SELF-ASSEMBLING COPOLYMERS AND THIN-FILM MEMBRANES COMPRISING SELF-ASSEMBLING COPOLYMERS AND 3D PRINTED SPACERS

FIELD OF THE DISCLOSURE

[0001] This disclosure relates generally to self-assembling copolymers and membranes made therefrom for reverse osmosis applications.

BACKGROUND

[0002] Membrane filtration is an important and promising method of water purification, reclamation and reuse. Membranes of various pore sizes can be used for a wide range of objectives, from simply removing disease-causing microorganisms to desalination by reverse osmosis (RO). Membranes also serve as an efficient, simple, scalable separation method in various industries, such as food, beverage, dairy, and bio/pharmaceutical industries.

[0003] Membranes with improved selectivity, or ability to separate solutes with better precision, offer to improve the economic feasibility and energy efficiency of several other processes. For instance, membranes with improved selectivity between sulfate and chloride anions could alter the composition of seawater and wastewater for use as drilling fluid in offshore oil wells while operating at lower applied pressures. Membranes with extremely small pore sizes but low salt rejection can lead to highly improved effluent quality for challenging wastewater streams, particularly those with high organic content, such as those from the food industry.

[0004] All of the aforementioned membrane processes are often severely impacted by fouling, defined as the degradation of membrane performance due to the adsorption and accumulation of feed components on the membrane surface. Severe declines in membrane permeability and changes in membrane selectivity are common. Fouling management is a significant component of costs associated with membrane systems, requiring increased energy use, regular cleanings involving downtime, maintenance and chemical use, and more complex processes.

SUMMARY

[0005] Provided herein are polymeric materials designed to create membranes with improved selectivity and fouling resistance, with potential capabilities that include tunable effective pore

size that can be reduced to <1 nm, exceptional fouling resistance, improved chemical resistance and thermal stability, and ion selectivity.

[0006] In various implementations, the present disclosure relates to self-assembling copolymers and membranes made therefrom. The present disclosure includes, without limitation, the following example implementations.

[0007] A self-assembling copolymer is used to spray-coat a thin-film membrane on a porous support material which has been augmented with 3D-printed spacers. Three-dimensional printing is intended to encompass any additive manufacturing process that involves the construction of a three-dimensional object from a CAD or other digital 3D model. The materials (e.g., plastics, liquids. or powders) are typically constructed layer by layer (e.g., deposited and joined or solidified together under computer control) and held together via binders, sintering, etc.

[0008] Embodiment 1: A filtration membrane comprising a porous support layer, at least one spacer disposed on the porous support layer via a three-dimensional printing process, and a self-assembling polymeric layer disposed on the porous support layer and the at least one spacer.

[0009] Embodiment 2: The filtration membrane of the preceding Embodiment, wherein the self-assembling polymeric layer is disposed on the porous support layer and the at least one spacer via spray-coating.

[0010] Embodiment 3: The filtration membrane of Embodiment 1 or 2, or any combination thereof, wherein the at least one spacer comprises a plurality of spacers distributed equidistant across a surface of the porous support layer. For example, in some embodiments, there may be 5,000 spacers per m^2, alternatively 25,000/m^2, or alternatively 125,000/m^2, where 10,000/m^2 is equal to one spacer for each square centimeter.

[0011] Embodiment 4: The filtration membrane of Embodiment 1 to 3, or any combination thereof, wherein the at least one spacer comprises a shape selected from the group consisting of radially symmetric dots, ellipses, or teardrops.

[0012] Embodiment 5: The filtration membrane of Embodiment 1 to 4, or any combination thereof, wherein the at least one spacer has a thickness of about 0.0005 to about 0.065 inches.

[0013] Embodiment 6: The filtration membrane of Embodiment 1 to 5, or any combination thereof, wherein the at least one spacer comprises at least one of a resin, an adhesive, a polymeric material, or a combination thereof.

[0014] Embodiment 7: The filtration membrane of Embodiment 1 to 6, or any combination thereof, wherein the porous support layer comprises at least one of a microfiltration or ultrafiltration membrane.

[0015] Embodiment 8: The filtration membrane of Embodiment 1 to 7, or any combination thereof, wherein the porous support layer comprises a flat sheet membrane or a hollow fiber membrane.

[0016] Embodiment 9: The filtration membrane of Embodiment 1 to 8, or any combination thereof, wherein the self-assembling polymeric layer comprises a zwitterionic copolymer.

[0017] Embodiment 10: The filtration membrane of Embodiment 1 to 9, or any combination thereof, wherein the self-assembling polymeric layer comprises a cross-linkable zwitterionic copolymer.

[0018] Embodiment 11: The filtration membrane of Embodiment 1 to 10, or any combination thereof, wherein the self-assembling polymeric layer is disposed on top of the porous substrate.

[0019] Embodiment 12: The filtration membrane of Embodiment 1 to 11, or any combination thereof, wherein the self-assembling polymeric layer comprises an average effective pore size of about 0.1 nm to about 2.0 nm, alternatively an average effective pore size of about 0.1 nm to about 1.2 nm, or alternatively an average effective pore size of about 0.5 nm to about 1.0 nm.

[0020] Embodiment 13: The filtration membrane of Embodiment 1 to 12, or any combination thereof, wherein the self-assembling polymeric layer comprises a thickness of about 10 nm to about 10 um, alternatively a thickness of about 100 nm to about 2 um.

[0021] Embodiment 14: The filtration membrane of Embodiment 1 to 13, or any combination thereof, wherein the filtration membrane rejects charged solutes and salts.

[0022] Embodiment 15: The filtration membrane of Embodiment 1 to 14, or any combination thereof, wherein the self-assembling polymeric layer exhibits sulfate (SO_4^{2-}) rejection of greater than 99%. Generally, the exact levels of rejection will vary depending on the membrane support, for example, whether the support is capable of ultrafiltration, microfiltration, nanofiltration, or superfiltration.

[0023] Embodiment 16: The filtration membrane of Embodiment 1 to 15, or any combination thereof, wherein the self-assembling polymeric layer exhibits sulfate (SO_4^{2-}) / chloride (Cl-) separation factor of greater than 50.

[0024] Embodiment 17: The filtration membrane of Embodiment 1 to 16, or any combination thereof, wherein the self-assembling polymeric layer exhibits sulfate (SO_4^{2-}) / chloride (Cl-) separation factor of greater than 75.

[0025] Embodiment 18: The filtration membrane of Embodiment 1 to 17, or any combination thereof, wherein the self-assembling polymeric layer exhibits different anion rejections for salts with the same cation.

[0026] Embodiment 19: The filtration membrane of Embodiment 1 to 18, or any combination thereof, wherein the self-assembling polymeric layer exhibits different anion rejections for salts selected among NaF, NaCl, NaBr, NaI, and $NaClO_4$.

[0027] Embodiment 20: The filtration membrane of Embodiment 1 to 19, or any combination thereof, wherein the self-assembling polymeric layer exhibits a fluoride (F-) / chloride (Cl-) separation factor of greater than 5.

[0028] Embodiment 21: The filtration membrane of Embodiment 1 to 20, or any combination thereof, wherein the self-assembling polymeric layer exhibits a fluoride (F-) / chloride (Cl-) separation factor of about 8.

[0029] Embodiment 22: The filtration membrane of Embodiment 1 to 21, or any combination thereof, wherein the filtration membrane has a molecular weight cut-off of at least 5000 Daltons, alternatively, 1000 Daltons, or alternatively 500 Daltons.

[0030] Embodiment 23: A process of filtering a liquid comprising providing a filtration membrane in accordance with any one of Embodiments 1-22, or any combination thereof, directing a liquid through the filtration membrane, first through the self-assembling polymeric layer and then through the porous support layer; and collecting the liquid that permeates through the filtration membrane.

[0031] Embodiment 24: A method of making a filtration membrane comprising providing a porous support; printing at least one spacer on the porous support via a three-dimensional printing process; providing a self-assembling polymer as described herein; and depositing the self-assembling polymer on to the at least one spacer and the porous substrate.

[0032] Embodiment 25: The method of the preceding Embodiment, wherein the self-assembling polymer is deposited on the at least one spacer and the porous support via spray coating.

[0033] Generally, additional treatment steps are contemplated and considered within the scope of the invention, such as, for example, quenching, surface modification, cleaning,

deactivating, etc., and may be carried out with different solvents, radiation ranges, and processing times.

[0034] These and other features, aspects, and advantages of the disclosure will be apparent from a reading of the following detailed description together with the accompanying drawings, which are briefly described below. The invention includes any combination of two, three, four, or more of the above-noted embodiments as well as combinations of any two, three, four, or more features or elements set forth in this disclosure, regardless of whether such features or elements are expressly combined in a specific embodiment description herein. This disclosure is intended to be read holistically such that any separable features or elements of the disclosed invention, in any of its various aspects and embodiments, should be viewed as intended to be combinable unless the context clearly dictates otherwise.

BRIEF DESCRIPTION OF THE FIGURES

[0035] Having thus described aspects of the disclosure in the foregoing general terms, reference will now be made to the accompanying drawings, which are not necessarily drawn to scale, and wherein:

[0036] FIG. 1 illustrates an enlarged cross-sectional side view of a portion of a membrane made in accordance with one or more embodiments of the present disclosure.

DETAILED DESCRIPTION

[0037] Disclosed are self-assembling copolymers that can be used in the preparation of reverse osmosis membranes having improved fouling resistance, chlorine tolerance, and stability (e.g. against chemical or thermal damage) and that may include non-planar topographies (e.g., incorporated 3D feed spacers). Generally, such membranes cannot be constructed by traditional methods, since those methods (e.g., slot die coating, gravure coating, etc.) require a flat substrate. Additionally, certain membrane chemistries, for example, polyvinylidene fluoride (PVDF) or polyethersulfone (PES) cannot be used to fabricate such a membrane, because they require a non-solvent or thermally induced phase inversion to become permeable to liquid. Only the unique combination of self-assembling copolymers as membrane materials and the "casting" of such materials via spray or electrospray coating can successfully create a functional membrane

on a support which has been augmented with feed spacers using additive manufacturing (i.e., 3D printing).

[0038] FIG. 1 depicts one example of a filtration membrane 100 manufactured in accordance with the present disclosure. As shown, the membrane 100 includes a porous support layer 104 with at least one spacer 106 disposed on a top surface 108 of the porous support layer 104 and then a self-assembling polymeric layer 102 disposed on the porous support layer 104 and the at least one spacer 106.

[0039] The porous support layer 104 can be any suitable porous surface. Typically, a microfiltration or ultrafiltration membrane is used; however, ceramic membranes, reverse osmosis membranes, porous (sintered) plastic, porous metal, or other materials are also contemplated and considered within the scope of the disclosure. The specific size, thickness, porosity, material, etc. of the support layer 104 will be selected to suit a particular application.

[0040] The support layer 104 may have features (i.e., feed spacers 106) added to it via additive manufacturing. See, for example, U.S. Pat. No. 7,291,002, the entire disclosure of which is hereby incorprorated herein by reference. However, other types of features or structures can be added to a support surface by alternative methods, such as, for example, extruded shapes (e.g., tubes) with ridges or similar features formed on a surface thereof. Typically these are "feed spacers" for later conversion of the material into a spiral-wound membrane, but in other cases three-dimensional features may be used in other types of membranes, such as features designed to disrupt the boundary layer in tubular membranes. See, for example, U.S. Pat. No. 10,471,391, the entire disclosure of which is hereby incorprorated herein by reference.

[0041] The features 106 are added prior to the coating of the self-assembling polymer system 102. This is important to ensure good anchoring to the porous support layer 104. In the case of zwitterionic materials, coating the support layer 104 prior to adding surface features 106 may result in surface features with poor adhesion, or they may not stick at all due to the anti-fouling nature of zwitterionic materials.

[0042] After the surface features have been added using well-documented processes, the support layer 104 is coated using spray-coating techniques. This may include electrostatic spray, ultrasonic spray, or conventional air-driven spray. See, for example, PCT Appl. No. PCT/US2020/032335, the entire disclosure of which is hereby incorprorated herein by reference. These techniques allow the fine control of layer thickness. The coating solution's properties, such

a boiling point, viscosity, and solids content are controlled by the addition of cosolvents as needed.

[0043] According to one aspect of the disclosure, the self-assembling copolymer is dissolved in an appropriate solvent such that the solvent can be removed by evaporation. The copolymer should be selected such that it will spontaneously form a permeable structure under these conditions. Examples of such copolymers include zwitterionic copolymers such as PMMA-r-SBMA, styrene-r-MPC, or TFEMA-r-SB2VP, as well as cross-linkable varieties of these polymers. Systems which require multiple coats of different polymers, such as amphiphilic polyelectrolyte complexes may also be considered. See, for example, U.S. Pat. No. 10,150,088 and PCT Appl. Nos. PCT/US2021/32793, PCT/US2022/25981, and PCT/US2022/41055, the entire disclosures of which are hereby incorprorated herein by reference.

[0044] The self-assembling polymeric layer 102 is sprayed over the 3D surface of the spacers 106 and support layer 104, forming a "skin" layer thereover. The skin layer provides the added benefit of imparting antifouling characteristics to the 3D printed spacers, further enhancing the benefits of those features.

[0045] After the coating is applied, dried, and cross-linked if necessary, the membrane can be used to assembly a variety of module forms, such as spiral wound, tubular, or plate and frame. Additional details regarding the manufacture of the membranes disclosed herein may be found in PCT Publication Nos. WO2021/232018 and WO2020/231797, and the following articles: Lounder, S. J., Asatekin, A. *Zwitterionic Ion-Selective Membranes with Tunable Subnanometer Pores and Excellent Fouling Resistance*. Chem. Mater. 2021, 33, 12, 4408–4416 and Lounder, S. J., Asatekin, A. *Interaction-Based Ion Selectivity Exhibited by Self-Assembled, Cross-Linked Zwitterionic Copolymer Membranes*. Proc Natl Acad Sci USA (In Proof, 2021); the entire disclosures of which are hereby incorpoated by reference herein.

WHAT IS CLAIMED IS:

1. A filtration membrane comprising:

a porous support layer;

at least one spacer disposed on the porous support layer via a three-dimensional printing process; and

a self-assembling polymeric layer disposed on the porous support layer and the at least one spacer.

2. The filtration membrane of claim 1, wherein the self-assembling polymeric layer is disposed on the porous support layer and the at least one spacer via spray-coating.

3. The filtration membrane of anyone of the preceeding claims, wherein the at least one spacer comprises a plurality of spacers distributed equidistant across a surface of the porous support layer.

4. The filtration membrane of any one of the preceeding claims, wherein the at least one spacer comprises a shape selected from the group consisting of radially symmetric dots, ellipses, or teardrops.

5. The filtration membrane of any one of the preceeding claims, wherein the at least one spacer has a thickness of about o.oo5 to about 0.065 inches.

6. The filtration membrane of any one of the preceeding claims, wherein the at least one spacer comprises at least one of a resin, an adhesive, a polymeric material, or a combination thereof.

7. The filtration membrane of anyone of the preceeding claims, wherein the porous support layer comprises at least one of a microfiltration or ultrafiltration membrane.

8. The filtration membrane of anyone of the preceeding claims, wherein the porous support layer comprises a flat sheet membrane or a hollow fiber membrane.

9. The filtration membrane of anyone of the preceeding claims, wherein the self-assembling polymeric layer comprises a zwitterionic copolymer.

10. The filtration membrane of anyone of the preceeding claims, wherein the self-assembling polymeric layer comprises a cross-linkable zwitterionic copolymer.

11. The filtration membrane of anyone of the preceeding claims, wherein the self-assembling polymeric layer is disposed on top of the porous substrate.

12. The filtration membrane of anyone of the preceeding claims, wherein the self-assembling polymeric layer comprises an average effective pore size of about 0.1 nm to about 2.0 nm, alternatively an average effective pore size of about 0.1 nm to about 1.2 nm, or alternatively an average effective pore size of about 0.5 nm to about 1.0 nm.

13. The filtration membrane of anyone of the preceeding claims, wherein the self-assembling polymeric layer comprises a thickness of about 10 nm to about 10 um, alternatively a thickness of about 100 nm to about 2 um.

14. The filtration membrane of anyone of the preceeding claims, wherein the filtration membrane rejects charged solutes and salts.

15. The filtration membrane of anyone of the preceeding claims, wherein the filtration membrane has a molecular weight cut-off of at least 500 Daltons.

16. The filtration membrane of anyone of the preceeding claims, wherein the self-assembling polymeric layer exhibits sulfate (SO_4^{2-}) rejection of greater than 99%.

17. The filtration membrane of anyone of the preceeding claims, wherein the self-assembling polymeric layer exhibits sulfate (SO_4^{2-}) / chloride (Cl-) separation factor of greater than 50.

18. The filtration membrane of anyone of the preceeding claims, wherein the self-assembling polymeric layer exhibits sulfate (SO_4^{2-}) / chloride (Cl-) separation factor of greater than 75.

19. The filtration membrane of anyone of the preceeding claims, wherein the self-assembling polymeric layer exhibits different anion rejections for salts with the same cation.

20. The filtration membrane of anyone of the preceeding claims, wherein the self-assembling polymeric layer exhibits different anion rejections for salts selected among NaF, NaCl, NaBr, NaI, and $NaClO_4$.

21. The filtration membrane of anyone of the preceeding claims, wherein the self-assembling polymeric layer exhibits a fluoride (F-) / chloride (Cl-) separation factor of greater than 5.

22. The filtration membrane of anyone of the preceeding claims, wherein the self-assembling polymeric layer exhibits a fluoride (F-) / chloride (Cl-) separation factor of about 8.

23. A process of filtering a liquid, the process comprising:

providing a filtration membrane of of any one of claims 1-22;

directing a liquid through the filtration membrane, first through the self-assembling polymeric layer and then through the porous support layer; and

collecting the liquid that permeates through the filtration membrane.

24. A method of making a filtration membrane comprising:

providing a porous support;

printing at least one spacer on the porous support via a three-dimensional printing process;

providing a self-assembling polymer as described herein; and

depositing the self-assembling polymer on to the at least one spacer and the porous substrate.

25. The method of claim 24, wherein the self-assembling polymer is deposited on the at least one spacer and the porous support via spray coating.