

CLAIMS

1. A composite hydrophilic/hydrophobic membrane comprising a hydrophilic polymer layer and a hydrophobic polymer layer comprising a fluorinated surface-modifying macromolecule (SMM), wherein said composite membrane has
 - a) vapour flux of at least 10 kg/m² h at 10°C bulk temperature difference, at a feed temperature of 45°C and a permeate temperature of 35°C, and
 - b) criterion parameter (f_i) of less than 1.
2. The composite membrane of claim 1, wherein said hydrophilic polymer layer comprises polysulfone, polyether sulfone, polyetherimide polyvinylidene fluoride or cellulose acetate.
3. The composite membrane of claim 1, wherein said SMM is poly(urethane propylene glycol) or poly(urea dimethylsiloxane urethane).
4. The composite membrane of claim 3, wherein the SMM is poly(urea dimethylsiloxane urethane) prepared using a two step polymerization method comprising a first polymerization step to form a polyurea pre-polymer from 4,4'-methylene bis(phenyl isocyanate) (MDI) and α,ω -aminopropyl poly(dimethylsiloxane) (PDMS), and a second polymerization step to end-cap the polyurea pre-polymer by the addition of 2-(perfluoroalkyl)ethanol (FAE).
5. The composite membrane according to claim 4, wherein the ratio of MDI:PDMS:FAE is about 2:1:2, about 3:2:2 or about 4:3:3.
6. The composite membrane of claim 3, wherein the SMM is poly(urethane propylene glycol) prepared using a two step polymerization method comprising a first polymerization step to form a polyurethane pre-polymer from 4,4'-methylene bis(phenyl isocyanate) (MDI) and polypropylene glycol (PPG), and a second polymerization step to end-cap the polyurethane pre-polymer by the addition of 2-(perfluoroalkyl)ethanol (FAE).
7. The composite membrane of claim 6, wherein the ratio of MDI:PPG:FAE is about 3:2:2.
8. A membrane distillation system comprising a composite hydrophilic/hydrophobic membrane according to claim 1.
9. The membrane distillation system of claim 8, wherein said hydrophilic polymer layer comprises polysulfone, polyether sulfone, polyetherimide polyvinylidene fluoride or cellulose acetate.
10. The membrane distillation system of claim 8, wherein said SMM is poly(urethane propylene glycol) or poly(urea dimethylsiloxane urethane).
11. The membrane distillation system of claim 10, wherein the SMM is poly(urea dimethylsiloxane urethane) prepared using a two step polymerization method

comprising a first polymerization step to form a polyurea pre-polymer from 4,4'-methylene bis(phenyl isocyanate) (MDI) and α,ω -aminopropyl poly(dimethylsiloxane) (PDMS), and a second polymerization step to end-cap the polyurea pre-polymer by the addition of 2- (perfluoroalkyl)ethanol (FAE).

12. The membrane distillation system of claim 11, wherein the ratio of MDI:PDMS:FAE is about 2:1:2, about 3:2:2 or about 4:3:3.

13. The membrane distillation system of claim 10, wherein the SMM is poly(urethane propylene glycol) prepared using a two step polymerization method comprising a first polymerization step to form a polyurethane pre-polymer from 4,4'-methylene bis(phenyl isocyanate) (MDI) and polypropylene glycol (PPG), and a second polymerization step to end-cap the polyurethane pre-polymer by the addition of 2-(perfluoroalkyl)ethanol (FAE).

14. The membrane distillation system of claim 13, wherein the ratio of MDI:PPG:FAE is about 3:2:2.

15. The membrane distillation system of claim 8, which is a direct contact membrane distillation system, a vacuum membrane distillation system, a sweeping gas membrane distillation system or an air gap membrane distillation system.

16. The membrane distillation system of claim 15, which is a direct contact membrane distillation system.

17. A method of manufacturing a composite hydrophilic/hydrophobic membrane comprising a hydrophilic polymer layer and a hydrophobic polymer layer, said method comprising the steps of:

(a) blending a host hydrophilic polymer with a fluorinated surface-modifying macromolecule and a non-solvent additive in a solvent;

(b) casting the polymer blend and allowing the solvent to evaporate at room temperature for a predetermined time; and

(c) immersing the cast film produced in step (b) in water to allow gelation wherein the method further comprises maximizing porosity of the hydrophobic polymer layer of the composite membrane, minimizing the thickness of the hydrophobic polymer layer, and maximizing the thickness, the porosity, and thermal conductivity of the hydrophilic polymer layer in order to generate the composite membrane with i) vapour flux of at least 10 kg/m² h at 10°C bulk temperature difference, at a feed temperature of 45°C and a permeate temperature of 35°C, and ii) criterion parameter (f_i) of less than 1.

18. The method of claim 17, wherein the host hydrophilic polymer is polysulfone, polyether sulfone, polyetherimide polyvinylidene fluoride, cellulose acetate or a mixture thereof.

19. The method of claim 17, wherein said SMM is poly(urethane propylene glycol) or poly(urea dimethylsiloxane urethane).

20. The method of claim 17, wherein the non-solvent additive is γ -butyrolactone or ethanol.

21. The method of claim 17, wherein the solvent is N,N-dimethylacetamide or 1-methyl-2-pyrrolidinone.

22. A method of optimizing the MD performance of a composite hydrophilic/hydrophobic membrane comprising a hydrophilic polymer layer and a hydrophobic polymer layer comprising a fluorinated surface-modifying macromolecule (SMM), said method comprising the steps of:

(a) maximizing porosity of the top hydrophobic layer of the composite membrane;

(b) minimizing the thickness of the top hydrophobic layer of the composite membrane; and

(c) maximizing the thickness, the porosity and the thermal conductivity of the bottom hydrophilic layer, wherein the composite membrane has i) vapour flux of at least 10 kg/m² h at 10°C bulk temperature difference, at a feed temperature of 45°C and a permeate temperature of 35°C, and ii) criterion parameter (f_i) of less than 1.

23. A composite hydrophilic/hydrophobic membrane comprising a hydrophilic polymer layer and a hydrophobic polymer layer comprising a fluorinated surface-modifying macromolecule (SMM), wherein said composite membrane has a criterion parameter (f_i) of less than 1.

24. A method of manufacturing a composite hydrophilic/hydrophobic membrane comprising a hydrophilic polymer layer and a hydrophobic polymer layer, said method comprising the steps of:

(a) blending a host hydrophilic polymer with a fluorinated surface-modifying macromolecule and a non-solvent additive in a solvent;

(b) casting the polymer blend and allowing the solvent to evaporate at room temperature for a predetermined time; and

(c) immersing the cast film produced in step (b) in water to allow gelation wherein the method further comprises maximizing porosity of the hydrophobic polymer layer of the composite membrane, minimizing the thickness of the hydrophobic polymer layer, and maximizing the thickness, the porosity, and thermal conductivity of the hydrophilic polymer layer in order to generate the composite membrane with a criterion parameter (f_i) of less than 1.

25. A method of optimizing the MD performance of a composite hydrophilic/hydrophobic membrane comprising a hydrophilic polymer layer and a hydrophobic polymer layer comprising a fluorinated surface-modifying macromolecule (SMM), said method comprising the steps of:

(a) maximizing porosity of the top hydrophobic layer of the composite membrane;

(b) minimizing the thickness of the top hydrophobic layer of the composite membrane; and

(c) maximizing the thickness, the porosity and the thermal conductivity of the bottom hydrophilic layer, wherein the composite membrane has a criterion parameter (β) of less than 1.

CLAIMS

1. A composite hydrophilic/hydrophobic membrane comprising a hydrophilic polymer layer and a hydrophobic polymer layer comprising a fluorinated surface-modifying macromolecule (SMM), wherein said composite membrane has

a) vapour flux of at least 10 kg/m² h at 10°C bulk temperature difference, at a feed temperature of 45°C and a permeate temperature of 35°C, and

b) criterion parameter (f_i) of less than 1

wherein said composite membrane has a flux and a morphology conceived to maximize said flux, said morphology being conceived by compiling mathematical parameters representing a thickness, a porosity density and a thermal conductivity of said hydrophobic layer, and a thickness, a porosity density and a thermal conductivity of said hydrophilic layer, wherein said morphology is conceived in accordance with the formula:

$$f_i = \frac{[k_g \varepsilon_t + k_t (1 - \varepsilon_t)] + B_m \delta_t \left(\frac{dp}{dT} \right)_{T_m} \Delta H_v}{k_w \varepsilon_s + k_s (1 - \varepsilon_s)}$$

where f_i reflects said morphology.

2. The composite membrane of claim 1, wherein said hydrophilic polymer layer comprises polysulfone, polyether sulfone, polyetherimide polyvinylidene fluoride or cellulose acetate.

3. The composite membrane of claim 1, wherein said SMM is poly(urethane propylene glycol) or poly(urea dimethylsiloxane urethane).

4. The composite membrane of claim 3, wherein the SMM is poly(urea dimethylsiloxane urethane) prepared using a two step polymerization method comprising a first polymerization step to form a polyurea pre-polymer from 4,4'-methylene bis(phenyl isocyanate) (MDI) and α,ω -

aminopropyl poly(dimethylsiloxane) (PDMS), and a second polymerization step to end-cap the polyurea pre-polymer by the addition of 2-(perfluoroalkyl)ethanol (FAE).

5. The composite membrane according to claim 4, wherein the ratio of MDI:PDMS:FAE is about 2:1:2, about 3:2:2 or about 4:3:3.

6. The composite membrane of claim 3, wherein the SMM is poly(urethane propylene glycol) prepared using a two step polymerization method comprising a first polymerization step to form a polyurethane pre-polymer from 4,4'methylene bis(phenyl isocyanate) (MDI) and polypropylene glycol (PPG), and a second polymerization step to end-cap the polyurethane pre-polymer by the addition of 2- (perfluoroalkyl)ethanol (FAE).

7. The composite membrane of claim 6, wherein the ratio of MDI:PPG:FAE is about 3:2:2.

8. A membrane distillation system comprising a composite hydrophilic/hydrophobic membrane according to claim 1.

9. The membrane distillation system of claim 8, wherein said hydrophilic polymer layer comprises polysulfone, polyether sulfone, polyetherimide polyvinylidene fluoride or cellulose acetate.

10. The membrane distillation system of claim 8, wherein said SMM is poly(urethane propylene glycol) or poly(urea dimethylsiloxane urethane).

11. The membrane distillation system of claim 10, wherein the SMM is poly(urea dimethylsiloxane urethane) prepared using a two step polymerization method comprising a first polymerization step to form a polyurea pre-polymer from 4,4'methylene bis(phenyl isocyanate) (MDI) and α,ω -aminopropyl poly(dimethylsiloxane) (PDMS), and a second polymerization step to end-cap the polyurea pre-polymer by the addition of 2- (perfluoroalkyl)ethanol (FAE).

12. The membrane distillation system of claim 11, wherein the ratio of MDI:PDMS:F AE is about 2:1:2, about 3:2:2 or about 4:3:3.
13. The membrane distillation system of claim 10, wherein the SMM is poly(urethane propylene glycol) prepared using a two step polymerization method comprising a first polymerization step to form a polyurethane pre-polymer from 4,4'methylene bis(phenyl isocyanate) (MDI) and polypropylene glycol (PPG), and a second polymerization step to end-cap the polyurethane pre-polymer by the addition of 2-(perfluoroalkyl)ethanol (FAE).
14. The membrane distillation system of claim 13, wherein the ratio of MDI:PPG:F AE is about 3:2:2.
15. The membrane distillation system of claim 8, which is a direct contact membrane distillation system, a vacuum membrane distillation system, a sweeping gas membrane distillation system or an air gap membrane distillation system.
16. The membrane distillation system of claim 15, which is a direct contact membrane distillation system.
17. A method of manufacturing a composite hydrophilic/hydrophobic membrane comprising a hydrophilic polymer layer and a hydrophobic polymer layer, said method comprising the steps of:
 - (a) blending a host hydrophilic polymer with a fluorinated surface-modifying macromolecule and a non-solvent additive in a solvent;
 - (b) casting the polymer blend and allowing the solvent to evaporate at room temperature for a predetermined time; and
 - (c) immersing the cast film produced in step (b) in water to allow gelation wherein the method generates the composite membrane with i) vapour flux of at least 10 kg/m² h at 10°C

bulk temperature difference, at a feed temperature of 45°C and a permeate temperature of 35°C, and ii) criterion parameter (f_i) of less than 1,

wherein said composite membrane has a flux and a morphology conceived to maximize said flux, said morphology being conceived by compiling mathematical parameters representing a thickness, a porosity density and a thermal conductivity of said hydrophobic layer, and a thickness, a porosity density and a thermal conductivity of said hydrophilic layer, wherein said morphology is conceived in accordance with the formula:

$$f_i = \frac{[k_g \varepsilon_t + k_t (1 - \varepsilon_t)] + B_m \delta_t \left(\frac{dp}{dT} \right)_{T_m} \Delta H_v}{k_w \varepsilon_s + k_s (1 - \varepsilon_s)}$$

where f_i reflects said morphology.

18. The method of claim 17, wherein the host hydrophilic polymer is polysulfone, polyether sulfone, polyetherimide polyvinylidene fluoride, cellulose acetate or a mixture thereof.

19. The method of claim 17, wherein said SMM is poly(urethane propylene glycol) or poly(urea dimethylsiloxane urethane).

20. The method of claim 17, wherein the non-solvent additive is γ -butyrolactone or ethanol.

21. The method of claim 17, wherein the solvent is N,N-dimethylacetamide or 1-methyl-2-pyrrolidinone.

22. A method of optimizing the MD performance of a composite hydrophilic/hydrophobic membrane comprising a hydrophilic polymer layer and a hydrophobic polymer layer comprising a fluorinated surface-modifying macromolecule (SMM), said method comprising the steps of:

- (a) maximizing porosity of the top hydrophobic layer of the composite membrane;
- (b) minimizing the thickness of the top hydrophobic layer of the composite membrane; and

(c) maximizing the thickness, the porosity and the thermal conductivity of the bottom hydrophilic layer, wherein the composite membrane has i) vapour flux of at least $10 \text{ kg/m}^2 \text{ h}$ at 10°C bulk temperature difference, at a feed temperature of 45°C and a permeate temperature of 35°C , and ii) criterion parameter (f_i) of less than 1

wherein said optimization is conceived in accordance with the formula:

$$f_i = \frac{[k_g \varepsilon_t + k_t (1 - \varepsilon_t)] + B_m \delta_t \left(\frac{dp}{dT} \right)_{T_m} \Delta H_v}{k_w \varepsilon_s + k_s (1 - \varepsilon_s)}$$

where f_i reflects morphology of the composite membrane.

23. A composite hydrophilic/hydrophobic membrane comprising a hydrophilic polymer layer and a hydrophobic polymer layer comprising a fluorinated surface-modifying macromolecule (SMM), wherein said composite membrane has a criterion parameter (f_i) of less than 1,

wherein said composite membrane has a flux and a morphology conceived to maximize said flux, said morphology being conceived by compiling mathematical parameters representing a thickness, a porosity density and a thermal conductivity of said hydrophobic layer, and a thickness, a porosity density and a thermal conductivity of said hydrophilic layer, wherein said morphology is conceived in accordance with the formula:

$$f_i = \frac{[k_g \varepsilon_t + k_t (1 - \varepsilon_t)] + B_m \delta_t \left(\frac{dp}{dT} \right)_{T_m} \Delta H_v}{k_w \varepsilon_s + k_s (1 - \varepsilon_s)}$$

where f_i reflects said morphology.

24. A method of manufacturing a composite hydrophilic/hydrophobic membrane comprising a hydrophilic polymer layer and a hydrophobic polymer layer, said method comprising the steps of:

(a) blending a host hydrophilic polymer with a fluorinated surface-modifying macromolecule and a non-solvent additive in a solvent;

- (b) casting the polymer blend and allowing the solvent to evaporate at room temperature for a predetermined time; and
- (c) immersing the cast film produced in step (b) in water to allow gelation to generate the composite membrane with a criterion parameter (f_i) of less than 1,

wherein said composite membrane has a flux and a morphology conceived to maximize said flux, said morphology being conceived by compiling mathematical parameters representing a thickness, a porosity density and a thermal conductivity of said hydrophobic layer, and a thickness, a porosity density and a thermal conductivity of said hydrophilic layer, wherein said morphology is conceived in accordance with the formula:

$$f_i = \frac{[k_g \varepsilon_t + k_t (1 - \varepsilon_t)] + B_m \delta_i \left(\frac{dp}{dT} \right)_{T_m} \Delta H_v}{k_w \varepsilon_s + k_s (1 - \varepsilon_s)}$$

where f_i reflects said morphology.

25. A method of optimizing the MD performance of a composite hydrophilic/hydrophobic membrane comprising a hydrophilic polymer layer and a hydrophobic polymer layer comprising a fluorinated surface-modifying macromolecule (SMM), said method comprising the steps of:

- (a) maximizing porosity of the top hydrophobic layer of the composite membrane;
- (b) minimizing the thickness of the top hydrophobic layer of the composite membrane; and
- (c) maximizing the thickness, the porosity and the thermal conductivity of the bottom hydrophilic layer, wherein the composite membrane has a criterion parameter (f_i) of less than 1

wherein said optimization is conceived in accordance with the formula:

$$f_i = \frac{[k_g \varepsilon_t + k_t (1 - \varepsilon_t)] + B_m \delta_i \left(\frac{dp}{dT} \right)_{T_m} \Delta H_v}{k_w \varepsilon_s + k_s (1 - \varepsilon_s)}$$

where f_i reflects morphology of the composite membrane.