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Association of Polyethylene Glycol Solubility with Emerging Membrane Technologies, Wastewater Treatment, and Desalination

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Abstract

Forward osmosis (FO) and membrane distillation (MD) are two emerging membrane technologies, and both have advantages of low membrane fouling, ability to use for highly saline desalination, and feasibility to integrate with a low-grade heat source like solar collector. Because polyethylene glycol (PEG) is a flexible, water-soluble polymer, it is an essential material used for membrane fabrication and enhancement of membrane properties. Low-molecular-weight PEG sometimes is used as pore constrictor and pore former for developing MD membranes and support layer of FO membranes. Due to the affinity of PEG chains to water molecules, PEG, its derivatives, and copolymers have been widely used in the fabrication/modification of FO and MD membranes, which are currently applied to bioseparation, wastewater treatment, and desalination in academia and industry at the pilot scale. This chapter covers direct PEG and its membrane separation applications in wastewater treatment and desalination. The advancement of PEG in membrane science and engineering is reviewed and discussed comprehensively. We focus on the effectiveness of PEG on membrane antifouling and the stability of PEG-modified membranes when applied to wastewater treatment and desalination.

Keywords: polyethylene glycol, forward osmosis, membrane distillation, draw solute, pore-forming additive

1. Chemistry of polyethylene glycol, its derivatives, and copolymers

Poly(ethylene glycol) or PEG is a synthetic water-soluble polymer with the formula $C_{2n}H_{4n+2}O_{n+1}$ which is available in a wide range of molecular weights where n value can go up to thousands. The molecular weight of PEG has a significant effect on its properties. Low-molecular-weight compounds (molecular weight < 1000) exist in liquid form, whereas higher molecular weight compounds are in waxlike solid form. The highest melting point of the solid-state material is reached at around 67°C , depending on the molecular weight [1]. In certain instances, PEG is also denoted as poly(oxyethylene) (POE) and polyoxirane. Additionally, PEG

is called poly(ethylene oxide) (PEO), when the molecular weight exceeds 20000. Other than water PEG is also soluble in certain organic solvents like acetone, ethylene dichloride, carbon tetrachloride, trichloroethylene, methylene dichloride, and dimethylformamide [2]. The favorable properties of PEG such as solubility in both aqueous and organic solvents, nontoxicity, and reduced immunogenicity have made it a good candidate to be used for conjugation with other molecules [3].

PEG is available as linear or branched chain polymers with terminal hydroxyl groups. The structure of PEG allows the attachment of varying functional groups at the end groups of the polymer. The attachment of different molecules to PEG is known as PEGylation, and it provides means of improving the solubility, stability, and biocompatibility of the attached molecules/compounds. PEG is commonly synthesized starting with ethylene oxide via an anionic ring-opening reaction, through a nucleophilic attack on the epoxide ring by the hydroxide ion. Conjugation of PEG to other molecules can be categorized into two groups as (1) first-generation PEGylation and (2) second-generation PEGylation. The first-generation PEGylation involves random attachment of PEG polymers to other molecules and is widely used with modifying polypeptides. This method can usually generate various undesired products as the attachment is nonselective. Also, it is mostly limited to low-molecular-weight derivatives and unstable bonds. On the other hand, the second-generation PEGylation is site-specific and leads toward the production of more stable and pure derivatives [4].

1.1 Hetero- and homobifunctional PEG derivatives

Various hetero- and homobifunctional products of PEG can be synthesized by different methods. Bentley et al. have shown a method to synthesize heterobifunctional PEG derivatives in high purity and high yield, by going through an intermediate with an easily removable group [5]. Here, they have first attached a benzyloxy group as the removable group to one end of PEG. Then, after modifying the other terminal OH group with a required molecule, the first group was removed by hydrogenolysis or hydrolysis. Afterward, another functional group can be attached to the newly available OH group, or the new OH can be converted to a different functional group. Also, another group has synthesized a heterobifunctional PEG with acetal and thiol groups starting with polymerization of ethylene oxide with potassium 3,3-diethoxypropanolate. Then, an excess of methanesulfonyl chloride was used to convert a terminal alkoxide group to a methanesulfonyl groups [6]. Within the two procedures above, the polymerization-based process is the most frequently used method in the synthesis of heterobifunctional derivatives. Although the second method is more cost-effective and efficient than the intermediate based method, it requires the availability of proper anionic polymerization initiators and precautions to avoid the formation of PEG diols [4].

A homobifunctional PEG derivative of α -lipoic acid (LA) ester was synthesized by Lu et al. to improve its properties for potential medical applications [7]. In this synthesis an esterification reaction driven by 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide was carried out with PEG in the presence of 4-(dimethylamino) pyridine as a catalyst. Additionally, homobifunctional PEG has been used in metal nanoparticle synthesis as a stabilizing agent. For instance, Ge et al. have synthesized supramagnetic nanoparticles to be used as draw solutes in forward osmosis (FO) membrane using polyethylene glycol activated with two carboxylic acid groups at the terminal ends [8].

1.2 Monofunctional PEG derivatives

Monomethoxy PEG (mPEG), where one terminal of the PEG is capped with a relatively inert methoxy group, is commonly utilized in producing monofunctional PEG derivatives. The synthesis of mPEG is carried out via anionic ring-opening polymerization reaction initiated by methoxide ions. The presence of trace amounts of water during the synthesis process of mPEG can result in the formation of PEG diols, which can reach above 15% in the composition. Hence, during the synthesis of monofunctional PEG, necessary steps must be taken to remove PEG diols from the starting materials. Otherwise, the final product will contain bifunctional PEG as impurities. Therefore, conversion of diols to inert compounds such as PEG-dimethyl ether or PEG carboxylic acids followed by purification was used as a strategy to overcome this issue [4, 9].

A group of monofunctional PEG derivatives called NHS esters, where N-hydroxysuccinimide based group is attached to mPEG, are widely used in

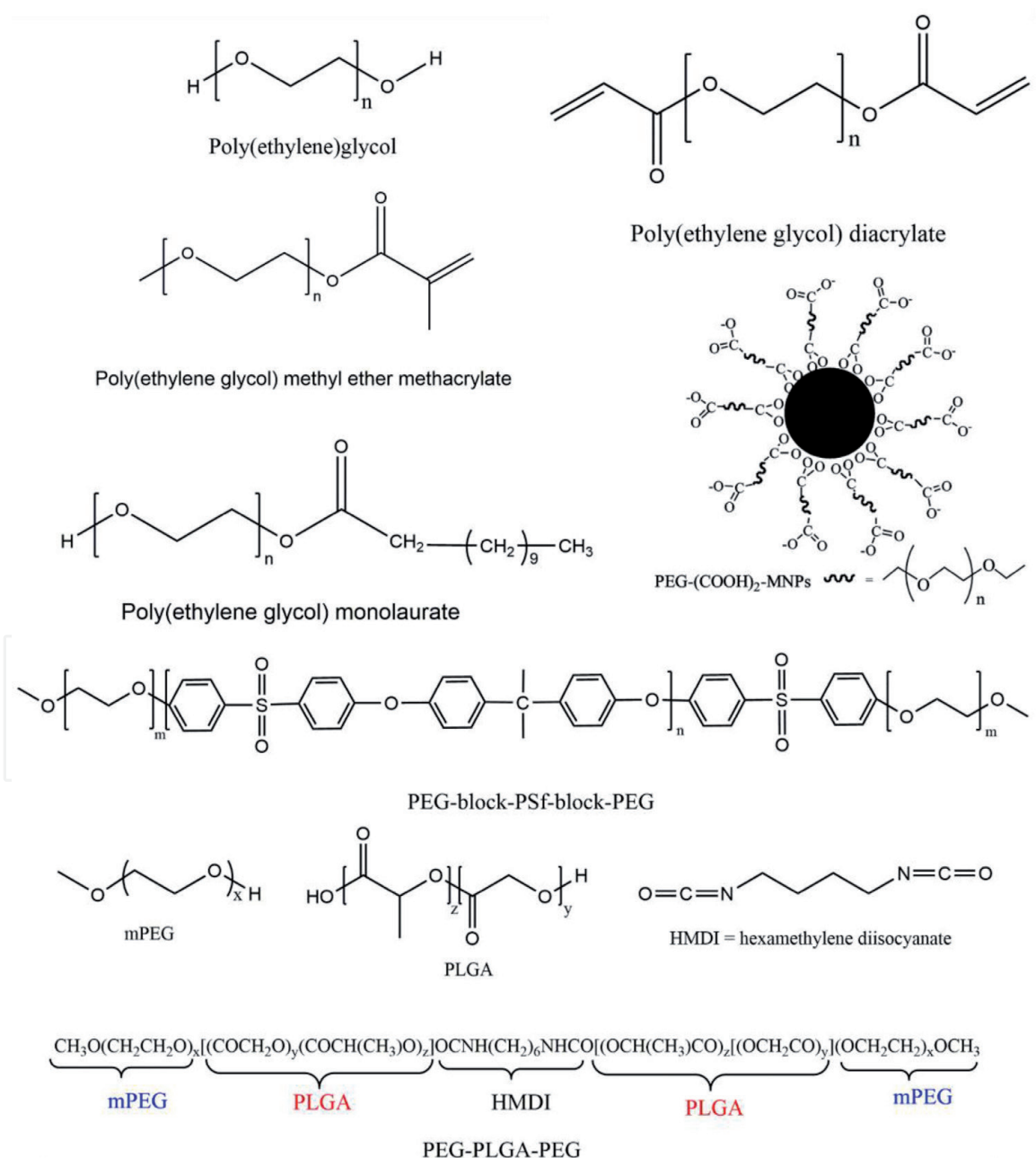


Figure 1. Structures of PEG, PEG derivatives, and copolymers used in membranes (PEG-(COOH)-MNPs adapted from [8]).

protein and peptide modifications. This type of PEG derivatives is commonly used as acylating agents to modify amino groups of lysine residues and also has some reactivity with histidine imidazole and tyrosine hydroxyl groups. For example, PEG succinimidyl succinate (PEG-SS) produced by reacting mPEG with succinic anhydride followed by carboxylic acid activation to form succinimidyl ester is an NHS ester that has been successfully coupled to the enzyme asparaginase [4, 9]. Also, PEG derivatives such as trichlorophenyl carbonate and carbonylimidazole were synthesized by reacting mPEG hydroxyl group with chloroformates or carbonylimidazole. Alkylating reagents derived from mPEG include PEG tresylate and PEG dichlorotriazine. Other examples of monofunctional PEG derivatives that are specific to sulfhydryl groups include PEG-maleimide, PEG-vinylsulfone, and PEG-iodoacetamide [10]. In addition to protein modifications, monofunctional PEG derivatives were also used in osmosis membrane-related applications. For instance, PEG conjugated to fatty acid and PEG monolaurate was used as draw solutes to test forward osmosis membranes [10].

According to the abovementioned chemistry and properties of PEG, it has been widely used in many different areas such as biomedical, biotechnology, and membrane technology-based applications. The main focus of this chapter is to discuss the usage of PEG, its derivatives, and copolymers (**Figure 1**) in emerging membrane technologies, such as forward osmosis and membrane distillation, as their applications relate to wastewater treatment and desalination.

2. Principle of forward osmosis

Forward osmosis is an emerging technology using a semipermeable ultrathin membrane to treat water or wastewater, and the membrane is typically thinner than RO membranes. Similar to the structure of thin film RO membranes, an FO membrane typically consists of an active layer and a support layer. In a commercially available thin film composite (TFC) FO membrane, the active layer is polyamide (PA), and the support layer is mainly made of polysulfone (PSf) or polyethersulfone (PES). An FO system generally consists of an FO module/cell for holding FO membranes, a draw solute recovery unit and pumps for circulating feed and draw solution (**Figure 2**). The FO module/cell is classified into flat sheet, hollow fiber, and spiral wound configurations, mainly depending on the operating scale. Although FO takes some advantages of an osmotically driven process, such as less membrane fouling, low energy requirement and operating cost, over

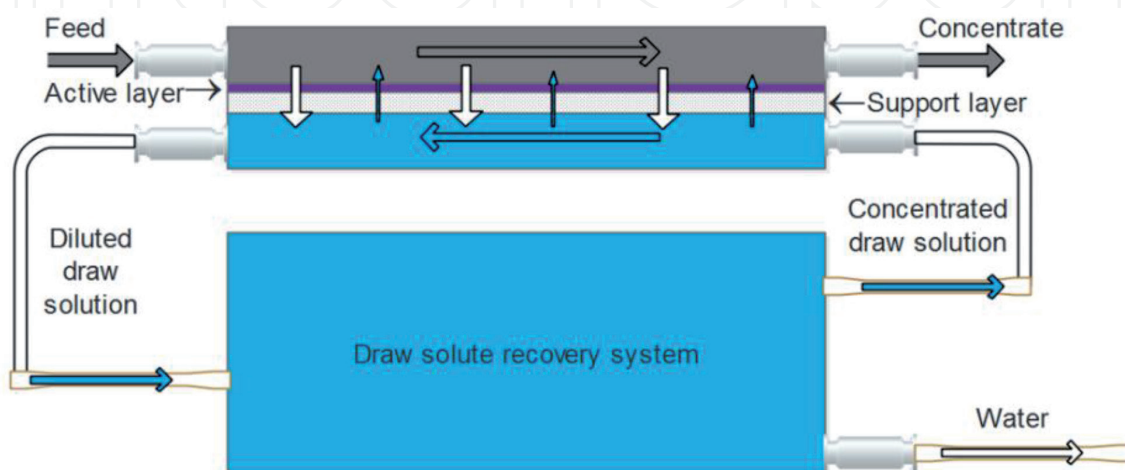


Figure 2.
Schematic of a forward osmosis system with draw solute recovery.

pressure-driven processes of nanofiltration (NF), and reverse osmosis (RO) in a similar membrane separation range, it still encounters some challenges in a wide range of practical applications for wastewater treatment and desalination. Jampani and Raghavarao purified and concentrated red cabbage (*Brassica oleracea* L.) anthocyanins by integrating osmotic membrane distillation and FO processes with a PEG-4000 and MgSO_4 (14.8/10.3%, w/w) extraction system [11]. Later, they used similar technologies to separate and concentrate Jamun anthocyanins by using PEG 6000 in the extraction system [12]. To test the performance of FO membranes, a series of PEG (10 and 20 kDa) and PEO (100, 600 and 1000 kDa) were used to determine molecular weight cutoff (MWCO), pore size, and distribution of a hydrophilic support layer during the fabrication of a TFC FO membrane [13].

3. Principle of membrane distillation

Membrane distillation (MD) is another emerging technology in membrane separation, which uses a hydrophobic, microporous membrane to treat water or wastewater through a thermally driven separation process. In an MD process, the

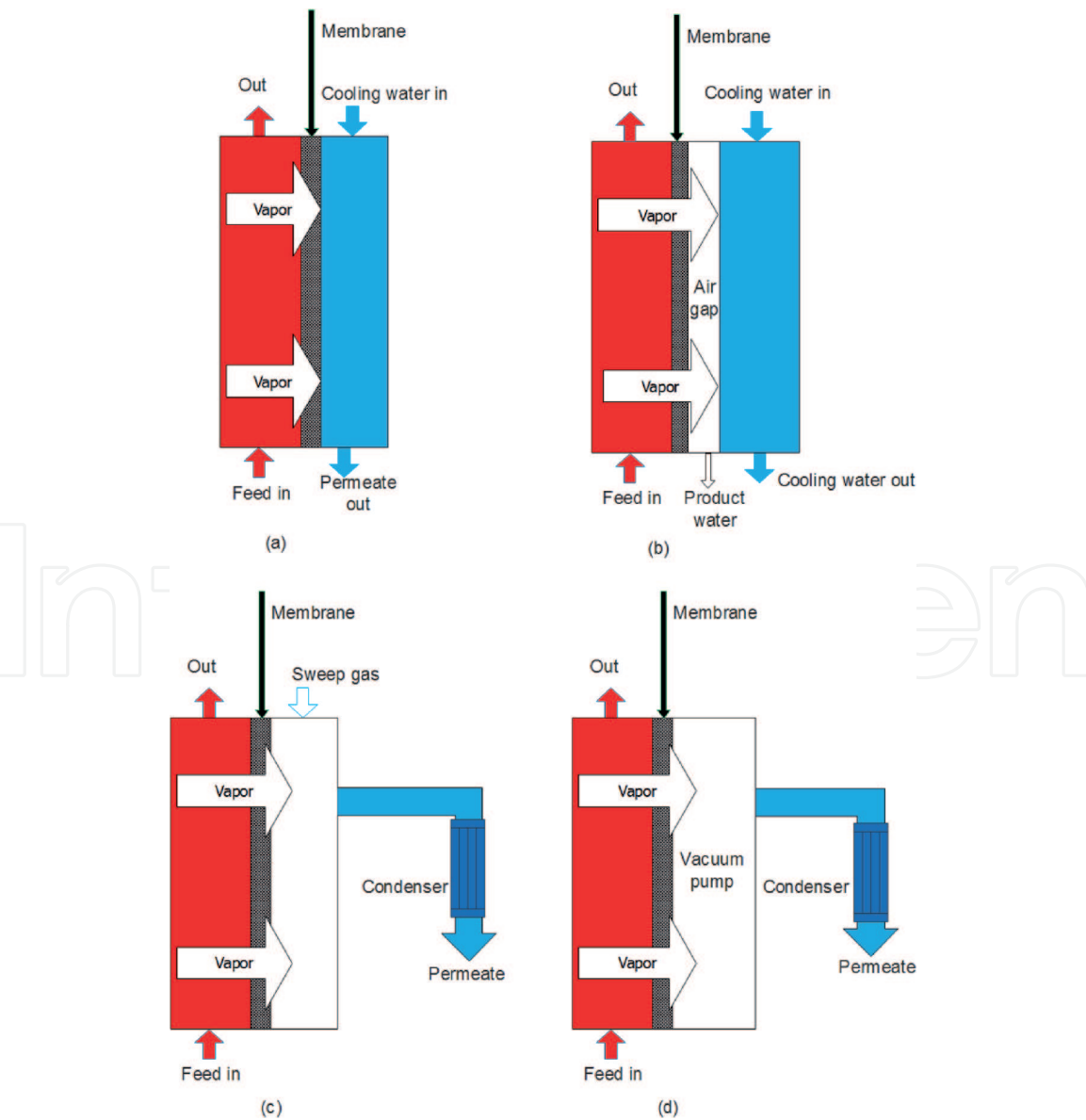


Figure 3.
Configurations of membrane distillation. (a) DCMD. (b) AGMD. (c) SGMD. (d) VMD.

feed solution is usually heated up, and the produced vapor passes through the pores of the membrane and condenses on the distillate side by cooling. MD is considered cost-effective and promising because it can achieve almost 100% dissolved solid rejection specifically in desalination. Similar to an FO module, an MD module can also be constructed as flat sheet, hollow fiber, and spiral wound forms. According to different configurations of the distillate side [14], MD can be classified into direct-contact MD (DCMD), air-gap MD, sweeping-gas MD (SGMD), and vacuum MD (VMD) shown in **Figure 3**. Conventional microporous membrane with pore size (0.1–1 μm) can be used for MD, and there also are some membranes specifically designed for MD. PEG and its derivatives can be used to improve the hydrophilicity of the membrane surface facing the feed solution during the fabrication of some specific MD membranes [15, 16].

4. PEG associated with forward osmosis

4.1 PEG used as/in draw solute

One of the challenges of FO applications in wastewater treatment and desalination is the selection of high-performance draw solutes. Among several hundreds of draw solute explored in the FO process, PEG is also evaluated for the FO process. Beside electrolyte NaCl, neutral PEG polymers at different molecular weights (M.W. = 100, 200, 600, 2000, 3000, 8300, and 10000) were used as model draw solute to evaluate the performance of a commercially available cellulose triacetate (CTA) FO membrane and a homemade porous UF-like FO membrane [17, 18]. Wei et al. fabricated a double-skinned selective thin film composite (TFC) FO membrane consisting of a top thin polyamide (PA) layer, a middle porous cellulose ester layer, and another bottom thin PA layer and tested its performance using several viscous draw solutes such as PEG monolaurate (PEG 640ML), sucrose, and ferric citric acid complex (Fe-CA) [19]. The novel membrane can minimize the effects of internal concentration polarization (ICP) because the bottom thin PA layer prevents viscous draw solute from entering the pores of the middle layer.

Hydrophilic magnetic nanoparticles (HMNPs) are a type of promising draw solutes, which may easily be recycled under a magnetic field. There exist some reports that HMNPs were fabricated from PEG and magnetic nanoparticles. Ge et al. synthesized a series of PEG-(COOH)₂-coated MNPs with narrow size distribution through a thermal decomposition process [8]. Mishra et al. specifically synthesized HMNPs with PEG 400 and evaluated their performances in an FO process where synthetic saline water (NaCl solution) at different concentrations of 0, 5, 10, 20 and 35 g/L was used as feed solution. About 35 g/L is close to the level of total dissolved solids (TDS) in seawater. When these HMNPs were used as draw solute in a fundamental FO process of deionized water, they could significantly eliminate the draw solute reverse diffusion problems which are common in the applications of general salts, such as NaCl, KCl, MgCl₂, MgSO₄, etc., as draw solute [20, 21]. Biodegradable and biocompatible temperature-sensitive triblock copolymer hydrogels PEG-PLGA-PEG/GO-0.09 wt%, PEG-PLGA-PEG/GO-0.18 wt%, PEG-PLGA-PEG/G-0.09 wt%, and PEG-PLGA-PEG/G-0.18 wt% were fabricated and used as draw solute in FO by Nakka and Mungray [22], where GO represents graphene oxide and G is graphene. PEG-PLGA-PEG was synthesized from D,L-lactide, 1,4-dioxane-2,5-dione, methyl ether polyethylene through ring-opening polymerization using stannous octane as catalyst. However, much smaller water fluxes were achieved when feed solutions are DI water and 2 g/L NaCl solutions than the previous HMNPs as draw solute.

4.2 PEG in the support layer of an FO membrane

In order to improve the performance of an FO membrane, the support layer can be reconstructed, and the active layer can be modified with PEG or its copolymer. Addition of PEG 400 to the support layer was conducted to fabricate a TFC FO membrane, and it was found that the addition of 6 wt% PEG was needed to reach the highest water flux [23] when DI water and 2 M NaCl were used as feed and draw solution. PEG 400 and dimethyl sulfone (DMSO_2) were used as an additive and a crystallizable diluent to fabricate the CTA support layer of an FO membrane through thermally induced phase separation, and the FO membrane exhibited better antifouling properties than PSf-based FO membranes [24]. Sharma et al. used PEG 4000 and 6000 as additive to prepare cellulose acetate flat asymmetric FO membranes, and the modified FO membranes were used to evaluate power density performance in pressure-retarded osmosis [25].

Liu et al. fabricated the support layer from PSf with 5-, 10-, and 15-wt% PEG or PEGMA (poly(ethylene glycol) methyl ether methacrylate) and evaluated the corresponding FO membranes by using DI water and 1 M NaCl as feed and draw solution [26]. The PSf-PEG support layer was made by blending PEG with PSf, and in the second type, it was PEGMA grafted on PSf. The FO membrane containing 10 wt% PEG achieved relatively steady performance for a long time operation process due to its better salt rejection, and the FO membrane with 5% PEGMA grafting possessed a high intrinsic permeability and a low structural parameter. Recently, amphiphilic PEG-block-PSf-block-PEG copolymers were used to cast the support layer, and the fabricated TFC FO membrane achieved some significant improvements on water flux, antifouling, and permeability selectivity [27].

4.3 PEG in the active layer of an FO membrane

When the active layer of a TFC FO membrane is modified with PEG, the surface hydrophilicity of the membrane can be improved, thus enhancing the membrane antifouling properties. Elimelech et al. functionalized the active layer of a TFC FO membrane with PEG diepoxides through surface grafting, and their dynamic experiments showed that the membrane fouling was significantly reduced when testing with alginate as model organic foulant [28]. The same research group later used a post-fabrication technique to graft a PEG-block copolymer on the active layer of commercial TFC FO membranes, and the PEG density was optimized to the best membrane performance by compromising the increased membrane hydrophilicity and reduced water flux [29]. Interestingly, a novel design of FO membranes by impregnating the support layer with hydrophilic cross-linked poly(ethylene glycol) diacrylate (PEGDA) was proposed by Zhao et al., and there is no additional PA layer needed [30]. The newly designed FO membrane had the ability to mitigate internal concentration polarization which is commonly for typical two-layer FO membranes and to improve the performance ratio by 50% compared to those of state-of-the-art commercial FO membranes. Recently, Chen et al. tethered the active PA layer of a TFC FO membrane with PEGMA, and the membrane ICP was greatly mitigated with only slightly flux reduction from 10.99 to 9.32 LMH during synthetic sewage treatment [31].

The antifouling ability and performance of CTA FO membranes can also be improved by applying PEG to the membrane surface. The surface of a CTA FO membrane was modified by firstly coating polydopamine (PD) and then grafting PEG, and the submerged osmotic membrane bioreactor using the FO membrane possessed better flux behaviors than the pristine reactor and anti-adhesion abilities of biopolymers and bio-cake [32].

5. PEG associated with membrane distillation

5.1 PEG used as pore-forming additive

In the early 1990s, PEG was used as pore-forming additive to fabricate microporous polyvinylidene fluoride (PVDF) membrane for MD of wastewater discharged from the taurine production [33]. The effects of a series of PEG 400, 1000, 1540, 2000, and 6000 on the pore structure and permeate performance of poly(vinylidene fluoride-co-hexafluoropropylene) (F2.6) flat-sheet membranes were investigated by evaluating average pore radius, porosity, and morphology, and the membranes reached better higher distilled flux than the PVDF membrane during the DCMD test [34]. Dayanandan et al. studied the influence of the various additions of PEG (0–4 wt%) in the coagulation bath composition during the preparation of PVDF membranes, and they found that the bath-based MD membrane with 4 wt% PEG had relative superior overall performance than other membranes based on various evaluations of elongation-at-break, tensile strength, liquid entry pressure, hydrophobicity, porosity, and water flux [35]. Combined effects of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and the concentrations of the additive PEG 10000 were studied by using a statistical approach, and the optimized membrane achieved salt rejection of 99.5% in the DCMD of 0.1 M NaCl solution at 65°C [36]. Two pore-forming additives PEG and LiCl both at 4 wt% were used in the fabrication of hydrophobic flat sheet and hollow fiber PVDF and PVDF-co-chlorotrifluoroethylene (PVDF-CTFE) membranes for membrane distillation [37, 38]. The effect of mass ratio of PEG and LiCl was further investigated for making PVDF-CTFE membranes for MD [39]. Recently, more effective additives such as organic acids, LiCl, MgCl₂, and LiCl/H₂O mixtures along with PEG were investigated in the fabrication of flat-sheet hydrophobic PVDF-CTFE membranes used for MD [38]. Hou et al. prepared hydrophobic PVDF flat-sheet membranes for DCMD by using various non-solvent additives such as acetone, phosphoric acid, glycerine, LiCl, and PEG 400 [40]. They found that the membrane fabricated with 5 wt% acetone and 3 wt% phosphoric acid exhibited the highest water flux among the various fabricated membranes and showed great performance stability in the 240 h desalination of synthetic seawater. There exist more novel additives, such as calcium carbonate nanoparticles and TamiSolve® NxG along with PEG and LiCl, applied to the fabrication of hydrophobic membranes for MD [41, 42].

During the fabrication of microporous PVDF hollow fiber membranes, two non-solvent additives PEG 400/1500 and LiCl were added to the feed N,N-dimethylacetamide (DMAc) solution containing PVDF powder [43–46]. The experiment factors such as dope extrusion rate, take-up speed, air-gap concentration of polymer and additives, and bore liquid temperature were investigated in the membrane fabrication through a dry-jet wet phase inversion process, and the obtained membranes were suitable for DCMD than VMD. Recently, Zhang et al. further discovered the regulatory role of coagulation bath temperature during PVDF membrane fabrication when PEG 400 and triethyl phosphate were used [47]. In the fabrication process of PVDF hollow fiber membranes via complex thermally integrated phase separation at 80°C for MD, triethylphosphate (TEP) and PEG 200 were used as weak solvent and weak bore fluid, respectively [48]. PEG 6000 was used to fabricate hollow fiber MD membranes by Garcia-Payo et al. [49, 50]. They also dissolved PEG 10000 in DMAc to prepare PVDF-HFP hollow fiber membranes, and the optimized membrane had high permeate flux and salt rejection [51, 52]. Similarly, the concentration effects of PEG 600 (0–20 wt%) on the performance of PVDF-HFP membranes for MD were also investigated, and the suitable range of 5–20 wt% was found for fabricating hollow fiber MD membranes with acceptable

performance [53]. Recently, Wang et al. developed hydrophobic flat sheet and hollow fiber membranes PVDF and PVDF-CTFE for DCMD using PEG 400 and LiCl as the additives [54].

5.2 PEG applied to surface modification of MD membrane

In order to explore new applications of microfiltration (MF) membrane in MD, a hydrophobic PVDF membrane with pore size of 0.2 μm and thickness of 125 μm was surface-casted with hydrophilic polymer gel made from a polymer solution containing 20% PEG and 3% polyvinyl alcohol (PVA) [15]. The modified membrane exhibited the excellent abilities to keep high constant flux at high salt concentration of 20–25% NaCl for a long time MD running and to prohibit the wetting problem when testing with 25% ethanol even. Recently, Zuo and Wang modified a PVDF membrane with a pore size of 0.22 μm and thickness of 125 μm by grafting PEG and depositing TiO_2 micro-balloon-shaped particles on the membrane surface [16]. In the desalination test of synthetic seawater containing 0.01 wt% of mineral oil over the 1-day operation, the fabricated membrane with a highly hydrophilic surface kept a stable water flux with negligible fouling and wetting. Later, Meng et al. investigated the effect of templating agents, such as PEG 1000, Pluronic F-127, Wacker IM-22, and cetyltrimethylammonium bromide, on the properties and MD performance of TiO_2 -coated PVDF membranes [55]. Their MD membrane templated with PEG achieved the most promising overall performance of water flux, salt rejection, and extended operation time due to the optimum reduction of pore wetting induced by the templating agent PEG. They further developed superhydrophobic nanocomposite PVDF membranes for DCMD by modifying the conventional PVDF membrane with a pore size of 0.45 μm , and a dip coating of sol-gel containing PEG was used after a TiO_2 and fluoro-silane coating in the modification [56].

6. PEG-assisted membranes in wastewater treatment and desalination

As emerging membrane technologies, FO and MD have received increased attentions for wastewater treatment and desalination [14, 57–60]. FO takes some

Membrane type	PEG	Wastewater/desalination	Performance improvement	Ref.
FO	PEGDE	Synthetic wastewater	Alleviation of flux reduction by 50%	[28]
FO	Jeffamine ED-2003	Synthetic secondary wastewater	Complete removal of organic foulant with NaCl solution	[29]
MD	PEG 2000	Taurine wastewater	Nonvolatile solute can be concentrated by MD	[33]
MD	PEG 2000 and 10000	NaCl solution	Remain 91% flux for 3.5 NaCl; almost unchanged flux for 20% NaCl	[15]
MD	PEG 1500	3.5% NaCl	Flux: 40.5 $\text{kg}/\text{m}^2 \text{ h}$; NaCl rejection: 99.99% at 81.8°C	[45]
MD	PEG 1000	10% NaCl	Recovery ratio: about 68%	[55]
MD	PEG 200 and 400	Formulated seawater	Flux: 61.6 $\text{kg}/\text{m}^2 \text{ h}$; NaCl rejection: 99.99% at 71°C	[48]

Table 1.
PEG-assisted FO and MD membranes used in wastewater treatment and desalination.

advantages of low membrane fouling, feasibility to treat high salinity water, possibility to run at low voltage electricity, and applications in osmotic dilution at low energy demand. When thermal volatile draw solute is used, FO can easily be integrated with low-grade heat, such as waste heat in a power plant and thermal heat gathered by highly efficient solar collector, for draw solute recovery [57, 58]. MD as a thermal membrane separation process has the nature to utilize low-grade heat easily, and it also possesses distinctive advantages of low membrane fouling and low operation energy demand of heating the feed and cooling the permeate when integrating with low-grade heat source and high quality of product water when using VMD and AGMD in the desalination of highly saline water [59]. The utilization of PEG, its derivatives, and copolymers in FO and MD membranes can improve the overall membrane performance, thus enhancing the abilities of these membranes in various applications. **Table 1** summarizes the performance of PEG-assisted FO and MD membranes used in wastewater treatment and desalination.

7. Summary

PEG, its derivatives, and copolymers are water soluble depending on their molecular weights, terminal, and copolymer blocks. They have widely been utilized in membrane fabrications and performance tests of some membranes due to the nature of hydrophilicity of these polymers. This chapter focuses on PEG applications in two emerging membrane technologies FO and MD. With regard to FO, PEG can not only be integrated into some draw solutes for easy draw solute recovery but can also be applied to the support and active layers for improving membrane anti-fouling properties. On the other hand, PEG is mainly used as pore-forming additive in the MD membrane fabrication. Compared to the control membranes in the various studies which are summarized here, PEG-assisted FO and MD membranes exhibit better overall performance for wastewater treatment and desalination according to water flux, flux recovery after cleaning, and antifouling behaviors.

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Conflict of interest

The authors declare no conflict of interest.

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