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Novel PVDF membranes comprising n-butylamine functionalized graphene oxide for direct contact membrane distillation

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ABSTRACT

To enhance the mechanical properties and wetting resistance of poly(vinylidene fluoride) (PVDF) membranes for membrane distillation (MD) of seawater, we have added n-butylamine modified graphene oxide (GO-NBA) in PVDF flat-sheet and hollow fiber membranes. For the first time, it is found that the addition of GO-NBA leads to PVDF flat sheet membranes with greater mechanical properties than that of conventional GO because of better compatibility, dispersity and crystalline structure. The addition of the GO-NBA also improves the mechanical properties of PVDF hollow fiber membranes in both tensile and hoop directions. With a small loading of 0.5 wt% GO-NBA in PVDF hollow fiber membranes, the maximum tensile stress, maximum tensile stain and Young's modulus increase by 32%, 63% and 71%, respectively, while the liquid entry pressure (LEP) and burst pressure jump by 67% and 15%, respectively. Under direct contact membrane distillation (DCMD), the 0.5 wt% GO-NBA incorporated membrane shows a flux of 61.9 kg m^{-2} h^{-1} and a salt rejection of 99.9% using a model seawater as the feed at 80 °C. This work might provide useful insights to fabricate robust MD membranes for seawater desalination.

1. Introduction

Membrane distillation (MD) is an emerging technology for seawater desalination. It is a thermally driven separation process which involves the transport of water vapor across a hydrophobic membrane [1–3]. This technology possesses several unique advantages: (1) larger contact area and lower operating temperature compared to the conventional distillation; (2) lower operating pressure than pressure driven membrane processes such as reverse osmosis (RO); (3) 100% theoretical rejections to non-volatile solutes; (4) less vulnerable to high feed concentration; (5) lower energy consumption when powered by industrial waste energy or solar energy [4–8].

The key component of the MD system is the hydrophobic membrane which serves as the phase barrier to ensure high rejections to non-volatile impurities [9–11]. Among the hydrophobic polymeric materials, PVDF has received significant attention due to its intrinsic hydrophobicity, excellent processability and good thermal stability [12,13]. PVDF membranes are mainly produced by phase inversion methods such as the thermally induced phase separation (TIPS) and the non-solvent induced phase separation (NIPS). Each of them has its advantages and disadvantages [14,15]. In this work, the NIPS method has been chosen because: (1) it does not involve high temperature spinning and (2) it can produce asymmetric membranes with distinct surface and substrate morphology and properties, making it possible to fabricate membranes with highly porous substrates and relatively dense surfaces [15–17]. However, membranes fabricated via NIPS usually suffer from weak mechanical properties [15]. It is difficult to improve the mechanical properties of MD membranes because of the requirements of high porosity (> 75%) and large pore size (100–300 nm) [4,18,19]. During MD operations, membrane mechanical integrity will be further impaired due to the elevated operation temperature. In normal operations, a hydraulic pressure must be applied to the fluid to counterbalance the pressure drop. The hydraulic pressure can be high if the process is operated at a high flow rate with a long and congested module. Therefore, a technology to improve the mechanical properties of PVDF MD membranes remains a hot subject in the field.

One of the possible solutions is to produce multi-bore hollow fibers because the resultant membranes exhibit superior mechanical properties and minimal fiber breakage. The multi-bore concept was firstly commercialized by inge GmbH (part of BASF) which produced seven-bore hollow fiber membranes with improved operation stability for ultra-filtration (UF) applications [20]. Since then, PVDF multi-bore hollow fibers with different geometries have been fabricated and explored for MD applications [21–23]. Although these multi-bore hollow fibers show enhanced mechanical properties, the enhancive effect is still limited by the intrinsic properties of the PVDF material

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Nomenclature

Ra	mean roughness
N_w	permeation flux
ΔW	change in the permeate mass
A	effective membrane area
t	test duration
β	rejection
C_p	permeate concentration
C_f	feed concentration
C_0	initial salt concentration of the cold stream
C_1	final salt concentration of the cold stream
m_0	initial mass of the cold stream
m_1	final mass of the cold stream
N_{w0}	permeation flux for pristine membrane

[24]. The other method to improve the mechanical properties is to fabricate membranes by using mixed matrix materials where inorganic or carbon fillers are incorporated into the polymer matrix. The superior characteristics of the fillers or their unique interactions with the host substrate may reinforce the physicochemical properties of the polymer matrix and bring desirable features to the membranes [25–27].

Graphene and its derivatives are new reinforced materials for polymers due to their excellent mechanical properties [28]. Woo and his co-workers showed that by incorporating graphene into PVDF, the mechanical properties and anti-wetting ability of the membranes could be significantly improved [29]. Graphene can be produced by four major methods: micro-mechanical exfoliation of graphite, chemical vapor deposition, epitaxial growth, and the reduction of graphene oxide (GO) [30]. The first three techniques can produce relatively perfect graphene structures; however, mass production of graphene from these methods is still questionable [30,31]. In comparison, GO can be produced by cost-effective methods with a high yield by using cheap graphite as the raw material. It shows attractive physical properties similar to those of graphene [30]. In addition, GO possesses many functional groups such as hydroxyls and epoxides, which make it molecularly tunable on surface properties to ensure good compatibility with various polymer materials. However, since GO is inherently hydrophilic, incorporating GO into PVDF membranes would lower the contact angle and wetting resistance [32]. In addition, the different surface tensions between GO and PVDF may engender GO agglomeration and result in poor mixing in casting solutions. Therefore, surface modification of GO is necessary to increase its hydrophobicity and interaction with PVDF. Recently, some studies have successfully rendered hydrophobicity to GO via alkyl amine functionalization [33,34]. The modified GO has been blended with polymers such as polyethylene to form nanocomposites with significantly high mechanical properties [28,35,36]. However, there are few studies on the effect of adding the modified GO into the PVDF matrix. To our best knowledge, there is also no study to explore its potential for MD applications.

In this work, GO would be modified with n-butylamine (NBA) and incorporated into both PVDF flat sheet and hollow fiber membranes. A systematical comparison would be conducted among the pristine PVDF membrane, GO and modified GO (i.e., GO-NBA) embedded membranes in order to investigate the effects of GO-NBA on membrane morphology, mechanical properties and performance. If the membrane morphology would be significantly changed and the mechanical properties could be greatly improved with a small amount of GO-NBA loading, this study may open up a new approach to design stronger and better MD membranes for seawater desalination.

2. Experimental

2.1. Materials

The polymer PVDF Kynar® HSV 900 powder (specific gravity: 1.76–1.79) was acquired from Arkema Inc. N-methyl-2-pyrrolidone (NMP, > 99.5%), ethylene glycol (EG, > 99.5%), isopropanol (IPA, > 99.5%), *n*-butylamine (NBA, > 99.0%) and sodium chloride (NaCl, 99.5%) were purchased from Merck. Ethanol (> 99.98%) and PTFE particles (< 1 µm) were ordered from VWR and Sigma–Aldrich, respectively. All the above chemicals were used as received. The GO solution (5 mg/mL) was purchased from Angstron Materials Inc. In order to get dry GO for later usage, the GO solution was frozen in a refrigerator for 4 h followed by being freeze dried in a freeze dryer (S61-Modulyo-D, Thermo Electron Corp.). De-ionized (DI) water used in this work was produced by a Milli-Q unit (MilliPore).

2.2. Functionalization of GO and preparation of GO and GO-NBA films

GO of 100 mg was dispersed in 100 mL ethanol containing 400 mg NBA. The mixture was sonicated for 90 min to complete the reaction. The stable suspension was then filtered with a 0.2 µm Whatman™ Anodisc™ membrane in a dead-end permeation cell. The GO-NBA film left on the filter membrane was collected and washed by 50 mL ethanol followed by vacuum dry for 12 h. The GO film was obtained through the same method without the addition of NBA.

2.3. Dope preparation and membrane fabrication

Before the dope preparation, the PVDF polymer was firstly dried for 24 h in a vacuum oven at 80 °C to remove the moisture. GO or GO-NBA was grinded into fine powders using an agate mortar and pestle. The powders were then sonicated in a mixture of NMP and EG for 90 min. Subsequently, the suspension was transferred into a round-bottom flask agitated by an overhead stirrer and the PVDF polymer was gradually added into it. For comparison, the PVDF polymer was also added into a mixture of NMP and EG to prepare pure PVDF membranes. The dope concentrations for flat sheet membranes were summarized in Table 1. Each dope solution was stirred for 24 h at 60 °C to form a homogeneous polymer solution, it was then set aside for 12 h to degas air bubbles. The pure PVDF membrane, GO and GO-NBA added membranes were labeled as FS, FS-GO and FS-GO-NBA, respectively.

The effect of GO or GO-NBA addition was firstly demonstrated on the flat sheet membranes. The content of GO or GO-NBA nano-fillers was set to be 0.5 wt% of the total solid loading. The flat sheet membranes were cast by a casting knife with a gap of 150 µm and then immersed in a coagulant of 60/40 (wt/wt) IPA/water [23] for 8 min before being transferred to a water coagulant bath for 3 days to complete the phase inversion. The resultant membranes were named as FS, FS-GO and FS-GO-NBA, respectively.

GO-NBA was added in the PVDF hollow fiber membranes which were fabricated via a dry-jet wet phase inversion process as described elsewhere [37]. The concentration of GO-NBA in the total solid varied from 0, 0.5, 1, 1.5–2 wt%, and the corresponding hollow fibers were

Table 1
Dope formulations and casting conditions for flat sheet membranes.

Membrane ID	FS	FS-GO
Dope composition (wt%)	PVDF/NMP/EG = 15/80/5	PVDF/NMP/EG/GO = 14.925/80/5/0.075
Coagulant composition (wt %)	IPA/Water = 60/40	
Casting knife thickness (µm)	150	
Time in the coagulant (min)	8	