the first molecular weight is lower than the second molecular weight and the ~~OSN~~ OSRO membrane has a molecular weight cut-off that prevents the second solvent from passing through the membrane, thereby separating the first and second ~~compounds~~solvents.

31. A method of forming an organic solvent reverse osmosis (OSRO) membrane comprising a mixed matrix material as described in any one of Clauses 1 to 25, wherein the method comprises the steps of:

(a) providing a material comprising:

a partially crosslinked solvent-resistant polymeric matrix with functional groups suitable for crosslinking; and

an inorganic material homogeneously dispersed throughout the polymeric matrix, where the material has a first region comprising a surface of the material and a second region; and

(b) exposing the first region of the material to a vapour comprising a crosslinking agent that generates further crosslinks in said first region to provide the organic solvent reverse osmosis (OSRO) membrane.

Drawings

FIG. 1 shows the 3D and chemical structures of (1) N,N′-Bis(3-aminopropyl)-1,3-propanediamine (APPD); (2) 1,4-Bis(3-aminopropyl)piperazine (BAPP); and (3) Polyethylenimine (PEI), simulated by Materials Studio 2018 version.

FIG. 2 depicts the OSN performance testing setup.

FIG. 3 depicts the pure isopropanol (IPA) permeance and Rose Bengal (RB) rejection in IPA of (a) APPD-; (b) BAPP-; and (c) PEI-modified vapour-phase crosslinking (VPC)/mixed matrix membranes (MMMs) as a function of reaction duration (Feed: pure IPA and 50ppm RB in IPA; Pressure: 10.0 bar).

FIG. 4 shows the surface and cross-sectional field emission scanning electron microscopy (FESEM) images of BAPP-modified MMMs with 0.1 wt% UiO-66-NH_2 as a function of reaction duration: 10 min, 20 min, 30 min and 45 min (Reaction temperature: 120 °C; Pressure: 1 atm).

FIG. 5 depicts the pore size distributions of the BAPP-modified MMMs as a function of reaction duration deduced by the probability density function (μ_p: the mean effective pore size).

More particularly, the membrane may have one or more of the following pure solvent permeance values:

(a) from 2 - 4 L m^{-2} h^{-1} bar^{-1} for methanol;

(b) from 0.5 - 1.5 L m^{-2} h^{-1} bar^{-1} for isopropanol (IPA);

(c) from 0.6 - 4 L m^{-2} h^{-1} bar^{-1} for hexane;

(d) from 0.9 - 1.5 L m^{-2} h^{-1} bar^{-1} for toluene;

(e) from 0.8-1.3 L m^{-2} h^{-1} bar^{-1} for tetrahydrofuran (THF); and

(f) from 0.2-1 L m^{-2} h^{-1} bar^{-1} for dimethylformamide (DMF).

As will be appreciated, the membranes disclosed herein may be used in nanofiltration. As such, there is also disclosed a method of nanofiltration using an organic solvent nanofiltration (OSN) membrane as described hereinbefore, comprising the steps of

(a) providing a solution comprising a first compound having a first molecular weight and a second compound having a second molecular weight; and

(b) subjecting the solution to nanofiltration using an OSN membrane as described in any one of ~~Claims~~ Clauses 1 to 25, such that the first and second compounds are separated from one another, wherein

the first molecular weight is lower than the second molecular weight and the OSN membrane has a molecular weight cut-off that prevents the second compound from passing through the membrane, thereby separating the first and second compounds. Further details of the method of use may be obtained from the examples section below and by analogy to the methods disclosed therein.

In certain embodiments of the invention, the first and second compounds may be solvents and so the solution does not need a separate solvent. As such, the nanofiltration may relate to solvent-solvent extraction. Alternatively, the method may be one in which the solution may further comprise an organic solvent and the first and second compounds are not organic solvents. In this instance, the nanofiltration may relate to the separation of two compounds.

Also disclosed herein is a method of forming an organic solvent nanofiltration (OSN) membrane and/or an organic solvent reverse osmosis (OSRO) membrane comprising a mixed matrix material as described hereinbefore, wherein the method comprises the steps of:

(a) providing a material comprising:

a partially crosslinked solvent-resistant polymeric matrix with functional groups suitable for crosslinking; and

an inorganic material homogeneously dispersed throughout the polymeric matrix, where the material has a first region comprising a surface of the material and a second region; and

(b) exposing the first region of the material to a vapour comprising a crosslinking agent that generates further crosslinks in said first region to provide the organic solvent nanofiltration (OSN) membrane. Further details of the method of manufacture may be obtained from the examples section below and by analogy to the methods disclosed therein.

Also disclosed herein is a method of nanofiltration using an organic solvent reverse osmosis (OSRO) membrane as described hereinbefore, comprising the steps of

(a) providing a solution comprising a first solvent having a first molecular weight and a second solvent having a second molecular weight; and

(b) subjecting the solution to nanofiltration using an OSRO membrane as described in any one of ~~Claims~~ Clauses 1 to 25, such that the first and second solvents are separated from one another, wherein

the first molecular weight is lower than the second molecular weight and the ~~OSN~~ OSRO membrane has a molecular weight cut-off that prevents the second solvent from passing through the membrane, thereby separating the first and second ~~compounds~~solvents. Further details of the method of use may be obtained from the examples section below and by analogy to the methods disclosed therein.

Also disclosed herein is a method of forming an organic solvent reverse osmosis (OSRO) membrane comprising a mixed matrix material as described hereinbefore, wherein the method comprises the steps of:

(a) providing a material comprising:

a partially crosslinked solvent-resistant polymeric matrix with functional groups suitable for crosslinking; and

an inorganic material homogeneously dispersed throughout the polymeric matrix, where the material has a first region comprising a surface of the material and a second region; and

(b) exposing the first region of the material to a vapour comprising a crosslinking agent that generates further crosslinks in said first region to provide the organic solvent reverse osmosis (OSRO) membrane. Further details of the method of manufacture may be obtained from the examples section below and by analogy to the methods disclosed therein.

Further aspects and embodiments of the invention will now be discussed by reference to the following non-limiting examples.

Claims

1. An organic solvent nanofiltration (OSN) membrane and/or an organic solvent reverse osmosis (OSRO) membrane comprising a composite mixed matrix material that comprises:

a solvent-resistant polymeric matrix with functional groups suitable for crosslinking; and

an inorganic material homogeneously dispersed throughout the polymeric matrix, where the mixed matrix material has a first region comprising a surface of the membrane and a second region, wherein:

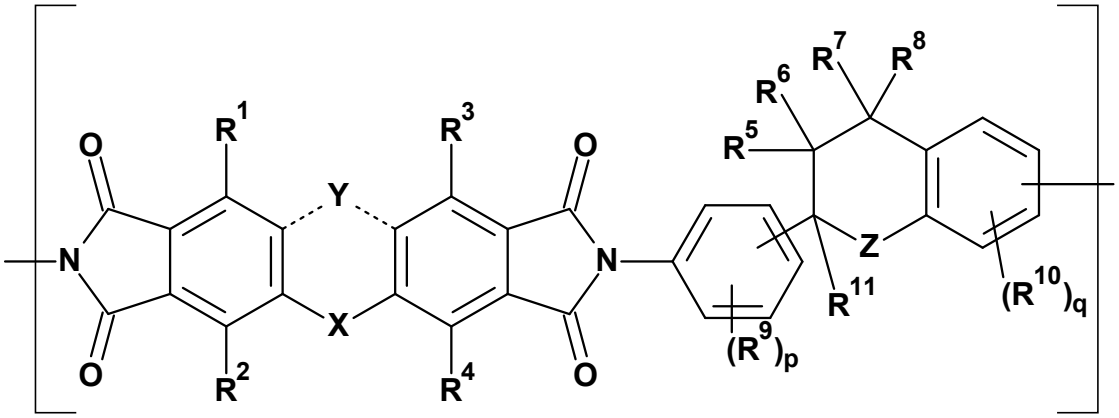
the first region of the mixed matrix material further comprises a crosslinking agent that crosslinks the polymeric matrix in said first region *via* the functional groups suitable for crosslinking; and

the first region has a mean effective pore size of from 0.2 to 2 nm.

2. The membrane according to Claim 1, wherein the solvent-resistant polymeric matrix with functional groups suitable for crosslinking is a polymeric matrix formed from one or more of the group selected from a polybenzimidazole (PBI), a poly(ether ether ketone) (PEEK), a polyacrylonitrile (PAN), and a polyimide (PI), optionally wherein the solvent-resistant polymeric matrix with functional groups suitable for crosslinking is a polymeric matrix formed from one or more of the group selected from a polybenzimidazole (PBI) or a polyimide (PI).

3. The membrane according to Claim 2, wherein the polymeric matrix is formed by a polyimide.

4. The membrane according to Claim 3, wherein the polyimide has a repeating unit of formula I:



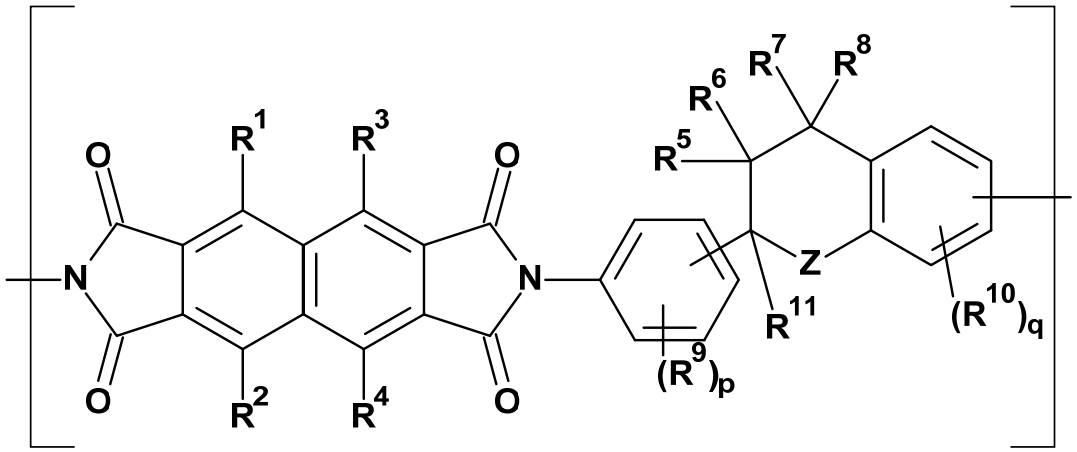
I

each of R^1 to R^8 and R^{11} is independently selected from H, C_{1-3} alkyl, C_{1-3} haloalkyl and halo;

X is a bond or is –C(=O)-;

Y is absent or is –C(=O)-; or

X and Y are each absent so as to form a fused aromatic structure of formula (Ia):



Ia

each R^9, when present, is independently selected from the group comprising: C_{1-3} alkyl, C_{1-3} haloalkyl and halo;

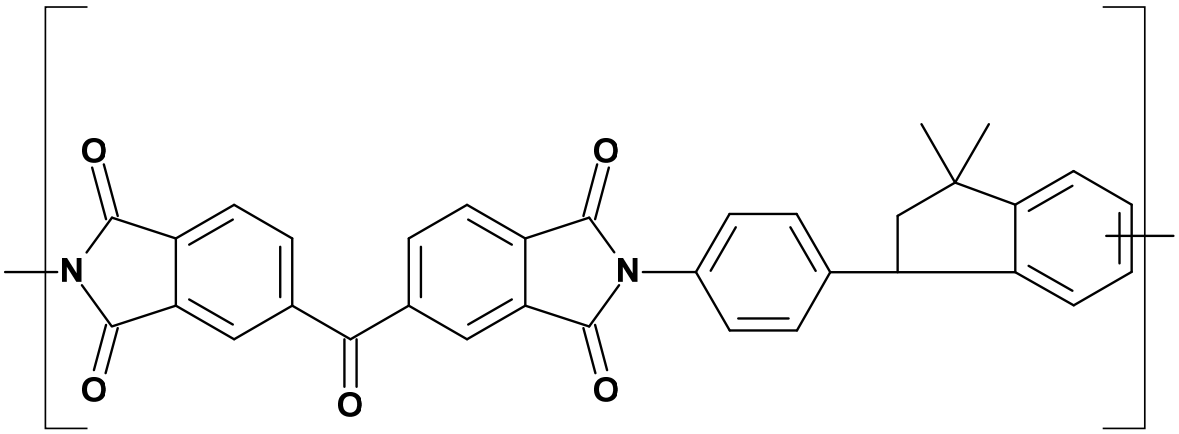
each R^{10}, when present, is independently selected from the group comprising: C_{1-3} alkyl, C_{1-3} haloalkyl and halo;

Z is selected from the group comprising: a bond and $-C(R^1)_2-$;

p is from 0 to 4; and

q is from 0 to 3.

5. The membrane according to Claim 4, wherein the polyimide has a repeating unit of formula II:



II

.

6. The membrane according to any one of the preceding claims, wherein the inorganic material is selected from one or more of a metal organic framework (MOF), carbon nanotubes, zeolites, titanium dioxide (TiO_2), nanoalumina, silica nanoparticles, silver nanoparticles, and a graphene oxide.

7. The membrane according to Claim 6, wherein the inorganic material is a MOF.

8. The membrane according to Claim 7, wherein the MOF has one or more of the following properties:
(a) a porosity of greater than or equal to 50% of the MOF crystal volume, such as from 55 to 80%, such as from 60 to 70%;
(b) a surface area of from 1,000 to 10,000 m^2/g, such as from 2,000 to 8,000 m^2/g, such as from 4,000 to 6,000 m^2/g;
(c) a diameter of the particle of from 10 to 1,000 nm, such as from 25 to 500 nm, such as from 50 to 150 nm.

9. The membrane according to Claim 7 or Claim 8, wherein the MOF is selected from one or more of a UiO-66 MOF (e.g. UiO-66-COOH or, more particularly, UiO-66, UiO-66-F_4 and UiO-66-NH_2), a MIL-53(Al) MOF, a ZIF-8 MOF, and a HKUST-1 MOF.

10. The membrane according to any one of the preceding claims, wherein the weight to weight ratio of the polyimide polymeric matrix material to the inorganic material is from 100:1 to 1000:1, such as from 100:1 to 25:1, such as from 150:1 to 200:1, such as 180:1.

11. The membrane according to any one of the preceding claims, wherein the polymeric matrix material is partially crosslinked by a diamine (e.g. 1,6-hexanediamine), optionally

wherein the polymeric matrix material is a polyimide polymeric matrix material is partially crosslinked by a diamine (e.g. 1,6-hexanediamine).

12. The membrane according to any one of the preceding claims, wherein the crosslinking agent is selected from one or more of the group consisting of a polyamine, and a hydrazine.

13. The membrane according to Claim 12, wherein crosslinking agent is a polyamine.

14. The membrane according to Claim 11 or Claim 12, wherein the polyamine is selected from one or more of the group consisting of ethylenediamine (EDA), trimethylamine (TEA), tris(2-aminoethyl)amine (TAEA), N,N′-bis(3-aminopropyl)-1,3-propanediamine (APPD), 1,4-bis(3-aminopropyl) piperazine (BAPP), and polyethylenimine (PEI), optionally wherein the polyamine is selected from one or more of the group consisting of N,N′-bis(3-aminopropyl)-1,3-propanediamine (APPD), 1,4-bis(3-aminopropyl) piperazine (BAPP), and polyethylenimine (PEI).

15. The membrane according to Claim 14, wherein the polyamine is selected from APPD or PEI, optionally wherein, when present, PEI has a weight average molecular weight of from 100 to 1,000 g mol^{-1}, such as 800 g mol^{-1}.

16. The membrane according to any one of the preceding claims, wherein the first region has a mean effective pore size of from 0.4 to 1.2 nm, such as from 0.5 to 1.13 nm, such as 0.6 to 0.9 nm.

17. The membrane according to any one of the preceding claims, wherein the mixed matrix material has a thickness of from 20 to 150 μm, such as from 25 to 110 μm.

18. The membrane according to any one of the preceding claims, wherein the first region has a thickness of from 100 to 5,000 nm, such as from 200 to 3,500 nm, such as from 300 to 3,000 nm, such as from 500 to 2,500 nm.

19. The membrane according to any one of the preceding claims, wherein the membrane further comprises a non-woven substrate.

20. The membrane according to Claim 19, wherein the non-woven substrate is formed from one or more from the group consisting of a polyester (PET) and a polypropylene (PP).

21. The membrane according to Claim 20, wherein the non-woven substrate is formed from polyethylene terephthalate.

22. The membrane according to any one of the preceding claims, wherein the membrane displays a molecular weight cut-off value of from 100 to 500 Daltons, optionally wherein:
(a) when the membrane is an OSN membrane it displays a molecular weight cut-off value of from 400 to 500 Daltons or when the membrane is an OSRO membrane it displays a molecular weight cut-off value of less than or equal to 200 Daltons, such as from 100 to 200 Daltons; and/or
(b) a rejection rate for a material having a molecular weight that is at least 10% above the molecular weight cut-off value of the membrane is at least 90%.

23. The membrane according to any one of the preceding claims, wherein the membrane is suitable for use in nanofiltration applications using one or more solvents selected from two or more of the solvent classes: polar protic, polar aprotic and non-polar organic solvents.

24. The membrane according to Claim 23, wherein the membrane is suitable for use in nanofiltration applications using one or more solvents selected from polar protic, polar aprotic and non-polar organic solvents.

25. The membrane according to any one of the preceding claims, wherein the membrane has a pure solvent permeance value of from 0.1 to 4 Lm^{-2} h^{-1} bar^{-1}, optionally wherein, the membrane has one or more of the following pure solvent permeance values:
(a) from 2 - 4 L m^{-2} h^{-1} bar^{-1} for methanol;
(b) from 0.5 - 1.5 L m^{-2} h^{-1} bar^{-1} for isopropanol (IPA);
(c) from 0.6 - 4 L m^{-2} h^{-1} bar^{-1} for hexane;
(d) from 0.9 - 1.5 L m^{-2} h^{-1} bar^{-1} for toluene;
(e) from 0.8-1.3 L m^{-2} h^{-1} bar^{-1} for tetrahydrofuran (THF);
(f) from 0.2-1 L m^{-2} h^{-1} bar^{-1} for dimethylformamide (DMF); and
(g) from 1 - 2 L m^{-2} h^{-1} bar^{-1} for ethanol.

26. A method of filtration using an organic solvent nanofiltration (OSN) membrane as described in any one of Claims 1 to 25, comprising the steps of
(a) providing a solution comprising a first compound having a first molecular weight and a second compound having a second molecular weight; and

(b) subjecting the solution to filtration using an OSN membrane as described in any one of Claims 1 to 25, such that the first and second compounds are separated from one another, wherein

the first molecular weight is lower than the second molecular weight and the OSN membrane has a molecular weight cut-off that prevents the second compound from passing through the membrane, thereby separating the first and second compounds.

27. The method according to Claim 26, wherein the first and second compounds are solvents.

28. The method according to Claim 26, wherein the method further comprises an organic solvent and the first and second compounds are not organic solvents.

29. A method of forming an organic solvent nanofiltration (OSN) membrane and/or an organic solvent reverse osmosis (OSRO) membrane comprising a mixed matrix material as described in any one of Claims 1 to 25, wherein the method comprises the steps of:

(a) providing a material comprising:

a partially crosslinked solvent-resistant polymeric matrix with functional groups suitable for crosslinking; and

an inorganic material homogeneously dispersed throughout the polymeric matrix, where the material has a first region comprising a surface of the material and a second region; and

(b) exposing the first region of the material to a vapour comprising a crosslinking agent that generates further crosslinks in said first region to provide the organic solvent nanofiltration (OSN) membrane.

30. A method of filtration using an organic solvent reverse osmosis (OSRO) membrane as described in any one of Claims 1 to 25, comprising the steps of

(a) providing a solution comprising a first solvent having a first molecular weight and a second solvent having a second molecular weight; and

(b) subjecting the solution to filtration using an OSRO membrane as described in any one of Claims 1 to 25, such that the first and second solvents are separated from one another, wherein

the first molecular weight is lower than the second molecular weight and the ~~OSN~~ OSRO membrane has a molecular weight cut-off that prevents the second solvent from passing through the membrane, thereby separating the first and second ~~compounds~~solvents.

31. A method of forming an organic solvent reverse osmosis (OSRO) membrane comprising a mixed matrix material as described in any one of Claims 1 to 25, wherein the method comprises the steps of:

(a) providing a material comprising:

a partially crosslinked solvent-resistant polymeric matrix with functional groups suitable for crosslinking; and

an inorganic material homogeneously dispersed throughout the polymeric matrix, where the material has a first region comprising a surface of the material and a second region; and

(b) exposing the first region of the material to a vapour comprising a crosslinking agent that generates further crosslinks in said first region to provide the organic solvent reverse osmosis (OSRO) membrane.