



## Recent Membrane Development for Pervaporation Processes

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# Recent Membrane Development for Pervaporation Processes

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## Abstract:

Pervaporation has been regarded as a promising separation technology in separating azeotropic mixtures, solutions with similar boiling points, thermally sensitive compounds, organic–organic mixtures as well as in removing dilute organics from aqueous solutions. As the pervaporation membrane is one of the crucial factors in determining the overall efficiency of the separation process, this article reviews the research and development (R&D) of polymeric pervaporation membranes from the perspective of membrane fabrication procedures and materials.

**Keywords:** Pervaporation; review; membranes; hydrophobic; hydrophilic; organics

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## Nomenclature

$A$	membrane area ( $\text{m}^2$ )
$f$	fugacity (kPa)
$J$	flux ( $\text{kg}/\text{m}^2\text{-h}$ )
$l$	membrane selective layer thickness ( $\mu\text{m}$ )
$M$	molar mass ( $\text{g}/\text{mol}$ )
$P$	permeability ( $\text{g m}/\text{m}^2 \text{ h kPa}$ )
$P^{\text{sat}}$	saturated vapor pressure (kPa)
$P/l$	permeance ( $\text{g}/\text{m}^2 \text{ h kPa}$ )
$Q$	weight of the collected permeate
$t$	time (h)
$x$	mass fraction in liquid feed solution
$y$	mass fraction in the permeate

## Greek Letter

$\alpha$	selectivity
$\beta$	separation factor
$\gamma$	activity coefficient

## Subscript

$evap$	evaporation
$f$	feed
$i$	component $i$ at feed or permeate
$j$	component $j$ at or permeate
$p$	permeate
$pervap$	pervaporation

## Abbreviations

6-FDA	4,4'-(Hexafluoroisopropylidene)diphthalic anhydride
ABE	acetone-butanol-ethanol
$\text{Al}_2\text{O}_3$	alumina oxide
BuOH	n-butanol
$\beta$ -CD	$\beta$ -cyclodextrin
CMS	carbon molecular sieve
COF	covalent organic framework
CS	chitosan
DABA	3,5-diaminobenzoic acid
DM	dimethylcarbonate
DMAc	N,N-dimethylacetamide

DMF	N,N-dimethylformamide
DMSO	N,N-dimethylsulfoxide
EDA	ethylenediamine
EG	ethylene glycol
ETBE	ethyl tert-butyl ether
EtOH	ethanol
FFV	fractional free volume
GA	glutaraldehyde
GFT	Gesellschaft für Trenntechnik
GO	graphene oxide
HF	hydrofluoric acid
HPEI	hyper-branched polyethyleneimine
HTPB	polybutadiene
I <sup>2</sup> PS	immiscibility induced phase separation
ICD	ionic complexation degree
IPA	isopropanol
IPN	interpenetrating polymer network
LBL	layer-by-layer
MDEGMA	poly(methyl diethylene glycol methacrylate)
MeOH	methanol
MgO	magnesium oxide
MMM	mixed matrix membrane
MOF	metal organic frameworks
MPD	m-phenylenediamine
MPDSA	sulfonated MPD
mPEEK	modified poly(ether ether ketone)
MTBE	methyl tert-butyl ether
MTR	Membrane Technology & Research
MWCNT	multiwalled carbon nanotubes
NaAlg	sodium alginate
NaCMC	sodium carboxymethyl cellulose
NDA	1,5-naphthalene diamine
NF	nanofiltration
NR	natural rubber
NRF	National Research Foundation
NTAC	5-nitrobenzene-1,3-diyl dichloride

OA	octaanion
OAPS	octaaminophenyl
OAS	octaammonium
ONPS	octanitrophenyl
P(AANa-co-SSNa)	poly(sodium acrylate-co-sodium styrenesulfonate)
PAA	polyacrylic acid
PAN	poly(acrylonitrile)
PAS	positron annihilation spectroscopy
PBI	polybenzimidazole
PBO	polybenzoxazole
PBOZ	polybenzoxazinone
PBPP	poly[bis(phenoxy)phosphazene]
PDDA	poly(diallyldimethylammonium chloride)
PDMC	poly(2-methacryloyloxy ethyl trimethylammonium chloride)
PDMS	polydimethylsiloxane
PEBA	polyether-block-polyamides
PEC	polymer polyelectrolyte complex
PEEK	poly(ether ether ketone)
PEI	polyethyleneimine
PEVP	poly (N-ethyl-4-vinylpyridinium bromide)
PIM	polymer of intrinsic microporosity
PMePP	poly[bis(p-methyl phenyl) phosphazene]
POC	porous organic cage
POSS	polyhedral oligomeric silsesquioxane
PSS	poly(sodium-p-styrenesulfonate)
PTA	phosphotungstic acid
PTFEP	poly[bis(trifluoroethoxy) phosphazene]
PTMSP	poly(1-trimethylsilyl-1-propyne)
PU	polyurethaneurea
PVA	polyvinyl alcohol
PVDF	polyvinylidene fluoride
PZSNT	polyphosphazene nanotube
QP4VP	quaternized poly(4-vinylpyridine)
R&D	research and development
RO	reverse osmosis
SA	sulfosuccinic acid

SCMC	sulfated sodium carboxymethyl cellulose
SPES	sulfonated polyethersulfone
SiO <sub>2</sub>	silica oxide
TBAC	5-tert-butylbenzene-1,3-dioyl dichloride
TDI	2,4-diisocyanate
TETA	triethylenetetramine
TFC	thin film composite
TMC	trimesoyl chloride
TiO <sub>2</sub>	titanium dioxide
TR	thermal rearrangement
VLE	vapor-liquid equilibrium
VTES	vinyltriethoxysilane
ZIFs	zeolitic imidazolate frameworks
ZrO <sub>2</sub>	zirconium dioxide



## 1. Introduction

The vision of a green and sustainable future has spurred the interests around the world in advancing the current separation technologies to conserve energy, as well as to achieve waste minimization and zero discharge. Energy/process integration and recycling/recovery of valuable products from waste streams are considered of paramount importance to accomplish this vision. In this regard, membrane technologies may serve as promising alternatives over conventional separation processes in the industries. Membrane-based separation processes are emerging and advanced separation technologies that may be widely applied in water, energy, food, chemical and healthcare sectors [1].

Pervaporation, a membrane-based separation technology, provides competitive advantages over conventional separation techniques such as distillation and absorption processes in separating azeotropic mixtures, thermally sensitive compounds and organic–organic mixtures, as well as in removing dilute organic compounds from wastewater [2-6]. This process requires the feed liquid mixture to contact one side of a semi-permeable membrane, while either vacuum or a sweep gas is applied at the permeate side of the membrane to generate a chemical potential difference for the separation to occur (Figure 1) [7].

### Figure 1

The separation mechanism of the pervaporation process predominantly relies on the preferential sorption and diffusion of the target component through the membrane [8]. Therefore, it is not restricted by the limitation of thermodynamic vapor-liquid equilibrium (VLE) [9]. As compared with conventional separation technologies,

pervaporation inherits the advantages of membrane-based separation technologies such as small footprint, simplicity and flexibility [5, 10]. In addition, it is considered to consume less energy as only the latent heat of evaporation is required for the separation [5, 8, 11]. For example, the dehydration of organics via conventional distillation process requires the heat energy to be supplied to the whole feed solution for the separation to occur. In contrast, the heat energy required in the pervaporation process is merely the latent heat of evaporation for the component that permeates through the membrane. Also, it can eliminate the ternary component (entrainer) that is usually required in azeotropic distillation or extractive distillation and hence prevents contamination in the final products [3].

The history of the pervaporation process can be traced to the 1910s when Kober defined the term of 'pervaporation' from the abbreviation of 'permeation' and 'evaporation' after observing the selective permeation of water through the collodion and parchment membrane [12]. Early lab-scale pervaporation experiments at laboratory scales were subsequently reported [13-17]. The pervaporation membrane ventured for its debut commercialization when Gesellschaft für Trenntechnik (GFT) launched the first pervaporation membrane. This membrane utilized a composite configuration where a thin layer of crosslinked polyvinyl alcohol (PVA) was coated on a porous poly(acrylonitrile) (PAN) support cast on a non-woven fabric [18]. The first industrial installation of a pervaporation plant was reported for dehydration of ethanol in Brazil in 1983 [19].

Thereafter, over 100 pervaporation systems were installed worldwide and most of them were for the dehydration of organic solvents [20]. On the other hand, the

application of commercial-scale pervaporation systems for organic-organic separations remained challenging due to the lack of suitable membranes and modules that are able to withstand continuous exposure of organic mixtures during the separation process [1, 21]. In contrast, pervaporation for specialty organics recovery has found its niche application for the recovery of thermal sensitive aroma in the food industry [1]. Also, separation of alcohols from organic solvents has been industrially explored. For example, methanol is being separated out from an azeotropic mixture with trimethylborate. Pervaporation allows separation without the need of adding a third component (e. g. water) to break the azeotrope, a procedure which is frequently used, but can lead to unwanted effects like hydrolysis. For example, the separation of 1,3-butadiene from C4 mixtures usually requires the addition of water and acetonitrile to break the azeotrope. However, the additives would facilitate hydrolysis, which causes the loss of acetonitrile and corrosion of equipment [22]. In addition, pervaporation has been recently investigated and referred as a green drying process for tetrahydrofuran recovery in the pharmaceutical industry [23].

To date, a significant number of reviews on this separation process have been published from the aspects of membrane materials [2, 5, 11, 24, 25], the process itself [8, 26] and its applications [3, 7, 27-33]. Although process intensification and module construction play important roles in the attempt of advancing the pervaporation process, the material engineering and fabrication methods of pervaporation membranes should not be neglected as the membrane is the heart of the separation process. The pervaporation membranes available in the market nowadays are fabricated from a wide variety of materials which comprise polymeric, inorganic and hybrid materials consisting of both organic and inorganic substances. However,

polymers remain as the most versatile and feasible candidate among them due to the ease of fabrication as well as relatively low production costs as compared with inorganic and hybrid materials [5]. Therefore, this article attempts to provide a review on the recent research progress in polymeric pervaporation membranes from the perspectives of membrane materials and membrane fabrication procedures.

## **2. Fundamentals of the pervaporation process**

A fundamental understanding of the mass transfer phenomena is vital for researchers to identify the preferred membrane materials and design the desired membrane structure and configuration. A summary of the main concepts and terminology applied to pervaporation has been published by Bøddeker [34]. The permeation of a component through a pervaporation membrane can be elucidated from both thermodynamic and kinetic perspectives. Thermodynamically, it involves the solubility of the component into the membrane material, while kinetically it engages the diffusion of the penetrant across the membrane. The coupled transport among different penetrants also affects each individual permeation [35]. In addition, these penetrants may swell up the membrane, change its microscopic structure and significantly enhance diffusion rates as compared with those through a dry membrane [17, 36].

The solution diffusion model is the most widely accepted transport mechanism for pervaporation as well as for reverse osmosis and gas separation processes [1, 8, 35, 37]. This model was first proposed by Thomas Graham to describe the gas transport

through the diaphragms. In this model, the transport of a permeating component through a membrane consists of three constructive steps (Figure 2):

- (i) Sorption of the permeating component from the feed liquid into the membrane;
- (ii) Diffusion of the permeating component through the membrane;
- (iii) Desorption of the permeating component to the vapor phase on the downstream of the membrane.

### Figure 2

Therefore, the separation performance of pervaporation membranes can be increased via enhancements of (1) solubility selectivity and/or (2) diffusivity selectivity of the penetrants across the membranes.

Crespo and Bøddeker reported that the sorption selectivity of the membranes favors the more condensable molecules or the ones which have special interactions with the membrane materials [38]. In order to identify such interaction strength or the affinity of the solute molecules towards the membrane materials, their Hildebrand and Hansen solubility parameters are commonly applied [5, 11]. Generally, the closer the solubility parameters of a membrane material and a solute are, the more the preferential sorption of the solute into the membrane is. Elastomeric membranes, which are easily swollen by the feed component mixture, need to be thicker than low swelling glassy membranes in order to maintain selectivity. Membranes with a very low thickness might enhance the flux but complicate the system when maintaining low permeate pressure and controlling concentration polarization [34].

On the contrary, the diffusion selectivity is greatly dependent on the size and shape of the permeating components, the mobility of polymer chains and the interstitial space among them, the interactions among the permeating components as well as between the components and the membrane material [39]. More specifically, the diffusivity of a permeant through a membrane is closely related to the fractional free volume (FFV) of the membrane which could be estimated through the Bondi's method [40] or the positron annihilation spectroscopy (PAS) [41-45].

As a result, the pervaporation membranes can be tailored into either an organic-selective (organics preferentially permeate through the membranes) or a water-selective (water preferentially permeates through the membranes) by means of material selection and morphological engineering during the membrane fabrication process. Both of them will be discussed later in this article.

The performance of a pervaporation membrane is generally evaluated according to its productivity and capability to separate the components from the feed mixture. This performance can be expressed by two different reporting parameters: (1) process performance [indicated by flux ( $J$ ) and separation factor ( $\beta$ )] or (2) driving force normalized performance [indicated by permeability ( $P$ ) or permeance ( $P/l$ ) and selectivity ( $\alpha$ )].

### 2.1. *Flux vs. permeability/permeance*

The flux, permeability and permeance are used to express the productivity of the membranes, whereby the flux of a membrane ( $J$ ) can be directly determined from the

experiment by evaluating the total weight of the permeate ( $Q$ ) collected at a specific period ( $t$ ) over the effective surface area ( $A$ ) of the membrane:

$$J = \frac{Q}{A \times t} \quad (\text{Eq. 1})$$

On the other hand, permeability ( $P$ ) or permeance ( $P/l$ ) reflects the driving force normalized productivity (i.e., known as the intrinsic productivity) of a dense or an asymmetric membrane, respectively. According to the solution-diffusion model, the relationship between permeability or permeance and the trans-membrane permeation flux of a particular component can be described as [46, 47]:

$$J_i = \frac{P_i}{l} (f_{i,f} - f_{i,p}) \quad (\text{Eq. 2})$$

where  $P_i$  is the permeability of component  $i$  across the membrane,  $l$  is the thickness of the selective layer,  $f_{i,f}$  and  $f_{i,p}$  are fugacities or partial vapor pressures of component  $i$  on feed and permeate sides of the membrane, respectively. The fugacity of component  $i$  in the feed side based on its liquid concentration can be determined by:

$$f_{i,f} = x_i \gamma_i p_i^{sat} \quad (\text{Eq. 3})$$

where  $x_i$ ,  $\gamma_i$  and  $p_i^{sat}$  are the mass fraction, activity coefficient and saturated vapor pressure of component  $i$  in the feed, respectively. Both of the activity coefficient and saturated vapor pressure can be obtained from computer simulation software.

## 2.2. Separation factor vs. selectivity

The separation efficiency of the membrane can be expressed using the term of separation factor ( $\beta$ ) or selectivity ( $\alpha$ ). The separation factor of the pervaporation process ( $\beta_{pervap}$ ) can be defined as:

$$\beta_{pervap, a/b} = \frac{y_j / y_i}{x_j / x_i} \quad (\text{Eq. 4})$$

The  $x$  and  $y$  are mass fractions of components 1 and 2 in the feed and permeate, respectively. In addition, the separation factor of the pervaporation process ( $\beta_{pervap}$ ) can be further decoupled into separation factor due to the evaporation process ( $\beta_{evap}$ ) and separation factor of the membrane ( $\beta_{membrane}$ ) [1]:

$$\beta_{pervap} = \beta_{evap} \times \beta_{membrane} \quad (\text{Eq. 5})$$

In certain cases, the ‘enrichment factor’ is used to describe the concentration ratio of the preferentially permeating component in both permeate and feed [34, 48]. Conversely, the intrinsic separation efficiency of the membrane is defined as the selectivity ( $\alpha$ ) which is the ratio of the permeabilities of components  $i$  and  $j$ . The selectivity can be further divided into mass-based selectivity and mole-based selectivity:

$$(\alpha_{ij})_{mass} = \left( \frac{P_i}{P_j} \right)_{mass} \quad (\text{Eq. 6})$$

$$(\alpha_{ij})_{mole} = \left( \frac{M_j}{M_i} \right) \times \left( \frac{P_i}{P_j} \right)_{mass} \quad (\text{Eq. 7})$$



The mole-based selectivity decouples the effect of the molar mass ( $M$ ) of components  $i$  and  $j$  in the calculation. In addition, the selectivity ( $\alpha$ ) of the asymmetric membranes can be defined as the ratio of the permeance of components  $i$  and  $j$  since the actual selective layer's thickness is unknown:

$$\alpha_{ij} = \frac{P_i/l}{P_j/l} \quad (\text{Eq. 8})$$

### 3. Common fabrication methods for pervaporation membranes

Membranes for pervaporation can be either completely dense or asymmetric with a thin dense and selective layer. Dense membranes are generally used in the laboratory to characterize the intrinsic properties of the materials, but their applications in industrial separation processes are hampered due to the relatively low trans-membrane flux. In contrast, asymmetric membranes possess a thin selective layer supported by a relatively thick microporous substrate. The microporous structure of the substrate greatly reduces the sub-structure resistance for penetrant transport and therefore enhances the trans-membrane flux.

A good comparison example is the removal of phenol from mixtures with water using polyether-block-polyamide co-polymer (PEBA) membranes [48]. Asymmetric composite membranes of PEBA with a selective layer thinner than 30  $\mu\text{m}$  on polyetherimide supports had a permeate flux higher than 526  $\text{g/m}^2\text{h}$  and an

enrichment factor lower than 31, while the membrane with a dense layer of 100  $\mu\text{m}$  had a permeate flux of 140  $\text{g}/\text{m}^2 \text{ h}$  and an enrichment factor of 121.

### 3.1 *Solution casting*

Solution casting is the most common method employed to fabricate flat-sheet membranes for various applications. The polymer and potential additives are first dissolved in a solvent to form a solution and the polymer solution is spread onto a flat surface followed by removal of the solvent through evaporation and/or phase inversion processes. Multilayered membranes can be prepared by multi-solution coatings with or without porous supports.

Dense membranes are prepared by the solvent removal via slow and complete evaporation processes, whereas asymmetric membranes with interconnected cell structures are obtained when the solvent removal procedure involves a phase inversion process, by immersion in a non-solvent bath. Addition of high volatile solvents to the casting solution with an evaporation step before the phase inversion promotes the formation of a top dense layer.

For the case of mixed matrix membranes (MMMs), the fillers are added into a polymer dope solution followed by thoroughly stirring and sonication to prevent the fillers from agglomeration. Subsequently, MMMs are formed by the similar procedures as aforementioned.

### 3.2 *Hollow fiber spinning*

Hollow fiber membranes possess several advantages over flat-sheet membranes for pervaporation such as higher packing density, self-supporting structure and self-containing vacuum channel if the shell feed mode is applied. The hollow fiber spinning process comprises a large number of process parameters throughout the entire chain of dope formulation, coagulation chemistry, spinneret design and spinning conditions such as air gap, temperature and take-up speed.

During spinning, the membrane is formed through phase inversion when the nascent fiber contacts with the coagulant. Since the polymer dope is extruded simultaneously with the bore fluid in the lumen side of the nascent fiber, coagulation occurs right away at its internal surface after the nascent fiber emerging from the spinneret. Meanwhile, partial coagulation starts at the outer surface when the nascent fiber goes through the air gap region as a result of humidity presence in air. The whole phase inversion process is completed once the fiber is fully precipitated in the external coagulation bath. The thickness and morphology of the selective layer can be manipulated by varying compositions of the spinning dope, bore fluid and external coagulant as well as take up speed.

The complexity of hollow fiber spinning increases as the spinning method advances from single-layer to dual-layer co-extrusion. The dual-layer hollow fibers possess the advantages of cost reduction as well as freedom in customization of materials and morphology for the selective and supporting layers [49, 50].

### 3.3 *Solution coating*

Solution coating is frequently applied to fabricate composite membranes by depositing a thin selective layer on top of microporous substrates or supports which can be in either flat-sheet, hollow fiber or tubular configuration. The substrate has to be fully porous in order to minimize the substructure resistance so that the membrane resistance is mainly controlled by the coated selective layer [51-54]. The pore size distribution of the substrate surface should be preferentially sharp and free of large defects to prevent intrusion of the coating solution. Pre-wetting the substrate with a low boiling point solvent (immiscible with the coating solvent) prior to the coating process can minimize the intrusion [51, 53, 54]. The coated membrane is then obtained by removing the pre-wetting solvent through a drying process. Most of the membranes for pervaporation are in the flat-sheet configuration. It is challenging to coat hollow fibers uniformly because of small fiber diameters. Uneven coated fibers may affect the separation process in a negative way.

### 3.4 *Interfacial polymerization*

Interfacial polymerization [55-57] is a well-established process for the preparation of thin composite membranes for reverse osmosis (RO) and nanofiltration (NF). The method however has been much less applied for pervaporation, except for dehydration. Interfacial polymerization has been widely used since 1960s for RO [55-57]. The polymerization process involves the rapid reaction between amine- and acyl chloride-based monomers to form a continuous polyamide layer at the interface of two immiscible liquids as shown in Figure 3. Since the acyl chloride-based monomer has a good solubility in the organic phase while the amine-based monomer has a

strong solubility in the aqueous phase, it is hypothesized that the growth of the thin polyamide layer at the bi-solution interface starts from the water phase towards the organic phase [55]. By using this technique, the selective layer formed on top of the substrate is very thin, which greatly augments the membrane flux. In addition, by selecting suitable monomers for the interfacial polymerization, enhanced chemical resistance, thermal stability and long term durability of the thin selective layer could be achieved [58].

### Figure 3

#### 3.5 *Physicochemical modifications*

Post-modification processes are commonly applied to improve the performance and stability of pervaporation membranes. Since pervaporation membranes are contacted with feed mixtures which consist of organic solvents, chemical crosslinking is the most common technique employed to stabilize the membranes and to suppress the swelling phenomenon. Hydrophilic and hydrophobic modifications of the membranes can also be utilized to improve the affinity between the permeating molecules and the membranes by incorporating or grafting the relevant functional groups into the polymer chains. On the other hand, post-annealing represents a versatile and efficient technique to eliminate the potential defects on the selective layer of the membranes.

## 4. **Pervaporation membranes**

As mentioned in the Introduction, this review focuses on the recent development of polymeric pervaporation membranes and hence this section is categorized into (i) polymeric membranes and (ii) mixed matrix membranes (MMMs), then further split

into sub-sections based on their respective applications in dehydration of organics, recovery of organics or organic-organic separations.

#### *4.1 Polymeric pervaporation membranes*

##### *4.1.1 Dehydration of organics*

Early development of pervaporation membranes for dehydration of organic solvents was mainly using hydrophilic polymers such as poly(vinyl alcohol), cellulose, chitosan, alginate, etc. that would enhance the solubility selectivity of water towards the membrane through hydrogen bonding interactions [2, 18, 31, 59, 60]. However, these membranes are susceptible to swell, crosslinking processes are generally employed to stabilize the membranes. These hydrophilic materials have been extensively reviewed in the literature [2, 24, 31] and therefore are beyond the scope of this article.

##### *4.1.1.1 Materials*

In recent years, research on pervaporation membranes for solvent dehydration applications has shifted towards the exploration of new chemically and thermally stable materials to dehydrate aggressive solvents at elevated operating temperatures. In this regard, polymers with stiff and rigid chains have been considered as the promising candidate in this application [5]. In addition, the glassy characteristic of these polymers could improve the diffusivity selectivity of the membranes during the dehydration process as the water molecule is smaller than most of the organic molecules.

Amorphous perfluoropolymer is a class of high free-volume materials that possess superior thermal and chemical stability to effectively handle aggressive solvents. The chemical structures and the trade names of some amorphous perfluoropolymers are shown Figure 4. The perfluoropolymer-based membranes have been studied by several research groups for dehydration of butanol, isopropanol, ethanol, N,N-dimethylformamide (DMF), N,N-dimethylsulfoxide (DMSO), N,N-dimethylacetamide (DMAc) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) [61-66]. Despite of their intrinsic hydrophobicity, the size exclusion mechanism has been proposed for these amorphous perfluoropolymer membranes as the dominant separation mechanism in dehydration applications [62].

#### Figure 4

On the other hand, aromatic polymers such as polybenzoxazole (PBO), polybenzoxazinone (PBOZ) and polybenzimidazole (PBI) have also been reported to show a great potential in solvent dehydration because of their excellent chemical and thermal resistance. The chemical structures of the aforementioned polymers are portrayed in Figure 5. Both PBO and PBOZ membranes were synthesized through the thermal rearrangement process from their respective precursors and were found to be applicable in dehydration of alcohols [9, 67, 68]. Ong et al. reported that the thermally rearranged PBO exhibited a stable performance in dehydration of isopropanol (IPA) and n-butanol (BuOH) at 80°C throughout the experimental period of 250 h [9] whereas Pulyalina et al. found that the diffusivity of water molecules was significantly enhanced in the PBOZ membrane as compared with its precursor [67]. Meanwhile, PBI-based pervaporation membranes were pioneered by Chung and co-workers [69-72]. They have fabricated PBI membranes in the forms of flat-sheet and

hollow fiber configurations for dehydration of various solvents such as alcohols, glycols and acetone. In addition, PBI was employed as a filler to improve the performance of Matrimid<sup>®</sup> membranes through polymer blending [73]. The N-H functional groups of PBI was identified to interact with the carbonyl groups of Matrimid<sup>®</sup> through hydrogen bonding as shown in Figure 6 [73]. Han et al. modified the surface of PBI membranes with chitosan for dehydration of IPA [74]. The hydrophilic layer of chitosan was reported to improve the dehydration performance of PBI membranes through the enhancement of solubility selectivity of water over IPA [74]. A performance comparison of polymeric membranes for dehydration of organics is tabulated in Table 1.

**Figure 5**

**Figure 6**

**Table 1**

#### *4.1.1.2 Modification processes*

Sulfonation [75-81] and crosslinking [82-88] are popular modification methods to augment the performance of pervaporation membranes. Figures 7 and 8 provide examples of sulfonation [79] and crosslinking mechanism on polymer chains [85]. Two-step sulfonation can occur by first immersing PBI membranes into sulfuric acid and subsequently treating the membranes at high temperatures. In this first step, the amidine cations and sulfonate anions are formed in the imidazole groups of PBI. Thermal treatment in the second step transfers sulfonate groups into the neighbor aromatic rings. This step is critical because it converts the ionic bonds between the sulfonate groups and nitrogen atoms in the imidazole groups to permanent covalent bonds with aromatic rings, which sustains the sulfonate groups after washing by



water. Although general perceptions agree that the performance enhancement of sulfonated membranes are owing to better hydrophilicity or affinity of water towards the membrane because of the sulfonic groups, some studies observed that the diffusion selectivity is dominant in determining the separation efficiency owing to the large differences in molecular size between water and solvents [75, 76, 80]. Meanwhile, crosslinking can tighten the polymer chains and improve the dehydration performance through suppressing the degree of swelling. Crosslinking can be classified into thermally and chemically induced routes based on the reaction mechanisms. As depicted in Figure 8, thermal crosslinking can be applied for carboxylic-containing polymer chains, where carboxylic groups can be removed at high temperatures for the formation of free radicals responding to the crosslinking reaction. Carboxylic-containing polymers also can perform crosslinking reaction through esterification between their carboxylic groups and diol-substances at high temperatures. Le et al. performed various crosslinking approaches; namely, thermal, diamino and diol crosslinking processes on co-polyimide (6FDA-NDA/DABA) membranes for ethanol dehydration [85]. The separation factors of the crosslinked membranes followed the order of thermally treated diamino crosslinked membranes > thermally crosslinked membranes > diol crosslinked membranes and vice versa for their fluxes [85].

**Figure 7**

**Figure 8**

Instead of using common difunctional crosslinkers, Xiao et al. and Hyer et al. conducted crosslinking reactions by employing trimesoyl chloride (TMC) as the multifunctional crosslinker on the PVA-based membranes for dehydration of ethylene glycol and IPA [83, 84]. The crosslinked PVA membranes showed an asymmetric

structure at the molecular level if an appropriate crosslinking condition was utilized. Although the crosslinking process can improve the pervaporation performance in terms of separation factor, it may lower the permeation flux due to the excessive densification of the selective layer. Efforts have been made to modify the crosslinking procedure to improve the permeation flux while maintaining the selectivity. Mangindaan et al. succeeded in it by performing vapor phase crosslinking on P84<sup>®</sup> polyimide membranes using ethylenediamine (EDA) vapor [88]. This technique enables the crosslinking reaction to merely occur on the surface rather than into the membrane bulk. As a result, an ultrathin crosslinked layer was formed as the selective layer which provided an impressive permeation flux with reasonable separation efficiency for acetone dehydration [88]. Table 2 summarizes the performance of polymeric membranes with various modification methods for dehydration of organics.

**Table 2**

#### *4.1.1.3 Composite membranes*

Thin film composite (TFC) membranes are one of the prominent representatives under the category multilayered membranes. The thin selective layer of these membranes is fabricated via the interfacial polymerization on top of porous asymmetric supports. Hence, these membranes can achieve good separation performance in terms of both flux and separation factor. The interfacially polymerized TFC membranes have been previously applied for RO and NF processes [1, 39]. Recently, they have emerged as a potential candidate for dehydration of organics via pervaporation [89-103]. Most of these studies focused on interfacial polymerization as functions of monomer types, substrates, pre-treatment and post-treatment conditions

[89-102]. A list of typical monomers in both aqueous and organic phases for interfacial polymerization is shown in Table 3.

**Table 3**

The investigation on TFC flat membranes has been mostly conducted by a research group from Taiwan [89-95, 98]. Huang et al. explored the polyamide TFC membrane prepared from triethylenetetramine (TETA) and TMC on the hydrolyzed PAN substrate for isopropanol (IPA) dehydration [94]. The reaction conditions of the polymerization were optimized to improve the performance of the TFC membrane [94] and the resultant TFC membrane showed a permeation rate of 3.4 kg/m<sup>2</sup>h with a permeate water concentration of higher than 99 wt% in dehydrating the IPA/water (70/30 wt%) mixture at 70 °C. In addition, the annealing effects on TFC membranes were studied by varying (1) the temperature of the TETA solution used for the interfacial polymerization as well as (2) the annealing temperature after the interfacial polymerization [94]. It was found that annealing processes could greatly enhance the separation performance of TFC membranes. Kao et al. prepared the TFC membrane using m-phenylenediamine (MPD) and sulfonated MPD (MPDSA) with TMC for IPA dehydration [95]. The MPDSA-TFC membrane showed a higher crosslinking degree, higher surface hydrophilicity and lower active layer thickness than the MPD-TFC membrane due to the presence of the sulfonic acid group in MPDSA monomer.

Besides studying the effects of various amine monomers, different acyl chloride monomers (i.e. 5-nitrobenzene-1,3-dioyl dichloride (NTAC) or 5-tert-butylbenzene-1,3-dioyl dichloride (TBAC)) have also been investigated to prepare TFC membranes for alcohol dehydration [43]. The NTAC based TFC membranes showed better dehydration performance as compared with TBAC based TFC membranes due to the

greater degree of crosslinking when NTAC was used as the acyl chloride monomer. The effects of drying processes on TFC membranes were also examined by Albo et al. using commercially available reverse osmosis (RO) TFC membranes from Nitto Denko (SWC5, ESPA2 and CPA5) for dehydration of IPA [99]. They found that the membranes dried via ethanol–hexane solvent exchange route exhibited higher water permeance as compared with the one dried at room temperature and in an oven [99].

On the other hand, Chung and co-workers have investigated TFC based pervaporation membranes in the hollow fiber configuration [96, 97, 100-102]. Significant efforts have been made to improve the adhesion and uniformity of the polyamide selective layer on top of the cylindrical hollow fiber substrate. Shi et al. coated a gutter layer on top of the ceramic substrate using polydopamine and hyper-branched polyethyleneimine (HPEI) to reduce the surface pore size and increase the adhesion between the top selective layer and the substrate for IPA dehydration [97]. Meanwhile, Zhang et al. modified the surface of the polyvinylidene fluoride (PVDF) hollow fiber substrate with sodium hydroxide (NaOH) to increase its hydrophilicity and adhesion with the aqueous monomer solution prior to conducting interfacial polymerization for dehydration of ethanol [100]. In addition, they have studied various approaches to modify the thin polymerized layer for a higher and more stable pervaporation performance. Zuo et al. utilized HPEI as the amine source to fabricate TFC hollow fiber membranes for dehydration of IPA [96]. They found that the hyper branched structure of HPEI could enhance the fractional free volume and hydrophilicity of the polyamide layer [96]. They also incorporated the toluene 2,4-diisocyanate (TDI) crosslinker during the interfacial polymerization process followed by annealing to produce the TDI crosslinked TFC hollow fiber membrane for

dehydration of ethanol [101]. This TDI crosslinked TFC membrane was able to overcome the swelling issue of conventional TFC membranes and enhanced the separation performance of the TFC membrane. The performance of TFC membranes for dehydration of organics are summarized in Table 4.

**Table 4**

Besides the interfacial polymerization, composite membranes can be fabricated by depositing a protective layer on top of the selective layer of a membrane. This technique was first proposed by Membrane Technology & Research (MTR) Inc. for pervaporation applications. [65, 104]. The MTR's Aquarius membrane possesses a thin amorphous perfluoropolymer protective layer coated on top of a hydrophilic cellulose ester membrane. The protective layer was able to suppress membrane swelling by preventing the selective layer from direct contact with the feed mixture. As a result, the Aquarius membrane has high tolerance towards the feed mixtures with high water concentrations for ethanol dehydration [104]. Ong and Chung adopted this principle to fabricate hollow fiber composite membranes via novel immiscibility induced phase separation (I<sup>2</sup>PS) process for dehydration of ethanol [50, 105]. Both of the protective and selective layers were simultaneously extruded and formed during the phase inversion process via immiscibility between the dope solutions at both layers [105]. The asymmetric structure of the protective layer enabled the hollow fiber composite membranes to show a high permeance coupled with a reasonable high selectivity for dehydration of ethanol [50]. This I<sup>2</sup>PS concept may provide certain insights in designing and fabricating new pervaporation membranes.

#### 4.1.2 Recovery of organics

Pervaporation becomes feasible in removal of organic compounds from aqueous solutions when the concentration of organic compounds is relatively low. As opposed to dehydration, the removal of dilute organic compounds from aqueous solutions via pervaporation process requires the preferential permeation of organic compounds with larger molecule sizes through the membrane. Hence, the membrane has to be made of organophilic or hydrophobic materials in order to increase the affinity of organic compounds towards it. In addition, the application of pervaporation in recovery of aroma compounds may become important in the future since it has the advantage of low operating temperatures to avoid the degradation of these thermally labile but highly valued compounds [19]. The hydrophobic polymers applied in this application are portrayed in Figure 9.

### Figure 9

Polydimethylsiloxane (PDMS) or commonly known as silicon rubber is the most widely studied hydrophobic material and often regarded as the benchmark material in this application. The application of PDMS and other hydrophobic materials (such as styrene based polymers, polyvinylidene fluoride (PVDF), polyether-block-polyamides (PEBA), etc.) in this application has been previously reported [7, 25, 48, 106-110]. Since the PDMS-based membranes are prepared via crosslinking process, the permeation flux of these membranes is usually low. Hence, hydrophobic polymers with high free-volumes such as poly(1-trimethylsilyl-1-propyne) (PTMSP) and polymers of intrinsic microporosity (PIMs) have been investigated for this application [111-117]. However, the flux of the PTMSP membrane reduced as a function of operating time because of chain relaxation that decreased the free volume [116]. On the other hand, the PIM-1 membrane has a comparable permeability with PTMSP for ethanol recovery but without showing flux reduction with operating time, which made

it a prospective membrane material for recovery of organic compounds from aqueous solutions [117].

Due to the limitation of available hydrophobic materials for recovery applications, substantial researches have been conducted to improve the performance of pervaporation membranes through modifying the membrane fabrication process. In the case of PDMS, it has been utilized as the selective-layer material by coating it on various substrates [118-123]. The viscosity of PDMS solutions and the properties of substrates (i.e. pore size, porosity, etc.) play crucial roles in determining the overall performance of composite membranes [122]. The performance of polymeric membranes for recovery of organic compounds from aqueous solutions are shown in Table 5.

**Table 5**

Although hydrophobic pervaporation is very useful in many fields such as alcohol and other organic recovery, the number of hydrophobic materials suitable for organics recovery is limited at the present and their performance looks unattractive. Future research on this area may focus on synthesis or exploration of new materials with high hydrophobicity and free volume size to promote high permeability and selectivity towards organic compounds, which typically have bigger diameters than water. Glassy materials may be more interesting than rubbery ones because of their better processability and scalability in fabricating more practical configurations, i.e., hollow fiber, by employing a well-controlled and efficient dry-jet wet spinning line through a non-solvent-induced phase-inversion process.

#### *4.1.3 Organic-organic separations*

Organic-organic separations via pervaporation process are the most challenging and the least developed application. This may be due to the lack of robust membrane materials as well as the modules that are able to withstand the long-term exposure of organic solvents. The major applications in organic-organic separations are summarized in Figure 10 [3]. A detailed review regarding the background of this application was provided by Smitha et al. [3].

### Figure 10

Recent studies in this application have been focused on the separation of alcohols/tertiary butyl ethers and aromatic/aliphatic compounds, and on gasoline desulfurization [32, 124-134]. A series of new materials were synthesized and modified for the separation of methanol/methyl tert-butyl ether (MeOH/MTBE) and ethanol/ethyl tert-butyl ether (EtOH/ETBE) mixtures. Their respective performance are tabulated in Table 6. Billy et al. grafted poly(methyl diethylene glycol methacrylate) (MDEGMA) onto cellulose acetate to fabricate membranes for EtOH/ETBE separation [125]. The membranes fabricated from short-graft copolymers were found to be more selective and less permeable as compared with those fabricated with long grafts due to microstructure and phase segregation of the copolymers [125]. Zereski et al. incorporated cardo (lactone) group into the backbone of poly(ether ether ketone) (PEEK) to reduce its crystallinity and employed the modified poly(ether ether ketone) (mPEEK) membrane for the MeOH/MTBE separation [127]. They found that the mPEEK membrane was MeOH-selective and mechanically stable in the feed mixture [127]. Both flux and selectivity of the membrane were strongly correlated with MeOH concentration in the feed mixture [127]. Han et al. integrated fluorene containing segments into poly(arylene ether



sulfone) to enhance the hydrophilicity and free volume of the polymer for the removal of MeOH from the MeOH/MTBE mixture [133]. The membrane exhibited a permeation flux of 334 g/m<sup>2</sup>h and a MeOH/MTBE separation factor of 287 with the feed mixture of 15wt% MeOH at 40°C [133].

**Table 6**

On the other hand, Ribeiro et al. synthesized a series of polymers, ranging from aromatic polyimides, poly(siloxane-co-imide), poly(ether-co-imide) and polybenzoxazole for the separation of toluene/n-heptane and benzene/n-heptane mixtures for aromatic/aliphatic separation [128, 131]. All the materials were found as selective towards aromatic compounds. They also reported that the polybenzoxazole membrane fabricated through the thermal rearrangement (TR) route did not necessarily enhance the permeability of hydrocarbon as compared with its respective polyimide precursor [128]. Their subsequent work showed that the incorporation of siloxane groups into the polymer could improve the permeability of hydrocarbon with some scarifications in selectivity whereas the introduction of ether groups was found to have a negligible effect on membrane performance [131].

The application of pervaporation process in gasoline desulfurization has attracted huge interests due to the stringent rules that limit the sulfur content in gasoline [29]. The model feed mixtures of this application are formulated from hydrocarbons in gasoline such as olefins, alkanes, cycloparaffins and aromatics, and from the sulfur sources in gasoline such as mercaptans, sulfides, thiophenes, etc. [32]. The review on gasoline desulfurization via pervaporation process has been covered by Mortaheb et al. and Lin et al. [32, 124]. Yang et al. synthesized and modified series of polyphosphazene-based membranes for gasoline desulfurization (shown in Figure 11)

[129, 132]. They found that the poly[bis(trifluoroethoxy) phosphazene] (PTFEP) based membrane displayed a low flux due to the semi-crystalline nature of PTFEP that induced mass transfer resistance [129]. They further modified the base polymer into poly[bis(p-methyl phenyl) phosphazene] (PMePP) and poly[bis(phenoxy)phosphazene] (PBPP) by incorporating bulky phenyl groups into the base polymer to enhance membrane performance through the increment of free volume [129, 132]. Liu et al. coated poly(ether-block-amide) (PEBAX 2533) on top of the PVDF substrate to fabricate composite membranes for the removal of thiophene from n-heptane [133]. A trade-off behavior between flux and separation factor was found as functions of operating temperature and thiophene concentration in the feed [133]. In summary, most of recent studies on this application have been focused on exploring new membrane materials and fabrication processes to improve membrane stability and performance under harsh operating environments.

### Figure 11

#### 4.2 Mixed matrix pervaporation membranes

In order to combine the strengths of inorganic and polymeric membranes, mixed matrix membranes (MMMs) was first patented by Kulprathipanja et al. in 1988 [135]. Since the proposal of MMM concept, numerous inorganic fillers such as zeolites [136-144], multiwalled carbon nanotubes (MWCNTs) [145-147], silica [146, 148] and graphene oxide (GO) [149], porous organic cages (POCs) [150] and covalent organic frameworks [151] and many others have been studied and incorporated into polymeric matrices for enhancement of pervaporation performance. Homogeneous dispersion of inorganic particles in the polymeric matrix is challenging because agglomeration of inorganic fillers creates defects in the membranes, resulting in a

decrease in selectivity [135, 152, 153]. To circumvent the incompatibility of the polymeric phase and the inorganic phase as well as to improve the filler dispersion, recent works have focused on following approaches: (1) Modify inorganic fillers with coupling agents to covalently bond the two phases [154-157]; (2) Coat inorganic fillers with a thin polymeric layer [158, 159]; (3) Employ hybrid particles such as polyhedral oligomeric silsesquioxane (POSS) [160-164] or metal organic frameworks (MOFs) [165-169], which contain both organic and inorganic components for better compatibility with the polymeric matrix; and (4) Develop a new process for MMM fabrication [146, 168, 170]. Following sections will review recent studies on MMMs for various pervaporation applications.

#### 4.2.1 *Dehydration of organics*

Jiang et al. [171] incorporated porous magnesium oxide (MgO) particles into the Matrimid<sup>®</sup> matrix for IPA dehydration. The resultant MMMs had a higher selectivity, but a lower permeability than the neat Matrimid<sup>®</sup> dense membrane. The highest selectivity was obtained for the MMM containing 15 wt% MgO. Compared to PVA and sodium alginate based MMMs, Matrimid<sup>®</sup>/MgO membranes were proven to have higher thermal stability. A high pervaporation operation temperature of 100 °C was able to be applied for the MMMs and hence a high flux of about 600 g/m<sup>2</sup>h was achieved. Besides MgO, Jiang and Chung [172] developed molecular-level MMMs made of Matrimid<sup>®</sup> and  $\beta$ -cyclodextrin ( $\beta$ -CD) (Figure 12A) for dehydrating IPA by pervaporation. The separation performance of the resultant MMMs containing 2-10 wt%  $\beta$ -CD is much higher than the neat Matrimid<sup>®</sup> membrane in terms of both flux and separation factor because of its hydrophilicity, interior cavity size and good

interaction between it and the polymer matrix. Compared to mixed matrix membranes embedded with MgO, introducing a low amount of  $\beta$ -CD into the Matrimid<sup>®</sup> led to the enhanced and superior separation efficiency. However, a higher content of  $\beta$ -CD deteriorated the separation performance due to the formation of non-permeable  $\beta$ -CD networks.

### Figure 12

Choi et al. [145] embedded multiwalled carbon nanotubes (MWCNTs) into poly(vinyl alcohol) (PVA) membranes for ethanol dehydration. The results showed that the addition of MWCNTs mitigated the crystallinity, induced micro-orientation and decreased the free volume of the PVA matrix. Despite the reduction in free volume, the flux of the MMMs was improved because the inner hollow space of MWCNTs could act as the diffusion path for permeating molecules with relatively less resistance. Zhao et al. [146] also applied MWCNTs to develop MMMs using polymer polyelectrolyte complexes (PECs) as matrices. The MWCNTs was found to evenly disperse in PEC films. However, the cross-sectional image of the films showed that these MWNTs were broken which was probably caused by the load transfer from PEC to MWCNTs under stretching. In the same work, they also incorporated SiO<sub>2</sub> into the PEC by the ‘in situ’ integration during ionic complexation. By this facile method, a fine dispersion of SiO<sub>2</sub> in PEC was achieved. The PEC/SiO<sub>2</sub> (5 wt%) nanohybrid membranes showed good performance for IPA dehydration with a flux of 2.3 kg/m<sup>2</sup>h and a separation factor of 1721 at 75 °C with a feed containing 10 wt% water in IPA.

Amnuaypanich et al. [139] prepared MMMs from natural rubber (NR) and sulfosuccinic-acid (SA) crosslinked PVA semi-interpenetrating polymer networks

(IPNs) consisting of zeolite 4A for ethanol dehydration. NR was found to restrict membrane swelling while PVA increased the water absorption because of its hydrophilicity. Zeolite 4A provided an alternative pathway for water transport and simultaneously enhanced water selectivity because of its molecular sieve nature. It was observed that both flux and separation factor were improved with a zeolite loading of 30% in the membrane. However, the separation factor dropped significantly when the zeolite loading increased to 40 wt% because of particle agglomeration that created cracks or large holes to facilitate ethanol transport. Bhat and Aminabhavi [140] also employed zeolite 4A to fabricate MMMs but used crosslinked sodium alginate as the matrix. Similar to Amnuaypanich et al.'s observation, incorporation of zeolite 4A enhanced both flux and selectivity when the particle loading ranged in 3-10 wt%. However, the flux for ethanol dehydration in Bhat and Aminabhavi's work was much lower than that in Amnuaypanich et al.'s work, which may be attributed to the difference in their polymer matrices.

To compare the separation efficiency of zeolite 4A with other particles such as silica and carbon molecular sieve (CMS), Bakhtiari et al. [142] introduced these three types of particles into two polyimide matrices (Matrimid<sup>®</sup> and P84) for IPA dehydration. They found that the water selectivity is in the order of zeolite 4A > CMS > aerosil silica. Among these fillers, only zeolite 4A enhanced the flux of the MMMs while two others did not alter the flux significantly. Similar to zeolite 4A, zeolite 13X was proven to have the ability to enhance both flux and selectivity when being embedded into the polymer blend matrix of sodium carboxymethyl cellulose (NaCMC) and PVA [143].

Recently, metal-organic frameworks (MOFs) consisting of metal and organic components have attracted a great attention because of their controllable pore sizes and high porosities [165-169]. As a sub-class of MOFs, zeolitic imidazolate frameworks (ZIFs) exhibit exceptional thermal and chemical stability and are attractive for various pervaporation applications [164, 166-169]. The chemical structures of the ZIFs applied for pervaporation dehydration are depicted in Figure 12B. Kang et al. successfully incorporated ZIF-7 crystal particles into the chitosan matrix to form MMMs [169]. The ZIF-7 particles were found to exhibit good interface adhesion with the chitosan matrix because of the nature of their organic linkers. The resultant MMMs showed a higher flux and separation factor at a low loading of ZIF-7 (2.5 wt%). However, when a higher loading of ZIF-7 was introduced into the matrix, crosslinking between the Zn atom of ZIF-7 and the amino groups of the chitosan polymers may occur and reduce the flux.

Different from Kang et al.'s work, Shi et al. studied MMMs with high loadings of MOFs [167]. They incorporated 12-58 wt% ZIF-8 into PBI for dehydration of various alcohols. Their MMMs exhibited homogeneous structures even at high loadings of ZIF-8 because of small particle sizes (~50 nm) and excellent compatibility between ZIF-8 and PBI. Although the resultant MMMs displayed good separation performance for dehydration of IPA and butanol, their separation efficiency for ethanol dehydration was relatively low. However, the PBI/ZIF-8 MMMs were proven to successfully suppress ethanol-induced swelling, which demonstrated the potential of embedding MOFs in MMMs for alcohol dehydration. Hua et al. incorporated ZIF-90 nanoparticles into Matrimid® to fabricate MMMs for IPA dehydration [164]. Sulfonated polyethersulfone (SPES) was found to be an effective primer to coat the

ZIF-90 particles so that the affinity between ZIF-90 particles and P84 was enhanced and the resultant MMMs have synergistic separation performance.

Other than MOFs, polyhedral oligosilsesquioxane (POSS) (Figure 12C) has been recently proven as a potential filler for MMMs because it can modify the properties of polymers such as mechanical properties, thermal stability, oxidation resistance and rheological properties. Xu et al. [161] incorporated several types of POSS (octaanion (OA), octanitrophenyl (ONPS), octaaminophenyl (OAPS) and octaammonium (OAS)) into the chitosan matrix for ethanol dehydration. They found that the morphology and pervaporation performance of the resultant MMMs were governed by POSS type and content, or more fundamentally, the interactions between POSS and the matrix. Similar to the effect of POSS content on gas separation [156], a small amount of POSS loading (1-2 wt%) was proven to significantly improve the membrane selectivity. However, with a higher POSS content, the MMMs exhibited different behaviors depending on the POSS type. Their study has demonstrated the promising application of POSS for pervaporation.

Considering the small size of POSS (1-3 nm) and its separation efficiency, Le et al. [163] developed dual-layer hollow fiber membranes consisting of a mixed matrix layer embedded with POSS as a selective layer for ethanol dehydration. Similar to the conclusion made by Xu et al. [161] and Li et al.'s [156], Le et al. found that incorporating a suitable POSS amount (2 wt%) into the selective layer increased its free volume size and diffusion selectivity and hence resulted in simultaneous enhancements in both total flux and separation factor for the resultant hollow fibers. To elucidate the effects of POSS, they also proposed the diffusion mechanisms of

permeate molecules through polymer chains containing POSS nanoparticles such as the disruption of inherent chain packing of stiff polyimide chains, space occupation, chain motion restriction and diffusion path enhancement [163].

Compared to alcohol dehydration, studies on MMMs for other solvent dehydration are very limited. Lokesh et al. [156] prepared a novel mixed matrix membrane by incorporating a small amount (0.25-1 wt%) of polyaniline-modified titanium dioxide ( $\text{TiO}_2$ ) into glutaraldehyde (GA) crosslinked sodium alginate for the dehydration of 1,4-dioxane. The surface modification of  $\text{TiO}_2$  with polyaniline was to facilitate the dispersion of  $\text{TiO}_2$  into PVA and simultaneously increased its hydrophilicity. The introduction of  $\text{TiO}_2$  was proven to improve the anti-swelling property of the membrane and thus increased the separation factor. However, the flux of their MMM significantly decreased and diminished their overall performance. Veerapur et al. [173] promoted the separation ability of MMMs in terms of both flux and separation factor for 1,4-dioxane dehydration by incorporating microporous hydrophilic zeolite T into crosslinked PVA. Both flux and separation factor were enhanced when the filler loading increased to 15 wt% due to the overall hydrophilic nature of the membrane in the presence of zeolite T particles. Other works on 1,4-dioxane dehydration by PVA/aluminosilicate and sodium alginate/charcoal MMMs were done respectively by Singha et al. [174] and Aminabhavi et al. [175], and a similar observation was obtained for the separation performance. Beside 1,4-dioxane, pervaporation dehydration of other solvents such as acetic acid, ethylene glycol (EG) and acetonitrile by MMMs have been studied [176-178]. Table 7 summarizes the dehydration performance of MMMs for dehydration of various organic-water mixtures.



**Table 7***4.2.2 Recovery of organics*

Table 8 presents the summary of solvent recovery performance by pervaporation via MMMs. For recovery of solvents, ZSM-5 zeolite with a high ratio of Si:Al and silicalite-1 (an aluminum-free ZSM-5) are the mostly common inorganic fillers. Vane et al. verified that high-silica ZSM-5 molecular sieve particles had capacity to improve the recovery performance of silicone rubber membranes for ethanol solutions [138]. Their study also confirmed that uniform particle dispersion, high zeolite loading, and small particle size are three critical factors to form desirable MMMs for pervaporation as observed for gas separation [135, 152, 153]. Subsequently, Vane et al. continued their work on ZSM-5 zeolite/silicone rubber membranes and investigated their long-term stability [141]. It was found that the performance changed when exposing the membranes in aqueous ethanol solutions over long periods of time. To overcome this phenomenon, several pretreatment of particles was examined.

**Table 8**

Their results suggested that quenching the calcined particles in linear short-chain alcohols lead to stable pervaporation performance while treating them with longer chain linear alcohols or branched alcohols reduced the performance due to their interaction with the zeolite. The authors also investigated the performance of the MMMs for butanol removal from real fermentation broths. It was evident that other products in the broth may be adsorbed within the zeolite, competing with butanol for sorption sites and blocking butanol transport. As a result, the separation performance of MMMs declined significantly. Interestingly, the most effective regeneration

approach was found by soaking the MMMs in 100% n-butanol, which was able to fully recover the original performance.

More recently, Zhan et al. modified ZSM-5 zeolite particles by hydrofluoric (HF) acid etching and embedded them into PDMS as MMMs for ethanol recovery [144]. It was found that HF etching was effective to remove organic impurities in zeolite, enhance surface hydrophobicity and surface roughness. As a result, the MMMs filled with etched ZSM-5 showed a better selectivity than that filled with non-etched ones, with a slight decrease in permeability. In addition, the tensile strength and swelling resistance of the resultant MMMs were improved due to the enhanced zeolite-PDMS interfacial adhesion.

Gu et al. employed silicalite particles to fabricate MMMs with PEBA for ethanol recovery [179]. They reported that there was an optimal loading of silicalite (2 wt%) where both the flux and separation factor could reach their highest values. When the silicalite content exceeded 2 wt%, separation factor and flux declined due to the transport resistance of adsorbed molecules by the presence of silicalite. Fouad and Feng utilized a silicate-filled composite PDMS membrane (Pervap 1070) manufactured by GFT (now Sulzer Chemtech) for pervaporative separation of n-butanol from dilute aqueous solutions (0.01–0.5 wt%) [180]. The membrane consisted of a thin selective skin layer of PDMS filled with a certain amount of silicalite particles and a microporous asymmetric PAN substrate. Since the butanol flux showed a concave increment as a function of butanol concentration in feed mixture due to strong affinity between the silicalite and butanol molecules, they have proposed an empirical equation to represent the concentration dependence of butanol

flux. It would be useful for the application of membrane pervaporation into in situ butanol removal from fermentation process.

To improve the interaction between silicalite and the PDMS matrix, Yi et al. modified the silicalite particles by silylation with vinyltriethoxysilane (VTES) as in Figure 13 [157]. This modification created chemical bonds between particles and the matrix, suppressed the void formation at the polymer–silicalite interface and hence increased the thermal stability of hybrid membranes and mitigated membrane swelling. The effect of particle loading on pervaporation performance of the MMMs was investigated using dilute ethanol solutions. The silylation modification not only increased the maximum loading of silicalite from 60 wt% for the unmodified silicalite to 67 wt% for the modified silicalite, but also improved the selectivity of the MMMs. However, the dispersion of zeolite nano-crystals was still non-homogeneous. Instead of dispersing the particles directly into the polymer, Liu et al. developed a new method to fabricate silicalite/PDMS membranes. As illustrate in Figure 14 [170], an ultrathin and very homogeneous silicalite-PDMS active layer on a porous alumina capillary support was uniformly formed by depositing the silicalite nano-particles onto the porous alumina support, calcining them and subsequently filling the interspaces among the silicalite nano-particles with PDMS. The membrane possessed a very high flux (5.0–11.2 kg/m<sup>2</sup>h) and a good separation factor (25.0–41.6) for the pervaporative recovery of iso-butanol from aqueous solutions (0.2–3 wt%) at 80 °C.

**Figure 13**

**Figure 14**

Besides ZSM-5 and silicalite, other hydrophobic particles have also been investigated for alcohol recovery. Huang et al. fabricated MMMs consisting of a novel

polyphosphazene nanotube (PZSNT) and PDMS for ethanol recovery. The PZSNT nanotube was synthesized by the reaction between hexachlorocyclotriphosphazene and 4,4'-sulfonyldiphenol as shown in Figure 15 [159]. Compared to normal carbon nanotubes, PZSNT has many advantages: (1) good dispersion in the polymer matrix and (2) higher affinity toward ethanol owing to its organic component, and (3) reduced diffusion resistance owing to the nanopores on its wall. It was found that the diameter of PZSNT had a certain effect on separation performance. The flux and separation factor increased with smaller nanotubes because of the increase in interface surface, so do the liquid uptake and sorption selectivity. To improve the interaction between particles with the polymer matrix, Le et al. studied novel molecular-level MMMs made of Pebax and POSS [162]. Octa(3-hydroxy-3-methylbutyldimethylsiloxy) POSS (AL0136) and disilanolisobutyl POSS (SO1440) were chosen with the hypotheses that their hydroxyl groups, Si-OH groups may interact with the polymeric matrix and the feed components while their siloxyl groups and isobutyl groups may increase hydrophobicity of the MMMs. Similarly to previous findings [163], both flux and separation factor increased when a small amount of POSS (2 wt%) was employed. The high permeation flux was achieved because of the increased free volume and the enhanced interactions between the solvents and POSS nanoparticles while the improved separation factor may be attributed to micro-voids formed at the particle-polymer interface to facilitate ethanol transport and preferential sorption of the membrane towards ethanol.

### Figure 15

More recently, Claes et al. incorporated hydrophobic silica into poly[1-(trimethylsilyl)-1-propyne] (PTMSP) and prepared MMMs for pervaporative separation of dilute aqueous ethanol and butanol mixtures (5 wt.%) [181]. The

hydrophobic silica significantly increased permeation flux with a sacrifice in alcohol/water selectivity. Their MMMs displayed a flux of  $9.5 \text{ kg/m}^2\text{h}$  with a separation factor of 18.3 for ethanol/water separation and a flux of  $9.5 \text{ kg/m}^2\text{h}$  with a separation factor of 104 for butanol/water separation (at  $50^\circ\text{C}$ ). This performance is superior to commercially available PDMS-based membranes. However, the long-term stability is questionable because PTMSP-based membranes may not be stable as a function of time because of aging.

MMMs comprising hydrophobic ZIF for organic recovery have also been demonstrated. Liu et al. successfully fabricated Pebax-based MMMs with superhydrophobic ZIF-71 [182]. A homogeneous dispersion of ZIF-71 particles in the matrix was obtained because of the organic nature of ZIF. A simultaneous increment in both separation factor and flux was achieved by optimizing the amount of ZIF-71. The MMMs with 20 wt% ZIF-71 loading exhibited a high total flux of  $520 \text{ g/m}^2\text{h}$  and a separation factor of 18.8 at  $37^\circ\text{C}$  for n-butanol removal from the model acetone-butanol-ethanol (ABE) solution. In addition, the membrane displayed stable performance in the real ABE fermentation broth for 100 h operation.

Studies on the recovery of non-alcoholic organic compounds from aqueous solutions by MMMs are relatively limited. Zhang et al. examined the recovery of the aroma, isopropyl acetate, from its dilute aqueous solution (0.39 wt%) using ZSM-5 filled hydroxyl terminated polybutadiene (HTPB)-based polyurethaneurea (PU) membranes [183] while Liu et al. explored homogeneous ZIF-8-silicone rubber nanocomposite membranes prepared by a novel 'Plugging-Filling' method for recovery of furfural (1.0 wt%) from water [168]. These works confirmed that both flux and separation can

be improved simultaneously by optimizing the particle loading, structure and chemistry.

#### 4.2.3 *Organic-organic separation*

Compared to dehydration or recovery of organic compounds from aqueous solutions, studies on MMMs for organic-organic separations are very limited. Table 9 tabulates some of their performance [184-190]. Most of them focused on separating the mixtures of alcohols with other organic compounds, or the mixtures of isomers and aromatic compounds. Filled particles were found to suppress excessive membrane swelling and improve plasticization resistance. They also provided micro-scale effects and created a large surface area. None of the studies showed that embedded particles had selective interaction with one organic more than the other. In most of the cases, the enhanced selectivity was attributed to physical crosslinking created by the particles. Different from recovery or dehydration application where flux and separation can be increased simultaneously, a trade-off relationship between flux and separation factor was generally observed for the organic-organic separation by MMMs.

**Table 9**

In summary, the effects of fillers on MMMs are not straightforward. Some studies reported a trade-off relationship between flux and separation factor while others reported both enhancements in flux and separation factor [135]. The enhanced performance may be attributed to the chemical structure of fillers, the interfacial voids generated among fillers and the rigidification of polymer chains by the fillers. On the one hand, the increment in flux may be attributed to good interaction between the feed

component and the filler, high porosity and large pore size of the filler. The increase in separation factor for water/organics separation can be attributed to the sieving effect of the fillers and rigidification of the polymer chains which reduces permeability. Generally, the interfacial voids lead to a higher permeability but a lower selectivity for water. Due to the opposite effects in enhancing either separation factor or flux, inorganic fillers with suitable pore sizes and good compatibility with the polymers must be carefully screened to result in balanced enhancements in separation performance. In addition, more studies should be focused on (1) the interface between fillers and polymers and (2) the transport mechanism of permeating molecules across MMMs to comprehensively understand the role of fillers in MMMs. Since porous MOFs, covalent organic frameworks (COFs) and POCs have high compatibility with polymer matrices, more studies on their MMMs are needed in order to reveal their potential for pervaporation applications.

## 5. Emerging R&D on Pervaporation Membranes

### 5.1 *Polyelectrolyte complex (PEC) membranes*

Polyelectrolyte complexes (PECs) are composed of two oppositely charged poly-ions crosslinked via electrostatic force. Although they have been unveiled for more than half a century [191, 192], their application in pervaporation was not developed until 1990s [193-195]. Afterwards, PEC membranes prepared by the layer-by-layer (LBL) deposition method were gradually adopted for dehydration of aqueous organics owing to their preferential affinity towards water molecules which would foster water transport through the membranes [196]. However, the water-induced swelling due to their high hydrophilicity is an inevitable issue during the pervaporation process.

Besides, the long-term operating instability is another severe problem. The mobile counter-ion pair is reversible and may be replaced by  $H^+$  in the presence of water [2]. In the past few years, various approaches to suppress membrane swelling and improve operating stability have been proposed and demonstrated.

Compared to ionic crosslinking, chemical crosslinking tends to introduce irreversible covalent bonds among polymer chains. Some researchers have attempted to chemically crosslink the PEC membranes in order to improve their long-term stability. Liu et al. reported a glutaraldehyde (GA) crosslinked PEC membrane based on carboxymethyl cellulose (CMCNa) and poly(diallyldimethylammonium chloride) (PDDA) [197]. It was found that the resultant membranes showed very high water resistance and good selectivity. Long-term pervaporation tests for a 50 wt% water-IPA mixture indicated that the membrane could deliver a stable performance for at least 100 h. Similarly, Zhang et al. also adopted GA to crosslink the outmost polyethyleneimine (PEI) layer on the PEI/polyacrylic acid (PAA) PEC membranes [198]. After chemical crosslinking, the composite membranes with a few bilayer of ion pairs displayed a stable and relatively high performance for ethanol dehydration.

Dynamic LBL assemblies have also been developed to improve separation performance and reliability. Compared to static LBL assemblies, the dynamic assembly approach renders the membrane structure to be more compact. For example, Ji et al. reported a pressure-assisted filtration method to build the PEC layer [199]. The polycation and polyanion were alternatively filtrated in a dead-ended filtration cell. They found that the regularity of the membrane surface was improved and the resulting membrane can maintain a stable performance up to 52 h for dehydration of a



95 % ethanol aqueous solution. Another interesting work by Yin et al. revealed a method to assemble the PEC membrane at a vibration condition. It was observed that a denser and smoother layer was formed on the substrate as the vibration frequency increased [200].

Besides, homogeneous-PEC (HPEC) membranes were employed to tune the ionic complexation degree (ICD). This ICD plays a critical role in determining the packing pattern and the density of PEC aggregates. Generally, the HPEC membrane was attained by blending polycation and polyanion in an acidic solution and subsequently casting the solution on a substrate. Jin et al. reported a series of HPEC membranes synthesized from poly (n-ethyl-4-vinylpyridiniumbromide) (PEVP) and sodium carboxymethyl cellulose (CMC-Na) with different ICDs [201]. By increasing ICD, the microstructure of the PEC layer became compact and the separation performance could be easily optimized. Similar works and results can be found elsewhere [202, 203]. Liu et al. further modified the HPEC membranes by introducing alkyl side chains in quaternized poly(4-vinylpyridine) [204]. Interestingly, they found that the hydrophilicity decreased while the degree of swelling increased with an increase in side chain length. In addition, the membranes could maintain a stable selectivity over a temperature range from 40 to 70 °C. On the other hand, Wang et al. introduced sulfate groups in PEC membranes to enhance the electrostatic force [205-207]. It appeared that the stronger the ion pairs, the more the stable pervaporation performance. The membranes also showed stronger tensile strength.

Recently, the electric field driven LBL assembly has become a very active topic [208-210]. For example, Zhang et al. assembled a layer of positively charged PEI on the

negatively charged PAN substrate under the action of an external electric force [209]. The resultant membrane possessed a more regular structure compared with the one assembled by the dynamic LBL adsorption. Zhang et al. unveiled that the membranes assembled in an electric field showed a smoother surface and a better storage stability within 60 days in a 90 wt% IPA aqueous solution at 25 °C [209, 210]. The structural regularity and stability endowed the PEC membrane significantly improved separation performance for alcohol dehydration.

Incorporation of inorganic particles is another strategy to improve separation performance for PEC membranes. Li et al. developed a series of organic-inorganic nanohybrid multilayer membranes by incorporating zirconium dioxide ( $\text{ZrO}_2$ ) and alumina oxide ( $\text{Al}_2\text{O}_3$ ) nanoparticles into polyelectrolyte complexes [211]. These hybrid membranes were used for dehydration of acetone and exhibited promising performance with a flux of  $0.69 \text{ kg/m}^2 \text{ h}$  and a water/acetone separation factor of 1880 at 50 °C. More recently, Wang et al. developed a graphene oxide (GO)-doped PEC membrane by assembling the positively charged PEI-modified GO and negatively-charged PAA on the hydrolyzed PAN substrate [149]. It was found that the water/ethanol selectivity, mechanical and thermal properties of the PEC nanohybrid membranes were significantly improved. Clearly, membranes made from organic-inorganic nanohybrids would be a promising strategy to improve the operation stability as well as to overcome the trade-off relationship in pervaporation. A summary on the performance of PEC membranes for pervaporation dehydration is tabulated in Table 10.

**Table 10**

## 5.2 Graphene-based membranes

Since the pioneering work on graphene from Geim and co-workers [212], it has attracted a great attention in various research fields because of its unique mechanical, electrical and thermal properties [213-217]. Its oxidized form, graphene oxide (GO), is even more attractive to researchers owing to its abundant oxygen-containing groups (Figure 16A) [218], which provides a good dispersion of its particles in water and an ability of chemically modifying it. Therefore, a variety of GO applications have been explored such as biosensing [219], photocatalysis [220], electronics and optoelectronics [221] and others. However, graphene/GO based membranes for separation applications is a relatively new topic, especially for their applications in pervaporation.

### Figure 16

Pure GO films can be self-assembled by means of filtration or spin coating without the aid of any chemicals [222-224]. GO films possess exceptionally good mechanical properties and flexibility. Hydrogen-bonding interactions between GO nanosheets enable the films to be highly stable in water once dried. Figure 16 shows some basic characteristics of a GO film assembled via filtration method [225]. GO films can be regarded as a novel type of carbon-based membrane and investigated with respect to its permeability to water and gases [226]. Recently, several researchers have reported the liquid separation properties of GO films [225, 227-231].

Yeh et al. employed a spin coating or vacuum filtration method to assemble a thin GO layer on a thin nanofibrous composite mat [227]. It was found that a 93 nm thick GO membrane had a permeate flux of  $2.2 \text{ kg/m}^2 \text{ h}$  and a separation factor of 308 for dehydration of an 80 wt% ethanol aqueous solution at  $70^\circ \text{C}$ . Hung et al. reported a

highly ordered layer of GO on PAN substrates by the pressure-assisted self-assembly technique [230]. The composite membrane showed high separation performance (flux:  $4.14 \text{ kg/m}^2 \text{ h}$  and separation factor: 1160) for dehydration of a 70 wt% of IPA aqueous solution at  $70^\circ\text{C}$ . These findings revealed that the GO membrane may be a good candidate to be applied in pervaporation due to its hydrophilic nature and decent inter-laminar spacing. Yang et al. reported the use of PDMS-graphene hybrid membranes for the desulfurization process [232]. As compared with the pristine PDMS membrane, the hybrid membranes exhibited a 66% flux enhancement while maintaining the enrichment factor in the separation of n-octane/thiophene. Efforts are needed to study the long-term stability of these GO membranes and to produce them in a larger scale.

## 6. Conclusions and Perspectives

This article summarizes the recent development of pervaporation membranes from the perspectives of membrane materials and membrane fabrication. The material strategies to design new polymers and hybrid materials with various modifications and the fabrication methods such as hollow fiber spinning, solution coating, interfacial polymerization, and LBL deposition to produce pervaporation membranes have been reviewed and discussed.

It has been almost a century since Kober observed the phenomenon of pervaporation. Numerous of researches have been reported on pervaporation membranes, transport mechanisms as well as their applications. Pervaporation is an energy efficient process over the conventional separation methods such as distillation and absorption processes

in separating azeotropic mixtures. However, the industrial adoption of this separation process is still rather limited. This could be due to the lack of stable and economic membrane modules under the industrial operating conditions that require the constant exposure of the membranes to the feed solution containing solvents under a relatively high temperature environment. Therefore, significant efforts must be positioned toward designing and fabricating suitable membranes and membrane modules (i.e., module sealants) that have good chemical and temperature resistance. Using organic-inorganic nanohybrids as membrane materials may be a promising strategy to overcome the bottlenecks in pervaporation. In addition, composite membranes consisting of a protective layer on top of the selective layer may be a promising membrane configuration in the future. The protective layer can shelter the selective layer beneath from direct contact with the feed mixtures and hence, minimizes the swelling effects to the selective layer.

Theoretically, the pervaporation process can be operated at a low feed temperature (i.e., room temperature). However, this operating condition leads to a low partial pressure (i.e., a possible low pressure ratio) in the feed side and a low driving force across the membrane. Hence, a higher vacuum condition (i.e., permeate pressure approaching 0 mbar) is often employed in academic research for pervaporation studies. However, such a high vacuum condition may be too costly and not economically feasible in industrial practices [233]. Since membranes and modules have to be stable under a relatively high operating temperature to maximize the pressure ratio across the membranes, future lab-scale experiments are preferable to be conducted at higher temperatures and weaker vacuum conditions for the separation of non-temperature sensitive components in order to investigate the true membrane

performance close to industrial conditions. Besides, the integration of distillation-membrane separation process can be simulated by conducting the vapor permeation experiments, which uses high-temperature pressurized vapor as the feed for the separation process.

To date, the application of pervaporation process in solvent dehydration remains as the most established and widely studied topic. The quest in exploring next-generation dehydration membranes should be focused on enhancing the permeability/permeance of the membrane while maintaining a satisfactory selectivity. This is because the high permeability/permeance membranes have the potential of reducing the membrane area needed to separation a similar capacity of feed mixture. On the other hand, the development of pervaporation membranes in recovery of organics and organic-organic separations is rather limited. More efforts should be focused on improving the selectivity and stability of the membranes in these applications, which have huge prospects in chemical, petrochemical, food and beverage industries.

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- Figure 1 Schematic of the vacuum pervaporation process.
- Figure 2 Graphical representation of the solution diffusion mechanism.
- Figure 3 Schematic procedure of TFC membranes formation via interfacial polymerization.
- Figure 4 The chemical structures and trade names of the perfluoropolymers. [65], Copyright 2013. Reproduced with permission from the American Chemical Society.
- Figure 5 The chemical structures of PBI, PBO and PBOZ.
- Figure 6 The interaction between PBI and Matrimid. [73], Copyright 2006. Reproduced with permission from Elsevier Ltd.
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- Figure 8 Crosslinking mechanisms of carboxylic-containing polymer chains via thermal treatment and esterification reaction [85], Copyright 2012. Reproduced with permission from Elsevier Ltd.
- Figure 9 Hydrophobic polymers applied in recovery of organics via pervaporation process.
- Figure 10 Major applications of pervaporation process in organic-organic separation. [3], Copyright 2004. Reproduced with permission from Elsevier Ltd.
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- Figure 13 Silylation mechanism of the silicalite-1 particle.
- Figure 14 Fabrication procedure of silicalite-1/PDMS nanocomposite membranes by the packing-filling method.
- Figure 15 Synthesis of polyphosphazene nanotubes.
- Figure 16 (A) The Lerf-Klinowski Model of the GO nanosheet structure; (B) Photo of a 10- $\mu\text{m}$ -thick GO film; (C) FESEM morphology of the layered structure of the GO film; (D) X-ray diffraction spectrum of the GO film.

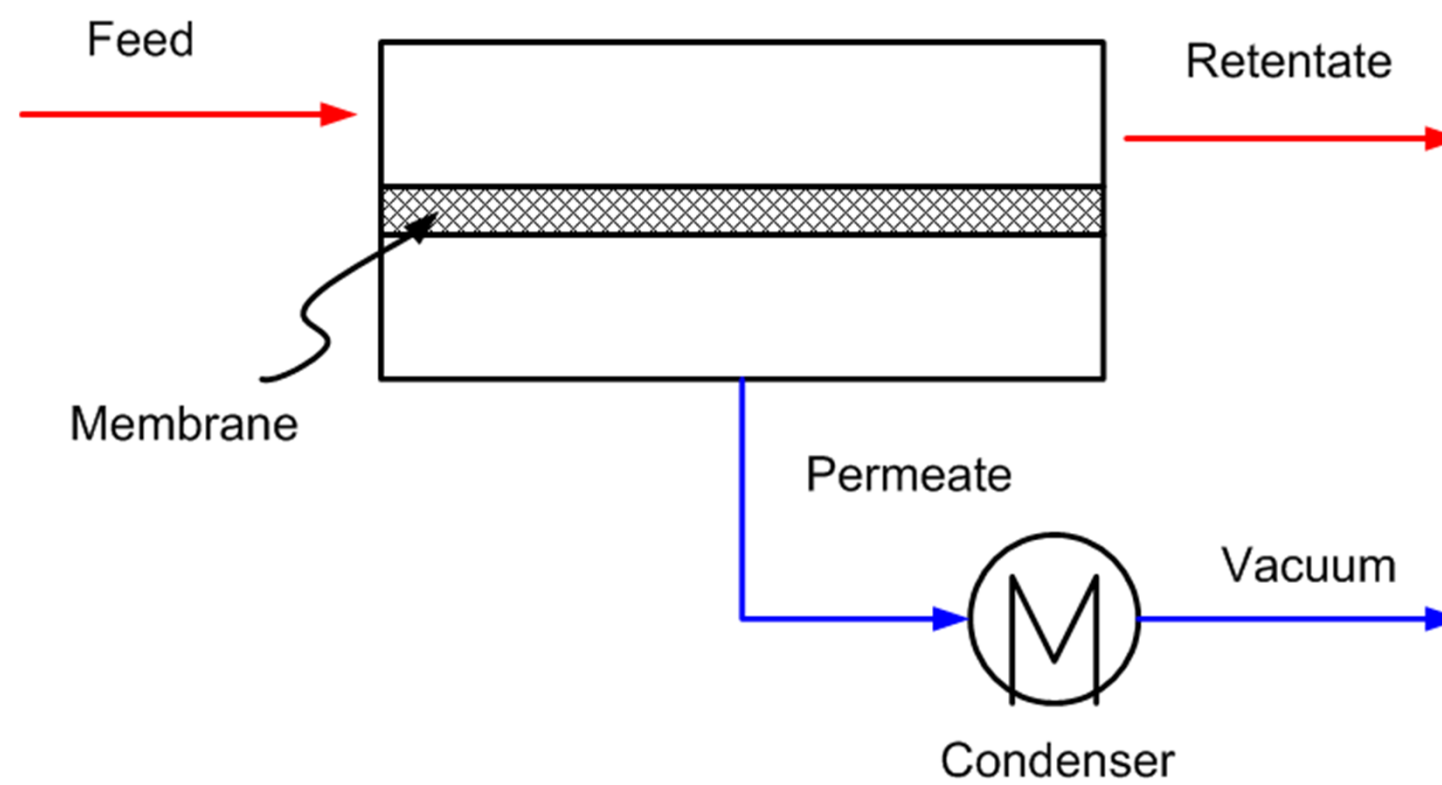
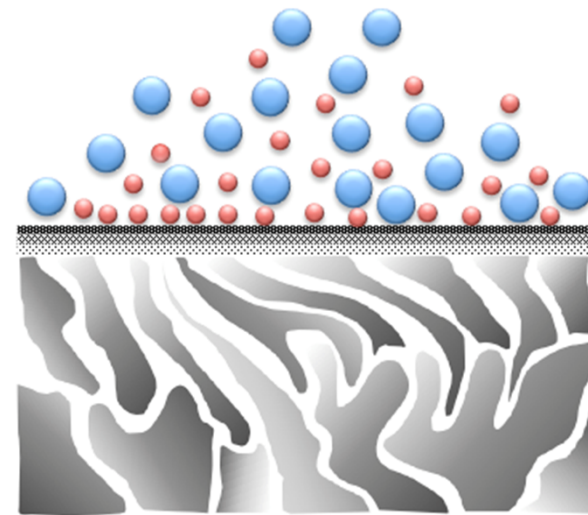
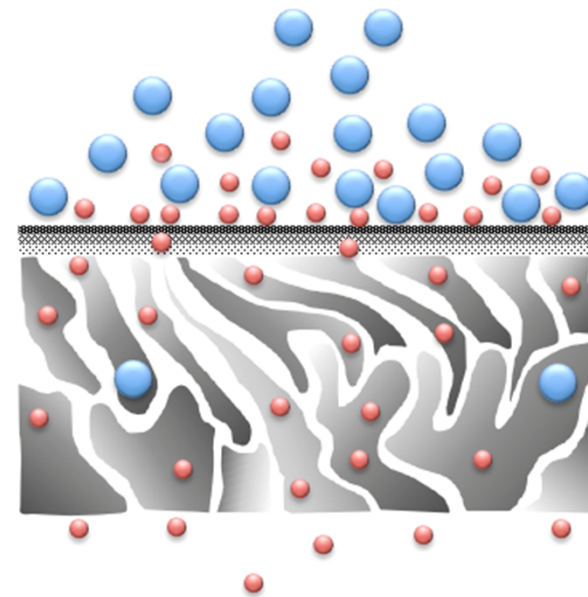


Figure 1.



(i) Sorption



(ii) Diffusion

(iii) Desorption

Figure 2.

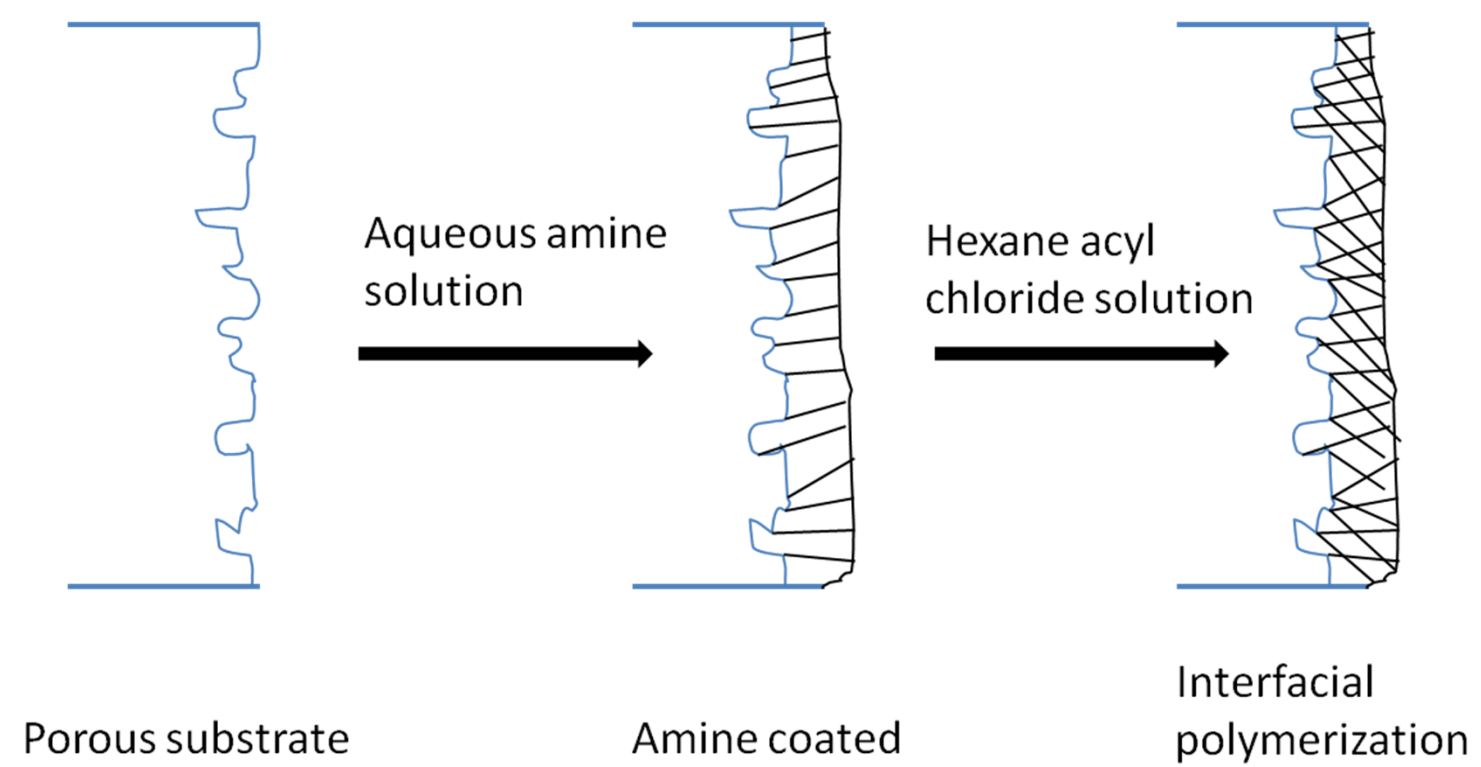
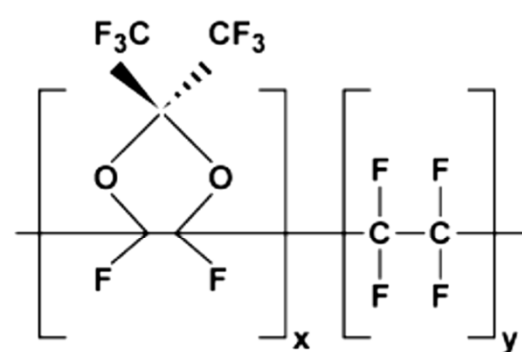
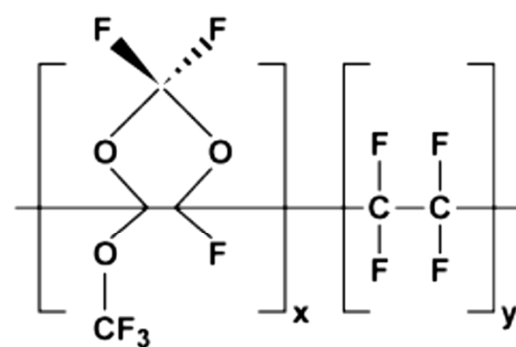


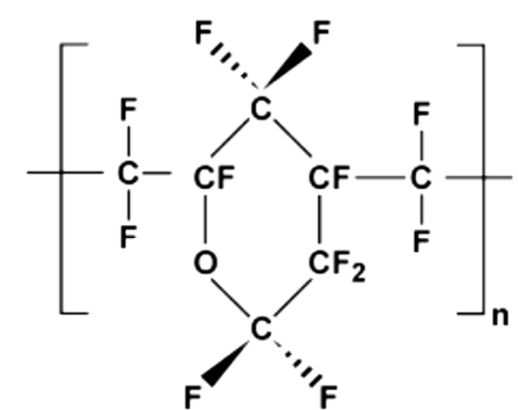
Figure 3



Teflon<sup>®</sup> AF (DuPont, USA)



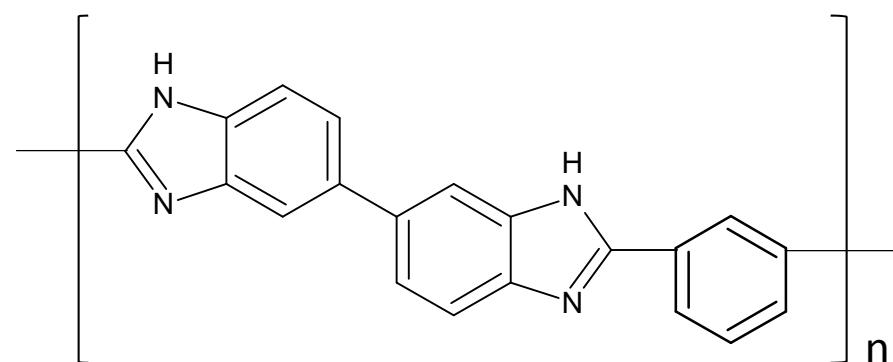
Hyflon<sup>®</sup> AD (Ausimont, Italy)



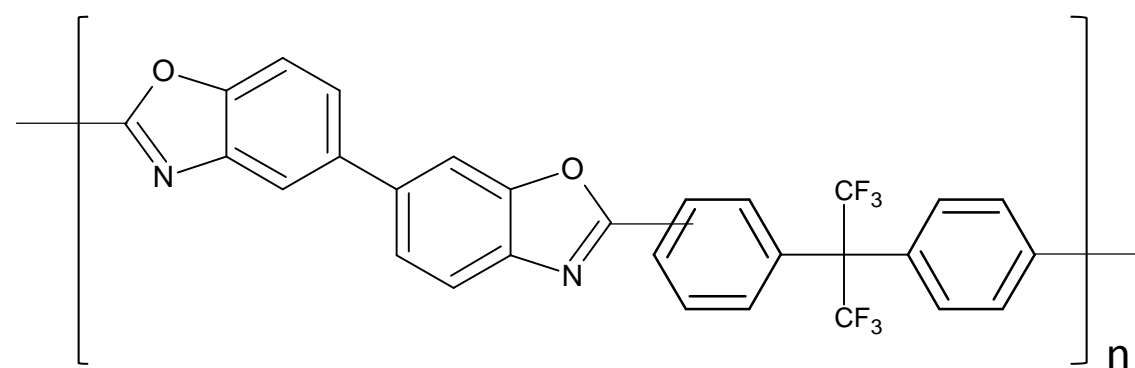
Cytop<sup>™</sup> (Asahi Glass, Japan)

Figure 4

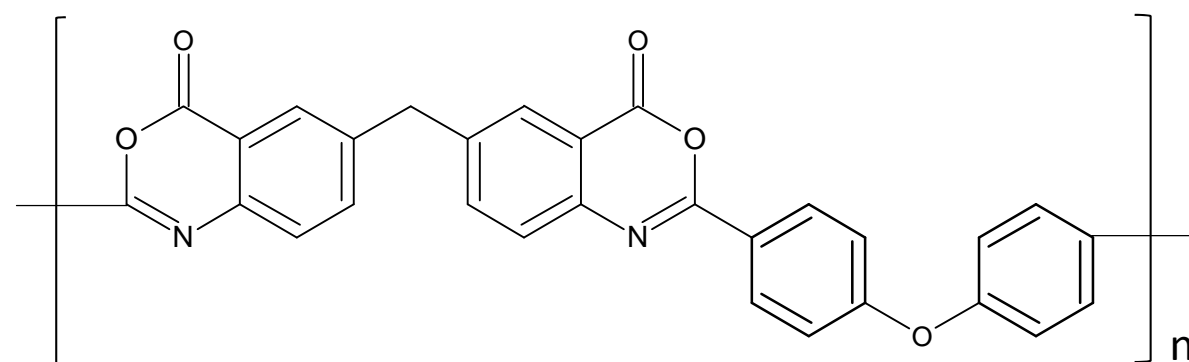




Polybenzimidazole (PBI)



Polybenzoxazole (PBO)



Polybenzoxazinone (PBOZ)

Figure 5.

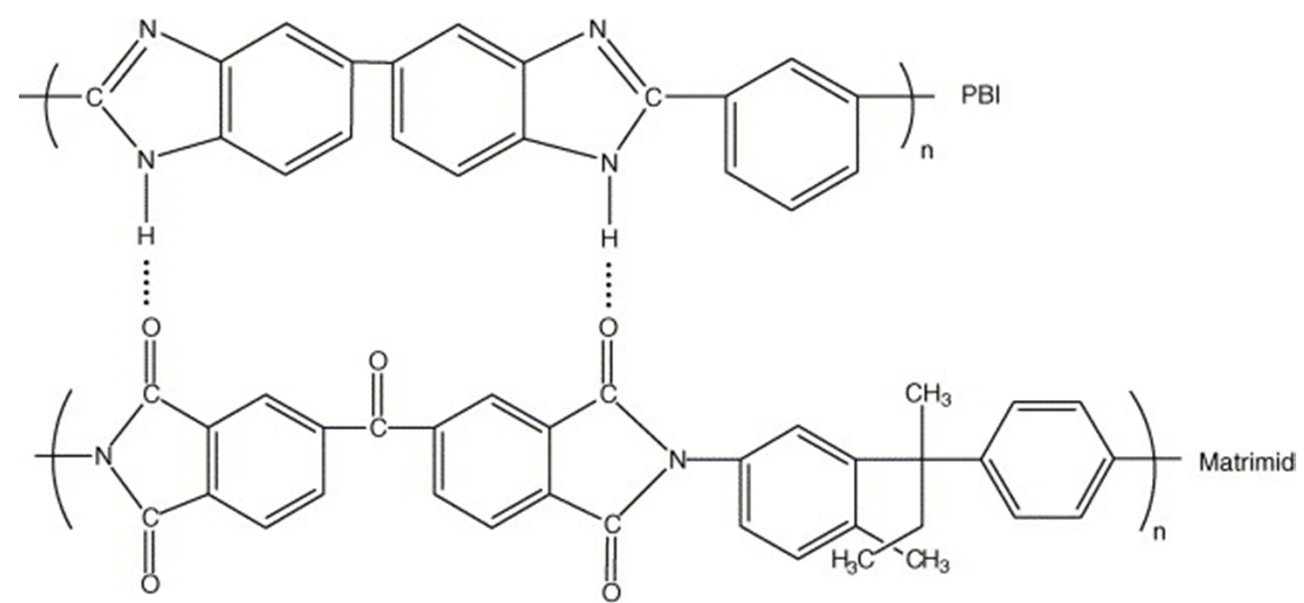


Figure 6

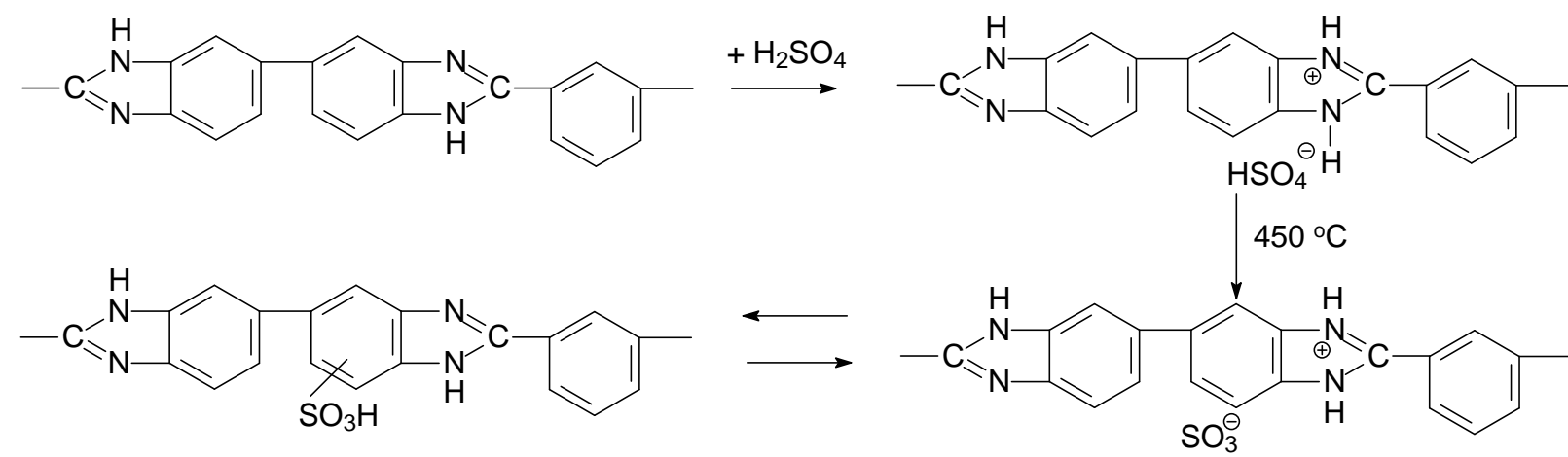


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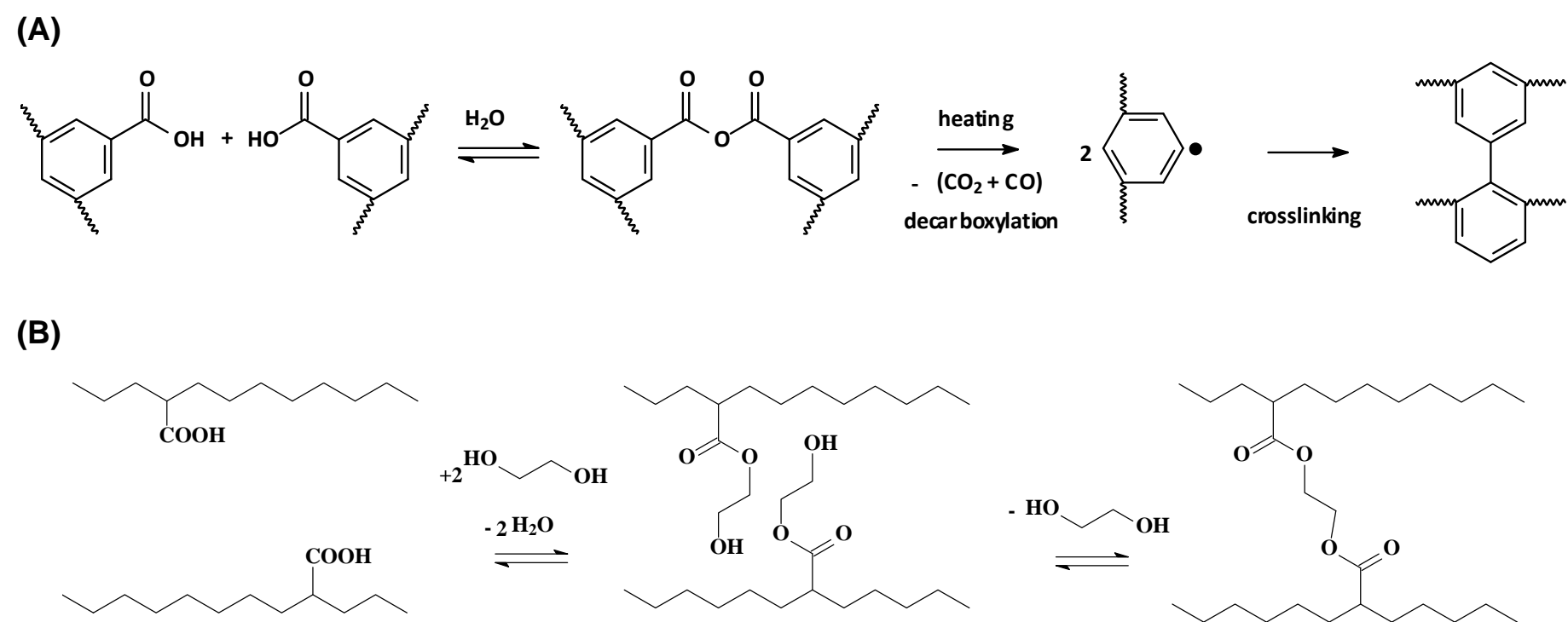
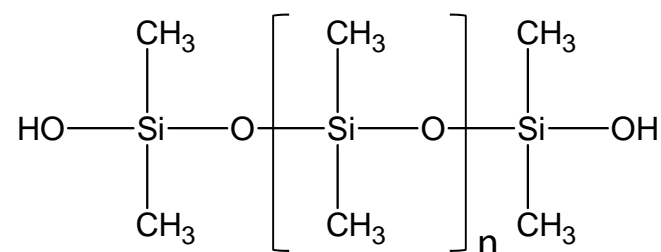
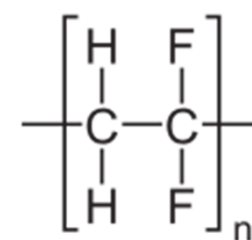


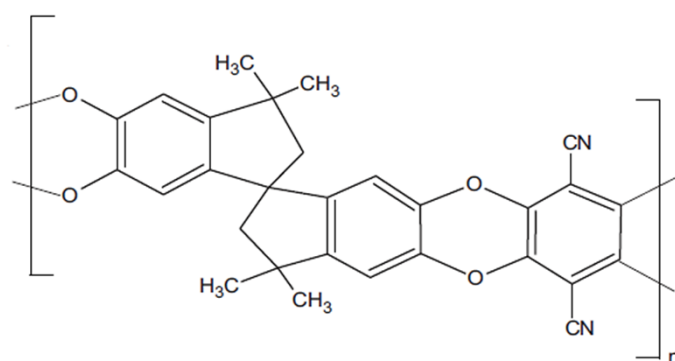
Figure 8



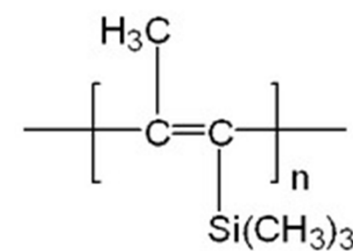
Polydimethylsiloxane (PDMS)



Polyvinylidene fluoride (PVDF)



Polymer of intrinsic microporosity-1 (PIM-1)



Poly(1-trimethylsilyl-1-propyne) (PTMSP)

Figure 9

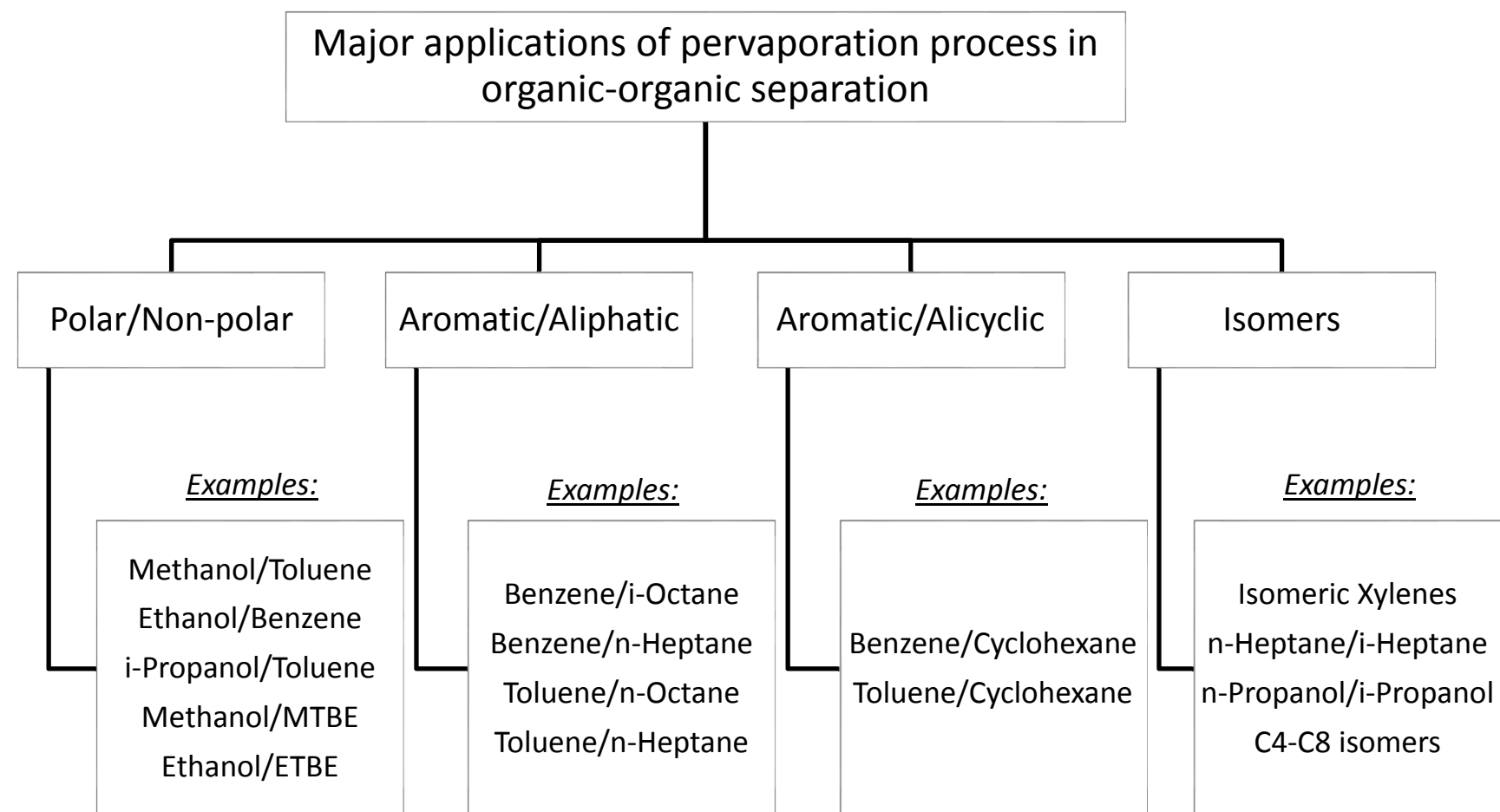
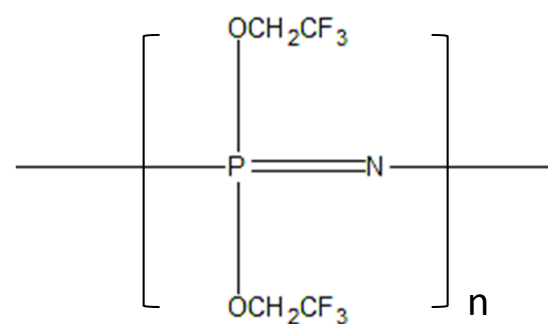
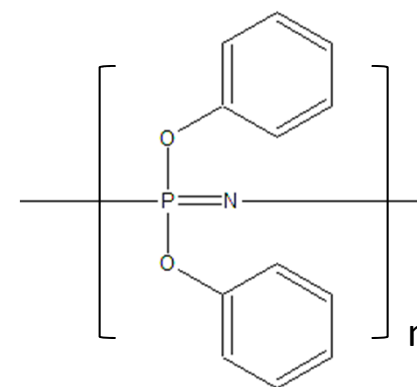


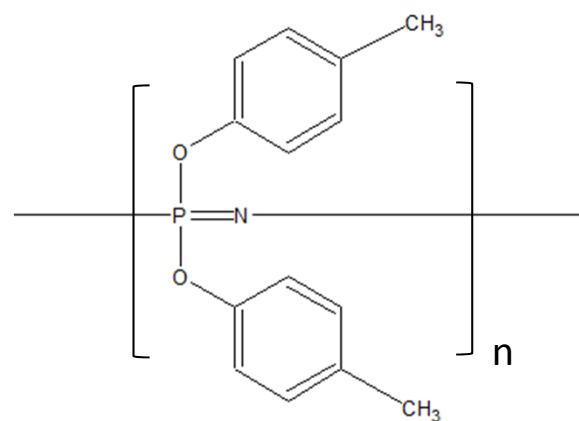
Figure 10]



Poly[bis(trifluoroethoxy) phosphazene]  
(PTFEP)



Poly[bis(phenoxy)phosphazene]  
(PBPP)



Poly[bis(p-methyl phenyl) phosphazene]  
(PMePP)

Figure 11

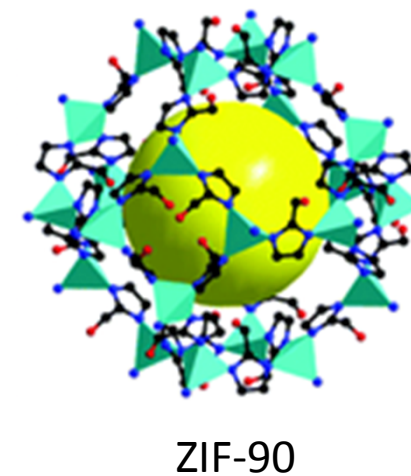
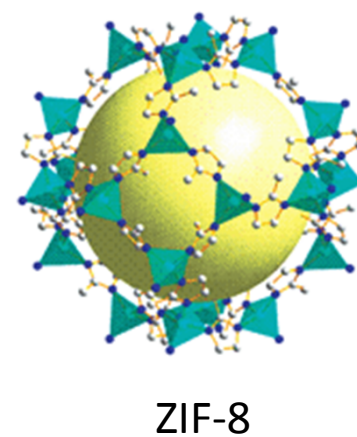
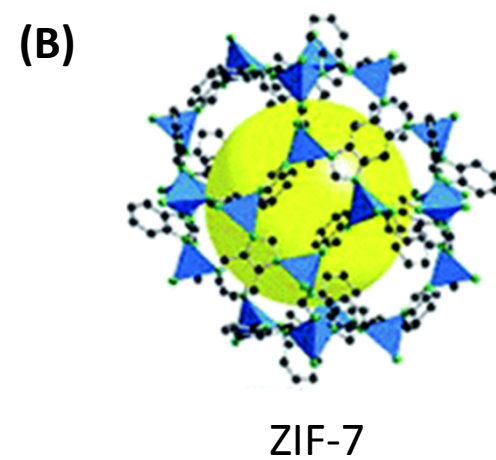
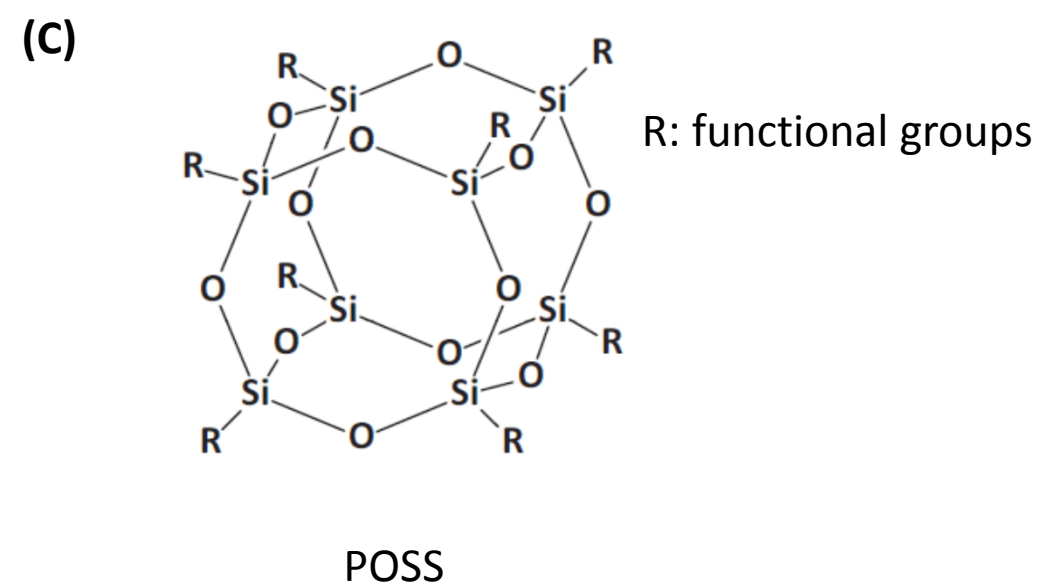
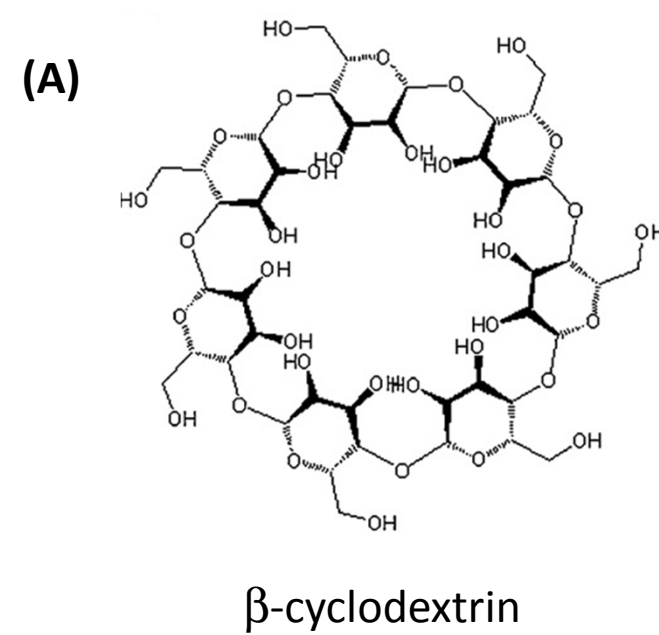


Figure 12.



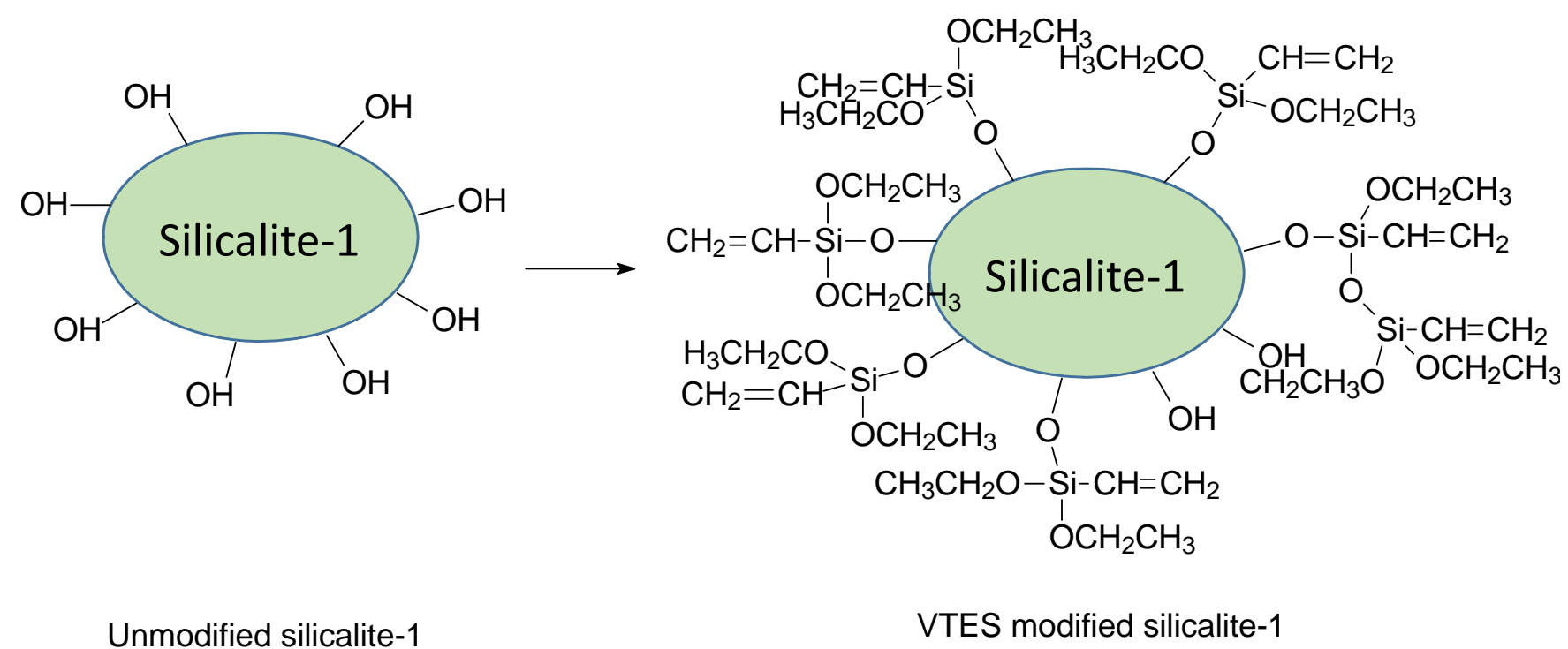
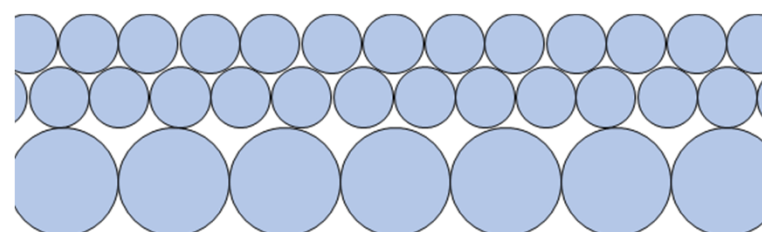
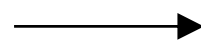


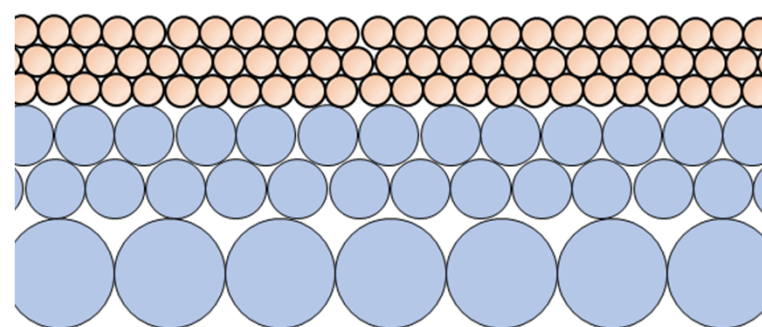
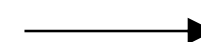
Figure 13

Porous alumina



Packing

Silicalite-1 layer



Filling

Mixed matrix layer

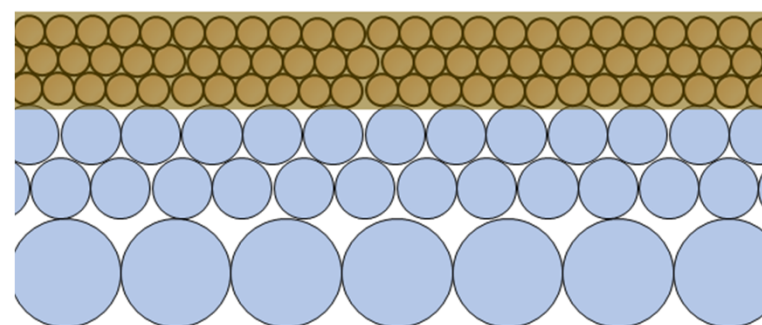
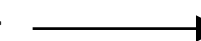


Figure 14

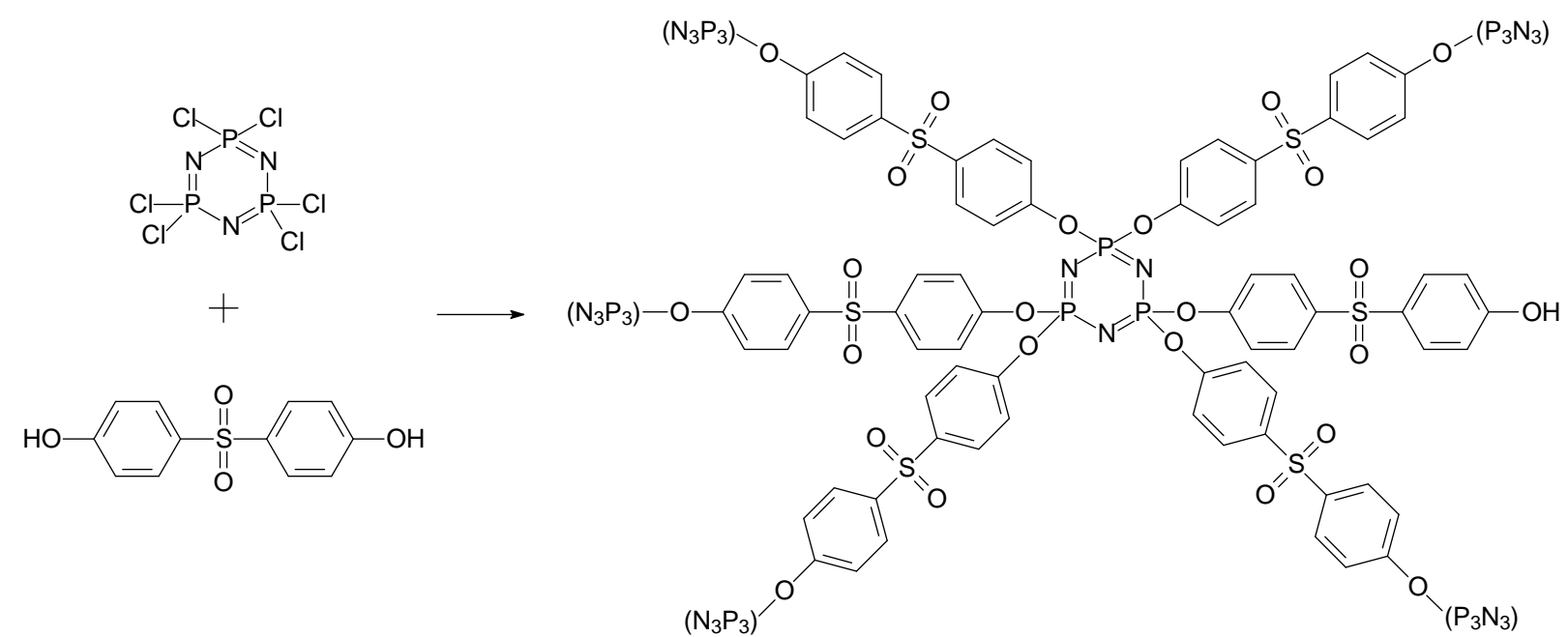


Figure 15

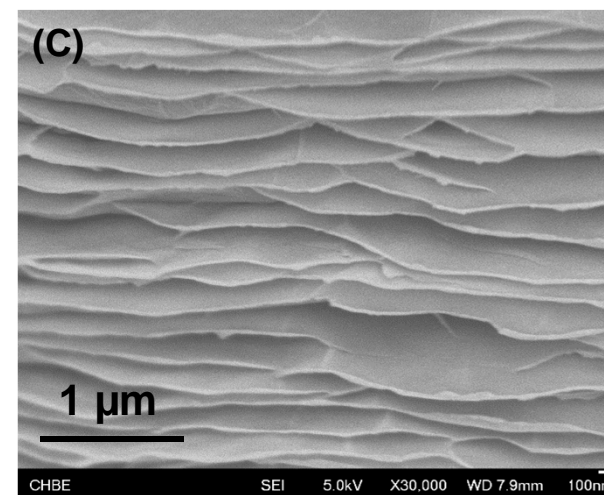
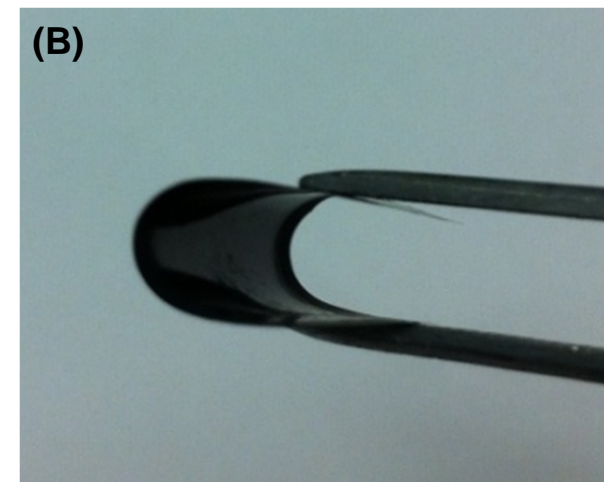
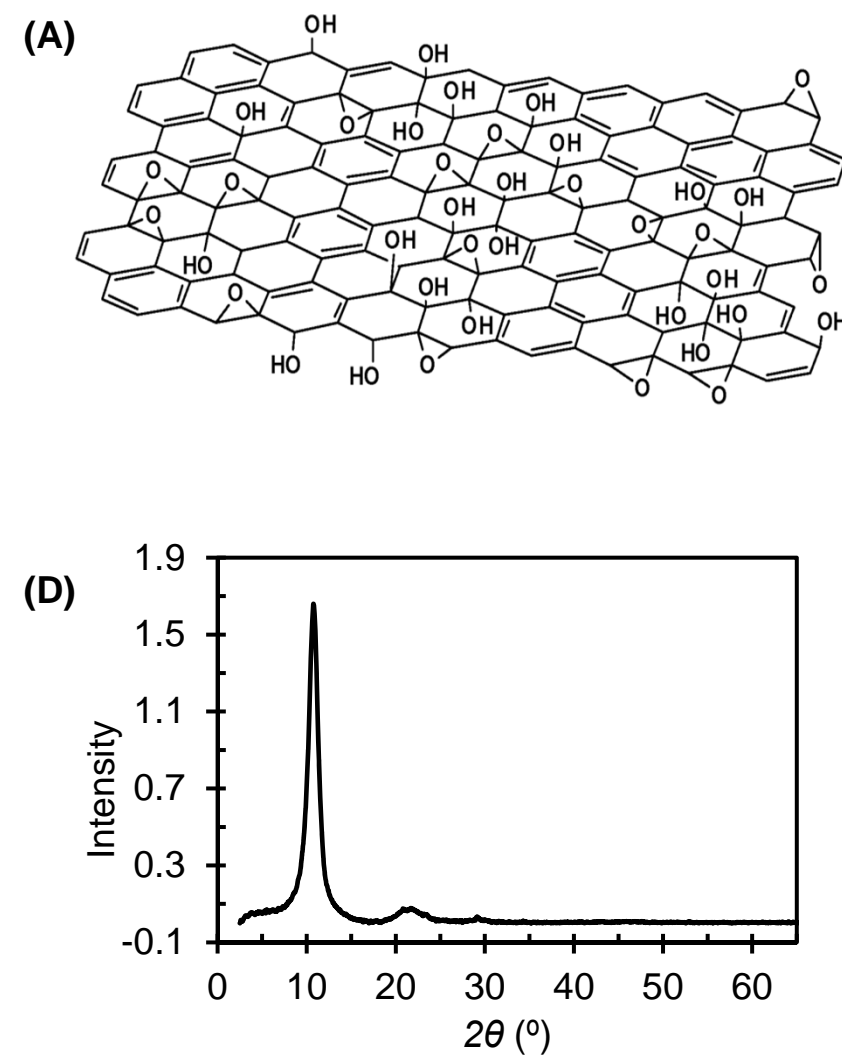


Figure 16.

Table 1. Polymeric membranes for dehydration of organics.

Feed mixture (mass ratio)	Membrane	Configuration	Temperature (°C)	Flux (g/m <sup>2</sup> h)	Separation factor (water/organic)	Reference
EtOH/H <sub>2</sub> O (90/10)	Pervap® 2201	Flat-sheet	60	~100	~100	[60]
IPA/H <sub>2</sub> O (85/15)	Pervap® 2201	Flat-sheet	60	~220	~400	[60]
EtOH/H <sub>2</sub> O (98.7/1.3)	Perfluoropolymer coated on PAN (CMS-3)	Flat-sheet	50	1650	387	[62]
IPA/H <sub>2</sub> O (98.7/1.3)	Perfluoropolymer coated on PAN (CMS-3)	Flat-sheet	22	50	500	[62]
DMAc/H <sub>2</sub> O (90/10)	Perfluoropolymer membrane (CMS-3)	Flat-sheet	60	~8	~1000	[64]
DMF/H <sub>2</sub> O (90/10)	Perfluoropolymer membrane (CMS-3)	Flat-sheet	60	~60	>5000	[64]
DMSO/H <sub>2</sub> O (90/10)	Perfluoropolymer membrane (CMS-3)	Flat-sheet	60	~9	~1000	[64]
EtOH/H <sub>2</sub> O (85/15)	Polybenzoxazole (PBO)	Flat-sheet	22	82	85	[9]
IPA/H <sub>2</sub> O (90/10)	Polybenzoxazole (PBO)	Flat-sheet	80	135	140	[9]
IPA/H <sub>2</sub> O (90/10)	Polybenzoxazinone (PBOZ)	Flat-sheet	50	3	5000	[67]
TFP/H <sub>2</sub> O (85/15)	Polybenzimidazole (PBI) on P84 support	Hollow fiber	60	332	1990	[69]
EG/H <sub>2</sub> O (64/36)	Polybenzimidazole (PBI) on polyetherimide support	Hollow fiber	60	758	592	[70]
Acetone/ H <sub>2</sub> O (85/15) Abbreviations: N,N-dimethylacetamide: DMAc; N,N-dimethylformamide: DMF; N,N-dimethylsulfoxide: DMSO; Ethylene glycol: EG; Ethanol: EtOH; Isopropanol: IPA; Tetrafluoropropanol: TFP;	Polybenzimidazole (PBI) on P84 support cross-linked with p-xylene dichloride followed by thermal treatment at 250 °C	Hollow fiber	50	300	490	[72]
IPA/H <sub>2</sub> O (70/30)	Chitosan modified	Flat-sheet	70	~250	~102	[74]

Table 2. Polymeric membranes with various modification for dehydration of organics.

Feed mixture (mass ratio)	Membrane	Modification methods	Configuration	Temperature (°C)	Flux (g/m <sup>2</sup> h)	Separation factor (water/organic)	Reference
Acetic acid/H <sub>2</sub> O (90/10)	Cardo polyetherketone (PEK-C)	Sulfonation (Sulfonation degree: 0.75)	Flat-sheet	50	248	103	[76]
EtOH/H <sub>2</sub> O (90/10)	Polysulfone	Sulfonation (Sulfonation degree: 0.92)	Flat-sheet	25	~600	~98	[77]
IPA/H <sub>2</sub> O (90/10)	Poly(vinyl alcohol)	Crosslink/graft with 15 wt% of sulfophthalic acid (SPTA)	Flat-sheet	40	35	3452	[78]
Acetic acid/H <sub>2</sub> O (50/50)	Polybenzimidazole (PBI)	Sulfonation with 2.5 wt% sulphuric acid solution followed by a thermal treatment at 450 ° C for 30 s	Flat-sheet	60	207	5461	[79]
MeOH/H <sub>2</sub> O (85/15)	Polyphenylsulfone (PPSU)	Sulfonation (copolymerization with 5 mol% 3,3'-disulfonate-4,4'-dichlorodiphenyl sulfone (sDCDPS) monomer)	Flat-sheet	60	33	11	[80]
IPA/H <sub>2</sub> O (80/20)	Poly(vinyl alcohol)	Crosslinked with trimesoyl chloride	Flat-sheet	60	320	~400	[83]
EG/H <sub>2</sub> O (90/10)	Poly(vinyl alcohol)	Crosslinked with trimesoyl chloride	Flat-sheet	25	~100	> 1000	[84]
EtOH/H <sub>2</sub> O (85/15)	6FDA-NDA/DABA co-polyimide (NDA/DABA: 9/1)	Thermally crosslinked at 425 ° C, 30 min	Flat-sheet	25	133	119	[85]
EtOH/H <sub>2</sub> O (85/15)	6FDA-NDA/DABA co-polyimide (NDA/DABA: 9/1)	Crosslinked with p-xylenediamine and treated at 200 ° C	Flat-sheet	25	51	632	[85]
EtOH/H <sub>2</sub> O (85/15)	6FDA-NDA/DABA co-polyimide (NDA/DABA: 9/1)	Crosslinked with 1,4-benzenedimethanol at 300 ° C	Flat-sheet	25	183	33	[85]
EtOH/H <sub>2</sub> O (85/15)	Chitosan/polyvinylpyrrolidone polymer blend (91/9 wt%)	UV-crosslinked ( $\lambda_{\text{max}}$ : 254 nm, distance: 15 cm, time: 4 min)	Flat-sheet	50	~900	~170	[86]
Acetone/H <sub>2</sub> O (85/15)	P84® co-polyimide	Crosslinked with ethylenediamine vapor	Flat-sheet	50	~1800	~54	[88]

Abbreviations:

Ethylene glycol: EG; Ethanol: EtOH; Isopropanol: IPA; Methanol: MeOH

Table 3. A list of typical monomers in both aqueous and organic phases for the interfacial polymerization.

Aqueous Phase Monomers	Organic Phase Monomers
<div data-bbox="342 378 537 613"> </div> <div data-bbox="373 667 470 708">MPD</div> <div data-bbox="690 378 884 625"> </div> <div data-bbox="680 667 827 708">MPDSA</div> <div data-bbox="348 797 863 911"> </div> <div data-bbox="562 940 659 980">TETA</div> <div data-bbox="243 1081 972 1352"> </div> <div data-bbox="573 1386 663 1427">HPEI</div>	<div data-bbox="1115 558 1371 764"> </div> <div data-bbox="1203 808 1308 849">NTAC</div> <div data-bbox="1518 542 1774 773"> </div> <div data-bbox="1612 813 1707 854">TMC</div> <div data-bbox="1121 972 1386 1187"> </div> <div data-bbox="1209 1211 1314 1252">TBAC</div> <div data-bbox="1499 984 1797 1182"> </div> <div data-bbox="1612 1211 1682 1252">TDI</div>

Table 4. TFC membranes for dehydration of organics

Feed mixture (mass ratio)	Active layer	Support	Configuration	Temperature (°C)	Flux (g/m <sup>2</sup> h)	Separation factor (water/organic)	Reference
EtOH/H <sub>2</sub> O (90/10)	TETA-NTAC	Modified polyacrylonitrile (PAN)	Flat-sheet	25	537	491	[43]
EtOH/H <sub>2</sub> O (90/10)	TETA-TBAC	Modified polyacrylonitrile (PAN)	Flat-sheet	25	452	301	[43]
EtOH/H <sub>2</sub> O (90/10)	TETA-TMC	Modified polyacrylonitrile (PAN)	Flat-sheet	25	1151	1491	[94]
IPA/H <sub>2</sub> O (90/10)	TETA-TMC	Modified polyacrylonitrile (PAN)	Flat-sheet	25	370	~171	[94]
EtOH/H <sub>2</sub> O (90/10)	<i>m</i> -tolidine-H-TMC	Modified polyacrylonitrile (PAN)	Flat-sheet	25	2191	1791	[98]
IPA/H <sub>2</sub> O (90/10)	MPD-TMC	Modified polyacrylonitrile (PAN)	Flat-sheet	25	181	22	[91]
IPA/H <sub>2</sub> O (90/10)	EDA-TMC	Modified polyacrylonitrile (PAN)	Flat-sheet	25	213	105	[92]
IPA/H <sub>2</sub> O (70/30)	MPDSA-TMC	Modified polyacrylonitrile (PAN)	Flat-sheet	25	1669	775	[95]
IPA/H <sub>2</sub> O (90/10)	CPA5 commercial RO membrane	A polysulfone and a polyethylene terephthalate layer	Flat-sheet	16	140	40	[99]
EtOH/H <sub>2</sub> O (85/15)	MPD-TMC	Polyvinylidene fluoride	Hollow fiber	50	1288	40	[100]
EtOH/H <sub>2</sub> O (85/15)	TDI cross-linked MPD-TMC	Ultem®	Hollow fiber	50	2000	130	[101]
EtOH/H <sub>2</sub> O (85/15)	TDI cross-linked MPD-TMC	Ultem®	Hollow fiber	80	6800	61	[101]
EtOH/H <sub>2</sub> O (85/15)	MPD-TMC-silicone coating	Polyethersulfone	Hollow fiber	50	7501	60	[102]
IPA/H <sub>2</sub> O (85/15)	HPEI-TMC	Torlon®	Hollow fiber	50	1282	624	[96]
IPA/H <sub>2</sub> O (85/15)	HPEI-TMC with post treatment	Torlon®	Hollow fiber	50	1980	349	[96]
IPA/H <sub>2</sub> O (85/15)	MPD-TMC	α-alumina	Hollow fiber	80	6050	1396	[97]

## Abbreviations:

Ethylene glycol: EG; Ethanol: EtOH; Ethylenediamine: EDA; Hyperbranched polyethyleneimine: HPEI; Isopropanol: IPA; *m*-phenylenediamine: MPD; sulfonated MPD: MPDSA; 2,2'-dimethylbenzidine hydrochloride: *m*-tolidine-H; 5-Nitrobenzene-1,3-dioyl dichloride: NTAC; 5-tertbutylbenzene-1,3-dioyl dichloride: TBAC; toluene 2,4-diisocyanate: TDI; Triethylenetetraamine: TETA; Trimesoyl chloride: TMC



Table 5. Polymeric membranes for recovery of organics

Feed mixture (mass ratio)	Membrane	Configuration	Temperature (°C)	Flux (g/m <sup>2</sup> h)	Separation factor (organic/water)	Reference
EtOH/H <sub>2</sub> O (5/95)	Polydimethylsiloxane (PDMS)	-	20-90	-	9-10	[7]
EtOH/H <sub>2</sub> O (4/96)	Polydimethylsiloxane (PDMS) on polyamide support	Flat-sheet	45	1850	8.5	[25]
BuOH/H <sub>2</sub> O (1/99)	Polydimethylsiloxane (PDMS) on macroporous ceramic support	Hollow fiber	40	1282	43	[122]
BuOH/H <sub>2</sub> O (1/99)	Poly(1-trimethylsilyl-1- propyne) (PTMSP) on cellophane	Flat-sheet	70	~1000	70	[111]
EtOH/H <sub>2</sub> O (10/90)	Poly(1-trimethylsilyl-1- propyne) (PTMSP)	Flat-sheet	50	~800	~17	[113]
EtOH/H <sub>2</sub> O (5/95)	Poly(vinylidene fluoride) (PVDF)	Hollow fiber	50	3500-8800	5-8	[109]
EtOH/H <sub>2</sub> O (10/90)	Polymer of intrinsic microporosity-1 (PIM-1)	Flat-sheet	60	1400	9	[117]
n-BuOH/H <sub>2</sub> O (1/99)	Poly ether block amide (PEBA)	Flat-sheet	50	278	20*	[106]
t-BuOH/H <sub>2</sub> O (1/99)	Poly ether block amide (PEBA)	Flat-sheet	50	199	6*	[106]
Phenol/H <sub>2</sub> O (0.0001/99.9999)	Poly ether block amide (PEBA)	Flat-sheet	50	526	31*	[48]

\* Result reflects the enrichment factor of the membrane

Abbreviations:

n-Butanol: BuOH; Ethanol: EtOH

Table 6. Polymeric membranes for organic-organic separations.

Feed mixture (A/B)	Membrane	Configuration	Temperature (°C)	Flux (g/m <sup>2</sup> h)	Separation factor (B/A)	Reference
ETBE/EtOH (80/20 wt%)	Cellulose acetate-g-poly(MDEGMA) (short graft)	Flat-sheet	50	55	91	[125]
MTBE/MeOH (97/3 wt%)	Modified poly(ether ether ketone) (mPEEK)	Flat-sheet	50	~98	~30	[127]
MTBE/MeOH (85/15 wt%)	Fluorene-containing poly(arylene ether sulfone) block co-polymer	Flat-sheet	40	334	287	[133]
Toluene/Heptane (40/60 wt%)	Polybenzoxazole (Est. thickness: 20 µm)	Flat-sheet	80	~70	3.7	[128]
Heptane/Thiophene (Sulfur content 500 ppm)	Poly[bis(trifluoroethoxy) phosphazene] (PTFEP)	Flat-sheet	80	~42	~11.5	[130]
Heptane/Thiophene (Sulfur content 400 ppm)	Poly[bis(phenoxy)phosphazene] (PBPP)	Flat-sheet	85	~400	~7.5	[130]
Heptane/Thiophene (Sulfur content 400 ppm)	Poly[bis(p-methyl phenyl) phosphazene] (PMePP)	Flat-sheet	85	~3500	~4.5	[132]
Heptane/Thiophene (Sulfur content 1000 ppm)	Poly ether block amide (PEBAX 2533)	Flat-sheet	40	3800	4 (sulfur/heptane)	[133]

Abbreviations:

Ethanol: EtOH; Ethyl tert-butyl ether: ETBE; Methanol:MeOH; Methyl tert-butyl ether: MTBE

Table 7. Mixed matrix membranes (MMMs) for dehydration of organics.

Feed mixture (mass ratio)	Membrane	Particle/ Hybrid component loading (wt%)	Configuration	Temperature (°C)	Flux (g/m <sup>2</sup> h)	Separation factor (water/organic)	Reference
EtOH/H <sub>2</sub> O (95/5)	PVA/NR/zeolite 4A (crosslinked with sulfosuccinic- acid)	40	Flat-sheet	30	3600	300	[139]
EtOH/H <sub>2</sub> O (90/0)	NaAlg/zeolite 4A (crosslinked with glutaraldehyde)	10	Flat-sheet	30	138	1334	[140]
IPA/H <sub>2</sub> O (90/10)	P84®/aerosil silica	10	Flat-sheet	30	121	80	[142]
IPA/H <sub>2</sub> O (90/10)	P84®/zeolite 4A	5	Flat-sheet	30	125	220	[142]
IPA/H <sub>2</sub> O (90/10)	Matrimid®/ zeolite 4A	10	Flat-sheet	30	159	890	[142]
IPA/H <sub>2</sub> O (82.5/17.5)	NaCMC/PVA/zeolite 13X (crosslinked with glutaraldehyde)	20	Flat-sheet	35	408	1852	[143]
IPA/H <sub>2</sub> O (82/18)	Matrimid®/MgO	50	Flat-sheet	100	630	700	[171]
1,4-dioxane/H <sub>2</sub> O (80/20)	NaAlg/polyaniline-coated TiO <sub>2</sub> (crosslinked with glutaraldehyde)	0.25	Flat-sheet	30	92	972	[156]
1,4-dioxane/H <sub>2</sub> O (80/20)	PVA/zeolite T (crosslinked with glutaraldehyde)	15	Flat-sheet	30	213	1689	[173]
Acetic acid/H <sub>2</sub> O (90/10)	NaAlg/ zeolite 4A (crosslinked with glutaraldehyde)	10	Flat-sheet	30	188	991	[140]
Acetic acid/H <sub>2</sub> O (99.5/0.5)	Poly(acrylonitrile butyl acrylate (PANBA)/montmorillonite	3	Flat-sheet	30	3970	1292	[177]
EG/ H <sub>2</sub> O (80/20)	PVA/zeolite 4A	5	Flat-sheet	70	2800	~2000	[178]
Acetonitrile/H <sub>2</sub> O (80/20)	PVA/iron oxide	10	Flat-sheet	45	102	38.4	[176]
IPA/H <sub>2</sub> O (86/14)	Matrimid®/β-CD	10	Flat-sheet	22	52	>5000	[172]
EtOH/H <sub>2</sub> O (90/10)	PVA/MWCNT	1	Flat-sheet	60	100	280	[145]
EtOH/H <sub>2</sub> O (90/10)	Chitosan (CS)/ZIF-7	2.5	Flat-sheet	25	1206	538	[169]

Cont.

Table 7 Cont.

Feed mixture (mass ratio)	Membrane	Particle/ Hybrid component loading (wt%)	Configuration	Temperature (°C)	Flux (g/m <sup>2</sup> h)	Separation factor (water/organic)	Reference
EtOH/H <sub>2</sub> O (85/15)	Polybenzimidazole (PBI)/ZIF-8	58.7	Flat-sheet	60	992	10	[167]
IPA/H <sub>2</sub> O (85/15)	Polybenzimidazole (PBI)/ZIF-8	58.7	Flat-sheet	60	246	310	[167]
BuOH/H <sub>2</sub> O (85/15)	Polybenzimidazole (PBI)/ZIF-8	58.7	Flat-sheet	60	226	698	[167]
IPA/H <sub>2</sub> O (85/15)	P84 <sup>®</sup> /ZIF-90/ sulfonated polyethersulfone	30	Flat-sheet	60	109	>5000	[164]
EtOH/H <sub>2</sub> O (90/10)	CS/OA POSS	5	Flat-sheet	30	28	310	[161]
EtOH/H <sub>2</sub> O (90/10)	CS/OAS POSS	5	Flat-sheet	30	37	200	[161]
EtOH/H <sub>2</sub> O (90/10)	CS/ONPS POSS	5	Flat-sheet	30	41	130	[161]
EtOH/H <sub>2</sub> O (90/10)	CS/OAPS POSS	5	Flat-sheet	30	30	370	[161]
EtOH/H <sub>2</sub> O (90/10)	Ultem <sup>®</sup> /polyimide/POSS	2	Hollow fiber	60	1800	160	[163]

Abbreviations:

n-Butanol: BuOH; Ethylene glycol: EG; Ethanol: EtOH; Isopropanol: IPA;

Table 8. Mixed matrix membranes (MMMs) for recovery of organics.

Feed mixture (mass ratio)	Membrane	Particle/ Hybrid component loading (wt%)	Configuration	Temperature (°C)	Flux (g/m <sup>2</sup> h)	Separation factor (organic/water)	Reference
EtOH/H <sub>2</sub> O (5/95)	PDMS/HF etched ZSM-5	30	Flat-sheet	50	125	17	[144]
EtOH/H <sub>2</sub> O (5/95)	Pebax/silicalite	2	Flat-sheet	40	833	3.6	[179]
BuOH/H <sub>2</sub> O (0.05/99.95)	PDMS/silicalite	N.A	Flat-sheet	45	240	36	[180]
EtOH/H <sub>2</sub> O (5.3/94.7)	PDMS/VTES modified silicalite	67	Flat-sheet	50	87	33	[157]
EtOH/H <sub>2</sub> O (5/95)	PTMSP/silica	25	Flat-sheet	50	9500	18.3	[181]
BuOH/H <sub>2</sub> O (5/95)	PTMSP/silica	25	Flat-sheet	50	9500	104	[181]
EtOH/H <sub>2</sub> O (5/95)	Pebax/POSS	2	Flat-sheet	65	427	5.7	[162]
BuOH/H <sub>2</sub> O (1/99)	Pebax/ZIF-71	25	Flat-sheet	40	60	22.1	[182]
Isopropyl acetate / H <sub>2</sub> O (0.39/9.61)	polyurethaneurea/ZSM-5	20	Flat-sheet	60	289	53	[183]
Fufural/H <sub>2</sub> O (1/99)	PDMS/ZIF-8	75.8	Flat-sheet	80	900	53.3	[168]

Abbreviations:

n-Butanol: BuOH; Ethanol: EtOH;

Table 9. Mixed matrix membranes (MMMs) for organic-organic separation.

Feed mixture (A/B)	Membrane	Particle/ Hybrid component loading (wt%)	Configuration	Temperature (°C)	Flux (g/m <sup>2</sup> h)	Separation factor (B/A)	Reference
Cyclohexane/ benzene (60/40 wt%)	Polyvinylchloride /H- $\beta$ -zeolite	10	Flat-sheet	30	11.5	19.3	[184]
Cyclohexane/ benzene (60/40 wt%)	Polyvinylchloride /Rh/H- $\beta$ -zeolite	10	Flat-sheet	30	18.5	17	[184]
EtOH/toluene (90/10 wt%)	CS/silicalite	5	Flat-sheet	30	1810	217	[185]
MeOH/toluene (90/10 wt%)	CS/silicalite	5	Flat-sheet	30	1700	200	[185]
t-BuOH/n-BuOH(50/50 wt%)	Polyamide-imide/ $\beta$ -cyclodextrin	15	Flat-sheet	60	4.4	1.53	[186]
Butanediol/BuOH (52.6/47.4 wt%)	PDMS/ZSM-5	80	Flat-sheet	N.A	16	18.4	[187]
MeOH/DMC (70/30 wt%)	PDMS/silica	15	Flat-sheet	40	702	4	[189]
o-xylene/p-xylene (85/15 wt%)	Poly(acrylic acid) sodium/silane-modified silicalite	6	Flat-sheet	30	38	1.8	[188]
m-xylene/p-xylene (85/15 wt%)	Poly(acrylic acid) sodium/silane-modified silicalite	6	Flat-sheet	30	36	2.2	[188]
Benzene/MeOH (80/20 wt%)	PVA/H-ZSM-5	5	Flat-sheet	30	71	47	[190]

Abbreviations:

Butanol: BuOH; Dimethylcarbonate: DMC; Ethanol: EtOH; Methanol:MeOH;

Table 10. Polyelectrolyte complexes (PECs) membranes for dehydration of alcohol and other solvents

Feed mixture (mass ratio)	Polyelectrolyte pair	Support	Modification methods	Temperature (°C)	Flux (g/m <sup>2</sup> h)	Separation factor (water/organic)	Reference
IPA/H <sub>2</sub> O (50/50)	PDDA/CMC-Na	Polysulfone	Glutaraldehyde crosslinking	70	2110	>1800	[197]
IPA/H <sub>2</sub> O (95/5)	PEI/PAA	Hydrolyzed PAN	Dynamic LBL assembly with the aid of pressure	70	340	833	[199]
IPA/H <sub>2</sub> O (90/10)	PDDA/PSS	Polyamide	LBL assembly at vibration condition	40	1800	190	[200]
IPA/H <sub>2</sub> O (90/10)	PDDA/PSS (PEC+)/PDMC/CMCNa (PEC-)	Polyamide reverse osmosis membrane	Assembly of opposite charged polyelectrolyte complex colloidal nanoparticles into multilayer films	60	1180	1010	[203]
IPA/H <sub>2</sub> O (90/10)	PVA/PDDA/CMC-Na	Polysulfone	PVA blend with PEC to increase hydrophilicity and suppress swelling	70	1350	1000	[202]
IPA/H <sub>2</sub> O (90/10)	QP4VP/CMC-Na	Polysulfone	Alkyl side chains with different length	60	1490	>2000	[204]
IPA/H <sub>2</sub> O (90/10)	Chitosan/P(AANa-co-SSNa)	PAN	Dual anion groups to enhance the ionic crosslinking	40	1250	1490	[205]
IPA/H <sub>2</sub> O (90/10)	PEI/PAA	Polyamide RO membrane	Electric field assisted assembly	70	4050	1075	[210]
EtOH/H <sub>2</sub> O (95/5)	Chitosan/PAA	IP polyamide	Crosslinking of the outmost layer to improve the operating stability	22	1000	80	[198]

Cont. next page

Table 10 Cont.

Feed mixture (mass ratio)	Polyelectrolyte pair	Support	Modification methods	Temperature (°C)	Flux (g/m <sup>2</sup> h)	Separation factor (water/organic)	Reference
EtOH/H <sub>2</sub> O (95/5)	PEI/PAA	Hydrolyzed PAN	Dynamic LBL assembly with the aid of pressure	70	310	604	[199]
EtOH/H <sub>2</sub> O (90/10)	PEVP/CMC-Na	Polysulfone	Homogeneous PECs coat on a substrate	70	930	1420	[201]
EtOH/H <sub>2</sub> O (90/10)	PDDA/SCMC	Polysulfone	Incorporation of sulfate groups	70	1760	683	[206]
EtOH/H <sub>2</sub> O (90/10)	Sulfated Chitosan/CMC-Na	Polysulfone	Incorporation of sulfate groups	70	1390	1570	[207]
EtOH/H <sub>2</sub> O (95/5)	PEI/PAN	Hydrolyzed PAN	Electric field assisted assembly	75	510	304	[209]
EtOH/H <sub>2</sub> O (95/5)	Chitosan/PAN	Hydrolyzed PAN	One step dynamic assembly	60	230	420	[209]
EtOH/H <sub>2</sub> O (95/5)	PEI/PAA-GO	PAN	Incorporation of GO nanosheets in the polyelectrolyte layers	50	270	394	[149]
Acetone/H <sub>2</sub> O 95/5	PDDA-ZrO <sub>2</sub> /PSS-ZrO <sub>2</sub>	PAN	Organic-inorganic hybrid PEC membranes	50	690	1880	[211]
Acetone/H <sub>2</sub> O 95/5	PDDA/PSS	PAN	N.A.	50	370	773	[211]
n-BuOH/H <sub>2</sub> O 90/10	QP4VP/CMC-Na	Polysulfone	Alkyl side chains with different length	60	2240	1120	[204]

## Abbreviations:

Butanol: BuOH; Sodium carboxymethyl cellulose: CMC-Na; Ethanol: EtOH; Graphene oxide: GO; Isopropanol: IPA; Polyacrylic acid: PAA; Polyacrylonitrile: PAN; Poly(sodium acrylate-co-sodium styrenesulfonate): P(AANa-co-SSNa); Poly(diallyldimethylammonium chloride): PDDA; Poly(2-methacryloyloxy ethyl trimethylammonium chloride): PDMC; Polyethyleneimine: PEI; Poly (N-ethyl-4-vinylpyridinium bromide): PEVP; Poly(sodium-p-styrenesulfonate): PSS; Phosphotungstic acid: PTA; Quaternized poly(4-vinylpyridine): QP4VP; Sulfated sodium carboxymethyl cellulose: SCMC