



# Carboxylic polyethersulfone: A novel pH-responsive modifier in support layer of forward osmosis membrane

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## ABSTRACT

Carboxylic polyethersulfone (CPES) was synthesized through a facile acetylation reaction followed by an oxidation treatment and used as a modifier in support layer composition of forward osmosis (FO) membrane. The hydrophilic CPES polymer could ameliorate thin film composite (TFC) membrane performance in water permeation. The inferior sponge-like structure of the pristine PES substrate was changed to appropriate long finger-like one, when the CPES modified polymer dope solution was casted in a basic coagulation bath. In such operational condition, attached carboxylic functional groups were almost deprotonated and the electrostatic repulsion forces among them resulted in the formation of a substrate with open pores and less dense morphology. To prove pH-responsive characteristics of the CPES blended membranes, pH of coagulation bath was switched from 3 to 12. By doing so, water flux drastically increased from 14.23 to 28.03 LMH and from 27.80 to 46.17 LMH in FO mode (active layer facing feed water) and PRO mode (active layer facing draw solution), respectively. Further studies showed that such pH treatments could also lower the unfavorable structure parameter ( $S$ ) from 1423.54 to 653.94  $\mu\text{m}$ . The pH-reversibility of the obtained membranes were evaluated using different draw solution pH values. In an acidic draw solution ( $\text{pH} = 3$ ), the protonated carboxylic functional groups started shrinking and thus could open the substrate's pores, which facilitate rapid water transportation. This investigation may open up a new class of pH-responsive and pH-reversible material for promising FO process, in which permeability and selectivity of a FO membrane could be readily controlled through fluctuation in pH of coagulation bath or draw solution.

## 1. Introduction

According to the estimates provided by United Nations Food and Agriculture Organization (UNFAO), absolute water scarcity will be experienced by more than 1.9 billion people over the next ten years [1]. To combat increasing water crisis, higher water productivity is believed to be one of the best strategy [2]. Among numerous emerging technology, membrane-based water desalination technique is perhaps the most promising one to locally and globally mitigate drinking water scarcity stress [3,4]. Forward osmosis (FO) as an osmotically-driven membrane process is a natural phenomenon, in which water moves across a semi-permeable membrane from a relatively diluted feed solution (FS) to a relatively concentrated draw solution (DS). Recently, FO has been gained extensive attentions in numerous applications such as desalination, water purification, power regenerations, brackish and liquid food processing, and so on [5,6]. Compared to the conventional pressure driven membrane processes such as reverse osmosis (RO), FO benefits from a lower fouling propensity, easy cleaning, high water

recovery and low equipment costs [7].

Thin film composite (TFC) membrane, as the heart of FO process, consists of an active thin layer deposited on a porous substrate. The top active layer is commonly made from polymeric polyamide (PA) thin film, which plays a significant role in the membrane selectivity [8,9]. The underlying thick porous substrate has a mechanically robust structure and provides adequate membrane stability in aqueous environment. Despite the substantial progress in FO process, there still remains some technical challenges, which hinder its widespread applications. With water permeation across the support layer, back solute diffusion simultaneously occurs from the bulk DS side toward the active surface of the FO membrane to compensate DS dilution [10,11]. A dense, thick and tortuous support layer impedes facile compensation process, leading to make internal concentration polarization (ICP) problem. The ICP is a deleterious phenomenon, which significantly reduces water flux from ideal values obtained by theoretical measurements [12–14]. To better assess the ICP effect, membrane substrate structure parameter ( $S = \text{thickness} \times \text{tortuosity/porosity}$ ) has been

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defined as a function of solute resistivity and diffusion coefficient of ionic salt solutions [15]. A smaller *S* value should be obtained through fabrication of a support layer, which has lower tortuosity, higher porosity and thinner structure.

So far, different procedures have been utilized to minimize the unfavorable ICP effect [16]. It is well-known that increasing the membrane hydrophilicity is an effective method to improve water flux as well as the ICP reduction [17–20]. Despite the fact that polyethersulfone (PES), as a traditional material used for the fabrication of TFC membrane substrate, has excellent chemical resistance, mechanical robustness, and thermal stability, its further applications in FO process have been hindered mainly due to intrinsic hydrophobic nature [21]. Therefore, increasing the hydrophilicity of the PES substrate followed by significant ICP reduction is an interesting research field, which will guarantee its long-term application in the FO process. In recent years, prevalent methodologies including surface and bulk modifications are utilized to improve the TFC membrane substrate hydrophilicity. The surface modification is conducted after membrane formation, in which the hydrophilic surfaces create via a proper physical or chemical treatments. Photo-induced grafting [22], gamma ray [23], electron beam-induced grafting [24], plasma treatment and plasma-induced grafting [25–27], thermal-induced grafting and immobilization [28,29], and surface-initiated atom transfer radical polymerization [30] are some of the chemical methods, which were successfully implemented to modify membrane surface.

The bulk modification of PES is chemically or physically carried out through addition of hydrophilic inorganic nanomaterials or functional groups into polymer matrix before membrane fabrication. In inorganic additives procedure, uniform distribution of fillers within the PES polymeric matrix is a great challenge, which causes a serious obstacle ahead for its development. But in the case of hydrophilic functional group addition, despite compromising mechanical properties of the obtained membrane, it is still considered as a more beneficial method. Using various procedures, many hydrophilic functional groups including hydroxyl, amine, carboxyl, and sulfone could be introduced on the main polymer chain. It is worth noting that the bulk modification methods are more straightforward than the surface ones, making a membrane with lower net effect [31]. Sulfonation of the PES is an electrophilic aromatic substitution reaction, in which sulfonic groups are added to the polymer backbone. Because of electron repulsing effect of the sulfonic group, the aromatic rings are deactivated for substitution, making the sulfonation of PES matrix so difficult. Therefore, strong sulfonating agents such as chlorosulfonic acid [32,33], sulfuric acid [34], trimethyl silylchlorosulfate [35,36], and sulfur trioxide [37] have to be used to sulfonate the PES polymer. Carboxylation of substrate polymer backbone is another appropriate choice, leading to fabricate a membrane with more proper characteristics.

Higher hydrophilicity as well as other excellent properties like pH-sensitivity and biocompatibility could be achieved through membrane substrate carboxylation [38,39]. Recently, polymeric pH-responsive membranes open up a new platform to control the permeability and separation performances [40]. To prepare a pH-sensitive membrane, gamma-ray irradiation method was utilized to graft acrylic and methacrylic acid as a monomer onto the PES chain [23,41]. Acetylation reaction followed by an oxidation step was recently suggested as a feasible way to graft carboxyl group onto the PES matrix [42]. Acetyl chloride and potassium permanganate were used as acetylating and oxidizing agents, respectively. Herein, carboxylic polyethersulfone-polyethersulfone (CPES-PES) with different weight ratio as novel pH-responsive TFC membrane substrates were successfully synthesized and their FO performances have been systematically investigated for the first time. The objectives of this study is to (1) investigate the effect of CPES as a modifier in the fabrication of TFC membrane substrate on FO performance; (2) study on the pH-responsible characteristics of membrane substrate by changing coagulation bath pH; (3) explore the pH-reversibility of CPES modified FO membranes by variation pH values of

the DS. This report provides a scalable and simple solution method to control and lower the unpleasant ICP effect from FO membrane substrates.

## 2. Materials and methods

### 2.1. Materials

Carboxylic polyethersulfone (CPES) was synthesized by acetylation and oxidation reactions on polyethersulfone (PES, molecular weight: 58,000, Ultrason<sup>®</sup> E 6020, BASF Co, Germany) using acetic anhydride (Merck), aluminium trichloride anhydrous (Merck) Potassium permanganate (Sigma Aldrich), and sodium hydroxide (Sigma Aldrich). Then, the obtained material was used for fabrication of final membrane support layers using N-methyl-2-pyrrolidone (NMP, Merck) as a solvent and polyethylene glycol 400 (PEG-400, Merck) as a pore-forming agent. M-Phenylenediamine (MPD) and 1,3,5-Benzenetricarbonyl chloride (TMC) and n-hexane were obtained from Merck and used for the synthesis of the polyamide (PA) active layer using interfacial polymerization (IP) reaction. Sodium hydroxide and hydrochloric acid were purchased from Merck and without further purification were used for adjusting the pH of coagulation bath and DS. Additionally, aqueous solutions containing 1 M sodium chloride (NaCl, Iran Mineral Salts Company, purity  $\geq$  99.2%) and distilled water (DI) were respectively utilized as DS and FS for FO experiments.

### 2.2. Preparation of carboxylic polyethersulfone

Carboxylic polyethersulfone (CPES) was prepared by controlled sequential acetylation and oxidation reactions in accordance with Wang et al. reported work [42]. In the acetylation reaction step, 10 g of PES was added into a flask and dissolved in 50 ml NMP solvent under vigorous stirring at room temperature. Then, a solution including acetic anhydride (8 ml, used as acetylation reagent), NMP (100 ml, used as solvent), and  $AlCl_3$  (6.5 g, used as catalyzer) was added dropwise (1 drop per second) into the above solution under stirring at 90 °C for about 24 h. The whole process was carried out under  $N_2$  atmosphere to inhibit the side reactions. The product precipitate was then collected by three times filtration and rinsing with DI water. Finally, the obtained PES-COCH<sub>3</sub> (COPEs) was dried at 60 °C for 24 h under vacuum condition before final oxidation reaction. In the oxidation step, COPEs (10 g) was dissolved in NMP with the concentration of 20 wt%. The solution of  $KMnO_4$  (1.2 g), NaOH (3.7 g), DI water (9 g), and NMP (40 ml) was added gradually into the COPEs solution under stirring at 80 °C for 4 h. The obtained deposit was separated from the solution using centrifugation 2500 RCF for 30 min. Finally, the solution was dried in a vacuum oven for overnight to obtain the deep red CPES polymer.

### 2.3. Membrane preparation

#### 2.3.1. Preparation of CPES-PES asymmetric support layer

CPES-PES asymmetric porous support layers were fabricated using non-solvent induced phase inversion via immersion precipitation method. First, the CPES and PES with various weight ratios were dissolved in NMP (42.5%) and PEG-400 (42.5%) at 70 °C for 4 h to get a 15 wt% polymer solution. The formed homogeneous polymer solution was then cooled down to room temperature and degassed overnight before casting operation. The porous support layers were casted on a glass plate with a casting knife setting at a gate height of 150  $\mu$ m. Finally, they were immersed into a coagulation bath of DI water with different pH values for 12 h. Solutions of HCl (1 M) and NaOH (1 M) were used to adjust pH of coagulation bath. The casting solution compositions used for different FO support layer preparations are summarized in Table 1.

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