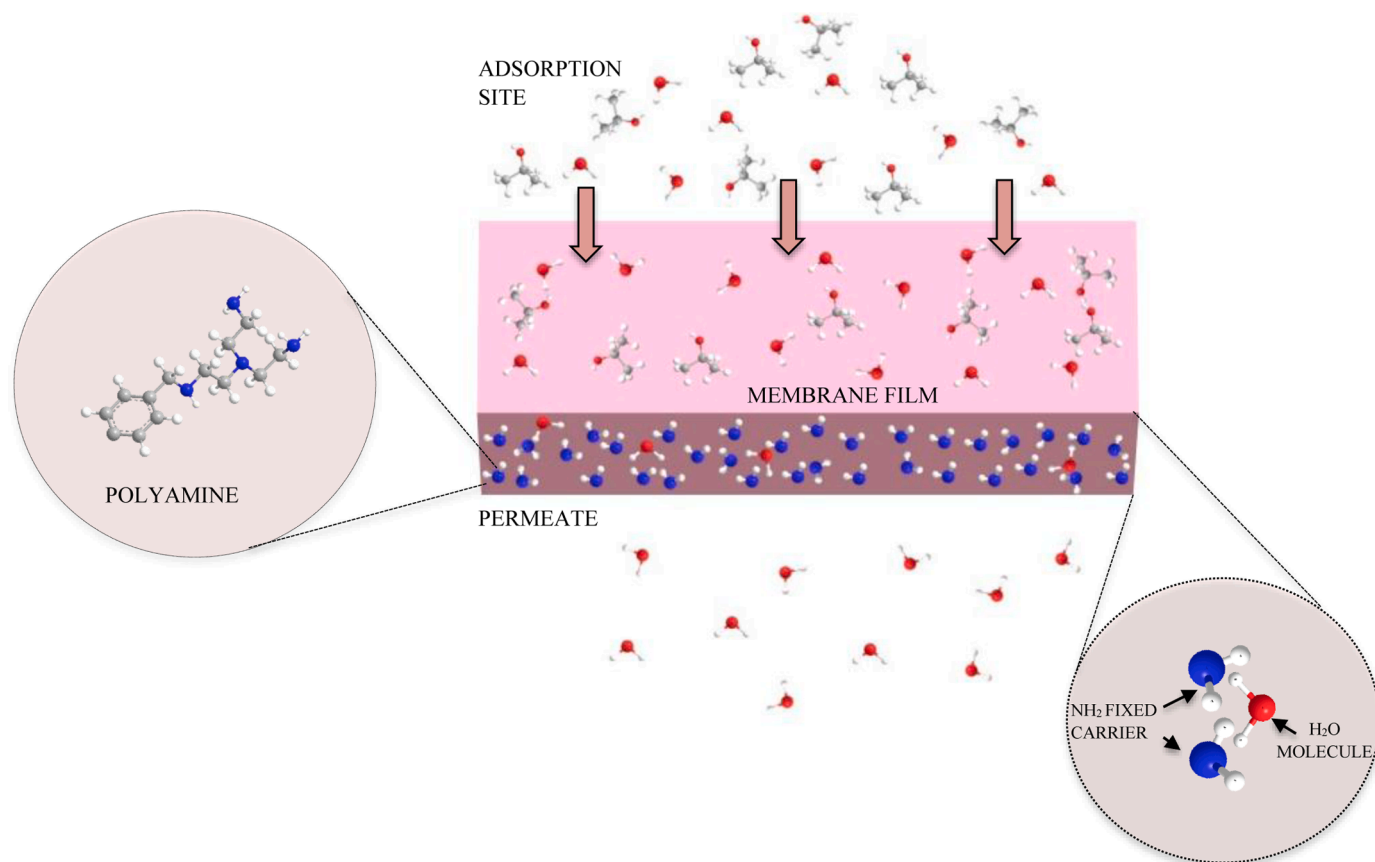


Fig. 3. Polymeric membrane with amine fixed carrier.

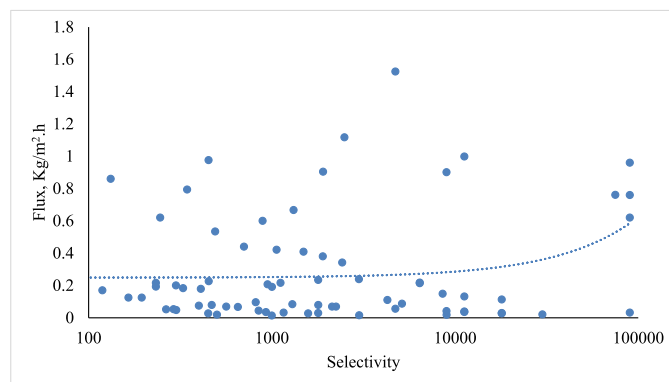
**Table 1**

10 years progress of IPA dehydration via polymeric membranes with 10% water in feed at 30 °C.

NO	Material	Selectivity	Flux, Kg/m <sup>2</sup> .h	References
1	PA/TiO <sub>2</sub> /CHF	800	1.5	[21]
2	Crosslinked PVA	77.3	0.475	[22]
3	PVA/PMMA	400	0.075	[23]
4	PVA/PANI	564	0.069	[24]
5	NaAlg/PVA (75:25)	195	0.125	[25]
6	NaAlg/PVA (50:50)	119	0.17	[25]
7	NaAlg/PVA (25:75)	91	0.195	[25]
8	PVA/KA	410	0.179	[26]
9	PVA/NaA	328	0.183	[26]
10	PVA/CaA	233	0.193	[26]
11	PVA/NaX	233	0.216	[26]
12	NaAlg/silicalite-1 5%	11241	0.039	[27]
13	NaAlg/silicalite-1 10%	17991	0.027	[27]
14	PVA/silicalite-1 5%	1295	0.084	[27]
15	PVA/silicalite-1 10%	2241	0.069	[27]
16	NaAlg	653	0.067	[27]
17	PVA	77	0.095	[27]
18	PVA/ZEOLITE	1900	0.38	[3]
19	PA/PAN	49	3.21	[28]
20	PA-GO/PAN TFNC	564	1.557	[28]
21	PVA-CNTs-1	817	0.096	[29]
22	PVA-CNTs-2	1794	0.079	[29]
23	PVA-CNTs-1/PAN	948	0.207	[30]
24	NaAlg-CNTs-2	6419	0.2176	[31]
25	PVA-3-Aminopropyl triethoxysilane-Tetraethoxysilane	891	0.6	[32]
26	PVA-3-Aminopropyl triethoxysilane	1580	0.027	[33]
27	PVA/chitosan 60:40	6419	0.214	[34]
28	PVA/chitosan 40:60	8562	0.149	[34]
29	PVA/chitosan 20:80	17991	0.113	[34]
30	Chitosan	5134	0.087	[34]
31	PVA	77	0.095	[34]
32	PVA, 4.5% Fe(II)/Fe(III)	470	0.079	[35]
33	Matrimid, 15% Zeolite 4 A	29991	0.021	[36]
34	PVA-Gelatin (M-1)	1160	0.0319	[37]
35	PVA-Gelatin (M-2)	1791	0.0292	[37]
36	PVA-Gelatin (M-3)	929	0.0352	[37]
37	PVA-Gelatin (M-4)	848	0.0439	[37]
38	PVA-CA	291	0.053	[38]
39	PVA/AA	300	0.2	[39]
40	PVA/GA/CS-Ag+ (2.4 × 10 <sup>-2</sup> mol.)	89991	0.62	[40]
41	PVA/GA/CS-Ag+ (4.7 × 10 <sup>-2</sup> mol.)	89991	0.76	[40]
42	PVA/GA/CS-Ag+ (7.1 × 10 <sup>-2</sup> mol.)	89991	0.96	[40]
43	PVA/GA/CS-Ag+ (9.4 × 10 <sup>-2</sup> mol.)	89991	1.44	[40]
44	PVA/GA/CS-Ag+(1.17 × 10 <sup>-1</sup> mol.)	89991	1.97	[40]
45	Pristine PVA	77	0.132	[41]
46	PVA/HPA-7	90000	0.032	[41]
47	MAT-4A	9000	0.018	[42]
48	MAT-ZSM5	3000	0.0155	[42]
49	MAT	1000	0.014	[42]
50	PVA	165	0.125	[43]
51	PVA-ZIF 8	132	0.86	[43]
52	Chitosan/PTFE	1490	0.409	[44]
53	GTMAC grafted chitosan	2133	0.0691	[45]
54	CS/PTA (M-4)	7490	1.17	[46]
55	CS/PTA (M-3)	11241	0.998	[46]
56	CS/PTA (M-2)	8991	0.901	[46]
57	CS/PTA (M-1)	74991	0.761	[46]
58	CS/TiO <sub>2</sub> (10 mass%)	1315	0.667	[47]
59	CS/TiO <sub>2</sub> (20 mass%)	1906	0.904	[47]
60	CS/TiO <sub>2</sub> (30 mass%)	2491	1.117	[47]
61	CS/TiO <sub>2</sub> (40 mass%)	4728	1.524	[47]
62	CS/HMDACS (10 mass%)	491	0.534	[48]
63	CS/HMDACS (20 mass%)	705	0.44	[48]
64	CS/HMDACS (30 mass%)	1062	0.421	[48]
65	CS/HMDACS (40 mass%)	2423	0.342	[48]

**Table 1 (continued)**

NO	Material	Selectivity	Flux, Kg/m <sup>2</sup> .h	References
66	CS/NaY zeolite (10 wt.%)	246	0.62	[49]
67	CS/NaY zeolite (20 wt.%)	345	0.794	[49]
68	CS/NaY zeolite (30 wt.%)	452	0.976	[49]
69	CS/NaY zeolite (40 wt.%)	603	1.23	[49]
70	PVA/TEOS modified with CS (5 wt.%)	1116	0.216	[50]
71	PVA/TEOS modified with CS (10 wt.%)	1791	0.234	[50]
72	PVA/TEOS modified with CS (15 wt.%)	2991	0.239	[50]
73	CS-HPC-10	4277	0.11	[51]
74	CS-HPC-20	11241	0.132	[51]
75	CS-HPC-30	1002	0.191	[51]
76	CS-HPC-40	453	0.226	[51]
77	Chitosan2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane (ETMS)	17990	0.0292	[52]
78	Chitosan2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane (ETMS)	8991	0.0414	[52]
79	Chitosan2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane (ETMS)	4727	0.056	[52]
80	Chitosan2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane (ETMS)	11,241	0.0355	[52]
81	CS-g-PANI (M-4)	502	0.019	[53]
82	CS-g-PANI (M-3)	450	0.027	[53]
83	CS-g-PANI (M-2)	301	0.048	[53]
84	Pure CS (M-1)	265	0.052	[53]
85	PA/TiO <sub>2</sub> /CHF	800	1.5	[54]

**Fig. 4.** Flux vs Selectivity of 10 years research data for IPA dehydration at 30 C and 10% water in the feed.

selectivity value, their flux rate is still below 1 kg/m<sup>2</sup>h. Clear judgment in achieving the objective to counter the trade-off cannot be based on the increase-decrease situation of the selectivity-flux relationship. We have collected 10 years of research data of selectivity and flux to plot our very own Membrane Performance Index, MPI curve, as a reference in membrane development. Having this curve not only can be a new guideline in experimental design and membrane development, but the researcher can always check and target the progress of their research, whether it successfully surpasses the 10 years' work. A study regarding new material and techniques can be made easily, as the progress can be straightly compared with this MPI curve and indirectly answered both objectives, which is to enhance selectivity and flux simultaneously.

### 3. New approach in composite membrane film

Here we highlight how using thermoplastic or elastomer in reducing membrane swelling could also enhance separation selectivity by combining nanomaterials and controlling experimental factors. Thermoplastic among the best engineered polymer that contains an active functional group for the purposed of alcohol dehydration such as amine,

ether, or carbonyl to tackle the azeotropic mixture at its highest selectivity. This section will discuss how nanomaterials such as Graphene oxide, Zeolite, Carbon molecular sieve, Metal oxide, and Metal organic framework could be the next material that can look further to be studied in combination with the latest engineered polymer.

### 3.1. Advance polymer for minimum swell membrane

#### 3.1.1. Polyether block amide (PEBA)

For the past ten years, Polyether Block Amide (PEBA) showed great interest in polymeric membrane development. Many researchers took advantage of the mechanically stable polyamide (PA) hard segment for longevity and continuous usage of the film aside from its soft polyether side, which generally drives the separation process. PEBA has been reported in several studies showing significant improvement in organic dehydration without compromising its flux rate.

Liu et al., 2005 mentioned that the PEBA membrane's success absorption is controlled by the strong affinity of PEBA- organic relationship [55]. For example, PEBAX 2533 is highly soluble in butanol, making it permeable and butanol selective in butanol-water separation. It is not just that, the unique characteristic of PEBA also make them water soluble but with the right solvent combination ratio. By taking advantage of this water-soluble nature, PEBA makes a perfect candidate for water selective separation. Hamouda et al. utilized this ability for desalination via pervaporation, and without surprise, pure water was extracted successfully from the binary system [56]. Another notable works in using PEBA as a water selective barrier such as the one did by Sridhar et al. where they found out more than 80 wt% of water in permeate for ethylene glycol and ethanol dehydration [57]. So, PEBA based membrane can always be tuned either for alcohol solvent recovery or alcohol dehydration and it all depends on the binary species for which species the selective barrier is in favor. PEBA comes in various configurations with a different trade name, solvent compatibility, and PA-PE contents, as summarized in Table 2: Different PEBA configuration in membrane processing. These five are among the top of the list in pervaporation application.

For whatever the types are, PEBA offers a dense nature membrane, thus making it possible for the solution diffusion mechanism of pervaporation application. Le et al. found out that adding surfactants like material or dispersant to PEBA based membrane, such as polyhedral oligosilsesquioxane (POSS), can improve pervaporation selectivity [63]. It is a crucial step for solution diffusion transport to have a good polymer dispersion due to the sorption of penetrant species at surface level is the first step of the mechanism. Any modification in the PEBA matrix should be targeting sufficient free volume for the penetrant diffusion.

#### 3.1.2. Polyamide-imide (PAI)

Other great candidates in this category are PAI, combining the greatness of PA and PI. This membrane usually tackles heavy duty processes due to its thermal stability, outstanding mechanical performance, and low thermal expansion coefficient [64,65]. The new trend rose in PAI membranes where researchers attempt to crosslink or layered this material to enhance its separation capability, mainly in pervaporation. PAI itself exhibits a distinct hydrophobic nature at around 76 (dynamic contact angle), where it usually possesses very low

**Table 2**  
Different PEBA configuration in membrane processing.

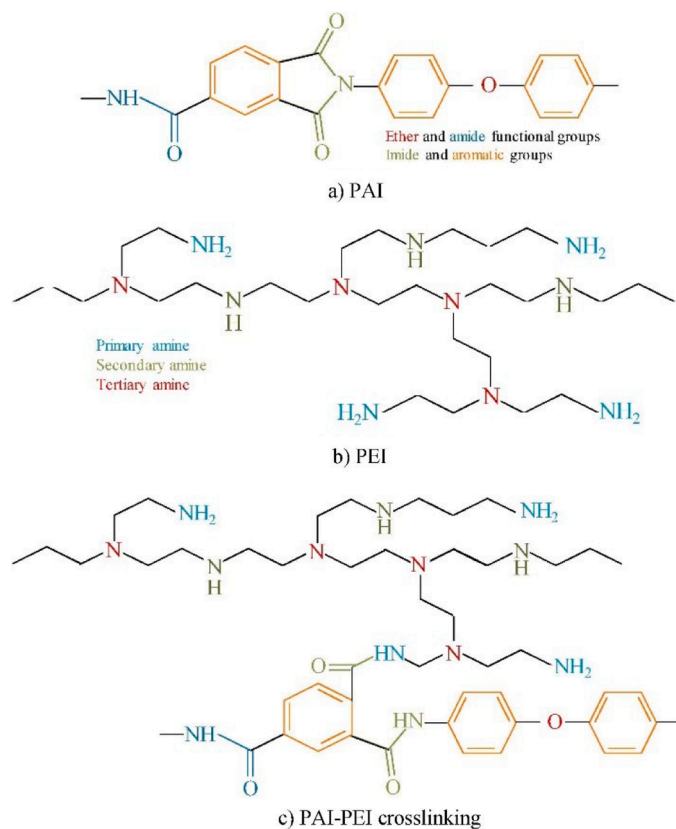
Peba types	PE-PA Ratio	Solvent	References
Pebax® 2533	80-20	n-butanol	[58]
Pebax® 3533	70-30	Dimethylacetamide	[59]
Pebax® 4033	53-47	70/30 1-butanol/1-propanol	[60]
Pebax® 5513	40-60	70/30 Ethanol/water	[61]
Pebax® MH 1657	60-40	dimethyl acetamide	[56]
		70/30 Ethanol/water	[62]

water adsorptive, but in return, offered a minimum surface swelling to a certain degree [66]. Wang et al. fabricated a dual layer Torlon® 4000T and polyetherimide to tackle the low fluxes in the PAI membrane [67]. Scoring an excellent flux rate up to 765 g/m<sup>2</sup>h, it proves that ether-amide-imide combination among the next best material to be considered in alcohol dehydration. There is also a study of PAI, where the crosslinking approach is introduced, as illustrated in Fig. 5.

The crosslinking approach proposed by Cihanoglu and Altinkaya, 2018 introduced polyethylenimine (PEI) into the PAI matrix and they manage to decrease the contact angle from 92° to 70°. Decreasing in water contact angle indicates that the membranes will have higher water uptakes, but the tendency of swelling also increases along the way, which for sure decreases the water selectivity as it will allow both species to pass through smoothly.

#### 3.1.3. Thermoplastic polyurethane (TPU)

TPU is another candidate suited for this challenging job. This material sat on its class with an equally important alternating soft and hard segment of the long polymeric chain. Containing stable hard segments of diisocyanates, diol or diamine chain extenders, PU is among the versatile polymer available for any pervaporation condition. On the other hand, it comes with an abundance of diamine terminated soft reactive oligomers choices, such as poly-ethers, poly-esters, poly-butadienes, and poly-acrylates [69]. This soft segment can always be manipulated to meet the needs of separation species and performances. TPU has been prepared by varying the ratio of soft and hard segment composition, which has affected the end result. Fig. 6 showed how increasing more hydrophilic monomer (2,3-(epoxypropyl)-methacrylate, EPMA) in TPU blending increases the hydrophilicity and thus increase its separation factor. Few physical changes in hydrophilicity affected by the pore formation, as bigger pore attributed to a lower contact angle, owing to that water could be transported faster due to less transport resistance.



**Fig. 5.** The chemical structures of PAI and PEI and the crosslinking reaction between PAI and PEI [68].

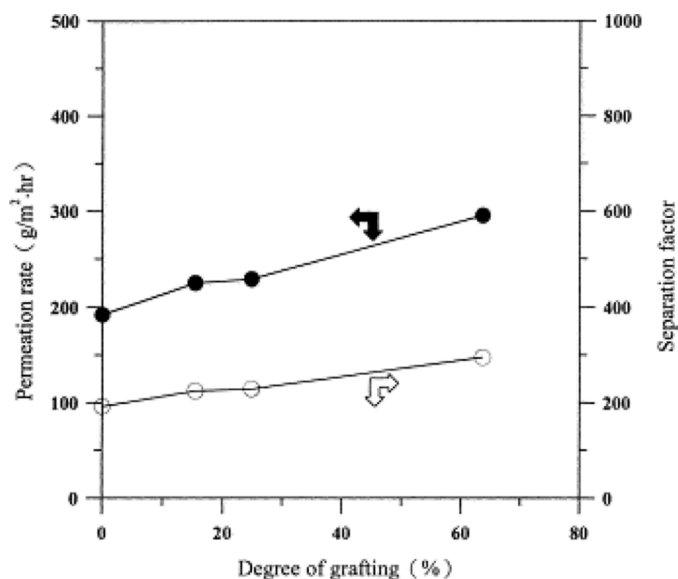


Fig. 6. Effect of the degree of grafting on the pervaporation performances through the chemical modified PU membrane [70].

Moreover, hydrophilic functional sites in a polymer chain add more and more free hydrogen bonding to interact between permeating species and membrane medium. That's been said, these unique polymers can always be fine tune to meet the specific need of the separation process.

### 3.1.4. Polyether ether ketone (PEEK)

Another engineered polymer that is worth mentioning is PEEK. This material possesses a very stable mechanical and chemical stability with a high glass transition temperature. Continuous modification and study on PEEK showed a great improvement in organic separation. Zereshki et al. observed a significant drop of around 20–50% alcohol in permeate by using chloroform as the evaporating solvent [71]. Some types of PEEK also come with a cardo lacton in its backbone, the unique structures where carbon is held by both polymeric chain and ring structure, as illustrated in Fig. 7.

By having so, this material is arranged in a loose polymeric chain but hardly moving to make them thermally stable for high temperature usage. PEEK mostly suitable for the pervaporation of organic species with different intermolecular interactions. Bearing a polar carbonyl group, PEEK can attract both dipole-dipole attraction, and hydrogen bonding makes it a bit tricky for a binary mixture of alcohol and carbonyl related organic separation. Many researches came with a solution by introducing more hydrophilic properties to PEEK- Sulfonated PEEK [72,73]. The presence of polar hydrophilic  $\text{SO}_3\text{H}$  attracts hydrogen bonding more than dipole-dipole attraction and further boosts the separation efficiency.

## 3.2. Nanomaterial in film synthesis

Aside from the main polymeric material in membrane development that we were talking about for the past 10 years, there are few more ways to alter film physicochemical, including nanomaterials. We all know how material and medium interaction capable of doing so. Since we were discussing membrane separation, the first step is site

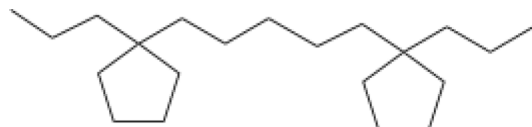


Fig. 7. Regular polymeric chain with cardo lacton structure.

adsorption, which occurs at the film's surface. It is the first thing to be considered in surface engineering. An increase in the surface area significantly provides a larger adsorption site for the permeating species.

Some nanomaterials often change the polymer's degree of cross-linking and crystalline phase, thus improving free space in the membrane matrix. Because of the separation mechanism in pervaporation, only allowing vapour to be diffuse through, free volume and chain mobility is considered crucial for improvement. The presence of nanoparticles in a membrane matrix disrupts the polymeric chain, and their tight arrangement subsequently allows a better permeation flux.

Previously, we discussed how the amide group is playing its role in amide-water affinity. In nanomaterial research, researchers tend to introduce a dominant polar group such as  $-\text{OH}$  and  $-\text{COOH}$  in the membrane matrix. It is believed that having prominent hydroxyl and carboxyl material will enhance the film's water sorptive. On top of that, nanomaterials such as graphene oxide (GO), zeolite, carbon molecular sieves (CMS), metal oxides, carbon nanotubes (CNTs), and metal organic framework (MOF) are gaining broad interests, especially by the researchers in membrane-based technology in order to provide and produce a well-developed membrane with excellent performance which can meet the requirements of current industry.

### 3.2.1. Graphene oxide

Graphene oxide (GO) is widely used as a hydrophilic enhancer due to the active OH terminal in its structure. The presence of GO in the pristine membrane proves a remarkable result in increasing the film hydrophilicity, as most recent works regarding these nanomaterials managed to reduce the contact angle measurement significantly. Fig. 8 illustrated GO's effect in polymeric membrane development towards its hydrophilicity in the function of the contact angle from the previous works.

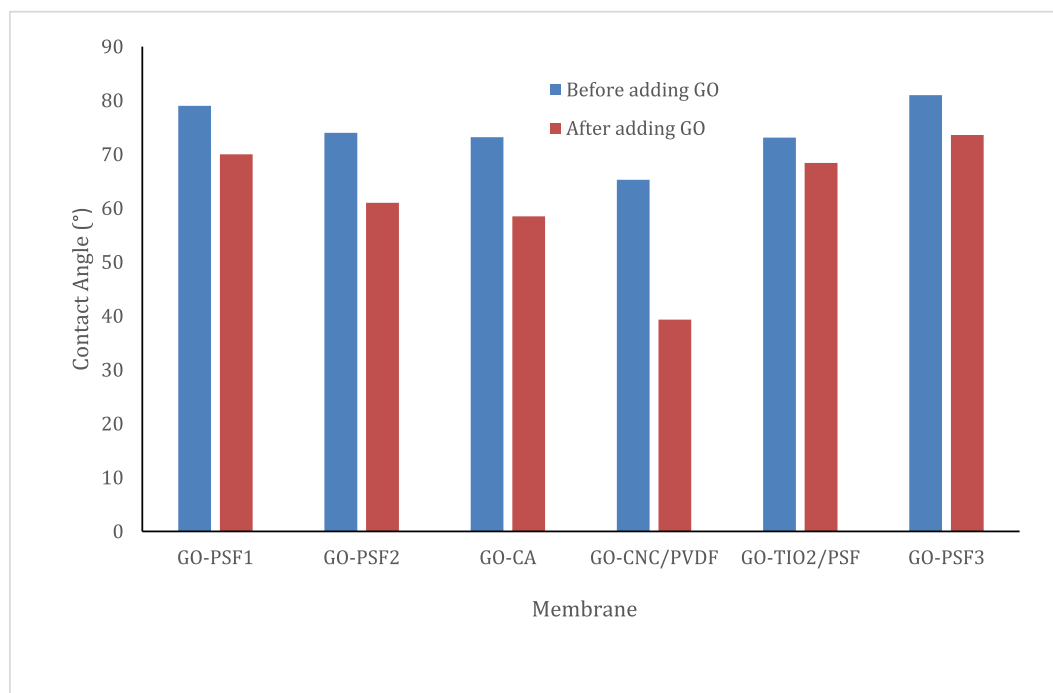
These recent studies utilize GO, taking advantage of its peculiar 2-dimensional (2D) nanostructure that is rich in oxygen functionalized groups such as hydroxyl, epoxy, and carboxyl, which make it very stable and strong affinity towards the water and most organic solvent. Wang et al. proved that the addition of GO flakes in their sodium alginate (SA) membranes had increased the ethanol dehydration up to 60% compared to the one with pristine alginate film [80]. This is due to less tortuous for water molecules to penetrate through the film. Not just that, the negatively charged  $-\text{COOH}$  in GO creating a surface with high electrostatic repulsion due to the coexistent with a polar water molecule. As the interaction of penetrant occurs at the surface of the membrane, it is critical to make sure the existent of GO is at the top rather than at the bottom. Presence of GO is normally randomized in between the polymer matrix; in this case, TFC is the most suitable configuration compared to MMM.

Preparing GO-polymer dope in membrane development could be tricky as excess GO in dope solution tends to form agglomeration in the final film [81,82]. Moreover, this unique material can be both hydrophilic and hydrophobic based on the preparation technique. Ashish et al. in their work of synthesizing graphene oxide membranes and studying its behaviour in water and isopropanol, successfully produced a composite membrane of Polysulfone and GO [83]. The comparison between wet and baked dry film showed that the dry film somehow increases the hydrophobicity from  $36^\circ$  to  $59^\circ$ . This is probably due to the GO basal plane's presence, which is dominated by the hydrophobic character of  $\text{sp}^2$  hybridized carbon.

Membrane hydrophilicity and flux rate in GO embedded membrane often related to material dispersion. The combination of polymer and GO compatibility must be taken into consideration. The porous polymer is the best base to hold GO nanostructure, so it can help overcome the poor dispersivity [76].

### 3.2.2. Zeolite

Incorporating this inorganic nanoparticle in membrane development also showed a great deal. Zeolite possesses a very distinct characteristic such as chemically stable in almost all polymer and all permeating

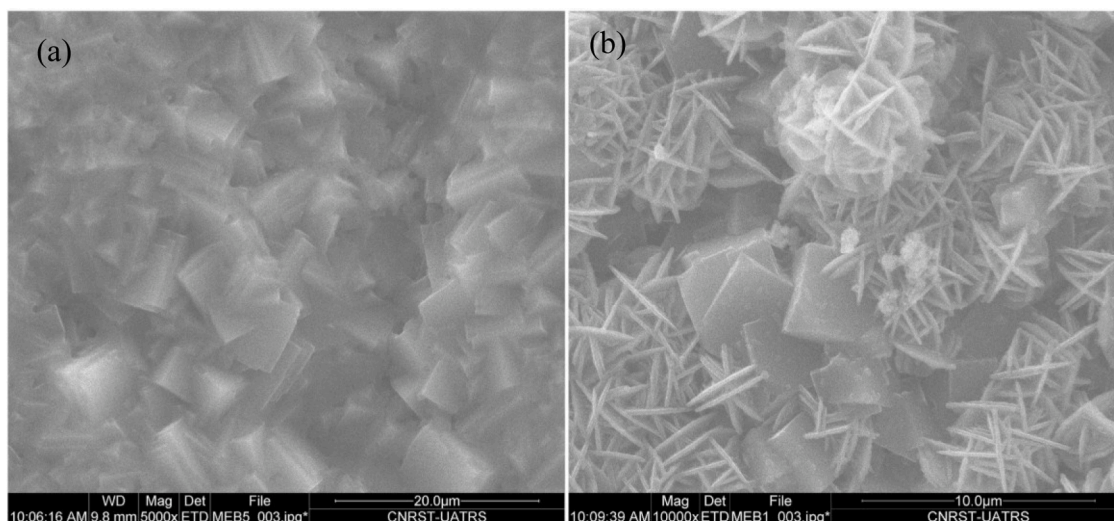


**Fig. 8.** Contact angle of several membranes with GO embedded; GO-PSF<sup>1</sup> [74], GO-PSF<sup>2</sup> [75], GO-CA[76], GO-CNC/PVDF [77], GO-TiO<sub>2</sub>/PVDF [78], GO-PSF<sup>3</sup> [79].

components, unique porous structure, and thermally stable for a wide range of operating conditions [84]. In the separation process, the separation ability of the zeolite membrane depends on both the molecular sieving and diffusibility of filtrated species mechanisms. Zeolite comes in various types and structures. NaA zeolite is one of the best candidates as membrane material, especially for separation processes involving azeotropic mixtures, such as a mixture of an organic compound and water due to its smallest pore size of approximately 0.42 nm and most hydrophilic as compared to other types of zeolite [85,86].

Achiou et al. managed to synthesize their own NaA zeolite on pozzolan support, and they found out that during the hydrothermal synthesis of zeolite membrane, different crystallization temperature produced different zeolitic morphology [87]. The formation rate of zeolite accelerates at high temperature, but too high temperature may cause alteration of the zeolite crystal structure. The SEM image showed that at 60 °C, a uniform well-structured cubic crystal lattice of NaA

zeolite was observed (Fig. 9a). However, at 80 °C, two different structures of zeolite were observed, indicating that another type of zeolite has been formed at the higher temperature, reducing the average size of NaA zeolite, which negatively influenced the membrane's performance (Fig. 9b). Therefore, choosing an appropriate crystallization temperature is essential to form a good quality zeolite membrane which increases the permeability without reducing the separation factor. They also discovered the correlation between surface roughness and hydrophilicity. Apparently, higher surface roughness produced greater hydrophilicity of the membrane. The cause for such behaviour was due to the addition of zeolite on the membrane surface which increased the surface roughness and the hydrophilic of the membrane due to numerous oxygen bonds available in zeolite which can absorb water molecules to form hydroxyl bond [88]. The experimental results confirmed that the water flux and separation factor for the zeolite membrane enhanced as compared to neat polymer membrane.



**Fig. 9.** SEM images of prepared membranes synthesized at (a) 60 °C and (b) 80 °C [87].



Similarly, as reported by Cao et al. in the preparation NaA zeolite membrane on ceramic hollow fiber supports for pervaporation process [89].

Fathizadeh et al. prepared a TFN membrane by incorporating NaX nano zeolite into polyamide (PA) top dense layer for the reverse osmosis process [90]. They reported that NaX zeolite is very hydrophilic, which led to interfacial free energy and contact angle improvement of the TFN membrane. The selective layer of the membrane became smoother and thinner as more nano-zeolite (0.004 to 0.2 w/v %) was added, creating an easier path for water passing through the membrane, which results in better water sorption and permeability. As can be observed in Fig. 10, the SEM images show the difference of thickness between pure PA TFC membrane and nano zeolite-PA TFN membrane. The dashed line represents the PA selective layer. The reasons for the changes were due to the existence of nano zeolite particles during the interfacial polymerization reaction, which had reduced the contact surface between the two monomers (TMC and MPD) and increased the reaction temperature, which can be ascribed to the heat of hydration for zeolite particles. Therefore, the diffusion between these two phases gets slower at a low temperature, which creates a thinner layer with a more stable surface.

### 3.2.3. Carbon molecular sieve, CMS

Similar to zeolite, carbon molecular sieve (CMS) is widely known as a promising adsorbent in many adsorption processes. Recently, the incorporation of CMS particles into polymeric materials are gaining increased attention by the researchers, especially in gas and liquid separations, as well as pervaporation due to its superior properties, having an amorphous structure which consists of a micro and sub-micrometer porous channel that improves the diffusibility and selectivity [91,92]. Despite having attractive features, their brittleness limits their application [93]. As an alternative, CMS membrane can be coated on top of a porous substrate, which strengthens the mechanical stability of the membrane. Hence, enabling the composite membrane to withstand harsh operating conditions in the industry.

However, poor polymer-sieve adhesion remains as one of the major challenges in preparing a well-developed membrane. Efforts have been made to solve the aforementioned issue, which includes modifying or treating the sieve surface with chemical reagents such as silanes. Rafizah and Ismail, proved that CMS treated with poly(vinyl pyrrolidone) kollidone 15 (PVP K-15) produced better polymer-sieve contact [94]. The FESEM image revealed that there are gaps or voids between the unmodified CMS and PSF matrix (Fig. 11a). The reason for such behaviour was due to weak interaction between CMS surface and PSF matrix. While the PVP-CMS particles adhered well with the PSF matrix (Fig. 11b) due

to the presence of PVP on the outer surface of CMS that introduced more reactive side groups such as amide carbonyl group, which formed specific interaction with sulfonate group of PSF.

Qadir et al. further addressed the influence of the different amount of CMS particles (1–5wt%) added into polyethersulfone (PES) matrix in the water treatment process and reported that even a small amount of CMS (1 wt%) could significantly enhance the membrane's performance [95]. The incorporation of 1 wt% CMS increased the pure water flux and salt rejection as compared to pure PES, from  $8.96 \text{ L m}^{-2} \text{ h}^{-1}$  to  $33.8 \text{ L m}^{-2} \text{ h}^{-1}$  and 20% to 26.13%, respectively. An increased in water flux shows that the presence of CMS particles increased the pore sizes, which provided a better pathway for the water to cross through the membrane, while the improvement of rejection indicates that the CMS has introduced a charge to the membrane hence enhancing the retention rate of the solute through Donnan exclusion mechanism [96]. However, increasing the amount of CMS to 5 wt% showed a decrement of the water flux performance, which could be due to aggregation of excess CMS in the macropores blocking the path for water permeation. A similar trend for rejection was observed at 5 wt% CMS, indicating that increasing the amount of CMS produced bigger pore size, which allowed the ions passing through effortlessly, resulting in low rejection. As such, we can tell that the amount of CMS particles played a crucial role in producing a defect-free membrane with excellent separation performance.

### 3.2.4. Metal oxides

TFN membranes composed of metal oxides have attracted much attention by the researchers due to their outstanding robustness in various applications such as water purification [97], desalination [98], reverse osmosis [99], and gas separation [100]. Shafiq et al. utilized titanium dioxide ( $\text{TiO}_2$ ) nanoparticles in the cellulose acetate TFN membrane and revealed that the incorporation of such nanoparticles improved the thermal stability and properties of the membrane [101]. As shown in Table 3, all of the  $\text{TiO}_2$  loaded membranes demonstrated a higher percent weight loss in comparison to the pure TFC membrane. The decomposition temperature increased with an increasing amount of  $\text{TiO}_2$  nanoparticles added, indicating that the TFN membrane with the highest concentration of  $\text{TiO}_2$  was the most thermally stable. As stated by Abedini et al. the  $\text{Ti}^{4+}$  and hydroxyl group in  $\text{TiO}_2$  nanoparticles may interact with the acetate group in cellulose acetate (CA) to form hydrogen and covalent bonds [102]. Due to good compatibility between  $\text{TiO}_2$  and CA, the rigidity of the polymer chain improved, which requires higher energy consumption to break the polymer chain, resulting in delayed decomposition of membrane.

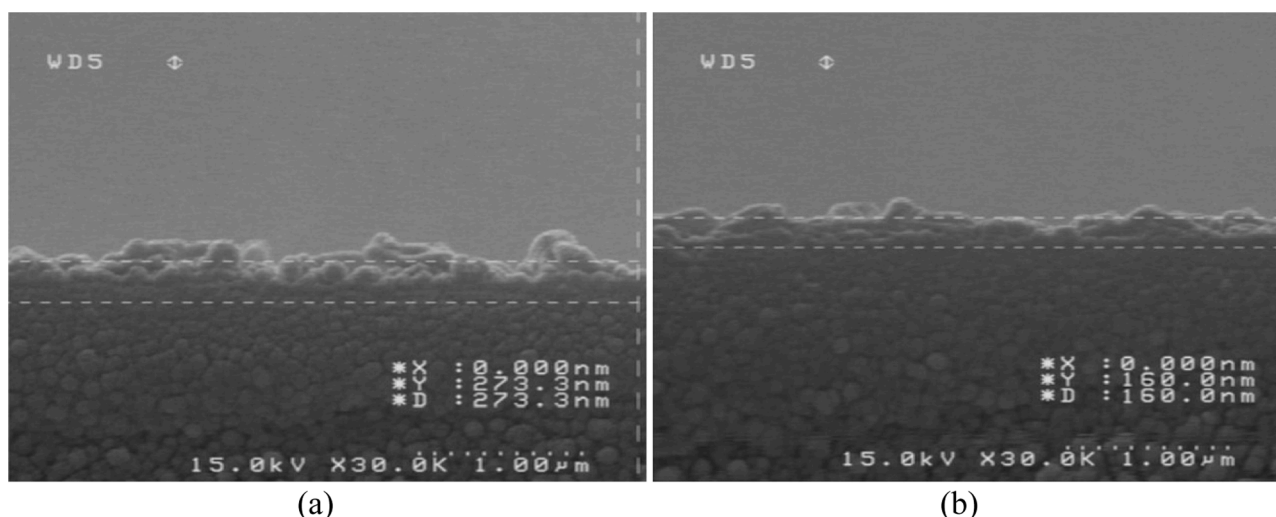


Fig. 10. Cross section images of (a) TFC membrane and (b) 0.2 w/v % nanozeolite TFN membrane.

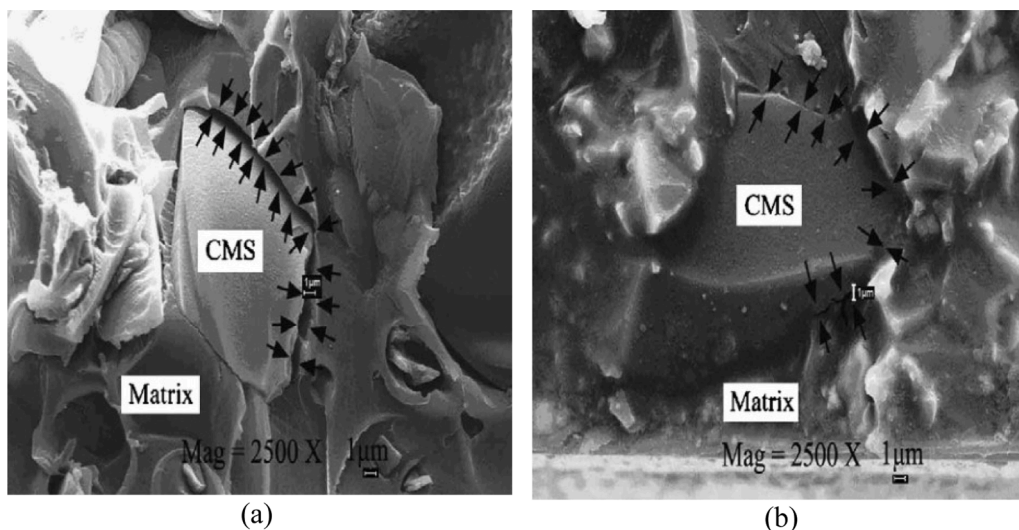


Fig. 11. Comparison of FESEM micrographs for the cross-section of PSF-CMS mixed matrix membrane with 30 wt% CMS loading: (a) containing unmodified CMS and (b) containing PVP-sized CMS [94].

Table 3  
Percentage of weight loss [101].

Samples	T <sub>30%</sub> (°C)	T <sub>50%</sub> (°C)	T <sub>70%</sub> (°C)
CA/PEG-400	330	354	369
CA/PEG-400 (5% TiO <sub>2</sub> )	335	360	385
CA/PEG-400 (15% TiO <sub>2</sub> )	362	387	404
CA/PEG-400 (25% TiO <sub>2</sub> )	373	395	409

\*T<sub>30%</sub>, T<sub>50%</sub> and T<sub>70%</sub> are the temperatures of 30, 50 and 70 % weight losses.

The performance of zinc oxide (ZnO) nanoparticles has been investigated by Isawi et al. in the preparation of PA/PSF composite membranes [103]. Similarly, they also reported that the addition of ZnO into the membrane had shifted the thermal degradation to a higher temperature as compared to other prepared membranes (Fig. 12). Overall, the results confirmed that the incorporation of these nanoparticles into a polymer matrix had strengthened the chemical bonds within the polymeric chain, which produced better thermal stability of the membrane.

### 3.2.5. Carbon nanotubes

Carbon nanotubes CNT offered a different route in film synthesis where they provide hydrophobic nanochannel for permeating species. The hydrophobic features help in increasing the flux rate, Tang et al. found out by adding CNTs to chitosan, it has improved the water transport rate by granting less clutter channel between CNTs walls and

the permeating species due to non-repulsive interaction of wall hydrophobicity [104]. Moreover, CNTs is a size-selective material, its smallest porous structure ranging from 4–12 Å, made it suitable to tackle the separation of contra molecular or atomic penetrant size [105]. Some studies tried to combine hydrophobic CNTs and a hydrophilic polymer such as PVA. By doing so, the ability to absorb water at a faster rate on the membrane surface while retaining a minimum swell could be achieved due to the hydrophobicity channel inside the membrane matrix. Focused work on this combination has been done by Shiarazi et al. where a significant improvement in reducing the swelling degree of PVA pristine with addition of CNTs is observed as illustrated in Fig. 13.

The theory behind membrane swelling is that the material exerts more water, but it can't bear the force of water-material interaction due to weak mechanical stability. CNTs, provides a rigidification in membrane matrix, decrease the chain mobility and membrane free volume and improved the intermolecular strength providing a robust structure.

### 3.2.6. Metal organic framework, MOF

Many have said that MOF is capable of breaking the permeability-selectivity trade-off in polymeric membrane separation. The robust, well-defined pores and tunable structure could increase the chemical affinity of the targeted penetrant and decrease the mass transfer resistance during solution diffusion. A functionalized chemical or bulky group could be added to the framework to form a well-defined pore

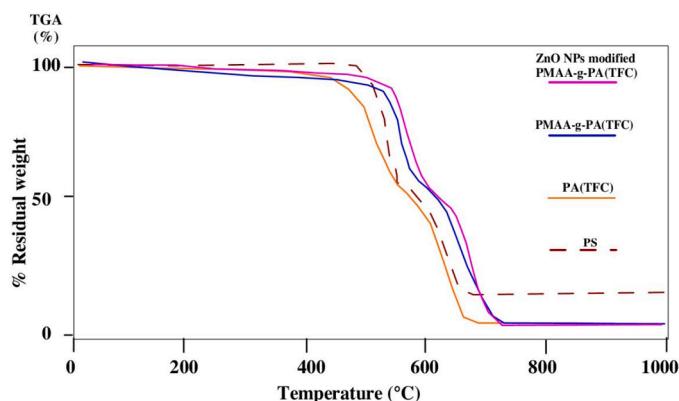


Fig. 12. TGA curves of PSF, PA/PSF, PMAA-g-PA/PSF, and ZnO loaded PA/PSF.

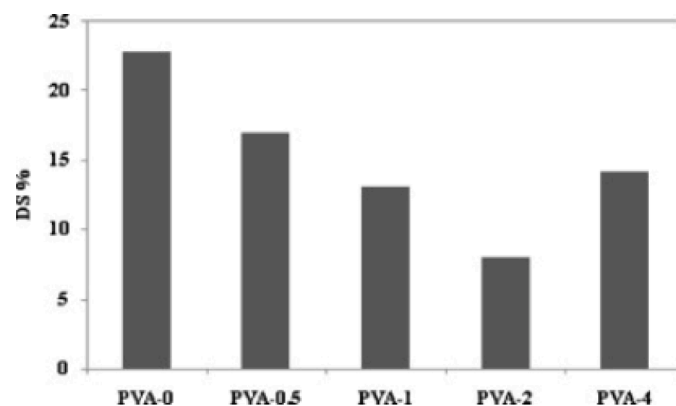


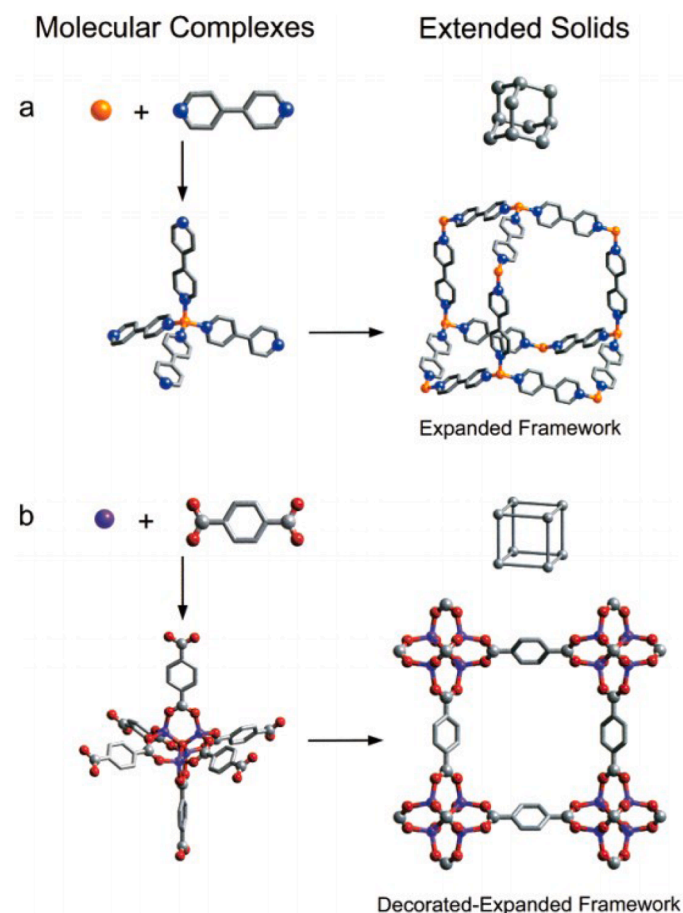
Fig. 13. Degree of swelling (DS) of different membranes in 20 wt.% water in IPA mixture at 30 °C, CNTs loading: PVA-0, 0% CNT, PVA-0.5, 0.5% CNT, PVA-1, 1% CNT, PVA-2, 2% CNT and PVA-4, 4% CNT [29].

aperture for molecular sieving. Adding functionalized bulky such as methyl or ethyl to MOF comes with the steric hindrance where it is purposely designed to clutter within the framework. The combination of suitable metal ions and organic ligands help to generate MOFs with surface areas of 1000–10,000 m<sup>2</sup>/g, which are greater than other porous materials [106].

Secondary based units, SBUs is one of the popular approach in MOFs development for membrane pervaporation as most of the synthesized MOFs reported to have a high water absorption. This is due to the transformation and arrangement of the molecular complex into 3-dimensional (3D) framework, as illustrated in Fig. 14 by combining organic and inorganic crystalline solid forming a well-structured controllable pore formation. Research in a self-standing MOF is still in progress by applying multilayered form film, such as TFC. MOF, in other words, works as a functional active layer for the TFC. Forming a thin selective layer with high interfacial bonding strength between the two surfaces remains a challenge. As an alternative, there is the idea of 'in-situ' nuclei growth [107–110]. This allows bridge intermolecular chain connection of pre-form MOF on the support surface with the later MOF layered coating.

### 3.3. Influenced factors in experimental design

TFC development consists of several vital factors starting from material selection, casting environment, and casting techniques. The material selection should meet the purpose of separation either it is for gas



**Fig. 14.** (a) organic bipyridine is used, where the host framework is collapsed due to the production of the cationic framework. B) SBUs is applied by introducing multi-hand linkers such as carboxylate group to form a robust M-O-C core. (a), M, orange; C, grey, N, blue; in (b), M, purple; O, red; C, grey. Structures were drawn using single-crystal X-ray diffraction data [111].

or liquid based on the physical characteristic of the material while casting environment such as bath temperature, casting temperature, evaporation, and quenching steps are the next level of a material alteration to further enhanced the separation capability of the materials. Having such an environment can sometimes improve the material morphological structure. Casting techniques focuses on the skin formation and thickness of the TFC to support the separation process.

It has been reported that the combination of relatively smooth, more hydrophilic, and negatively charged membrane surface typically produces a better separation efficiency [112]. In general, the most critical morphological parameters for a membrane are gravimetric porosity, pore size, pore size distribution, tortuosity, surface roughness, molecular weight cutoff, and thickness. Morphology control is the key factor in membrane fabrication since the membrane performances directly depend on their morphology, which is in terms of pore size and distribution. [113]

#### 3.3.1. Effect of Selective Skin Layer Thickness on Separation Efficiency

A basic structure of industrial grade TFC consists of a dense 200 Å to 1 µm selective layer with microporous support polymer. Primarily, the mass-transfer resistance dominant by the selective skin layer, so that the thickness of the layer much influence the performance of the entire membrane. In homogenous membranes, researcher agreed that the thicker the membrane is, the higher the permeation resistance, and the lower the flux will be [114]. The relationship between membrane thickness and flux is inversely proportional to each other [115]. To reduce the mass-transfer resistance in a membrane, the top selective layer might need to be as thin as possible without losing its stability. The thinner skin layer is also attributed to a better packed structure with well arrange molecular structure, which indirectly affects the skin density. As the density is taken into consideration, it was said to be the function of the distance of the skin from top surface (refer Fig. 15). As the distance (thickness) decreases, the density increases [116]. It is hard to produce and control the exact thickness of the selective skin layer because of the simplicity of the process itself. The incomplete coverage and solution penetration are among the few factors that contribute to skin defect. To avoid this issue, polymer with a larger chain dimension than the support was suggested as a selective material [117]. Theoretically, it makes sense, as the ultra-height molecular weight polymer creating perfect sealed to the support porosity. As the problem cantered on the solution penetration, alternatively, TFC could be produced by having several layers; porous support, seal layer, and selective layer so that defect free selective layer can be produced. Refer to the SEM image in Fig. 15 below, a uniform, dense skin layer on top of the PVDF porous structure can be entirely coated [1]. The support layer only provides pathways for the channeling species passes through with no separation occur as the top selective skin layer already acts as an active absorption side for the separation process. The porous support itself is an asymmetric configuration by having a very thin dense top layer followed with a porous structured underneath. Having the thin dense upper part could act as a seal layer to avoid selective solution to penetrate through the membrane.

#### 3.3.2. Effect of casting temperature on membrane morphology

Membranes morphology, in general, contribute a significant effect on separation performance. The surface properties could explain fouling, hydrophobicity, absorption, and further evaluate the separation factor. Membrane synthesis involves temperature to melt and recrystallize the polymer solution via solvent evaporation cause physical changes to the final product. As the solution subject to a certain amount of temperature, it might disrupt the molecule arrangement and orientation. Generally, six factors affect polymers' crystallinity: the polymer chain, degree of polymerization, intermolecular forces, pendant group, cooling rate, and molecular orientation.

Polymer morphology is dependents on its thermal history. Thermal annealing is a common, easiest, and economical treatment to rearrange

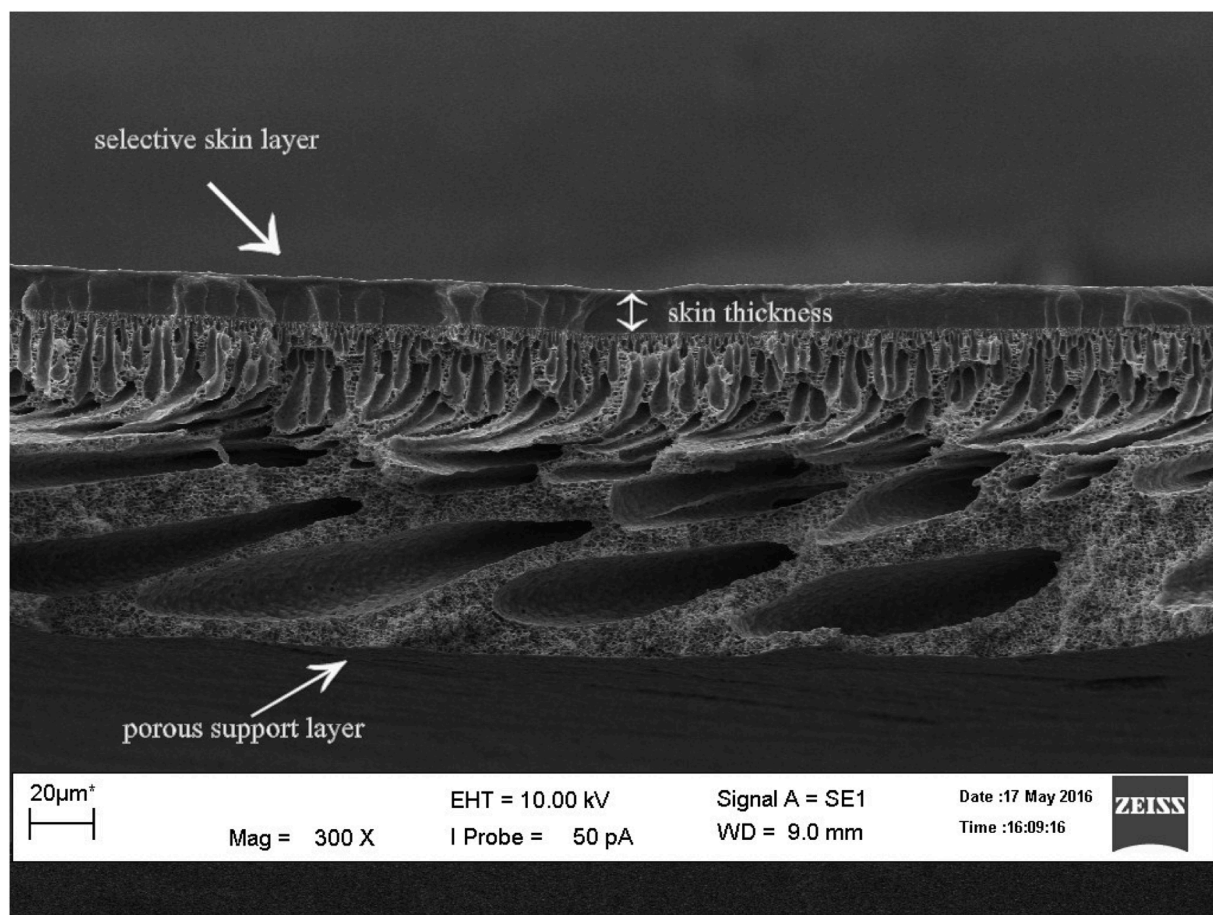


Fig. 15. PVDF/Pebax TFC membranes [1].

the polymer matrix [118]. This temperature approach process also could increase the crystallinity of the polymer and further improves the separation properties. Changes in crystallinity and polymer chain could be brought to surface reorganization [58]. A slower cooling rate will give a better chain arrangement and form a better crystalline phase compared to the immediate evaporation [119]. As the temperature alteration involved during the casting procedure, the evaporation rate of the solvent is increased, resulting in changes in chain arrangement.

Yeow et al. reported that the morphology of the membranes cast and coagulated at 20 °C showed an irregular fingerlike cross-sectional structure with macro voids and some isolated islands of a dense polymer phase also clearly seen. This could be due to the precipitation of highly localized concentrated polymer as a result of crystallization. The structure of these crystallization-associated precipitation behaviours was not observed when the membranes were cast and coagulated at

50 °C. Therefore, an elevated temperature favoured liquid-liquid demixing and resulted in membranes with a cellular morphology in the substrate and a regular fingerlike structure beneath the skin layer [120].

Buonomenna et al. stated that high casting solution temperature plays an essential role in increasing the crystallization's liquid-liquid demixing rate [121]. Membranes prepared at 25 °C and 60 °C exhibit highly inhomogeneous structure owing to the presence of a dense thin skin layer and large voids and cavities of different size and shape beneath the upper layer. The structure of the porous sublayer is characterized by interconnected cavities [121]. Fig. 16 showed a difference in voids and cavities size produced at casting temperature 25 °C and 60 °C.

This goes similarly to work done by Putthanarat et al. since the membranes cast at temperatures above 50 °C exhibit larger, more developed, and more closer grains. Furthermore, the packing densities

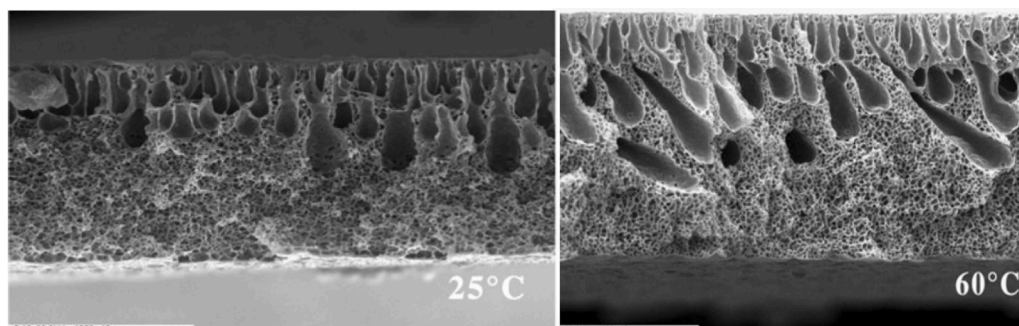


Fig. 16. SEM of membranes cast at two different temperatures [121].

of the 60 °C and 80 °C were greater than those for 20 °C, 40 °C and 50 °C [122].

By having a rougher surface, the membrane is said to have both pros and cons. A rough membrane will provide a large absorption site from the large surface area of the nodule aggregates formed, but at the same time, it will increase the fouling rates [123].

### 3.3.3. Effect of selective material concentration

Much research has been done on how material concentration contributes to a better membrane synthesis. Some said that porosity and void could be minimized with an increasing polymer concentration [124]. But that is in the case of porous media. Selective material works a bit differently as they will be coated on top of the porous substrate. The selective material was suggested to be very dilute as a concentrated solution could thicken the layer, increase the mass transfer resistance, and lead to a loss in gas selectivity.

As the concentration increase, the thickness of the selective layer also increases. This suggests that the proper concentration can synthesize the desired selective layer for optimum performances [125]. Yuliwati and Ismail testified that increasing the polymer concentration ranges from 16 to 22 wt. % demonstrated an obvious change of morphology and suppressed both inner and outer finger-like macro voids. The finger-like structure under the top layer, as this structure was prepared at higher concentration, was much less than the membrane structure prepared at a lower concentration. Furthermore, a more sponge-like substructure and a thicker top layer of the membranes were formed across the membrane wall. This can be explained by the fact that higher dope viscosity decreases the solvent (DMAc) and non-solvent (water from coagulation medium) exchange rates, resulting in higher resistance of diffusion from the polymer aggregation [126].

Defect in composite membranes is either incomplete coverage of the porous support or solution penetration by the thin selective solution. These two factors are related to each other because of the relationship between solution concentration and morphological changes. If the concentration is too low, the tendency of penetration is high; thus, incomplete coverage of the film structure could occur, but if it is too high, the TFC will have a thicker structure, and the performance will drop drastically. As mention before, a suitable range of Pebax should be around 3% to 5% in its respective binary solution [127–130]. In this range, the researcher believed that even though pore penetration is possible, it still allows penetrant species to transport excellently.

### 3.3.4. Effect of coagulation bath temperature (CBT)

Solvent and non-solvent interaction in membrane occur in a water bath where phase inversion is taking place. When the cast film was immersed in the distilled water bath, precipitation started because of the low miscibility between the polymer and the non-solvent (water). Simultaneously, the miscibility between the solvent (NMP) and the non-solvent (water) caused an exchange of solvent and non-solvent in several points of the film top layer and the substrate, which led to the formation of nuclei of the polymer-poor phase. Because of the continuation of the diffusional flow of solvent from the surrounding cast film, these nuclei continued to grow until the polymer concentration at their boundaries became so high, and the de-mixing process was completed [131].

Therefore, the condition of the precipitation bath could affect the morphological changes of the film form. Every structural change might be due to the molecular entanglement, restricting the changing mobility during film formation. The de-mixing process of the solvent and non-solvent rapidly occurs in the coagulation environment where the verification takes place, and the structure is completely frozen. Oprea and Ciobanu in their work on the effect of bath temperature towards membranes morphology, found out that at low bath temperature, there will be a porous cellular structure enclosed with continuous polymer matrix phase. As the bath temperature increase, they start to observe a very symmetric 'sponge structure' across the film [132].

The decrease in CBT levels intensively reduced the mutual

diffusivities between the non-solvent (water) and the solvent (NMP) in the casting solution during the solidification process. This caused the limited nuclei, which can form quickly after immersion of the cast film into the water bath, to grow slowly and to result in the formation of a large number of small nuclei in every part of the cast film. This caused the production of few and more pores/voids in the membrane top layer and the sub-layer, respectively, resulting in the defeat of macro voids formation and an approximately denser structure [131].

The aggregation of molecules at low bath temperature also decreases the formation of uniform porous structure and possibly forms a stiff, dense film. At elevated temperatures, molecules have a better chance and great mobility to arrange themselves faster and form a symmetrical film [132]. The morphological in dry-wet phase inversion techniques strongly depend on the de-mixing rate; either it is instantaneous or delays. Macrovoid (finger-like cavities) region is most associated with the instantaneous de-mixing of the solvent and non-solvent, while the formation of the spongy porous structure is appointed to the delay de-mixing. The study of the effect of CBT done by Amirilargani et al. jotted a significant finding when they said the increase of CBT from 0 °C to 25 °C had improved the formation of surface porosity from a dense region to fine pores structure from top to bottom [133]. Peng et al. also reported that as CBT increases, the pore size of the skin layer is increased and enlarged significantly [134].

### 3.3.5. Effect of evaporation times and quenching times on membranes porosity

These two periods; evaporation times and quench times, are the phase inversion steps in film development. The first period where the polymer precipitate is left to vaporize in the open air for a specific period of time on the casting support (glass) and then move to the second period, which is the quenching step in a non-solvent bath. Longer evaporation time will cause the film interface concentration and area with high polymer concentration to form thicker and dense skin. Tsay and McHugh observed an increasing anisotropic spongy sublayer with an increase of evaporation time. This pores formation behaviour is related to the nucleation and growth mechanism of the polymer [135].

The influence of solvent evaporation time prior to immersion in the coagulation step strongly affects the surface skin-layer thickness. Dry-phase separation happens at the initial stage of evaporation, where the volatile solvent is removed from the casting solution. As a result, the unstable top skin layer region of the developing membrane will be formed as a result of the selective loss of the volatile solvent and can be observed by the rapid beginning turbidity in this top skin layer. Wet-phase separation occurs when the developing membrane is immersed in the non-solvent bath. In this quench step, a bulky membrane structure is formed, and the remaining solvent and non-solvent are extracted [136].

Jami'an et al. and Shahbanu et al. reported that increasing solvent evaporation time decreases the membrane surface's porosity. This is because those membranes had enough time to rearrange membrane molecular chains and cause the membrane surface to become closely pack, thus decreasing the pore size on the membrane surface and reducing defects. That is why membrane with no evaporation time had higher porosity by the instantaneous de-mixing process, and a delayed de-mixing gives lower porosity due to evaporation of solvent before immersion on water. When the solvent evaporated, polymer solutions' concentration and viscosity were increase, resulting in restriction of the solvent-non solvent exchange [136,137].

The quenching method has been applied widely in the membrane fabrication process. The purpose of quenching is to make the polymer chains harden and shrink much slowly and gradually with the decrease of temperature [138]. The quenching step can take up to 48 hours as the procedure leads to membrane precipitation. The quenching period depends on the material used to prepare the dope solution and the dynamic movement of the solvent and non-solvent.

### 3.3.6. Effect of additive in polymer matrix

Another method to prepare a membrane with improved morphology and characteristics is to change the casting dope formulation using different additives such as mineral fillers, polymers, surfactants, and non-solvents. The proper choice of the additive may result in the formation of more desirable pore structures with better interconnectivity, which is an improvement to the surface properties [139]. It also has been reported by Mohammadali Baghbanzadeh et al. that nano-sized inorganic particles can be effectively used as an additive in a membrane matrix due to their small size and high surface area. Nano-materials bearing a large surface area increase the interfacial interactions between the particles and the polymer matrix and, consequently, improve the formed composite membranes' thermal and mechanical stabilities [139].

Hong-Bin Li et al. reported that applying different additives is vital to obtain the desired membrane pore structure since the resulted membrane with added additives exhibits excellent mechanical strength and thermal stability. Polymeric additives increase the membrane's properties and structure in terms of higher permeation flux and fouling resistance, whereas inorganic additives could accelerate the phase separation rate and contribute to a membrane structure with lots of interconnected pores [140]. The introduction of additives also has an important impact on the membrane surface hydrophilicity since the membrane surface hydrophilicity was gradually improved as the additive was added. It has also been reported that membranes without additives exhibited short finger-like pores compared to the membrane with some additive, which became long and gradually extended.

The previous study by Sen et al. found that polycarbonate membranes containing low molecular-weight compounds with multifunctional groups as an additive also improved the separation performance of the membranes. Despite the different functional groups of low molecular-weight compounds, their effect on the membrane performance was similar, which decreased the permeabilities and increased the membrane selectivity [141]. Activated carbon is a good example of large pore size inorganic fillers that can act as an additive in mixed-matrix membranes. Adding rigid materials with large pore sizes, which are the materials with pore dimensions much larger than the penetrants into the polymer matrix can induce a selective surface flow of targeted components in the particles' pores. Therefore, the more adsorbable component can be adsorbed and diffused selectively through the particles, and thus, the less adsorbable component permeates more slowly [138].

In brief, adding additives in membrane preparation with an appropriate amount can increase the performance and morphology of the membranes. However, the roles of different additives nevertheless differ in different polymer and solvent systems.

### 3.3.7. Effect of cross-linking agent

Cross-linking modification, including chemical cross-linking and thermal cross-linking, is known to be a promising method to improve and enhance the thermal and chemical stabilities of the polymeric membrane. In cross-linking modification, many research work at present focus on chemical cross-linking, in which the polymer reacts with the cross-linking agent in the presence of a catalyst to form a cross-linking or network structure. The chemical cross-linking mainly improved the properties of polymeric membranes, such as hydrophilicity and separation performance. However, the thermal cross-linking can enhance the thermal and chemical stabilities of the polymeric membrane because the thermal rearrangement and cross-linking occur in the chain segments of polymer to form a stable three-dimensional network structure during thermal cross-linking [142].

Cross-linking has also been suggested to improve gas separation membranes by improving the perm-selectivity while maintaining a high permeability and increasing resistance towards aggressive gases [143]. So, it also could be applied to a pervaporation environment. Li et al. reported that dopamine cross-linked with polyethyleneimine layer had

improved the membrane surface's hydrophilicity. Furthermore, both interaction between dopamine and substrate and the interaction between polyethyleneimine and dopamine layer rely on chemical bonds, which is not physical adsorption, which can certainly enhance the active's structural stability and compatibility layer and the substrate [144].

The chemistries of membrane materials and cross-linking agents and their interactions have great influence on the cross-linked structure, degree of cross-linking, and transport properties. However, different materials may need different cross-linking agents. Therefore, there is a requirement to identify novel cross-linking methods for the membranes and fundamentally understand the science of molecular structure, chain length, and flexibility of cross-linking agents on the cross-linking process and membrane performance [145].

### 3.4. Mass transfer resistant and diffusion

For all that, we know separation via pervaporation follow the solution diffusion mechanism applying the famous Fick's Law, but the resistant within a composite membrane could be explained based on the qualitative definition of the film. The first factor that governs and much influenced the resistant is the thickness of the selective dense layer. First, we take a look at Eq. 2 [146], because we are subjecting the binary mixture towards a multilayered membrane, it must go through several mass transfer resistants based on how many layers the composite is made of.

$$R_{composite} = \frac{1}{K_{composite}} \# \quad (2)$$

And, for an instant, if a composite layered composed of a single dense selective on top of a porous substrate, the mass transfer coefficient, K will be as follow.

$$\frac{1}{K_{composite}} = \frac{1}{K_{dense}} + \frac{1}{K_{substrate}} \# \quad (3)$$

$K_{dense}$  is defined as

$$K_{dense} = \frac{P.R.T}{e_{dense}} \# \quad (4)$$

$$K_{substrate} = \frac{D.\epsilon}{\tau.e_{substrate}} \# \quad (5)$$

where P, R, T and  $e_{dense}$  is the permeability, the ideal gas constant(J/mol), temperature (K), and the thickness (m) of the selective dense layer respectively. For the substrate on the other hand, the mass transfer resistant could be defined by the diffusion coefficient (D) ( $m^2/s$ ),  $\epsilon$  is the porosity,  $\tau$  is the tortuosity and  $e_{porous}$  is the thickness of the porous support.

Combining Eq 2 to 5, mass transfer resistant in a composite membrane can be written as in Eq 6,

$$R_{composite} = \frac{e_{dense}}{P.R.T} + \frac{\tau.e_{substrate}}{D.\epsilon} \# \quad (6)$$

A closed look to the equation revealed the relationship of every part of the film towards the resistant. Increase in selective dense layer will subsequently affected the mass transfer resistant while substrate thickness is not. To understand more on this statement, we are substituting tortuous in the substrate that defined by Eq 7 into 6.

$$\tau = \frac{L}{e_{substrate}} \# \quad (7)$$

Where L is the pore length. By doing so, a clear image of how dense layer thickness affected the resistant could be seen.

$$R_{\text{composite}} = \frac{e_{\text{dense}}}{P.R.T} + \frac{L}{D.\epsilon} \# \quad (8)$$

The substrate porous structured is well explained via tortuous pore diffusion model by Sakai 1994,

$$r_p = \sqrt{\frac{8\mu\tau^2\Delta x}{H}}.L_p \# \quad (9)$$

where  $\tau$  is the tortuosity,  $\Delta x$  is the membrane thickness,  $H$  is the water content,  $L_p$  is the pure water permeability,  $r_p$  is the pore radius, and  $\mu$  is the viscosity of pure water (0.695 cP). The tortuosity of the membrane used was assumed to be 1.6 empirically [147].

#### 4. Conclusion

Future work regarding alcohol dehydration via membrane pervaporation should be focusing on the experimental design and material choice. It is the key to having the best membrane. The combination of an advanced engineered polymer such as PEBA and nanomaterial could not be wrong, both holding the best of the best feature that is currently being paired with none. It is expected for the next 10 years, progressive work in membrane development manages to tackle the flux-selectivity trade-off via this approach.

#### Declaration of Competing Interest

The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript.

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