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# Green fabrication of a positively charged nanofiltration membrane by grafting poly(ethylene imine) onto a poly (arylene ether sulfone) membrane containing tertiary amine groups



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## ABSTRACT

A green method to prepare asymmetric positively charged poly(arylene ether sulfone) nanofiltration (NF) membranes was explored by grafting water-soluble poly(ethylene imine) (PEI) onto a poly(arylene ether sulfone) membrane containing tertiary amine groups (PES-TA) and cross-linking with poly(ethylene glycol) diglycidyl ether (PEGDGE). The modifications were shown to increase the positive charge and decrease the pore size of the PES-TA substrate. The optimized NF membrane displayed a pure water flux of  $15.5 \text{ L m}^{-2} \text{ h}^{-1}$ . Membrane rejection NaCl,  $\text{MgCl}_2$ , and methyl violet (MV) (at a constant pressure of 4 bar) were measured to be 46.2%, 94.9%, and 99.8%, respectively. Moreover, the membrane maintained excellent chlorine resistance during 100 h of exposure to chlorine. Thus, the membrane shows potential for water desalination and purification applications.

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## 1. Introduction

Membrane technologies have been implemented successfully in water purification for decades. There is a pressing need to purify water at lower cost and by using less energy [1]. Nanofiltration (NF) is a low-energy purification process used for water treatment. In addition to saving energy, the unique traits of NF include low environmental impact, high retention of multivalent ions, and a pore size range of 0.5–2 nm [2]. The separation mechanism of NF includes both size exclusion and the Donnan effect [3]. In the last decade, the field of NF has expanded rapidly, leading to significant applications such as desalination of brine and pharmaceutical preparations [4,5].

Methods to prepare NF membranes include interfacial polymerization (IP), coating technologies, and immersed coagulation phase inversion [6–9]. Polyamide membranes prepared by IP technology have an unrivalled flux and high retention of salt, which allows water purification operations at lower pressures and with low-energy consumption rates. However, polyamide membrane may not be appropriate for many water sources, because of their poor resistance to acids, bases and chlorine [8]. Coating technologies, including spin coating, dip coating, and spray coating, have been utilized to add a thin layer of polymer on a porous support membrane to enhance the functional performance of NF membranes [10]. These coating technologies address many of the shortfalls of polyamide membranes and provide the membrane with good resistance to the aforementioned conditions [11]. Unfortunately, the thinly coated layer has been shown to readily detach from the membrane, because of the different tolerance of the coating polymer and the support layer polymer during water purification under high pressure. Another shortcoming of the coating method is that the solvent used to coat the polymer must wet the membranes and must not dissolve or swell the ultrafiltration support [12]. Although membranes prepared via IP and coating techniques have been well received by industry, the ability to make integrally skinned asymmetric membranes via a single-step fabrication process [12–14] is of broad interest. Asymmetric membranes generated by phase inversion have been applied in the

*Abbreviations:* AFM, atomic force microscopy; A, effective membrane area ( $\text{m}^2$ );  $C_p$ , concentration of the permeation ( $\text{mg mL}^{-1}$ );  $C_f$ , concentration of the feed ( $\text{mg mL}^{-1}$ ); DMF, N,N-dimethylformamide; F, pure water flux ( $\text{L m}^{-2} \text{ h}^{-1}$ ); h, hour; IP, interfacial polymerization; L, liter; MW, molecular weight; MV, methyl violet; MWCO, molecular weight cut off; NF, nanofiltration; PEGDGE, poly(ethylene glycol) diglycidyl ether; PEI, polyethyleneimine; PEG, polyethylene glycol; RO, reverse osmosis;  $r_s$ , stokes radius; s, second;  $t$ , testing time (h); PES-TA, cardo poly(arylene ether sulfone) with pendant tertiary amine groups; THF, tetrahydrofuran; V, volume of permeate water (L); XPS, X-ray photoelectron spectroscopy

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desalination process [6] and organic solvent nanofiltration (OSN) [9,15]. High charge density and hydrophilicity are required to improve water permeability. However, NF membranes fabricated with charged polymers are susceptible to water swelling, which results in reduced salt rejection and degradation of the favorable mechanical properties [16,17].

Various post-modification methods have been investigated to improve the performance of asymmetric NF membranes without sacrificing mechanical properties. UV-photografting [18,19], ATRP grafting [20], and covalent bond grafting [21] have been widely used to obtain the desired high surface charge density to enhance the rejection of dyes and salts. Covalent bond grafting has also been shown to increase the antifouling properties of NF membranes [22]. In the grafting process, reducing the use of organic solvents is necessary to decrease manufacturing costs and to produce enable greener membrane-preparation processes [21].

Previous work in our laboratory has demonstrated that poly(arylene ether sulfone) with tertiary amine groups (PES-TA) is a promising candidate for achieving asymmetric NF membranes with reasonable rejection for multivalent salts and dyes [23]. In this work, a green surface-modification process for PES-TA was developed to achieve an asymmetric positively charged NF membrane. The tertiary amine groups of PES-TA at the membrane surface were quaternized by reaction with water-soluble poly(ethylene glycol) diglycidyl ether (PEGDGE). The residual epoxy groups were then end-capped with poly(ethylene imine) (PEI). The morphology, pore size, and performance of these membranes are characterized in this study.

## 2. Experimental

### 2.1. Chemicals

Cardo poly(arylene ether sulfone) with pendant tertiary amine groups (PES-TA) was prepared as previously described [23]. The chemical structure is shown in Fig. 1. Poly(ethylene glycol) diglycidyl ether (PEGDGE) (MW: 218 g mol<sup>-1</sup>) and poly(ethylene imine) (PEI) (average MW=1200 g mol<sup>-1</sup>, 50 wt% in H<sub>2</sub>O) were purchased from Sigma-Aldrich. Methyl violet (MV), NaCl, and MgCl<sub>2</sub> were purchased from Sinopharm Chemical Reagent Co., Ltd. All other chemicals were of analytical grade and purchased commercially.

### 2.2. Asymmetric membrane preparation

An asymmetric PES-TA NF membrane was prepared using a classical non-solvent induced phase inversion method [24]. The polymer PES-TA was dissolved in N,N-dimethylformamide (DMF) and tetrahydrofuran (THF) co-solvent to form a homogenous 22 wt% polymer solution at 60 °C. The ratio of solvent and co-solvent was 3–2 and the membrane preparation conditions were as referenced reported previously [23]. The polymer solution was cast onto a nonwoven polyester fabric with a 150-micron blade at 30 °C, and 30% relative humidity. A 5 s evaporation period was

allowed before immersion into a deionized (DI) water coagulation bath. THF is a volatile solvent and its partial evaporation before immersion into the coagulation bath is necessary for the formation of a tight top layer with elevated PES-TA concentration. After the evaporation period, the cast film was immersed into a 30 °C DI coagulation bath. The phase-separated films were taken out of the coagulation bath and rinsed with 50 °C DI water for 30 min to remove residual solvent. Samples were stored in DI water.

### 2.3. Membrane surface grafting

#### 2.3.1. Preparation of PEGDGE-modified PES-TA NF membranes

The PES-TA membrane was modified by immersion into an aqueous solution containing PEGDGE, to enable reaction between the PES-TA NF membrane's intrinsic tertiary amine groups and the epoxy groups of PEGDGE. The PEGDGE solutions were made up as 1, 2, 4, 8, and 10 g PEGDGE dissolved in 100 mL DI water to produce concentrations of 1, 2, 4, 8, and 10 wt%, respectively. PES-TA membranes were immersed in PEGDGE aqueous solutions with different concentrations and heated at 60 °C for 10 h. The membrane was then removed from the reaction solution and washed thoroughly with DI water. The membrane is designated as PES-TA-PEGDGE.

#### 2.3.2. Preparation of PES-TA-PEGDGE-PEI NF membranes

Residual epoxy groups in the chain terminal of PES-TA-PEGDGE NF membrane were end-capped with polyethylene imine (PEI) solution at 60 °C for 2 h, in order to enhance the density of the surface's positive charge, by protonation of the PEI molecules. The concentration of the PEI solution was determined to be in the range of 0–6 wt%. Finally, the resultant membrane, designated as PES-TA-PEGDGE-PEI was washed and stored in DI water for further characterization.

### 2.4. Membrane characterizations

X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 290 system) was used to analyze the surface composition of the membranes. Al/Kα (hν=1486.6 eV) was used as the X-ray source. Quantification was based on peak areas. The surface morphology of the unmodified and modified PES-TA membrane samples was observed by atomic force microscopy (AFM, Bruker Dimension ICON SPM). Nanoscope analysis software version 1.40 was used for image acquisition and the AFM images were captured as a 3D model. Static contact angles were recorded by the sessile drop method using Drop Shape Analysis DSA10 (Krüss GmbH, Germany) at ambient temperature. Water droplets (5 μL) were dropped carefully on to the membrane surface with a micro-syringe. The reported data were determined from the average of at least 10 measurements in different positions for each sample. The streaming potential measurement was determined using an electrokinetic analyzer (SurPASS, Anton Paar GmbH, Austria). The streaming potential was detected by Ag/AgCl electrodes. A 10 mM KCl background electrolyte solution was used and the pH was adjusted with 0.1 M HCl and 0.1 M NaOH.

### 2.5. Separation and permeation properties

Both the unmodified and modified PES-TA NF membranes were tested using flat-sheet cross-flow test cells with an effective area of 23.75 cm<sup>2</sup> at 4 bar and 25 °C. The membrane samples were pressurized with DI water at 4 bar for 4 h before data collection. The membrane flux was measured by collecting the pure water permeate for a given period. The permeation flux (F) was calculated according to the following equation:

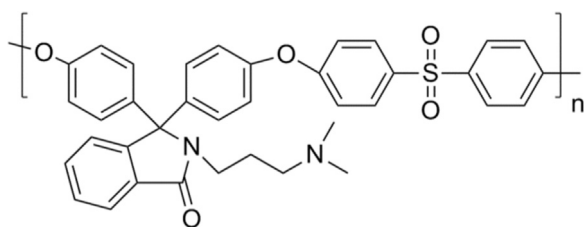


Fig. 1. The chemical structure of PES-TA.

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