

CLAIMS

1. A composite hydrophilic/hydrophobic membrane comprising a hydrophilic polymer layer, a hydrophobic polymer layer and fluorinated surface-modifying macromolecules (SMM).
2. The composite membrane as claimed in claim 1, wherein said hydrophilic polymer layer is selected from the group consisting of polysulfone, polyether sulfone, polyetherimide, polyvinylidenefluoride and cellulose acetate.
3. The composite membrane as claimed in any one of claims 1 to 2, wherein said fluorinated surface-modifying macromolecules (SMM) consist of oligomeric fluoropolymers synthesized using polyurethane chemistry and tailored with fluorinated end-groups.
4. The composite membrane as claimed in any one of claims 1 to 3, wherein said fluorinated SMM is blended with said hydrophilic polymer layer.
5. The composite membrane as claimed in claim 4, wherein said SMM is selected from the group consisting of poly(urethane propylene glycol) and poly(urea dimethylsiloxane urethane).
6. The composite membrane as claimed in claim 5, wherein said SMM is a 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(phenylisocyanate) (MDI) and polypropylene glycol (PPG), and a second polymerization step to end-cap the polyurethane pre-polymer by the addition of 2-(perfluoroalkyl)ethanol.
7. The composite membrane of claim 6, wherein the ratio of MDI:PPG:FAE is about 3:2:2.
8. The composite membrane as claimed in claim 5, wherein said SMM is a 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(phenylisocyanate) (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).

9. The composite membrane as claimed in claim 8, wherein the ratio of MDI:PDMS:FAE is about 2:1:2, about 3:2:2 or about 4:3:3.
10. The composite membrane as claimed in any one of claims 1 to 9, wherein said composite membrane has a flux and a morphology conceived to maximize said flux.
11. The composite membrane as claimed in claim 10, wherein said morphology is conceived by compiling mathematical parameters reflecting various characteristics of said morphology.
12. The composite membrane as claimed in claim 11, wherein said mathematical parameters comprise 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.
13. The composite membrane as claimed in claim 12, wherein said morphology is conceived in accordance with:

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

where f_i reflects said morphology.

14. The composite membrane as claimed in any one of claims 1 to 13, wherein said composite membrane has a high vapour flux.
15. A membrane distillation system comprising the composite membrane of any one of claims 1 to 14.

16. The membrane distillation system as claimed in claim 15, wherein said system is selected from the group consisting of a direct contact membrane distillation system, a vacuum membrane distillation system, a sweeping gas membrane distillation system and an air gap 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 fluorinated surface-modifying macromolecules (SMM) and a non-solvent additive in a solvent;
 - (b) casting said hydrophilic polymer blend and allowing said solvent to evaporate at room temperature for a predetermined time; and
 - (c) immersing said cast film produced in step (b) in water to allow gelation.
18. The method of manufacturing a composite membrane as claimed in claim 17, further comprising maximizing porosity and minimizing thickness of said hydrophobic polymer layer of said composite membrane in order to increase flux of said composite membrane.
19. The method of manufacturing a composite membrane as claimed in any one of claims 17 to 18, further comprising maximizing thickness, porosity and thermal conductivity of said hydrophilic polymer layer.
20. The method of manufacturing a composite membrane as claimed in any one of claims 17 to 19, wherein said host hydrophilic polymer comprises at least one of polysulfone, polyethersulfone, polyetherimide polyvinylidene fluoride and cellulose acetate.
21. The method of manufacturing a composite membrane as claimed in any one of claims 17 to 20, wherein said SMM is selected from the group consisting of poly(urethane propylene glycol) and poly(urca dimethylsiloxane urethane).
22. The method of manufacturing a composite membrane as claimed in any one of claims 17 to 21, wherein said non-solvent additive is selected from the group consisting of γ -butyrolactone and ethanol.

23. The method of manufacturing a composite membrane as claimed in any one of claims 17 to 22, wherein said solvent is selected from the group consisting of N,N-dimethylacetamide and 1-methyl-2-pyrrolidinone..
24. A method of optimizing the MD performance of a composite hydrophilic/hydrophobic membrane comprising a hydrophilic polymer layer and a hydrophobic polymer layer, 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.

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 $10 \text{ kg/m}^2 \text{ h}$ at 10°C bulk temperature difference, at a feed temperature of 45°C and a permeate temperature of 35°C , and
 - 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:F AE 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(urca dimethylsiloxane urethane).
11. The membrane distillation system of claim 10, wherein the SMM is id morphology is poly(urca 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 polymer with fluorinated surface-modifying 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 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.
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 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.
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 composite membrane has 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 (f_i) of less than 1.