

LOW ENERGY REINFORCED MEMBRANE FOR PRESSURE DRIVEN APPLICATION

Cross-Reference to Related Application

[0001] This application claims the benefit of priority of Singapore Patent Application No. 10201904021V, filed 3 May 2019, the content of it being hereby incorporated by reference in its entirety for all purposes.

Technical Field

[0002] The present disclosure relates to a reinforced flat sheet membrane operable to withstand vacuum pressure and a high pressure of up to 1500 psi. The present disclosure also relates to a method of fabricating such a reinforced flat sheet membrane.

Background

[0003] In a membrane module for processing a liquid (e.g. wastewater), there is typically a leaf set that comprises, amongst other components (permeate carrier, spacer, etc.), a membrane. Mechanical strength of the membrane and overall leaf set thickness are key factors that affect pressure driven membrane purification performance in terms of water flux, rejection, power density, and reverse salt flux permeability.

[0004] In high pressure applications, membrane area between feed spacers may deform if mechanical strength of membrane is insufficient. In this regard, while commercially available reverse osmosis (RO) membrane tends to have sufficient mechanical strength for operation at high pressures for up to 1500 psi, such membranes tend to suffer from severe internal concentration polarization (ICP) when operated in pressure retarded osmosis applications due to presence of various support layers and their structural parameters, which may result in very low permeability and power density.

[0005] For pressure retarded osmosis (PRO) membrane operated under high pressure (up to 25 bar, about 50% of osmotic pressure), the membrane may get severely deformed and the resultant water fluxes may be significantly lower than what is theoretically predicted.

[0006] A membrane suitable for use in pressure retarded osmosis may need to have a reasonable level of mechanical strength to avoid severe membrane deformation at high pressures. The PRO membrane may also have a dense active layer that rejects salt efficiently,

provides for high water flux and low reverse salt permeability. Therefore, a reinforced membrane may be potentially considered as a suitable membrane for PRO, and even for FO.

[0007] Besides mechanical strength of membrane, thickness of the leaf set has to be considered for fabrication of low-energy spiral wound membrane module (SWM) for all pressure-driven membranes. Conventionally, various mesh materials are included in a leaf set to provide channels for feed and permeate to flow. Due to the high applied pressures in pressure driven membrane operations, the mesh materials also act as support materials in the leaf set to protect membrane integrity. Even when the membrane backing where the polymeric membrane is coated on have sufficient mechanical strength, polymeric membrane may get deform due to elongation with age and with higher applied pressure. The mesh materials potentially reduce the amount of membrane material that may be fitted into the module. In other words, filtration output gets compromised due to fitting of various supporting materials. Additionally, the support materials may render module fabrication difficult and more expensive. For example, with the supporting materials, including the membrane, it tends to get more difficult to roll up all the components (i.e. more layers) to fit into a spiral wound module.

[0008] There is thus a need to provide for a solution that addresses one or more of the limitations mentioned above. The solution should at least provide for a reinforced flat sheet membrane having reasonable mechanical strength and thickness to operably withstand pressure conditions used in various membrane applications (RO, PRO, FO, etc.).

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Summary

[0009] In a first aspect, there is provided for a reinforced flat sheet membrane operable to withstand vacuum pressure and a high pressure of up to 1500 psi, wherein the reinforced flat sheet membrane comprises:

- a polymeric membrane;

- a permeate carrier which reinforces the polymeric membrane and has channels to direct permeate flow;

- wherein the polymeric membrane has the permeate carrier incorporated therein and the channels of the permeate carrier are partially exposed at a surface of the polymeric membrane.

[0010] In another aspect, there is provided for a method of fabricating a reinforced flat sheet membrane operable to withstand vacuum pressure and a high pressure of up to 1500 psi, wherein the reinforced flat sheet membrane comprises:

a polymeric membrane;

a permeate carrier which reinforces the polymeric membrane and has channels to direct permeate flow;

wherein the polymeric membrane has the permeate carrier incorporated therein and the channels of the permeate carrier are partially exposed at a surface of the polymeric membrane,
5 wherein the method comprises:

contacting the permeate carrier with a pre-wetting agent;

casting a polymer solution on the permeate carrier; and

forming the polymeric membrane from the polymer solution with the permeate carrier
10 incorporated in the polymeric membrane.

Brief Description of the Drawings

[0011] The drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the invention. In the following description, various embodiments
15 of the present disclosure are described with reference to the following drawings, in which:

[0012] FIG. 1 shows examples of materials that may be available and used as permeate carriers to mechanically reinforce a flat sheet polymeric membrane. The first column shows a TJ-30 material having pores of an average 400 micron mesh holes that may even include a few larger mesh hole sizes of up to 1200 micron mesh holes or more. The second column shows P16
20 material having pores of about 300 μm . The third column shows TF800 material having pores of about 100 μm . The fourth column shows BW30 material having pores of about 400 μm . The actual size is derived by using the scale shown in the photo to obtain a measurement and dividing the measurement by 4. The top row of images shows a surface of the permeate carriers that are not yet incorporated to the polymeric membrane. The bottom row of images shows the
25 opposing surface of the permeate carriers that are not yet incorporated to the polymeric membrane. Either surfaces of the permeate carrier may be exposed at the back surface of the polymeric membrane when the permeate carrier is incorporated in a polymeric membrane. The back surface of the polymeric membrane may be a surface which the permeate flows out from the polymeric membrane.

[0013] FIG. 2 shows a reinforced flat sheet membrane of the present disclosure formed with the permeate carrier in a handframe before scale-up. The polymer solution for forming the flat sheet membrane was coated on the permeate carrier.
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[0014] FIG. 3A shows a 60x magnification of the front and back view of a regular flat sheet membrane coated with a polyamide rejection layer. Specifically, FIG. 3A shows the regular flat sheet membrane formed with non-woven polyester backing. The top row image shows the polyamide rejection layer (front view) while the bottom row image shows the opposing side having the non-woven polyester backing (back view). The regular flat sheet membrane herein is not reinforced by a mesh, i.e. no permeate carrier incorporated therein.

[0015] FIG. 3B shows a 60x magnification of the front and back view of a reinforced flat sheet membrane coated with a polyamide rejection layer. Specifically, FIG. 3B shows the reinforced flat sheet membrane formed with a TJ-30 permeate carrier, wherein the curing of the polymer solution to form the flat sheet membrane was carried out with the polymer solution facing a direction which gravity acts (i.e. downwards curing). Said differently, the permeate channels of the permeate carrier was positioned upwards (i.e. in a direction that opposes gravity). The top row image shows the polyamide rejection layer (front view) while the bottom row image shows the opposing side having the permeate channels of the TJ-30 permeate carrier (back view).

[0016] FIG. 4A shows a 60x magnification of front and back view of a reinforced flat sheet membrane coated with a polyamide rejection layer. Specifically, FIG. 4A shows the reinforced flat sheet membrane formed with a TJ-30 permeate carrier, wherein the curing of the polymer solution to form the flat sheet membrane was carried out with the polymer solution facing against the direction which gravity acts (i.e. upwards curing) and a FO recipe was used. Said differently, the permeate channels of the permeate carrier was positioned downwards (i.e. in the same direction as gravity). The top row image shows the polyamide rejection layer (front view) while the bottom row image shows the opposing side having the permeate channels of the TJ-30 permeate carrier (back view). The term "FO recipe" herein refers to a polymeric membrane, including the reinforced flat sheet membrane, made using similar active components/materials except for compositional differences. Specifically, a particular composition of MPD and TMC were used for interfacial polymerization to form the polyamide rejection layer.

[0017] FIG. 4B shows a 60x magnification of front and back view of a reinforced flat sheet membrane a polyamide rejection layer. Specifically, FIG. 4B shows the reinforced flat sheet membrane formed with a TJ-30 permeate carrier, wherein the curing of the polymer solution to form the flat sheet membrane was carried out with the polymer solution facing a direction

which gravity acts (i.e. downwards curing) and a FO recipe was used. Said differently, the permeate channels of the permeate carrier was positioned upwards (i.e. in a direction that opposes gravity). The top row image shows the polyamide rejection layer (front view) while the bottom row image shows the opposing side having the permeate channels of the TJ-30 permeate carrier (back view).

[0018] FIG. 4C is a field emission scanning electron microscopy (FESEM) image showing the cross-sectional view of a reinforced flat sheet membrane of FIG. 4A. Scale bar denotes 100 μm .

[0019] FIG. 4D is a FESEM image showing the bottom view of the reinforced flat sheet membrane of FIG. 4C, wherein the bottom view is the side having the permeate channels of the permeate carrier. Scale bar denotes 100 μm .

[0020] FIG. 5A shows an industrial scale reinforced flat sheet membrane of the present disclosure, wherein the flat sheet membrane is reinforced using a P16 permeate carrier.

[0021] FIG. 5B shows a reinforced flat sheet membrane of the present disclosure, wherein the reinforced flat sheet membrane is fabricated at an industrial scale compared to the reinforced flat sheet membranes of FIG. 4A to 4D, which were produced using smaller sized handframes. The top left image shows the polyamide rejection layer and scale bar denotes 500 μm . The top right image shows the side having the permeate channels of the permeate carrier (back side) and scale bar denotes 500 μm . The bottom left image is a 10x magnification of the top right image and scale bar denotes 50 μm . Specifically, the reinforced flat sheet membrane has significant improvement in terms of the unblocked permeate channels at back side of the membrane.

[0022] FIG. 5C shows a reinforced flat sheet membrane fabricated for reverse osmosis (RO). The top left image shows the polyamide rejection layer and scale bar denotes 750 μm . The top right image shows the side having the permeate channels of the permeate carrier (back side) and scale bar denotes 250 μm . The bottom image is a 5x magnification of the top right image and scale bar denotes 50 μm . Specifically, the reinforced flat sheet membrane has significant improvement in terms of the unblocked permeate channels at back side of the membrane.

[0023] FIG. 6 is a table showing the RO performance of a reinforced flat sheet made on handframe tested under 225 psi (15 bar). * refers to the sample of reinforced membrane ID D050718HF23.4 made with polyester backing on a handframe. ** refers to the column having

the title “% reduction”, which indicates for the percentage of thickness reduction with respect to the reference membrane. The results are based on handframe data.

[0024] FIG. 7 is a table showing the RO performance of a reinforced flat sheet membrane made using phase inversion (PI) while interfacial polymerization (IP) was carried out on handframe.

5 Testing was carried out under 225 psi (15 bar) for the reinforced flat sheet membrane made using recipe B except for the samples having a membrane ID marked with * and **, wherein * denotes a resultant reinforced flat sheet membrane made from polymer coated on a thin film composite (TFC) line and where recipe D was used, and ** denotes a resultant reinforced flat sheet membrane made using recipe D. The term “line” in the present disclosure refers to a
10 production line that involves some level of automation for manufacturing the resultant reinforced flat sheet membrane. The term “TFC line” refers to a process used for making the salt rejection polyamide layer on the polymeric membrane. Recipes B and D refer to the chemical compositions use for making the polymeric membrane on the phase inversion (PI) line, wherein polysulfone (PS) is used for making the polymeric membrane. Recipes B and D
15 refer to compositions for making the polymeric membrane, wherein recipe B uses 1 wt% of polymer more than recipe D. However, the viscosity of the polymer solution (i.e. dope) used to form the polymeric membrane based on recipe B is 30% higher than that of recipe D even though an additional 1 wt% of polymer was used in the polymer solution.

[0025] FIG. 8 is a table showing power density and reverse salt flux of reinforced flat sheet
20 membranes (RM) made using a handframe (HF) and fabricated on the phase inversion (PI) coater line with different polymer dopes, i.e. recipe B involving polysulfone (PS-B) and recipe D involving polysulfone (PS-D), in comparison with a commercially available RO membrane at various pressures. Specifically, RO performance of the present reinforced flat sheet membrane (RM) made on handframe (HF) and lined with polysulfone (PS) dope is compared
25 with commercially available RO membranes.

[0026] FIG. 9 is a table showing FO performance of a reinforced flat sheet membrane of the present disclosure made on the coater line tested under FO (recipe B). For FO testing, the reinforced membrane used has interfacial polymerization carried out on a membrane fabricated using the coater line based on the following specifications: line speed - 3 MPM, pump speed -
30 13 Hz, pre-wetting agent – deionized (DI) water, wetting supplier – a peristaltic pump with 4 cartridges at 4x50 ml per min, reinforcing material: TJ-30 permeate carrier (tricot). Jw denotes water flux from feed to draw solute, and Js denotes reverse salt flux. The FO test is carried out

with feed facing active layer while PRO test is carried out with draw solute facing active layer. Coupons A and B refer to two different locations of a reinforced flat sheet membrane used in this example. Specifically, coupons A and B are both samples of a rectangular piece cut out from the reinforced flat sheet membrane having an area of 42 cm². This helps to gauge the uniformity of the reinforced flat sheet membrane.

[0027] FIG. 10A is a table showing the performance of 2514 RO elements at 15 bar and 2000 ppm NaCl. The RO elements are spiral wound membranes made using the present reinforced flat sheet membrane. For element testing, the polyamide was interfacially polymerized onto the reinforced flat sheet membrane that was cast on the coater line. Whether the interfacial polymerization was carried out using a handframe (HF) or the coater line (Line) is indicated under the IP mode in the table. The conditions used for testing are shown in FIG. 10A. The numbers 2514 indicate that each RO element has a diameter of 2.5 inch and a length of 14 inch.

[0028] FIG. 10B is a table showing the performance of 1812 RO elements at 3.4 bar and 500 ppm NaCl. The RO elements are spiral wound membranes made using the present reinforced flat sheet membrane. For element testing, the polyamide was interfacially polymerized onto the reinforced flat sheet membrane that was cast on the coater line. The interfacial polymerization was carried out using the coater line (Line) as indicated under the IP mode in the table. The conditions used for testing are shown in FIG. 10B. The numbers 1812 indicate that each RO element has a diameter of 1.8 inch and a length of 12 inch.

[0029] FIG. 11A compares a conventional spiral wound module (left image) to a spiral wound module comprising the reinforced flat sheet membrane of the present disclosure. The conventional spiral wound module consists of 3 separate components, which are the feed spacer, permeate carrier, and membrane. Meanwhile, the spiral wound module of the present disclosure has 2 separate components, i.e. the feed spacer and the reinforced flat sheet membrane, wherein the permeate carrier is incorporated into the reinforced flat sheet membrane to form as a single component.

[0030] FIG. 11B shows an element 1812 of a spiral wound module.

[0031] FIG. 11C shows an element 2514 of a spiral wound module.

[0032] FIG. 12A shows a spiral wound leaf set configuration for PRO, wherein the active layer faces the draw solution.

[0033] FIG. 12B shows a spiral wound leaf set configuration for RO, wherein active layer faces feed solution.

[0034] FIG. 13 shows a reinforced flat sheet membrane prepared without pre-wetting, wherein the reinforced flat sheet membrane was creased.

Detailed Description

5 [0035] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practised.

[0036] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments,
10 even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0037] The present disclosure relates to a reinforced flat sheet membrane operable for various treatment processes. The treatment processes may involve operating pressures ranging from
15 vacuum to high pressures. Non-limiting examples of treatment processes include reverse osmosis (RO), pressure retarded osmosis (PRO), forward osmosis (FO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF), pervaporation, membrane distillation, and/or gas separation. The present reinforced flat sheet membrane may be operable to withstand a wide range of operating pressures, including vacuum pressure and high operating pressures, such as
20 pressure in the range of 0 Pa and up to 1500 psi (about 10.34 MPa), or 1.5×10^{-11} psi to 1500 psi, and is hence versatile.

[0038] The reinforced flat sheet membrane includes a polymeric membrane and a permeate carrier incorporated to the polymeric membrane. In various instances, there may be a dense rejection layer formed on the polymeric membrane, away from the permeate carrier (i.e.
25 permeate carrier and rejection layer are formed on opposing sides of the polymeric membrane). The dense rejection layer may be herein interchangeably termed dense selective layer, dense active layer (or simply active layer), and active rejection layer.

[0039] The polymeric membrane herein may be interchangeably termed substrate layer, support layer, porous substrate layer, and membrane substrate. The polymeric membrane is the
30 layer that forms the bulk of the reinforced flat sheet membrane. In other words, the polymeric membrane contains the permeate carrier.

[0040] The permeate carrier may be a mesh having pores of varying or uniform size. The pores may be defined by holes formed between filaments woven to construct the mesh. The filaments may be woven or aligned to define channels. Such channels are termed herein permeate channels. The permeate channels may be configured to direct permeate flow in a desired direction. The permeate carrier may be substantially embedded in the polymeric membrane. For example, the permeate carrier may be partially embedded such that the permeate channels may be substantially exposed (e.g. entirely or partially exposed) for permeate flow to be directed away from the polymeric membrane.

[0041] The reinforced flat sheet membrane is advantageous as the polymeric membrane and permeate carrier are formed as a single component. This contrasts with conventional configurations wherein the polymeric membrane and permeate carrier are used as separate components. Even with the polymeric membrane and permeate carrier formed as a single component, not only is the mechanical strength of the polymeric membrane enhanced but also the overall thickness of a leaf set reduced. A leaf set, in the context of the present disclosure, includes a membrane and other filtration components such as feed spacer, permeate carrier, additional backing materials. For example, conventionally, the leaf set of a spiral wound element in a spiral wound membrane module may include a feed spacer and a permeate carrier with a polymeric membrane sandwiched between the feed spacer and permeate carrier. A membrane module interchangeably refers to the spiral wound element. The element may have a housing, wherein the housing refers to a casing for the spiral wound element.

[0042] Advantageously, with a permeate carrier formed into the polymeric membrane, this mitigates, or may even eliminate, deformation of the polymeric membrane arising from high pressure and vacuum pressure applied thereon. Deformation of the membrane may at least adversely reduce filtration output.

[0043] Advantageously, incorporation of the permeate carrier to the polymeric membrane reduces overall thickness of a leaf set compared to a conventional leaf set. With reference to FIG. 6 as an example, using the same method of membrane fabrication on a handframe, the overall leaf set thickness was reduced from 62 mil (D050718HF23.4) to 51 mil (D171218HF33.1), representing a 17% leaf set thickness reduction, even when a 11 mil thickness permeate carrier was used. The unit “mil” used herein refers to a thousandth of an inch. Moreover, a significantly desirable rejection of 97.1% remains attainable. This allows more of the present reinforced flat sheet membrane to be fitted into a module, increasing at

least the treatment efficiency per module. Moreover, by reducing the number of components involved and thickness of the leaf set, the leaf set and the various components may be more easily rollable for fabrication of the spiral wound configuration, rendering less fabrication efforts (less energy consumed to manufacture for the same or higher filtration output).

5 **[0044]** The present method also includes a method of fabricating the reinforced flat sheet membrane. The present method reinforces the polymeric membrane with a mesh (i.e. permeate carrier) which enables higher water permeability as incorporation of the permeate carrier may render the polymeric membrane to have less structure parameter, which helps in mitigating internal concentration polarization (ICP). The polymeric membrane has less structure
10 parameter because part of the polymeric membrane is replaced by the integrated permeate carrier. Conversely, a conventional polymeric membrane may have a porous layer and a dense rejection layer formed thereon, and while the porous layer may be more porous than the dense rejection layer, the porous layer is relatively denser and more tortuous than a permeate carrier. The term “structure parameter” herein is an intrinsic membrane parameter that may be a
15 function of the support layer thickness, tortuosity, and porosity. It may be a parameter that serves as an indication of the degree of internal concentration polarization in the porous support structure of, for example, a forward osmosis membrane, may be useful in evaluations of a membrane’s (e.g. forward osmosis membrane) performance. The structure parameter is usually a consistent parameter regardless of operating conditions. The support layer in this case may
20 be the permeate carrier incorporated in the polymeric membrane.

[0045] The present reinforced flat sheet membrane may also have the permeate carrier (mesh reinforcing material) replace a conventional non-woven substrate.

[0046] Details of various embodiments of the reinforced flat sheet membrane, its method of fabrication, and advantages associated with the various embodiments are now described below.

25 **[0047]** In the present disclosure, there is provided for a reinforced flat sheet membrane operable to withstand vacuum pressure and a high pressure of up to 1500 psi. The reinforced flat sheet membrane may comprise a polymeric membrane, and a permeate carrier which reinforces the polymeric membrane and has channels to direct permeate flow, wherein the polymeric membrane has the permeate carrier incorporated therein and the channels of the
30 permeate carrier may be partially exposed at a surface of the polymeric membrane.

[0048] In various embodiments, the permeate carrier may comprise a mesh. The mesh may comprise a woven mesh, a non-woven mesh, or a tricot mesh. The mesh may be formed of

cellulose, polyester, polypropylene, acrylic, nylon, sulfonated polysulfone, polysulfone, polyethersulfone, polyimide, polyamide, polybenzimidazole, polyacrylonitrile, polyarylsulfone, poly(vinyl butyral), polyetherimide, a derivative thereof, or a combination thereof.

- 5 [0049] In various embodiments, the mesh may have a pore size ranging from 100 μm to 5000 μm , 200 μm to 5000 μm , 500 μm to 5000 μm , 1000 μm to 5000 μm , 1500 μm to 5000 μm , 100 μm to 200 μm , 100 μm to 500 μm , 100 μm to 1000 μm , 200 μm to 1000 μm , 200 μm to 500 μm , 100 μm to 2000 μm , 200 μm to 2000 μm , 500 μm to 2000 μm , 1000 μm to 2000 μm , etc. In various instances, the pore size may be about or more than 1000 μm . In various instances, the pore size may be about 500 μm or about 200 μm . Regardless of the pore size of the mesh (i.e. permeate carrier), the reinforced flat sheet membrane remains producible.

- [0050] In various embodiments, the polymeric membrane may have a porous substrate layer which (i) an active rejection layer may be formed on, and/or (ii) the permeate carrier may be incorporated in the porous substrate layer. In various instances, the polymeric membrane may itself serve as the porous substrate layer.

- 15 [0051] The active rejection layer may comprise polyamide, polyamine, polyamide-imide, polyhydric alcohol, polyphenol, a derivative thereof, or a combination thereof. Such material may be easily fabricated through interfacial polymerization or any suitable crosslinking methods.

- 20 [0052] The porous substrate layer may comprise cellulose, polyester, polypropylene, acrylic, nylon, sulfonated polysulfone, polysulfone, polyethersulfone, polyimide, polyamide, polybenzimidazole, polyacrylonitrile, polyarylsulfone, poly(vinyl butyral), polyetherimide, a derivative thereof, or a combination thereof.

- [0053] In various embodiments, the reinforced flat sheet membrane may have a thickness ranging from 20 μm to 300 μm , 30 μm to 300 μm , 50 μm to 300 μm , 100 μm to 300 μm , 200 μm to 300 μm , 20 μm to 100 μm , 30 μm to 100 μm , 20 μm to 200 μm , 30 μm to 200 μm , etc. In addition to the reduced thickness relative to polymeric membrane and permeate carrier conventionally used as separate components), such thickness also renders better water flux without compromising salt rejection. For example, at least a 17% reduction in thickness may be achieved using the present reinforced flat sheet membrane compared to a conventional leaf set which has permeate carrier and polymeric membrane configured as separate components.

A rejection of at least 97.1% can still be achieved even when the permeate carrier is integrated into the polymeric membrane.

[0054] The reinforced flat sheet membrane may further comprise a pre-wetting agent coated on the permeate carrier. The pre-wetting agent may be applied to the permeate carrier prior to contacting the permeate carrier with the polymer solution to form a polymeric membrane having the permeate carrier therein. The pre-wetting agent renders the permeate carrier suitable for subsequent instantaneous pre-curing upon contact with the polymer solution (i.e. polymer dope) prior to phase inversion (complete curing) in a coagulation tank. The pre-wetting agent also mitigates formation of defects when the polymer solution coagulates to form the polymeric membrane in the presence of the permeate carrier.

[0055] In various embodiments, the reinforced flat sheet membrane may be operable to withstand a pressure from 0 psi to 1.5×10^{-11} psi, 0 psi to 1000 psi (about 6.89 MPa), 0 psi to 1500 psi, 1.5×10^{-11} psi to 1000 psi, or 1.5×10^{-11} psi to 1500 psi, etc.

[0056] In various embodiments, the reinforced flat sheet membrane may be operable for microfiltration, ultrafiltration, nanofiltration, reverse osmosis, pressure retarded osmosis, forward osmosis, pervaporation, membrane distillation, and/or gas separation.

[0057] Embodiments and advantages described for the present reinforced flat sheet membrane of the first aspect can be analogously valid for the present method of fabrication of the reinforced flat sheet membrane subsequently described herein, and vice versa. As the various embodiments and advantages have already been described above and examples demonstrated herein, they shall not be iterated for brevity.

[0058] The present disclosure also provides for a method of fabricating a reinforced flat sheet membrane operable to withstand vacuum pressure and a high pressure of up to 1500 psi, wherein the reinforced flat sheet membrane may comprise a polymeric membrane, a permeate carrier which reinforces the polymeric membrane and has channels to direct permeate flow, wherein the polymeric membrane has the permeate carrier incorporated therein and the channels of the permeate carrier are partially exposed at a surface of the polymeric membrane, wherein the method may comprise contacting the permeate carrier with a pre-wetting agent, casting a polymer solution on the permeate carrier, and forming the polymeric membrane from the polymer solution with the permeate carrier incorporated in the polymeric membrane.

[0059] In various embodiments, contacting the permeate carrier with the pre-wetting agent may comprise dispensing the pre-wetting agent onto the permeate carrier at a flow rate of 10

mL/min to 10 L/min, 100 mL/min to 10 L/min, 1 L/min to 10 L/min, etc. Such flow rates contribute to proper control of coating the permeate carrier sufficiently and/or homogeneously so that the no defects (e.g. pinhole defects or blocked permeate channels) get formed when the polymer solution is cast thereon. The dispensing of the pre-wetting agent may be carried out
5 by hand or on an industrial line. By hand, the permeate carrier may be laid on a frame where a user can control the frame for dispensing the pre-wetting agent thereon. As for an industrial line, machines and equipments such as conveyor belts for the permeate carrier to be laid thereon may be used to move the permeate carrier under a dispensing module that dispenses the pre-wetting agent onto the permeate carrier. Methods of dispensing the pre-wetting agent onto the
10 permeate carrier may be carried out by any suitable means, for example, spraying, misting, pouring, sponging, slot die, roller spreader, nip-roll spreader, dripping, and soaking.

[0060] The pre-wetting agent may comprise a liquid or a gaseous solution. The liquid or gaseous solution may contain (i) an anionic surfactant, wherein the anionic surfactant may comprise a detergent, a fatty acid, a foaming agent, or a dispersant, or (ii) a non-ionic surfactant,
15 wherein the non-ionic surfactant may comprise alcohol, ester, phenol, ether, or amide, or (iii) a cationic surfactant, wherein the cationic surfactant may comprise a salt solution, wherein the salt solution may comprise an organic solvent or an inorganic solvent, wherein the organic solvent may comprise N-methyl-2-pyrrolidone, dimethylformamide, hexane, or a combination thereof, wherein the inorganic solvent may comprise water, or (iv) a combination thereof.

[0061] The present method may further comprise removing excess pre-wetting agent from the permeate carrier. Removal of the excess pre-wetting agent may be carried out by different physical means, such as but not limited to, removal by using sponge, compressed air, vacuum suction, etc. The removal may be carried out prior to phase inversion.

[0062] The present method may further comprise dissolving a polymer in an organic solvent
25 to form the polymer solution for casting on the permeate carrier, wherein the organic solvent may comprise 1-methyl-2-pyrrolidinone, dimethyl-acetamide, dimethyl formamide, or a combination thereof.

[0063] The polymer in the organic solvent may have a concentration ranging from 5 wt% to 50 wt%, 10 wt% to 50 wt%, 20 wt% to 50 wt%, 30 wt% to 50 wt%, 40 wt% to 50 wt%, 10
30 wt% to 20 wt%, etc. The polymer solution may have a viscosity ranging from 100 to 100,000 cps, 1000 to 100,000 cps, 10,000 to 100,000 cps, etc. For example, the polymer solution may have a viscosity in a range of 1100 to 1600 cps. Such viscosities contribute to proper control

of coating the permeate carrier sufficiently and/or homogeneously so that the no defects (e.g. pinhole defects or blocked permeate channels) get formed when the polymer solution is cast thereon.

[0064] In various embodiments, forming the polymeric membrane may comprise coagulating the polymer solution by phase inversion in the presence of a non-solvent, e.g. water or aqueous solution of inorganic salts wherein the aqueous solution may contain 20 vol% (or less) of one or more organic solvents. The organic solvent in such aqueous solution may include, but not limited to, one or more alcohols like isopropanol, ethanol, polyethylene glycol (PEG), or a combination thereof. In various embodiments, coagulating the polymer solution by phase inversion may comprise having the polymer solution cast onto the permeate carrier, and immersing the polymer solution with the permeate carrier into the non-solvent, wherein the polymer solution and the permeate carrier are arranged to have the polymer solution face any direction in the non-solvent. For example, the phase inversion may be carried out with the permeate carrier and polymer solution arranged on a wetted mesh support with the polymer solution facing upwards, downwards, perpendicular, or enter a coagulant bath facing an angle to the surface of the coagulant in a coagulant bath. In other words, the permeate channels that are exposed face downwards, upwards, perpendicular, or enter a coagulant bath facing an angle to the surface of the coagulant in a coagulant bath, respectively. When either the polymer solution or permeate carrier face downwards, the polymer solution or permeate carrier faces the direction in which gravity acts. Advantageously, the present method is versatile in this regard.

[0065] In various embodiments, forming the polymeric membrane may comprise coagulating the polymer solution by phase inversion at a temperature ranging from -10°C to 150°C, 10°C to 150°C, 50°C to 150°C, 100°C to 150°C, etc. Such temperatures contribute to proper control of structures of the polymeric membrane (i.e. porous substrate layer). The coagulant used may comprise or may be with or without anti-freeze agent. The coagulant may comprise or may be steam or supersaturated steam. In some instance, prior to phase inversion, the polymer solution may have a layer that is already cured or may be partially cured (partially solidified/coagulated) as a polymer. In various instances, the curing (solidifying/coagulation) may occur in the phase inversion process.

[0066] The present method may further comprise subjecting the polymeric membrane to interfacial polymerization or chemical crosslinking to form an active rejection layer. The active

rejection layer may be formed on the polymeric membrane away from the permeate carrier that is incorporated in the polymeric membrane, such that channels of the permeate carrier are exposed or partially exposed at a surface of the polymeric membrane opposing (i.e. opposite to) the surface where the active rejection layer is formed.

- 5 [0067] Apart from the above, various embodiments may include modifying the phase inversion from a lab-scale to an industrial-scale phase inversion casting line. Various setting mentioned above (e.g. temperatures, flow rates, viscosities) may be looked at to translate lab-scale fabrication to industrial-scale fabrication, which involves fabricating the reinforced flat sheet membrane with a width ranging from 0 to at least 2 m and a length of more than 0 to at least 10 2000 m), such that the reinforced flat sheet membrane may be readily available for all pressure driven applications (e.g. reverse osmosis, forward osmosis and pressure retarded osmosis). As mentioned above, at the industrial-scale, a line speed of more than 0 MPM to at least 50 MPM may be considered. Such line speeds contribute to proper control of coating the permeate carrier sufficiently and/or homogeneously so that the no defects (e.g. pinhole defects or blocked 15 permeate channels) get formed when the polymer solution is cast thereon, and also control the coagulation rate and residence time of the polymer solution in a coagulant bath. In addition to line speed, other parameters already identified above (e.g. polymer solution viscosity, mesh pore size, wetting flow rate) help to fabricate the reinforced flat sheet membrane with sufficient permeate channels for good permeate flow rate. The present method allows for fabrication of 20 spiral wound membrane element having a length ranging from 12" to 2 m and a diameter ranging from 1" to 12", wherein the spiral wound membrane element includes the reinforced flat sheet membrane of the present disclosure.

- [0068] In the present disclosure, when used in the context of a unit of measurement, such as referring to a dimension or size (e.g. length, diameter, surface area), a number accompanied by 25 the symbol " (e.g. 12") refers to a value in inch. For example, 1" and 12" refer to 1 inch and 12 inch, respectively.

- [0069] The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from the definition of the invention.

- 30 [0070] In the context of various embodiments, the articles "a", "an" and "the" as used with regard to a feature or element include a reference to one or more of the features or elements.

[0071] In the context of various embodiments, the term “about” or “approximately” as applied to a numeric value encompasses the exact value and a reasonable variance.

[0072] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

- 5 [0073] Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

Examples

- 10 [0074] The present disclosure relates to a reinforced flat sheet membrane, which may be part of a thinner leaf set comprising the reinforced flat sheet membrane, for use in low energy pressure driven application. The present disclosure also relates to a method of making such a reinforced flat sheet membrane.

- [0075] The reinforced flat sheet membrane may be used for pressure driven water purification
15 applications, e.g. reverse osmosis (RO), pressure retarded osmosis (PRO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), and forward osmosis (FO).

- [0076] To fabricate the reinforced flat sheet membrane, the porous substrate layer may be part of a base layer having mechanical reinforcement (FIG. 1) from the permeate carrier, wherein the permeate channels of the permeate carrier are substantially exposed at the back side of the
20 reinforced flat sheet membrane. The back side of the reinforced flat sheet membrane herein refers to a side of the reinforced flat sheet membrane proximal to permeate flow or where the permeate channels are located. The reinforced flat sheet membrane may be independently used for low pressure applications or may be coated with a dense rejection layer for higher pressure salt rejection applications.

- 25 [0077] The present reinforced flat sheet membrane and its method of fabrication are described in further details, by way of non-limiting examples, as set forth below.

[0078] Example 1: General Discussion of the Reinforced Flat Sheet Membrane and Method – Pre-Wetting of Permeate Carrier

- [0079] The present disclosure describes a robust process of making a reinforced flat sheet
30 membrane for pressure driven application (e.g. including up to 1500 psi). The resultant membrane has a high salt rejection layer, low reverse salt permeability, high flux permeability, is resistant to deformation at high pressure, and has overall thickness reduction as a spiral

wound leaf set, all of which lead to an increase in overall efficiency of a spiral wound element comprising the present reinforced flat sheet membrane.

[0080] The fabrication method involves casting a polymer solution over a pre-wetted permeate carrier (e.g. mesh) and coagulating the polymer from the polymer solution via phase inversion.

5 Advantageously, wetting of the mesh allows for direct casting of polymer solution onto a mesh having a mesh size of more than 300 micron, which may otherwise produce membranes with pinhole and a mechanically weak phased inversed layer that fails under high pressure. Nevertheless, direct casting may work on permeate carrier with smaller mesh size of less than 300 micron, bearing in mind that permeate carriers having smaller mesh size may be more
10 expensive and/or not readily available. Direct casting on permeate carriers having mesh size of less than 300 micron may not be easily repeatable for scaling up membranes to industrial size, but this is rendered possible with the present method that involves pre-wetting of the permeate carrier. Moreover, without pre-wetting, the polymer solution may penetrate through the permeate carrier and blocks the channels of the permeate carrier.

15 **[0081]** For lab-scale fabrication, to cast a consistently good membrane without pinholes and blocked permeate channels (FIG. 3A) for a mesh having pore sizes of more than 300 micron, pre-wetting the mesh with a liquid of different constituent prior to casting and coagulating the polymer solution to form a porous membrane may be advantageous, especially with the cast polymer solution facing downwards (i.e in the same direction which gravity acts). A thin
20 coagulated layer formed almost instantly after casting and phase inversion, with the polymer solution facing down help to prevent the polymer solution that is still in its liquid form from seeping through the permeate carrier's pores, which in turn prevents formation of pinholes, renders unblocked permeate channels, and reduced polymer membrane thickness. Coagulating the membrane may also be carried out with the polymer solution facing a direction that opposes
25 the direction in which gravity acts (i.e. facing upwards) (FIG. 4A).

[0082] Accordingly, for lab-scale coating, the pre-wetting renders scaling up of the present method successfully to an industrial scale coating line for fabricating reinforced flat sheet membrane of the present disclosure. For example, an industrial-scale coating line of 1 m width and length of more than 100 m can be set up. In such an industrial-scale, the polymer solution
30 may be cast using, e.g. a slot die, in any direction or at any angle on to a substrate (e.g. perpendicularly on to a substrate). The process may depend on control of substrate wetting,

drying, polymer dope recipe and viscosity, dope dispenser pressure, pump speed, line speed, coagulation temperatures, rinsing tank temperatures, etc.

[0083] Subsequently, the resultant membrane's performance may be tested using a method that has been developed to enable flat-sheet flux and salt rejection determination without being affected by leakage from the non-active membrane area, which comprises the permeate carrier, wherein the method does not suffer from permeate leak or feed flow leak from pressure driven testing or from FO/PRO operation testing. The testing method may be termed herein a flat sheet coupon performance quality testing method to prevent leakage from the non-active layer of the present reinforced flat sheet membrane. Vacuum grease, silicon, blue tack, plasticine, any removable gel or fluid, or malleable solid, which may fill the tiny channels and/or pores of the tricot/mesh (i.e. permeate carrier) at the back side of the membrane may be carefully applied outside the active area but within the boundary of the testing cell prior to performance testing.

[0084] Example 2: Detailed Discussion of the Reinforced Flat Sheet Membrane and Method

[0085] A membrane is one of the factors affecting pressure driven performance in terms of water flux as well as power density, for example, in PRO. Conventional membranes for high pressure application may be fabricated by coating a porous polymer support layer directly onto a non-woven polyester substrate via phase inversion. The support layer then undergoes interfacial polymerization on another machine to make the dense rejection polyamide layer. The membrane may then be wound into a spiral wound element with the feed spacer facing the active rejection side and the permeate carrier facing the back side of the membrane, wherein the feed spacer and permeate carrier are not incorporated (i.e. remain as separate components) into the membrane.

[0086] A key consideration of the present reinforced flat sheet membrane is to have it fabricated and operable in pressure driven applications (for at least up to 1500 psi), wherein the reinforced flat sheet membrane may be a thin leaf set having a permeate carrier incorporated into a polymeric membrane, forming a single component instead of existing as separate components. A thin leaf set is advantageous for the fabrication of low-energy spiral wound module (SWM) for pressure-driven membranes, as the reduced thickness enables a single thinner component (polymeric membrane with permeate carrier incorporated) to be rolled with a feed spacer to form the spiral wound element, significantly reducing effort for element rolling (FIG. 11A). The present method of membrane fabrication reinforces the membrane with a

permeate carrier, that may be a mesh material, to enable higher water permeability through less structure parameter in the polymeric membrane and hence reduced internal concentration polarization (ICP). Typically, a polymeric membrane has a layer with porous structure that forms bulk of a membrane, and optionally, a dense rejection layer (i.e. dense selective layer, dense active layer). The layer with porous structure may be termed herein a support layer or substrate layer. With the permeate carrier incorporated into the polymeric membrane, especially the support layer, the thickness of the support layer may be reduced, which may mitigate ICP. The present reinforced flat sheet membrane may circumvent the use of conventional non-woven substrates, as the permeate carrier (mesh reinforced material) is already incorporated, wherein the permeate channels of the permeate carrier are substantially exposed at the back side of the polymeric membrane, such that the reinforced flat sheet membrane when rolled into a spiral wound module requires lower energy for the same treatment output, as more reinforced flat sheet membranes of the present disclosure can be rolled within the spiral wound module housing. The present reinforced flat sheet membrane also has a high salt rejection layer, low reverse salt permeability, high flux permeability, is resistant to deformation at high pressure, rollable into a spiral wound element with less effort, and reduces the overall thickness when all components are put together – allowing for more of the present reinforced flat sheet membranes to be fitted in a module.

[0087] In the present disclosure, the permeate carrier may be a hydrophilic or hydrophobic tricot mesh fabric with strong mechanical strength and high porosity embedded into the porous substrate layer for supporting the whole reinforced flat sheet membrane. A selective thin rejection layer may be formed at the top of the reinforced membrane layer, away from where the permeate carrier is incorporated. The reinforced flat sheet membrane can be fabricated into standard element sizes i.e. 1.8”, 2.5”, 4” and 8” for different applications.

[0088] In PRO, the available renewable osmotic power in nature is estimated to be in an order of 2000 TWh per year globally when released from mixing of seawater and river water in estuaries. In industry, tons of waste brine (such as seawater desalination brine) carries huge osmotic potential. PRO may be a promising technology for harvesting this renewable osmotic power. When water in the feed solution permeates through a membrane due to osmotic difference across the membrane, it increases the volume of the pressurized draw solution, which can then be used to drive a turbine to generate electricity or a pressure exchanger to reduce the energy consumption of seawater desalination process.

[0089] The PRO membrane is a consideration, as it affects PRO performance (both water flux and power density). However, to date, conventional spiral wound membrane may not be suitable for PRO, which impedes large-scale commercialization of PRO technology. As an alternative, high performance FO membranes were considered. However, a drawback of FO membranes used in PRO is severe membrane deformation due to high operating pressures in PRO. In PRO, the membrane area at the feed spacer grids is often unsupported and hence susceptible to deform easily at high pressures, even when the membrane has a reasonable level of mechanical strength for FO applications. Severe membrane deformation has adverse impacts on PRO performance and operation. First, it can deteriorate the membrane separation parameters, e.g. undesirably increase membrane solute permeability and decrease membrane selectivity, which may be reflected in a sharp increase in the rate of reverse solute diffusion at elevated pressures. Severe reverse solute diffusion adversely enhances ICP, which decreases water flux and power density in PRO. Second, a deformed membrane restricts or blocks the feed flow channel, which then adversely requires higher pressure at the feed side to maintain the feed flow and this detrimentally increases the energy consumption for operating PRO.

[0090] Even if self-supported hollow fiber membranes were considered, such hollow fiber membranes are unable to circumvent deformation, as its low mechanical stability only allows it to be operated at a maximum pressure of less than 20 bar. A low operation pressure for PRO compromises high power density for higher pressures applied (since the applied pressure for a theoretical peak power density is approximately half that of the osmotic pressure difference) and may also reduce the energy conversion efficiency at the post stage for osmotic power recovery.

[0091] The present reinforced flat sheet membrane is also advantageous for use in other high pressure applications, such as RO especially for seawater desalination wherein pressures can reach up to 1000 psi. The present reinforced flat sheet membrane eliminates the use of permeate carrier as a separate component from the polymeric membrane in RO/NF/UF/MF or additional feed spacers in PRO to mechanically support a PRO membrane. This enables more membranes to be fitted in within per membrane module, thereby providing more membrane surface area for filtration and rendering treatment cost per module more effective in pressure driven applications. Total leaf set thickness may be reduced by $(2 \times T_{m1} + T_{LCS}) - 2 \times T_{m2}$ if the present reinforced flat sheet membrane, with the permeate carrier incorporated therein, is sufficient to circumvent use of a low concentration spacer in PRO (see FIG. 6 and 12). In this instance, in

the context of PRO, a feed spacer may be equivalent to the permeate carrier used in RO. The “feed spacer in PRO” is configured to face the cleaner stream of liquid. FIG. 6 shows that using a 280 micron spacer, there can be 1% to 4% thickness saving in a RO leaf set. If a thinner permeate carrier of 100 micron is used, e.g. for RO, the thickness saved per leaf set may go up to about 18%, or even about 20%. The throughput for each spiral wound element may then increase significantly even with a thinner leaf set given that more of the present reinforced flat sheet membranes can be packed into an element, hence rendering an ultra-low energy membrane spiral wound element.

[0092] FIG. 7 shows that successfully cast reinforced flat sheet membrane using the present modified phase inversion coating line has an average flux of 3.1 LMH/bar and 95% rejection based on a range of process settings for casting on a 280 micron tricot spacer having an average 400 micron mesh holes that may even include a few larger mesh hole sizes of up to 1200 micron mesh holes or more. The larger mesh holes may potentially lead to pinholes if pre-wetting of the permeate carrier happens to be omitted. FIG. 8 shows the power density, reverse salt flux, and reverse osmosis performance of the present reinforced flat sheet membrane compared to a conventional RO membrane. The structure, material, chemistry of the polymeric support structure and rejection layers has been configured only for RO performance, hence power density and reverse salt flux of the present reinforced flat sheet membrane can be significantly improved. FIG. 9 shows the result of FO testing (in which coupons A and B refer to 2 different membrane samples) using FO-mode and PRO-mode. For the pressure retarded osmosis (PRO) testing, 2 different modes are used, i.e. the FO-mode and PRO-mode. In the FO-mode, the membrane active layer faces the feed solution. In the PRO-mode, the membrane active layer faces the draw solution. In other words, the difference between FO-mode and PRO-mode lies in the orientation of the membrane selective layer.

[0093] **Example 3: Non-Limiting Examples of Configuration and Materials Used**

[0094] The mesh fabric (i.e. permeate carrier) was partially embedded in the middle porous substrate layer to support the whole reinforced flat sheet membrane against applied hydraulic pressures. The permeate carrier may have, for example, a tensile modulus greater than 100 MPa and was selected from a group consisting of woven, non-woven, tricot and a combination thereof. Each strand of the permeate carrier was either monofilament or multifilament. Non-limiting examples of the materials for the permeate carrier include polyester, polypropylene,

acrylics, nylon, sulfonated polysulfone, and a combination thereof. The thickness of the permeate carrier ranged from, for example, 30 μm to 300 μm .

[0095] The permeate carrier was pre-wetted with, for example, water, one or more surfactant solutions, one or more salt solutions, one or more solvents, or a combination thereof. The surfactant solution include, for example, (i) anionic surfactant such as detergent, fatty acid, foaming agent, dispersant, (ii) non-ionic surfactant such as alcohol, ester, phenol, ether, amide, and/or (iii) cationic surfactant. The solvent may be, for example, water, N-methyl-2-pyrrolidone (NMP), hexane, or a combination thereof. The components used as or used to form the pre-wetting agent may be in any range from 0 to 100%, wherein all components used therein sums up to 100%. The pre-wetted mesh may be blown with compressed dry air at 0.1 to 10 bar to remove excess pre-wetting agent.

[0096] The middle porous substrate layer (i.e. the layer formed between a dense rejection layer and permeate carrier) was coagulated on the permeate carrier by the phase inversion method. The polymer used in forming the substrate layer was selected from, for example, polymeric materials such as polysulfone (PSU), polyethersulfone (PES), polyacrylonitrile (PAN), polyarylsulfone (PASf), poly(vinyl butyral) (PVB), sulfonated polysulfone (sPSU), polybenzimidazole (PBI), cellulose, a derivative thereof, and/or a combination thereof. The concentration of polymer in the polymer dope (i.e. polymer solution) ranged from, for example, 5.0 to 50.0 wt.% (preferably 15.0 to 20.0 wt.%). Solvents used for the polymer solution may include, as non-limiting examples, 1-methyl-2-pyrrolidinone (also termed NMP), dimethylacetamide (DMAc), dimethyl formamide (DMF), and a combination thereof. Macromolecule organics, small molecule organic, and inorganic salts, such as lithium bromide (LiBr), polyvinyl pyrrolidone (PVP), propylene glycol, polyethylene glycol (PEG), acetone, isopropanol, ethanol, lithium chloride (LiCl), etc., can be used as additives to adjust membrane porosity or hydrophobicity-hydrophilicity, of which their concentration in the polymer solution may range from 0.1 to 20.0 wt.%.

[0097] The top active layer was formed either by interfacial polymerization on the top of the substrate layer or by phase inversion during formation of substrate layer. However, formation of the top active layer is not limited to these two methods and may include, for example, crosslinking via chemical reaction or other suitable approaches. The polymer used in forming the active layer via interfacial polymerization was chosen from polyamine, polyhydric alcohol and polyphenol that were polymerized from monomers of (i) *o*-phenylenediamine (OPD), m-

phenylenediamine (MPD), bisphenol A (BPA), trihydroxypropane and (ii) molecules with polychloride and/or polysulfonylchloride such as trimesoyl chloride (TMC) and 1, 5-naphthalene-bisulfonyl chloride, wherein the monomers in (i) and (ii) may be dissolved in organic solvents e.g. hexane, cyclohexane, Isopar serials, etc., or a combination thereof.

- 5 Macromolecule organics, small molecule organics, and surfactants, such as dimethyl sulfoxide (DMSO), ϵ -carprolactam (CL), triethylamine (TEA), camphorsulfonic acid (CSA), sodium dodecyl sulfate (SDS) were used to increase miscibility of two immiscible phases or neutralize by products during interfacial polymerization.

[0098] Example 4A: Tricot Permeate Carrier (Average Mesh Size – 100 micron) With No

10 **Pre-Wetting**

[0099] For examples 4A to 4I, a polymer dope containing 17 wt% of PSU and 1 wt% LiBr dissolved in NMP was prepared in a round bottom flask and mixed at $55 \pm 5^\circ\text{C}$. The dope was cooled down to room temperature and degassed for 2 hours under vacuum conditioned. The dope serves as the polymer solution that is cast to form the polymeric membrane.

- 15 **[00100]** In this example, a permeate carrier with average tricot mesh size of 100 micron (TF800) is cast without pre-wetting. The results are in table 1 below.

[00101] Table 1 - Coating using TF800 permeate carrier mesh

Membrane ID	Backing (Reinforced material - RM)	Quench Temp. ($^\circ\text{C}$)	Backing Thickness (mil)	Total thickness (mil)	Total - backing thickness (mil)	Leaf set thickness	% reduction in leaf set thickness	Flux (LMH)	% Rejection
D070310HF14.2	TF800	25	9				~5.8	32.0	98.0
D270410HF17.1	TF800	25	9				~5.8	65.3	91.8
D040510HF18.1	TF800	8	9				~5.8	28.9	56.8
D040510HF18.2	TF800	8	9				~5.8	18.8	74.9

- 20 **[00102]** The performance is better when quench (i.e. coagulate) at room temperature. The cost of TF800 is high at USD4.30 per meter compared to TJ-30 at USD2.10 per meter. Reduction in leaf set thickness is about 5.8% (estimated from membranes coated with 100 and 150 μm blade gap). See example below for leaf set comparison calculation.

[00103] Coating Parameters

[00104] Active layer recipe: MPD 2.25 wt%, TMC 0.12 wt%

- 25 **[00105]** Blade gap: 250 μm

[00106] Coating angle: 45°

[00107] Curing direction: Polymer facing up

[00108] Dope viscosity: 1222 cps

[00109] Testing conditions**[00110]** Feed solution: 2000 ppm NaCl**[00111]** Pressure: 225 psi**[00112]** Feed temperature: 25°C5 **[00113]** **Example 4B: Tricot Permeate Carrier (Average Mesh Size – More Than 400 micron) With Pre-Wetting for RO**

[00114] In this example, a permeate carrier with average tricot mesh size of more than 400 micron (TJ-30) is cast with pre-wetting using DI water. The results are in table 2 below. Experiments using TJ-30 of such mesh size without pre-wetting may be susceptible in producing defective porous support layer and not desirably be used. In this example, a control

10 with the standard non-woven polyester backing was cast together to compute the savings in leaf set thickness (leaf set comparison calculation). Leaf set thickness was reduced by about 1.5%. The term “RO recipe” refers to a MPD and TMC composition used for interfacial polymerization to form the active layer for use in RO applications.

15 **[00115]** Table 2 – Coating Using TJ-30 Mesh with RO Recipe

Membrane ID	Backing (Reinforced material - RM)	Backing Thickness (mil)	Total thickness (mil)	Total - backing thickness (mil)	Leaf set thickness	% reduction	Flux (LMH)	% Rejection
D130618HF20.2	TJ-030	11				~1.47	21.0	97.4
D190618HF21.1	TJ-030	11				~1.47	24.4	94.8
D170718HF24.1	TJ-030	11	15.062	4.062	61.124	1.47	16.7	91.2
D050718HF23.4	Non-woven	4	10.019	6.019	62.038	0.00	25.8	94.8

[00116] Coating Parameters**[00117]** Active layer recipe: MPD 2.25 wt%, TMC 0.12 wt%**[00118]** Blade gap: 100 µm20 **[00119]** Coating angle: 45°**[00120]** Curing direction: Polymer facing down**[00121]** Dope viscosity: about 1100 cps**[00122]** Pre-Wetting agent: DI water**[00123]** Testing conditions25 **[00124]** Feed solution: 2000 ppm NaCl**[00125]** Pressure: 225 psi**[00126]** Feed temperature: 25°C

[00127] Example 4C: Tricot Permeate Carrier (Average Mesh Size – More Than 400 micron) With Pre-Wetting for FO

[00128] In this example, a permeate carrier with average tricot mesh size of more than 400 micron (TJ30) is cast with pre-wetting using DI water using FO recipe. The results are in table 3 below. FO recipe gave higher flux under same testing conditions.

[00129] Table 3 – Coating Using TJ-30 Mesh with FO recipe

Membrane ID	Backing (Reinforced material - RM)	Backing Thickness (mil)	Total thickness (mil)	Total - backing thickness (mil)	Leaf set thickness	% reduction	Flux (LMH)	% Rejection
D050718HF23.1	TJ-030	11	15.213	4.213	61.425	0.99	25.3	96.4

[00130] Coating Parameters

[00131] Active layer recipe: MPD 1.5 wt%, TMC 0.1 wt%

[00132] Blade gap: 100 µm

[00133] Coating angle: 45°

[00134] Curing direction: Polymer facing down

[00135] Dope viscosity: about 1100 cps

[00136] Pre-Wetting agent: DI water

[00137] Testing conditions

[00138] Feed solution: 2000 ppm NaCl

[00139] Pressure: 225 psi

[00140] Feed temperature: 25°C

[00141] Example 4D: Tricot Permeate Carrier (Average Mesh Size – More Than 400 micron) With Pre-Wetting and Polymer Facing up for RO

[00142] In this example, a permeate carrier with average tricot mesh size of 400 micron mesh holes that may even include a few larger mesh hole sizes of up to 1200 micron mesh holes or more is cast with pre-wetting using DI water and RO recipe but curing up and coating angle is 90°. The results are in table 4 below. Reduction in leaf set thickness is about 4.5%.

[00143] Table 4 – Coating Using TJ-30 Mesh with RO recipe but Polymer Facing Up

Membrane ID	Backing (Reinforced material - RM)	Backing Thickness (mil)	Total thickness (mil)	Total - backing thickness (mil)	Leaf set thickness	% reduction	Flux (LMH)	% Rejection
D050718HF23.2	TJ-030	11	14.144	3.144	59.289	4.43	22.7	97.2

[00144] Coating Parameters

[00145] Active layer recipe: MPD 2.25 wt%, TMC 0.12 wt%

[00146] Blade gap: 100 μm

[00147] Coating angle: 90°

[00148] Curing direction: Polymer facing up

[00149] Dope viscosity: about 1100 cps

5 [00150] Pre-Wetting agent: DI water

[00151] Testing conditions

[00152] Feed solution: 2000 ppm NaCl

[00153] Pressure: 225 psi

[00154] Feed temperature: 25°C

10 [00155] **Example 4E: Tricot Permeate Carrier (Average Mesh Size – About 64 micron) for RO**

[00156] In this example, a permeate carrier with average rectangular mesh size of about 64 micron (Sefar PETEX IEM-07-195/70) is cast with and without pre-wetting using DI water and RO recipe and curing face down. The permeate carrier in this instance is a polyester mesh of 45 μm thickness and have about 44.5% of open area. The results are in table 5 below. The membrane cast without pre-wetting (D260718HF26.1) has good rejection, flux and 10% reduction in leaf set thickness. However, the membrane looks creased (see FIG. 13).

[00157] Table 5 - Coating Using Ultrathin Sefar Mesh and RO recipe

Membrane ID	Backing (Reinforced material - RM)	Backing Thickness (mil)	Total thickness (mil)	Total - backing thickness (mil)	Leaf set thickness	% reduction in leaf set thickness	Flux (LMH)	% Rejection
D260718HF26.1	SEFAR	2.6	12.425	9.825	55.850	9.97	27.4	97.4
D260718HF26.2	SEFAR	2.6	8.550	5.950	48.100	22.47	53.8	62.8

20 [00158] Coating Parameters

[00159] Active layer recipe: MPD 2.25 wt%, TMC 0.12 wt%

[00160] Blade gap: 100 μm

[00161] Coating angle: 90°

[00162] Curing direction: Polymer facing up

25 [00163] Dope viscosity: about 1100 cps

[00164] Pre-Wetting agent: DI water

[00165] Testing conditions

[00166] Feed solution: 2000 ppm NaCl

[00167] Pressure: 225 psi

[00168] Feed temperature: 25°C

[00169] Example 4F: Tricot Permeate Carrier (Average Mesh Size – More Than 400 micron) With Pre-Wetting Using Water as Both Solvent and Surfactant for RO

- 5 [00170] In this example, a permeate carrier with average tricot mesh size of more than 400 micron (TJ-30) is cast with pre-wetting using solvent in water and surfactant in water and interfacial polymerized using RO recipe. For 20 wt% NMP in water, the reduction in leaf set thickness is about 4.5% and flux is higher.

[00171] Table 6 - Coating using TJ-30 Mesh with RO recipe but Polymer Facing Up

Membrane ID	Wetting solution	Backing {Reinforced material - RM}	Backing Thickness {mil}	Total thickness {mil}	Total - backing thickness {mil}	Leaf set thickness	% reduction in leaf set thickness	Flux {LMH}	% Rejection
D200718HF25.1	0.2% SLS	TJ-030	11	15.125	4.125	61.250	1.27	29.2	82.8
D200718HF25.3	20% NMP/H ₂ O	TJ-030	11	14.150	3.150	59.300	4.41	27.9	93.6

10

[00172] Coating Parameters

[00173] Active layer recipe: MPD 2.25 wt%, TMC 0.12 wt%

[00174] Blade gap: 100 µm

[00175] Coating angle: 45°

- 15 [00176] Curing direction: Polymer facing down

[00177] Dope viscosity: about 1100 cps

[00178] Pre-Wetting agent: 0.2 wt% SLS and 20 wt% NMP in DI water

[00179] Testing conditions

[00180] Feed solution: 2000 ppm NaCl

- 20 [00181] Pressure: 225 psi

[00182] Feed temperature: 25°C

[00183] Example 4G: P16 Permeate Carrier (Average Mesh Size – About 300 micron) With Pre-Wetting for RO

- 25 [00184] In this example, a permeate carrier with average tricot mesh size of about 300 micron (P16) is pre-wetted with DI water and interfacial polymerized using RO recipe. The results are in table 7 below. The pre-wetted membrane has good rejection and flux.

[00185] Table 7 - Coating using P16 Permeate Carrier with RO recipe

Reinforced Membrane ID	Wetting Solution	Backing (Reinforced Material - RM)	Backing Thickness (mil)	Total Thickness (mil)	Total - Backing Thickness (mil)	Leaf Set Thickness (mil)	**Thickness Reduction (%)	Coupon Flux (LMH)	Coupon Rejection (%)
B211218HF35.1	DI water	P16	6.8	10.6	4.0	51.0	17.8	37.5	93.5
B210119NF36.3	DI water	P16	6.9	15.7	8.7	62.5	-0.7	46.6	94.9

[00186] Coating Parameters

[00187] Active layer recipe: MPD 2.25 wt%, TMC 0.12 wt%

[00188] Blade gap: 200 μ m

5 **[00189]** Coating angle: 45°

[00190] Curing direction: Polymer facing down

[00191] Dope viscosity: about 1600 cps

[00192] Pre-Wetting agent: DI water

[00193] Testing conditions

10 **[00194]** Feed solution: 2000 ppm NaCl

[00195] Pressure: 225 psi

[00196] Feed temperature: 25°C

[00197] Example 4H: P16 Permeate Carrier (Average Mesh Size – About 300 micron)

Using Phase Inversion

15 **[00198]** In this example, a permeate carrier with average tricot mesh size of about 300 micron (P16) is cast on the present modified industrial phase inversion casting line. The permeate carrier is pre-wetted and cast using a slot die at 90°C coating angle. The results are in table 8 below. The reinforced membranes show 2.9 to 9.6 % thickness reduction as compared to *RO250918-01 coated on a non-woven backing.

20 **[00199]** Table 8 - Coating using P16 Permeate Carrier on the Present Modified Industrial Phase Inversion Casting Line, wherein * denotes that the interfacial polymerization was carried out on the thin film composite (TFC) line with active layer recipe comprising MPD 2.25 wt% and TMC 0.12 wt% for interfacial polymerization. ** refers to an improved active layer recipe with small molecule additives, such as sodium dodecyl sulfate (SDS), isopropanol, etc., used.

Reinforced Membrane ID	Total - Backing Thickness (mil)	Thickness Reduction (%)	Coupon Flux (LMH)	Coupon Rejection (%)
*RO250918-01	2.1	N.A.	20.5	98.0
**B100119P16/7.1	1.9	9.6	55.7	96.5
**B150119P16/8.1	1.9	9.6	52.8	96.2
**B180219P16/9.1	4.0	2.9	44.8	94.9

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[00200] Coating Parameters

[00201] Active layer recipe: MPD 2.25 wt%, TMC 0.12 wt%

[00202] Slot die lip gap: 100 μm

[00203] Coating angle: 90°

[00204] Dope viscosity: about 1600 cps

5 [00205] Pre-Wetting agent: DI water

[00206] Testing conditions

[00207] Feed solution: 2000 ppm NaCl

[00208] Pressure: 225 psi

[00209] Feed temperature: 25°C

10 [00210] **Example 4I: Reinforced Flat Sheet Membrane In 1812 Spiral Wound Element**

[00211] In this example, a reinforced flat sheet membrane was interfacial polymerized using RO recipe on an industrial-scale interfacial polymerization (IP) line. The results are in tables 9 and 10 below. The as-made reinforced flat sheet membrane is rolled into a full scale 1812-element. In this example, a P16 permeate carrier with average mesh size of about 300 micron

15 was used.

[00212] Table 9 - Interfacial Polymerization (IP) of Reinforced Flat Sheet Membranes on an Industrial-Scale IP line

Reinforced Membrane ID	IP Formula	IP Line Speed (MPM)	Dryer Speed (Hz)	Backing Thickness (mil)	Total Thickness (mil)	Total Backing Thickness (mil)	Leaf Set Thickness (mil)	Thickness Reduction (%)	Coupon Flux (LMH)	Coupon Rejection (%)
RM180219	SPA	0.8	N.A.	6.6	10.6	4.0	52.2	2.9	37.9	93.4
RM260219	18SPA	0.8	30	6.6	15.1	3.5	51.2	4.5	47.1	92.0

20 [00213] Table 10 - Element Rolling of Interfacial Polymerized Reinforced Flat Sheet Membrane

Reinforced Membrane ID	Element size	No. of membrane leaf	Active Area (m ²)	Testing Pressure (psi)	Testing Feed Solution	Recovery (%)	Permeate Flowrate (mL/min)	Rejection (%)
RM260219	1812	5	0.425	50	500ppm NaHCO ₃	15	24	86.6

[00214] Coating Parameters

[00215] Active layer recipe: MPD 2.25 wt%, TMC 0.12 wt%

[00216] Slot die lip gap: 100 μm

25 [00217] Coating angle: 90°

[00218] Dope viscosity: about 1600 cps

[00219] Pre-Wetting agent: DI water

[00220] Testing conditions

[00221] Feed solution: 2000 ppm NaCl

[00222] Pressure: 225 psi

[00223] Feed temperature: 25°C

[00224] The rejection layer of FO and RO membranes are polymerized using recipes B, C, and D, which comprise of m-phenylenediamine (MPD) in DI water and trimesoyl chloride in hexane or isopar serial with varying amount of small molecule additives such as sodium dodecyl sulfate (SDS), isopropanol, etc. Recipes B, C, and D differ in the type of solvents, composition of MPD and TMC, and amount of additives, all adjusted for different applications e.g. FO and RO.

10 [00225] **Example 5: Commercial and Potential Applications**

[00226] The present technology relates to structure of a membrane that can be configured for spiral wound membrane modules to increase productivity and reduce cost. Specifically, the present disclosure relates to a reinforced flat sheet membrane usable in a spiral wound membrane module, wherein the reinforced flat sheet membrane is rollable to form a spiral wound element. As the reinforced flat sheet membrane comprises a polymeric membrane having a permeate carrier incorporated formed as a single component, a thinner leaf set results, which provides for higher active area in pressure driven water purification applications at low energy requirement.

[00227] In summary, the present disclosure includes a reinforced flat sheet membrane for use in PRO or FO process. The reinforced flat sheet membrane may include (a) a low concentration (LC) spacer having permeate channels as one layer, (b) a porous substrate/support layer as second layer, adjacent and/or partially merged to the first layer, (c) wherein the LC spacer may be partially embedded in the porous substrate/support layer, (d) a selective/active layer as a third layer, adjacent and/or partially merged to the second layer, and/or a draw spacer adjacent to the third layer. A draw spacer may be used in PRO or FO where the spacer is placed in or proximal to the draw solution, hence termed draw spacer.

[00228] In some embodiments, the reinforced flat sheet membrane for use in RO, UF or MF process may include (a) a permeate carrier as a first layer, (b) a porous substrate/support layer as second layer, adjacent and/or partially merged to the first layer, wherein the permeate carrier may be partially embedded in the porous substrate/support layer. (c) a selective/active layer as a third layer, adjacent and/or partially merged to the second layer, and (d) a feed spacer adjacent to the third layer.

[00229] The present disclosure also includes a method of fabricating the reinforced flat sheet membrane. The method may include (a) pre-wetting a low concentration spacer or permeate carrier with pre-wetting agents, (b) casting a porous substrate/support layer on the permeate carrier by phase inversion method, (c) forming a selective/active layer on the porous substrate/support layer by (i) phase inversion method during formation of the porous substrate/support layer or (ii) interfacial polymerization method to form the reinforced flat sheet membrane.

[00230] In various embodiments, the backing layer used in conventional membrane is omitted and this results in an overall thickness reduction in spiral wound leaf set (thinner), so more of the present reinforced flat sheet membranes can be packed into a spiral wound membrane module. The omission of the backing layer also simplifies the fabrication process.

[00231] In various embodiments, the permeate carrier may be a hydrophilic or hydrophobic tricot mesh fabric.

[00232] In various embodiments, the pre-wetting agent used herein may be a liquid that comprises a surfactant solution.

[00233] While the invention has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. The scope of the invention is thus indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.

CLAIMS

1. A reinforced flat sheet membrane operable to withstand vacuum pressure and a high pressure of up to 1500 psi, wherein the reinforced flat sheet membrane comprises:

a polymeric membrane;

a permeate carrier which reinforces the polymeric membrane and has channels to direct permeate flow;

wherein the polymeric membrane has the permeate carrier incorporated therein and the channels of the permeate carrier are partially exposed at a surface of the polymeric membrane,

and further comprising a pre-wetting agent coated on the permeate carrier, wherein the pre-wetting agent comprises a constituent different from the polymeric membrane, wherein the pre-wetting agent comprises the constituent as a liquid or as a gaseous solution, and wherein the liquid or gaseous solution contains:

an anionic surfactant, wherein the anionic surfactant comprises a detergent, a fatty acid, a foaming agent, or a dispersant; or

a non-ionic surfactant, wherein the non-ionic surfactant comprises alcohol, ester, phenol, ether, or amide; or

a cationic surfactant, wherein the cationic surfactant comprises a salt solution, wherein the salt solution comprises an organic solvent or an inorganic solvent, wherein the organic solvent comprises N-methyl-2-pyrrolidone, dimethylformamide, hexane, or a combination thereof, wherein the inorganic solvent comprises water; or

a combination thereof.

2. The reinforced flat sheet membrane of claim 1, wherein the permeate carrier comprises a mesh, wherein the mesh comprises a woven mesh, a non-woven mesh, or a tricot mesh, and wherein the mesh is formed of cellulose, polyester, polypropylene, acrylic, nylon, sulfonated polysulfone, polysulfone, polyethersulfone, polyimide, polyamide, polybenzimidazole, polyacrylonitrile, polyarylsulfone, poly(vinyl butyral), polyetherimide, a derivative thereof, or a combination thereof.

3. The reinforced flat sheet membrane of claim 2, wherein the mesh has a pore size ranging from 100 μm to 5000 μm .

4. The reinforced flat sheet membrane of any one of claims 1 to 3, wherein the polymeric membrane has a porous substrate layer which:

- (i) an active rejection layer is formed on; and
- (ii) the permeate carrier is incorporated in the porous substrate layer;

wherein the porous substrate layer comprises cellulose, polyester, polypropylene, acrylic, nylon, sulfonated polysulfone, polysulfone, polyethersulfone, polyimide, polyamide, polybenzimidazole, polyacrylonitrile, polyarylsulfone, poly(vinyl butyral), polyetherimide, a derivative thereof, or a combination thereof.

5. The reinforced flat sheet membrane of claim 4, wherein the active rejection layer comprises polyamide, polyamine, polyamide-imide, polyhydric alcohol, polyphenol, a derivative thereof, or a combination thereof.

6. The reinforced flat sheet membrane of any one of claims 1 to 5, wherein the reinforced flat sheet membrane has a thickness ranging from 20 μm to 300 μm .

7. The reinforced flat sheet membrane of any one of claims 1 to 6, wherein the reinforced flat sheet membrane is operable to withstand a pressure from 1.5×10^{-11} psi to 1500 psi.

8. The reinforced flat sheet membrane of any one of claims 1 to 7, wherein the reinforced flat sheet membrane is operable for microfiltration, ultrafiltration, nanofiltration, reverse osmosis, pressure retarded osmosis, forward osmosis, pervaporation, membrane distillation, and/or gas separation.

9. A method of fabricating a reinforced flat sheet membrane operable to withstand vacuum pressure and a high pressure of up to 1500 psi, wherein the reinforced flat sheet membrane comprises:

- a polymeric membrane;
- a permeate carrier which reinforces the polymeric membrane and has channels to direct permeate flow;

wherein the polymeric membrane has the permeate carrier incorporated therein and the channels of the permeate carrier are partially exposed at a surface of the polymeric membrane, wherein the method comprises:

contacting the permeate carrier with a pre-wetting agent;
 casting a polymer solution on the permeate carrier; and
 forming the polymeric membrane from the polymer solution with the permeate carrier incorporated in the polymeric membrane,

wherein the pre-wetting agent comprises a constituent different from the polymer solution, wherein the pre-wetting agent undergoes pre-curing instantaneously upon contact with the polymer solution prior to complete curing in forming the polymeric membrane, wherein the pre-wetting agent comprises the constituent as a liquid or as a gaseous solution, and wherein the liquid or gaseous solution contains:

an anionic surfactant, wherein the anionic surfactant comprises a detergent, a fatty acid, a foaming agent, or a dispersant; or

a non-ionic surfactant, wherein the non-ionic surfactant comprises alcohol, ester, phenol, ether, or amide; or

a cationic surfactant, wherein the cationic surfactant comprises a salt solution, wherein the salt solution comprises an organic solvent or an inorganic solvent, wherein the organic solvent comprises N-methyl-2-pyrrolidone, dimethylformamide, hexane, or a combination thereof, wherein the inorganic solvent comprises water; or

a combination thereof.

10. The method of claim 9, wherein contacting the permeate carrier with the pre-wetting agent comprises dispensing the pre-wetting agent onto the permeate carrier at a flow rate of 10 mL/min to 10 L/min, wherein dispensing the pre-wetting agent onto the permeate carrier is carried out by spraying, misting, pouring, sponging, deposition from a slot die, roller-spreading, nip-roll spreading, dripping, or soaking.

11. The method of claim 9 or 10, further comprising removing excess pre-wetting agent from the permeate carrier.

12. The method of any one of claims 9 to 11, further comprising dissolving a polymer in an organic solvent to form the polymer solution for casting on the permeate carrier, wherein the organic solvent comprises 1-methyl-2-pyrrolidinone, dimethyl-acetamide, dimethyl formamide, or a combination thereof.
13. The method of claim 12, wherein the polymer in the organic solvent has a concentration ranging from 5 wt% to 50 wt%.
14. The method of any one of claims 9 to 13, wherein the polymer solution has a viscosity ranging from 100 to 100,000 cps.
15. The method of any one of claims 9 to 14, wherein forming the polymeric membrane comprises coagulating the polymer solution by phase inversion in the presence of a non-solvent.
16. The method of claim 15, wherein coagulating the polymer solution by phase inversion comprises having the polymer solution cast onto the permeate carrier, and immersing the polymer solution with the permeate carrier into the non-solvent, wherein the polymer solution and the permeate carrier are arranged to have the polymer solution face any direction in the non-solvent.
17. The method of claim 15 or 16, wherein forming the polymeric membrane comprises coagulating the polymer solution by phase inversion at a temperature ranging from -10°C to 150°C.
18. The method of any one of claims 9 to 17, further comprising subjecting the polymeric membrane to interfacial polymerization or chemical crosslinking to form an active rejection layer.