

STRENGTHENED HOLLOW FIBRE MEMBRANES AND METHODS FOR FABRICATING THE SAME

Field of the Invention

[0001] The present invention generally relates to filtration technologies, and more particularly to strengthened hollow fiber membranes that can be used for micro-filtration and ultra-filtration, and methods for fabricating the strengthened hollow fiber membranes.

Background of the Invention

[0002] Polymeric hollow fiber membranes have elongated central lumens so that they are useful in filtration, one of its broad applications. Filtration separates mixed components in either liquids or gases according to the sizes and/or charges of the components. Thus, polymeric hollow fiber membranes have been extensively used in material purification and wastewater treatment. For example, in the wastewater treatment, wastewater is passed through either the bore or shell sides of multiple microporous hollow fiber membranes. Some components (e.g., water) diffuse through the microporous walls of such fiber membranes into the shell or bore sides of the hollow fiber membranes, forming a permeate, while other components are selectively rejected by such microporous walls and therefore form a retentate. The porosity of such hollow fiber membranes determines the specific compositions of the permeate and retentate.

[0003] One known method for producing polymeric hollow fiber membrane rely on use of a spinnerette, which comprises an annular extrusion orifice and a central bore-forming tube, for extruding a polymeric material into hollow fiber membranes. See, e.g., U.S. Pat. No. 5,209,883. Specifically, a polymeric dope or extrudate, which is formed of either a molten polymeric material (as in melt extrusion) or a polymeric material dissolved in a solvent (as in solution extrusion), is pumped through the annular extrusion orifice of such spinnerette, and a bore-forming liquid or gas is concurrently forced through the central bore-forming tube of such spinnerette, to extrude a polymeric precursor article having a relatively "soft" tubular wall formed of the molten polymer or the polymeric

solution. Subsequently curing and/or drying of such tubular wall forms a polymeric hollow fiber membrane.

[0004] US 2004/0197557 A1 discloses another process for fabricating polymeric hollow fiber membranes. Specifically, a removable solid core fiber is provided for coating one or more layers of a polymeric membrane-forming material thereon. After treating the polymeric membrane-forming material layer to form a solidified polymeric membrane having a permanent tubular shape, the solid core fiber is selectively removed, leaving an elongated lumen inside the solidified polymeric membrane.

[0005] The cross section of the hollow fiber membrane is usually asymmetric. The membrane has a functional separation layer on the top of a porous support layer. However, membrane-forming polymer polyvinylidene fluoride (PVDF) is hydrophobic so that a dense layer of membrane may be formed to reduce the ability of passing water. In order to avoid this problem, it is possible to add various pore forming agents in the spinning solution.

[0006] In Japanese patent 62-017614, PVDF has mixed with pore forming agent polyethyleneglycol and surfactant Tween-80 and then used above phase transfer formation technique to form a hollow fiber membrane. The membrane formed by this method is not strong enough and the flux is low.

[0007] In Japanese patent 3-71168, 7.2% of polyethylene glycol is added as pore forming agent. However, the flux is still not high enough.

[0008] In Chinese patent CN1128176A, PVDF has been mixed with a solvent, a polymeric pore forming agent, a surfactant and other agents to produce hollow fiber membrane. When these agents interact with each other, a high flux hollow membrane is formed.

[0009] In Chinese patent CN1265048A, PVDF has been mixed with organic as well inorganic particles and then melted to produce a hollow fiber membrane with large inner diameter. The membrane can be used in high viscosity media.

[0010] All above-mentioned hollow fiber membranes are not strong enough to be used for separation processes in heavily polluted media. The fiber may break when air agitation is applied to clean the membrane.

[0011] The present invention has improved the composition of the spinning solution by adding nonsoluble high strength fibers to form a supporting frame. Therefore, a hollow fiber membrane with proper pore size, high flux, and high strength is formed.

Summary of the Invention

[0012] Therefore, one of the objectives of the present invention is provide to a hollow fiber membrane with improved strength so that it can be used in treating heavily polluted wastewater.

[0013] In one aspect of the present invention, there is provided a strengthened hollow fiber membrane that is formed from a composition, wherein the strength hollow fiber membrane has the following characteristics: external diameter of 0.3-3mm, wall thickness of 0.05-1mm, porosity of 50-90%, pore size of 0.01-1 μ m, break strength of 0.6-2Mpa, and water flux 400-4000L/m².h at 0.1MPa , 25°C.

[0014] In another aspect of the present invention, there is provided a composition for forming a strengthened hollow fiber membrane. In one embodiment, the composition comprises a membrane-forming polymer that is preferably 15-30 wt%; a solvent that is preferably 50-80 wt%; a non-soluble fiber that is preferably 0.5-10 wt%; and one or more components selected from the group consisting of an inorganic pore forming agent that is preferably 1.0-15 wt%; an organic pore forming agent that is preferably 4-20 wt%; and a surfactant that is preferably 0.05-3%wt%.

[0015] In another embodiment of the composition, the membrane-forming polymer is selected from the group consisting of PVDF, PVDF copolymer, and a mixture of both; wherein the PVDF copolymer has at least 60% or more vinylidenefluoride monomer units. In yet another embodiment of the composition, the membrane-forming polymer comprises a base polymer and an additive polymer; wherein the base polymer is selected from the group consisting of PVDF, PVDF copolymer having at least 60% or more vinylidenefluoride monomer units, and a mixture of both; and wherein the additive polymer is a hydrophilic polymer. In a further embodiment of the composition, the hydrophilic polymer is selected from the group consisting of polymethacrylate, polyvinylalcohol, a copolymer of ethylene and vinylacetate, polyvinylpyrrolidone, polyethyleneoxide, polyvinylacetate, polyacrylic acid, polyacrylonitrile, polyvinyl gutyral resin, and a mixture thereof; wherein the hydrophilic polymer is preferably 1 to 10 wt %.

[0016] In yet another embodiment of the composition, the solvent is a strong polar compound selected from the group consisting of dimethylformamide (DMF),

dimethylacetamide (DMAC), N-methylpyrrolidone, triethylphosphate, dimethylsulfoxide, cyclobutylsulfone, and a mixture thereof. In a further embodiment, the solvent is more preferably 50-80 wt%. In yet still another embodiment of the composition, the solvent comprises a strong polar compound and a weak polar compound; wherein the strong polar compound is selected from the group consisting of dimethylformamide (DMF), dimethylacetamide (DMAC), N-methylpyrrolidone, triethylphosphate, dimethylsulfoxide, cyclobutylsulfone, and a mixture thereof; wherein the weak polar compound is selected from the group consisting of dioxane, butanone, and a mixture thereof; wherein the weak polar compound is preferably 1-5 wt%. In still a further embodiment, the total solvent is more preferably 50-80 wt%.

[0017] In yet another embodiment of the composition, the non-soluble fiber is selected from the group consisting of glass fiber, carbon fiber, polyethylene, polypropylene, polyimide, polyaramide, polyethylene terephthalate and a mixture thereof.

[0018] In yet another embodiment of the composition, the inorganic pore forming agent is selected from the group consisting of LiNO_3 , NaCl , CaCl_2 , CaCO_3 , $\text{Ca}(\text{NO}_3)_2$, SiO_2 , Al_2O_3 , Clay, and a mixture thereof. In a further embodiment of the composition, the inorganic pore forming agent is more preferably 1-15 wt%; and wherein the size of the inorganic pore forming agent is preferably less than $10\mu\text{m}$.

[0019] In yet another embodiment of the composition, the organic pore forming agent is a water soluble compound. In a further embodiment of the composition, the water soluble compound is selected from the group consisting of polyethylene glycol, polyoxethylene, polyvinylpyrrolidone, polyvinylalcohol, methylcellulose, and a mixture thereof. In still further embodiment of the composition, the organic pore forming agent is more preferably 4-20 wt%.

[0020] In yet another embodiment, the surfactant is an organic surfactant selected from the group consisting of cationic surfactants, anionic surfactants, amphoteric surfactants, and nonionic surfactants. In a further embodiment of the composition, the surfactant is selected from the group consisting of dodecyl sodium sulphate, dodecyl benzosulphonate, hexadecyltrimethyl ammonium bromide, secocanol polyoxyethylene, dodecyl amino sulphonate, fluoro surfactant, Tween-20 and Tween-80, preferably 0.05-3%wt%.

[0021] In yet another aspect of the present invention, there is provided a method for fabricating a strengthened hollow fiber membrane, comprising the following steps of: mixing a membrane-forming polymer, a solvent, and one or more components selected from the group consisting an inorganic pore forming agent, an organic polymer pore forming agent, and a surfactant; adding a reinforcement fiber to form a composition; making hollow filament; and extracting pore forming agents with bases, acids, water or organic solvent; thereby the hollow fiber membrane produced has outer diameter 0.3-3 mm, wall thickness 0.05-1 mm, porosity 50-90%, pore size 0.01-1 μ m, breaking strength 0.4-2 Mpa, water flux 400-4000 L/m² at 0.1Mpa, 25°C; wherein the composition comprises: the membrane-forming polymer that is preferably 10-40 wt%; the solvent that is preferably 50-90 wt%; the non-soluble fiber that is preferably 0.5-20 wt%; and one or more components selected from the group consisting of the inorganic pore forming agent that is preferably 0.5-40 wt%; the organic pore forming agent that is preferably 2-30 wt%; and the surfactant that is preferably 0.01-5 wt%;

[0022] The above and other objectives and advantages of the invention will become apparent from the following detailed description of preferred embodiments thereof.

Detailed Description of the Invention

[0023] The present invention may be understood more readily by reference to the following detailed description of certain embodiments of the invention.

[0024] Throughout this application, where publications are referenced, the disclosures of these publications are hereby incorporated by reference, in their entireties, into this application in order to more fully describe the state of art to which this invention pertains.

[0025] While the present invention will be described in reference to the accompanying drawings, the specifics and details are provided for the sole purpose of illustrating the principles of the present invention. It is to be appreciated that the present invention may be practiced without employing the specifics and details. Furthermore, certain variations of the specifics and details in the practice are permissible without deviation from the principles of the present invention.

[0026] In one aspect, the present invention provides a strengthened hollow fiber membrane that has a high breaking strength resulting from the embedded reinforcement fibers. The strengthened hollow fiber membrane comprises a membrane-forming polymer and a reinforcement fiber, where the reinforcement fiber is embedded within the membrane-forming polymer. In one embodiment, the membrane-forming polymer is PVDF or PVDF copolymer or a mixture of both. PVDF copolymer has at least 60% or more vinylidene fluoride monomer units. In another embodiment, the membrane-forming polymer comprises a base polymer and an additive polymer, where the base polymer is PVDF or PVDF copolymer or a mixture of both, and the additive polymer imparts certain functionalities to the base polymer. For example, the additive polymer may be a hydrophilic polymer or a mixture of two or more hydrophilic polymers in order to impart a functionality such as a wettability with water and a resistance to contamination to the resultant hollow fiber membrane. Examples of the hydrophilic polymer include polymethacrylate, polyvinyl alcohol, a copolymer of ethylene and vinyl acetate, polyvinyl pyrrolidone, polyethylene oxide, polyvinyl acetate, polyacrylic acid, polyacrylonitrile, and polyvinyl butyral resin. In order for the functionality to be effectively imparted to the hollow fiber membrane without properties of the base polymer being adversely affected, the content of the hydrophilic polymer is preferably chosen to be within the range of 1 to 10 wt %.

[0027] The reinforcement fiber contributes the strength to the resultant hollow fiber membrane. As mentioned above, when a hollow fiber membrane is employed in wastewater treatment, it has to have the strength to endure the constant agitation and high pressure during the filtration. The PVDF hollow fiber membranes resulting from the known methods are not strong enough to meet the challenge of treating heavily polluted wastewater because the treatment has to be done under high turbulence and pressures. Surprisingly, the inventor of the present invention discovered that the embedded reinforcement fiber increased the strength of the PVDF hollow fiber membranes. In one embodiment, the reinforcement fibers are short fibers including glass fiber and carbon fiber. In another embodiment, the reinforcement fibers are organic polymer fibers including polyethylene, polypropylene, polyimide, and polyaramide if proper solvents are chosen during the fabrication process described in detail hereinafter.

[0028] The hollow fiber membrane provided by the present invention has an external diameter of 0.3-3mm, wall thickness of 0.05-1mm, porosity of 50-90%, pore size of 0.01-1 μ m, break strength of 0.6-2Mpa, and water flux 400-4000L/m².h at 0.1MPa , 25°C.

[0029] In another aspect, the present invention provides a composition from which a PVDF-based hollow fiber membrane can be fabricated. In one embodiment, the composition comprises a membrane-forming polymer, a solvent, an organic pore forming agent, an inorganic pore forming agent, a reinforcement fiber, and a surfactant. It is to be appreciated that the composition may have only one or more of the organic pore forming agent, the inorganic pore forming agent, and the surfactant. While specific chemicals and materials will be used hereinafter to illustrate the principles of the present invention, it is to be appreciated that the listed chemicals and materials are not inclusive and other suitable chemicals and materials may also be used.

[0030] The membrane-forming polymer comprises a base polymer that is PVDF or PVDF copolymer or a mixture of both. PVDF copolymer has at least 60% or more vinylidenefluoride monomer units. The membrane-forming polymer further comprises one or more additional polymers that impart to the hollow fiber membrane certain functionalities including wettability. In certain embodiment, the additional polymers are hydrophilic polymers including polymethacrylate, polyvinylalcohol, a copolymer of ethylene and vinylacetate, polyvinylpyrrolidone, polyethyleneoxide, polyvinylacetate, polyacrylic acid, polyacrylonitrile, and polyvinyl gutyral resin. The additional polymers may be about 1-10% by weight of the membrane-forming polymer. The membrane-forming polymer is preferably about 10-40% by weight of the composition, more preferably 15-30%.

[0031] The solvent is necessary for dissolving the polymers in order to make the composition suitable for extrusion. In one embodiment, the solvent for the composition comprises a strong polar compound selected from the group consisting of dimethylformamide (DMF), dimethylacetamide (DMAC), N-methylpyrrolidone, triethylphosphate, dimethylsulfoxide, cyclobutylsulfone, and a mixture thereof. The solvent is preferably about 50-90% by weight of the composition, more preferably 60-80%. In certain embodiments, the solvent further comprises one or more weak polar compounds

including dioxane, butanone, and a mixture thereof. The weak polar compound is preferably about 1-5% by weight of the composition.

[0032] Organic polymer pore forming agent such as polyethylene glycol can improve flow ability of spinning solution, pore forming performance and membrane hydrophilicity. In one embodiment, the organic polymer pore forming agent comprises one or more of the water soluble compounds selected from the group consisting of polyethylene glycol, polyoxethylene, polyvinylpyrrolidone, polyvinylalcohol, methylcellulose, and a mixture thereof. In certain embodiments, the molecular weight of polyethylene glycol is preferably between 200-20,000 Dalton; the molecular weight of polyoxyethylene preferably 100,000 Dalton or more; the molecular weight of polyvinylpyrrolidone preferably 10,000 to 1.2 million Dalton. The organic polymer pore forming agent is preferably about 2-30% by weight of the composition, more preferably 4-20%.

[0033] The organic polymer pore forming agent can help thickening and dispersion of the composition (spinning solution) but has low ability of diffusion and emulsion. Hence, the interface between spinning solution and coagulation solution cannot be fully wetting in order to make the two solutions diffusion each other. In addition, organic polymer pore forming agent is dissolved in the spinning solution in the molecule form and not easy to form through holes during coagulation. In order to form more through holes, a large amount of pore forming agent is needed. However, the addition of the large amount of organic polymer pore forming agent causes high density of pores and reduces the strength of the hollow fiber membrane. Therefore, in order to strengthen the hollow fiber membrane, reinforcement fibers discussed in detail hereinafter are introduced into the membrane-forming composition.

[0034] Inorganic pore forming agent such as calcium carbonate is dispersed in the spinning solution heterogeneously. After forming membrane, the trapped inorganic pore forming agent can be removed by acid, base, or solvent from the membrane to form pores. This method can form bigger size pores and through holes. Therefore, the membrane flux is high. In one embodiment, the inorganic pore forming agent is one or a mixture of the following compounds: LiNO_3 , NaCl , CaCl_2 , CaCO_3 , $\text{Ca(NO}_3)_2$, SiO_2 , Al_2O_3 , Clay, and the like. The total content of inorganic pore forming agent is preferably 0.5-20% by

weight of the composition, more preferably 1-15%. The size of the inorganic pore forming agent is preferably less than 10 μ m.

[0035] Low molecular surfactant such as Tween-20 is good for diffusion and emulsion. Organic surfactant is one or a mixture of the following: cationic surfactants, anionic surfactants, amphoteric surfactant or nonionic surfactant such as dodecyl sodium sulphate, dodecyl benzosulphonate, hexadecyltrimethyl ammonium bromide, secocetanol polyoxyethylene, dodecyl amino sulphonate, fluoro surfactant, Tween-20 and Tween-80. Total surfactant content is preferably 0.01-5% by weight of the composition, depending on the type of surfactant used. For example, nonionic surfactant is preferably 1-2% by weight of the composition, and fluoro surfactant is preferably 0.05-0.5% by weight of the composition.

[0036] The combination of the organic polymer pore forming agent, inorganic pore forming agent, and surfactant results in stable and strong hollow fiber membranes with good size of pores and high flux. Without wish to be bound by any particular theories, it is believed that the unique combination of all these components in the membrane-forming composition not only minimizes the shortcomings for each component when they are alone, but also brings all their advantages together. For example, the organic polymer pore forming agent alone helps thickening and dispersion of the composition (spinning solution) but has low ability of diffusion and emulsion, the inorganic pore forming agent alone results in an unstable composition that makes spinning process difficult, and the low molecular weight surfactant is not suitable for dispersion and thickening. Surprisingly, the combination of three components in the composition improves the compatibility of all components, makes even distribution of all components, and makes mass transfer in the interface between spinning solution and coagulation solution fast. Therefore, the hollow fiber membrane has even pore distribution.

[0037] A nonsoluble reinforcement fiber such as glass fiber is added in the spinning solution to improve mechanical strength of the hollow fiber membrane. In one embodiment, the nonsoluble reinforcement fibers are short fibers such as glass fiber and carbon fiber. In another embodiment, organic polymer fibers such as polyethylene, polypropylene, polyimide, and polyaramide can also be used if proper solvents are chosen. The nonsoluble reinforcement fiber is preferably about 0.5-20% by weight of the

composition. It is to be noted that the nonsoluble reinforcement fiber is mixed with the solution and thus forms in-situ strengthened fiber membranes.

[0038] In yet another aspect of the present invention, there is provided a method for fabricating the hollow fiber membrane. A technique called phase inversion of hollow fiber membrane may be employed in this invention. Briefly, membrane-forming polymer is dissolved proportionally with solvent and mixed with pore forming agent to form a spinning solution. This solution is then injected through a spinning nozzle into a bath containing coagulation solution. Solvent and pore forming agent is diffused into the coagulation solution. The polymer forms a hollow fiber membrane due to this phase transfer. The pore size of this hollow fiber membrane can be controlled by the composition of the spinning solution, spinning process and post treatment of the membrane.

[0039] In one embodiment, the hollow fiber membranes are prepared by a conventional phase inversion process. The membrane-forming polymer, inorganic pore agent, organic polymer pore agent, and surfactant are dissolved and mixed in a polar solvent. Then, reinforcement fibers are added into the composition. Then, make hollow filament and then extract pore agent with bases, acids, water or organic solvent. The hollow fiber membrane produced by this method has an external diameter of 0.3-3mm, wall thickness of 0.05-1mm, porosity of 50-90%, pore size of 0.01-1 μ m, break strength of 0.6-2Mpa, and water flux 400-4000L/m².h at 0.1MPa, 25°C.

[0040] The following examples are provided for the sole purpose of illustration of the principles of the present invention.

[0041] Examples

[0042] The following examples have used common spinning conditions. Melting index (MI) of PVDF is 2-15. The membrane-forming polymer, solvent, additives are warmed and stirred in a reactor to form a spinning solution; then solution is filtered. Reinforcement fibers are added and stirred to mix evenly. After the solution is degassed, it together with a core solution passes through a spinning nozzle and drops into the coagulation solution to form a hollow fiber membrane.

[0043] Example 1

[0044] 1000 grams of 2 μ m calcium carbonate particles were stirred vigorously in 5 kg dimethyl acetamide (DMAc); add 2kg more DMAc, 2kg PVDF resin, 500g polyethylene glycol, and 100g Tween-20 and mixed evenly. Filtered the solution. Added

100g glass fiber and stir. Degased the solution and then passed this spinning solution through a spinning nozzle into a coagulation bath with water as coagulation agent. Used 2% HCl solution to remove calcium carbonate and get hollow fiber membrane. This inner pressure PVDF hollow fiber membrane had inner diameter 0.8mm, wall thickness 0.25mm, break strength 1.12Mpa, water flux 970L/m².hr at 0.1Mpa, 25°C, pore size 0.1um, porosity 75%.

[0045] Comparison with example 1

[0046] The formulation above changed to, 1000 grams of 2um calcium carbonate particles 7kg DMAc, 2kg PVDF, 500g polyethylene glycol, 100g Tween-20, used the same process as example 1. A hollow fiber membrane obtained had inner diameter 0.8 mm, wall thickness 0.25mm, break strength 0.42Mpa, water flux 950L/m².hr at 0.1Mpa, 25°C, pore size 0.1um and porosity 80%.

[0047] Example 2

[0048] 500g Al₂O₃ sized from 20 to 80nm were stirred vigorously in 7kg N-methylpyrrolidone. Added 2kg PVDF resin, 500g polyvinyl pyrrolidone and 100g Tween-80 and stirred to mix evenly. Filtered the solution and add 100g polypropylene short fiber and stir. Degased the solution and carry out spinning as example 1. Used 4% NaOH solution to remove Al₂O₃ to get a hollow fiber membrane. This external pressure PVDF hollow fiber membrane had inner diameter 0.5mm, wall thickness 0.15mm, break strength 0.62Mpa, water flux 1270L/m².hr at 0.1Mpa, 25°C, pore size 0.2um, porosity 78%.

[0049] Comparison with example 2

[0050] The formation in example 2 changed to 500g Al₂O₃ sized from 20 to 80nm 7kg N-methylpyrrolidone, 2kg PVDF resin, 500g polyvinylpyrrolidone, 100g Tween-80. The external pressure PVDF hollow fiber membrane had inner diameter 0.5mm, wall thickness 0.15mm, break strength 0.32Mpa, water flux 1200L/m².h at 0.1Mpa, 25°C, pore size 0.2um, porosity 81%.

[0051] Example 3

[0052] 800g of 2um calcium carbonate particles were stirred vigously in 5kg DMAc. Added 1.8kg DMAc, 1.8kg PVDF, 780g polyvinylpyrrolidone and 20g flouro surfactant FC-4 and stir. Filtered the solution, add 100g glass fiber and stir. Degased and then carried out spinning as example 1. Used 2% HCl solution to remove calcium carbonate and obtain inner pressure PVDF hollow fiber membrane with inner diameter

0.8mm, wall thickness 0.3mm break strength 0.93Mpa, water flux 1310L/m².hr at 0.1Mpa, 25°C, pore size 0.5um.

[0053] Example 4

[0054] Added 7kg DMAc, 2kg PVDF resin, 1000g polyethylene glycol, and 100g Tween-20 and mixed evenly. Added 150g Nylon short fiber and stir. Degased the solution and then passed this spinning solution through a spinning nozzle into a coagulation bath with water as coagulation agent. This inner pressure PVDF hollow fiber membrane had inner diameter 0.8mm, wall thickness 0.25mm, break strength 0.62Mpa, water flux 450L/m².hr at 0.1Mpa, 25°C, pore size 0.1um, porosity 80%.

[0055] Comparison with example 4

[0056] The formulation above changed to 7kg DMAc, 2kg PVDF, 1000g polyethylene glycol, 100g Tween-20, using the same process as example 1. A hollow fiber membrane obtained had inner diameter 0.8 mm, wall thickness 0.25mm, break strength 0.42Mpa, water flux 470L/m².hr at 0.1Mpa, 25°C, pore size 0.1um and porosity 85%.

[0057] Example 5

[0058] Added 7kg N-methylpyrrolidone. Added 2kg PVDF resin, 500g polyvinyl pyrrolidone and 100g Tween-80 and stir to mix evenly. Filtered the solution and added 100g Polyethylene Terephthalate (PET) short fiber and stir. Degased the solution and carried out spinning as example 1. This external pressure PVDF hollow fiber membrane had inner diameter 0.5mm, wall thickness 0.15mm, break strength 0.45Mpa, water flux 700L/m².hr at 0.1Mpa, 25°C, pore size 0.2um, porosity 80%.

[0059] Comparison with example 5

[0060] The formation in example 5 changed to 7kg N-methylpyrrolidone, 2kg PVDF resin, 500g polyvinylpyrrolidone, 100g Tween-80. Degased the solution and carried out spinning as example 1. The external pressure PVDF hollow fiber membrane had inner diameter 0.5mm, wall thickness 0.15mm, break strength 0.32Mpa, water flux 770L/m².h at 0.1Mpa, 25°C, pore size 0.2um, porosity 85%.

[0061] While the present invention has been described with reference to particular embodiments, it will be understood that the embodiments are illustrative and that the invention scope is not so limited. Alternative embodiments of the present invention will become apparent to those having ordinary skill in the art to which the present invention pertains. Such alternate embodiments are considered to be encompassed within the spirit

and scope of the present invention. Accordingly, the scope of the present invention is described by the appended claims and is supported by the foregoing description.

CLAIMS

What is claimed is:

1. A strengthened hollow fiber membrane that is formed from a composition, wherein the strength hollow fiber membrane has the following characteristics: external diameter of 0.3-3mm, wall thickness of 0.05-1mm, porosity of 50-90%, pore size of 0.01-1 μ m, break strength of 0.6-2Mpa, and water flux 400-4000L/m².h at 0.1MPa , 25°C;

wherein the composition for forming the strength hollow fiber membrane comprises:

a membrane-forming polymer that is preferably 10-40 wt%;

a solvent that is preferably 50-90 wt%;

a non-soluble fiber that is preferably 0.5-20 wt%; and

one or more components selected from the group consisting of an inorganic pore forming agent that is preferably 0.5-40 wt%; an organic pore forming agent that is preferably 2-30 wt%; and a surfactant that is preferably 0.01-5 wt%;

2. The strengthened hollow fiber membrane of claim 1, wherein the membrane-forming polymer is selected from the group consisting of PVDF, PVDF copolymer, and a mixture of both; wherein the PVDF copolymer has at least 60% or more vinylidenefluoride monomer units.

3. The strengthened hollow fiber membrane of claim 1, wherein the membrane-forming polymer comprises a base polymer and an additive polymer; wherein the base polymer is selected from the group consisting of PVDF, PVDF copolymer having at least 60% or more vinylidenefluoride monomer units, and a mixture of both; and wherein the additive polymer is a hydrophilic polymer.

4. The strengthened hollow fiber membrane of claim 3, wherein the hydrophilic polymer is selected from the group consisting of polymethacrylate, polyvinylalcohol, a copolymer of ethylene and vinylacetate, polyvinylpyrrolidone, polyethyleneoxide,

polyvinylacetate, polyacrylic acid, polyacrylonitrile, polyvinyl butyral resin, and a mixture thereof; wherein the hydrophilic polymer is preferably 1 to 10 wt %.

5. The strengthened hollow fiber membrane of claim 1, wherein the solvent is a strong polar compound selected from the group consisting of dimethylformamide (DMF), dimethylacetamide (DMAC), N-methylpyrrolidone, triethylphosphate, dimethylsulfoxide, cyclobutylsulfone, and a mixture thereof.

6. The strengthened hollow fiber membrane of claim 5, wherein the solvent is more preferably 50-80 wt%.

7. The strengthened hollow fiber membrane of claim 1, wherein the solvent comprises a strong polar compound and a weak polar compound; wherein the strong polar compound is selected from the group consisting of dimethylformamide (DMF), dimethylacetamide (DMAC), N-methylpyrrolidone, triethylphosphate, dimethylsulfoxide, cyclobutylsulfone, and a mixture thereof; wherein the weak polar compound is selected from the group consisting of dioxane, butanone, and a mixture thereof; wherein the weak polar compound is preferably 1-5 wt%.

8. The strengthened hollow fiber membrane of claim 7, wherein the total solvent is more preferably 50-80 wt%.

9. The strengthened hollow fiber membrane of claim 1, wherein the non-soluble fiber is selected from the group consisting of glass fiber, carbon fiber, polyethylene, polypropylene, polyimide, polyaramide, polyethylene terephthalate and a mixture thereof.

10. The strengthened hollow fiber membrane of claim 1, wherein the inorganic pore forming agent is selected from the group consisting of LiNO_3 , NaCl , CaCl_2 , CaCO_3 , $\text{Ca}(\text{NO}_3)_2$, SiO_2 , Al_2O_3 , Clay, and a mixture thereof.

11. The strengthened hollow fiber membrane of claim 10, wherein the inorganic pore forming agent is more preferably 1-15 wt%; and wherein the size of the inorganic pore forming agent is preferably less than 10 μ m.
12. The strengthened hollow fiber membrane of claim 1, wherein the organic pore forming agent is a water soluble compound.
13. The strengthened hollow fiber membrane of claim 12, wherein the water soluble compound is selected from the group consisting of polyethylene glycol, polyoxethylene, polyvinylpyrrolidone, polyvinylalcohol, methylcellulose, and a mixture thereof.
14. The strengthened hollow fiber membrane of claim 13, wherein the organic pore forming agent is more preferably 4-20 wt%.
15. The strengthened hollow fiber membrane of claim 1, wherein the surfactant is an organic surfactant selected from the group consisting of cationic surfactants, anionic surfactants, amphoteric surfactants, and nonionic surfactants.
16. The strengthened hollow fiber membrane of claim 1, wherein the surfactant is selected from the group consisting of dodecyl sodium sulphate, dodecyl benzosulphonate, hexadecyltrimethyl ammonium bromide, secotanol polyoxyethylene, dodecyl amino sulphonate, fluoro surfactant, Tween-20 and Tween-80, more preferably 0.05-3 wt%
17. A composition for forming a strengthened hollow fiber membrane, comprising:
 - a membrane-forming polymer that is preferably 15-30 wt%;
 - a solvent that is preferably 50-80 wt%;
 - a non-soluble fiber that is preferably 0.5-10 wt%; and
 - one or more components selected from the group consisting of an inorganic pore forming agent that is preferably 1.0-15 wt%; an organic pore forming agent that is preferably 4-20 wt%; and a surfactant that is preferably 0.05-3%wt%;

18. The composition of claim 17, wherein the membrane-forming polymer is selected from the group consisting of PVDF, PVDF copolymer, and a mixture of both; wherein the PVDF copolymer has at least 60% or more vinylidene fluoride monomer units.

19. The composition of claim 17, the membrane-forming polymer comprises a base polymer and an additive polymer; wherein the base polymer is selected from the group consisting of PVDF, PVDF copolymer having at least 60% or more vinylidene fluoride monomer units, and a mixture of both; and wherein the additive polymer is a hydrophilic polymer.

20. The composition of claim 19, wherein the hydrophilic polymer is selected from the group consisting of polymethacrylate, polyvinyl alcohol, a copolymer of ethylene and vinyl acetate, polyvinylpyrrolidone, polyethylene oxide, polyvinyl acetate, polyacrylic acid, polyacrylonitrile, polyvinyl butyral resin, and a mixture thereof; wherein the hydrophilic polymer is preferably 1 to 10 wt %.

21. The composition of claim 17, wherein the solvent is a strong polar compound selected from the group consisting of dimethylformamide (DMF), dimethylacetamide (DMAC), N-methylpyrrolidone, triethylphosphate, dimethylsulfoxide, cyclobutylsulfone, and a mixture thereof.

22. The composition of claim 21, wherein the solvent is more preferably 50-80 wt%.

23. The composition of claim 17, wherein the solvent comprises a strong polar compound and a weak polar compound; wherein the strong polar compound is selected from the group consisting of dimethylformamide (DMF), dimethylacetamide (DMAC), N-methylpyrrolidone, triethylphosphate, dimethylsulfoxide, cyclobutylsulfone, and a mixture thereof; wherein the weak polar compound is selected from the group consisting of dioxane, butanone, and a mixture thereof; wherein the weak polar compound is preferably 1-5 wt%.

24. The composition of claim 23, wherein the total solvent is more preferably 50-80 wt%.
25. The composition of claim 17, wherein the non-soluble fiber is selected from the group consisting of glass fiber, carbon fiber, polyethylene, polypropylene, polyimide, polyaramide, polyethylene terephthalate and a mixture thereof.
26. The composition of claim 17, wherein the inorganic pore forming agent is selected from the group consisting of LiNO_3 , NaCl , CaCl_2 , CaCO_3 , $\text{Ca}(\text{NO}_3)_2$, SiO_2 , Al_2O_3 , Clay, and a mixture thereof.
27. The composition of claim 26, wherein the inorganic pore forming agent is more preferably 1-15 wt%; and wherein the size of the inorganic pore forming agent is preferably less than $10\mu\text{m}$.
28. The composition of claim 17, wherein the organic pore forming agent is a water soluble compound.
29. The composition of claim 28, wherein the water soluble compound is selected from the group consisting of polyethylene glycol, polyoxethylene, polyvinylpyrrolidone, polyvinylalcohol, methylcellulose, and a mixture thereof.
30. The composition of claim 29, wherein the organic pore forming agent is more preferably 4-20 wt%.
31. The composition of claim 17, wherein the surfactant is an organic surfactant selected from the group consisting of cationic surfactants, anionic surfactants, amphoteric surfactants, and nonionic surfactants.
32. The composition of claim 17, wherein the surfactant is selected from the group consisting of dodecyl sodium sulphate, dodecyl benzosulphonate, hexadecyltrimethyl

ammonium bromide, secocanol polyoxyethylene, dodecyl amino sulphonate, fluoro surfactant, Tween-20 and Tween-80, preferably 0.05-3%wt%.

33. A method for fabricating a strengthened hollow fiber membrane, comprising the following steps of:

mixing a membrane-forming polymer, a solvent, and one or components selected from the group consisting of an inorganic pore forming agent, an organic polymer pore forming agent, and a surfactant;

adding a reinforcement fiber to form a composition;

making hollow filament; and

extracting pore forming agents with bases, acids, water or organic solvent;

thereby the hollow fiber membrane produced has outer diameter 0.3-3 mm, wall thickness 0.05-1 mm, porosity 50-90%, pore size 0.01-1 μ m, breaking strength 0.4-2 Mpa, water flux 400-4000 L/m² at 0.1Mpa, 25°C;

wherein the composition comprises:

the membrane-forming polymer that is preferably 10-40 wt%;

the solvent that is preferably 50-90 wt%;

the non-soluble fiber that is preferably 0.5-20 wt%; and

one or more components selected from the group consisting of the inorganic pore forming agent that is preferably 0.5-40 wt%; the organic pore forming agent that is preferably 2-30 wt%; and the surfactant that is preferably 0.01-5 wt%;

34. The method of claim 33, wherein the membrane-forming polymer is selected from the group consisting of PVDF, PVDF copolymer, and a mixture of both; wherein the PVDF copolymer has at least 60% or more vinylidenefluoride monomer units.

35. The method of claim 33, the membrane-forming polymer comprises a base polymer and an additive polymer; wherein the base polymer is selected from the group consisting of PVDF, PVDF copolymer having at least 60% or more vinylidenefluoride monomer units, and a mixture of both; and wherein the additive polymer is a hydrophilic polymer.

36. The method of claim 35, wherein the hydrophilic polymer is selected from the group consisting of polymethacrylate, polyvinylalcohol, a copolymer of ethylene and vinylacetate, polyvinylpyrrolidone, polyethyleneoxide, polyvinylacetate, polyacrylic acid, polyacrylonitrile, polyvinyl gutyral resin, and a mixture thereof; wherein the hydrophilic polymer is preferably 1 to 10 wt %.

37. The method of claim 33, wherein the solvent is a strong polar compound selected from the group consisting of dimethylformamide (DMF), dimethylacetamide (DMAC), N-methylpyrrolidone, triethylphosphate, dimethylsulfoxide, cyclobutylsulfone, and a mixture thereof.

38. The method of claim 37, wherein the solvent is more preferably 50-80 wt%.

39. The method of claim 33, wherein the solvent comprises a strong polar compound and a weak polar compound; wherein the strong polar compound is selected from the group consisting of dimethylformamide (DMF), dimethylacetamide (DMAC), N-methylpyrrolidone, triethylphosphate, dimethylsulfoxide, cyclobutylsulfone, and a mixture thereof; wherein the weak polar compound is selected from the group consisting of dioxane, butanone, and a mixture thereof; wherein the weak polar compound is preferably 1-5 wt%.

40. The method of claim 39, wherein the total solvent is more preferably 50-80 wt%.

41. The method of claim 33, wherein the non-soluble fiber is selected from the group consisting of glass fiber, carbon fiber, polyethylene, polypropylene, polyimide, polyaramide, polyethylene terephthalate and a mixture thereof.

42. The method of claim 33, wherein the inorganic pore forming agent is selected from the group consisting of LiNO_3 , NaCl , CaCl_2 , CaCO_3 , $\text{Ca}(\text{NO}_3)_2$, SiO_2 , Al_2O_3 , Clay, and a mixture thereof.

43. The method of claim 42, wherein the inorganic pore forming agent is more preferably 1-15 wt%; and wherein the size of the inorganic pore forming agent is preferably less than 10 μ m.

44. The method of claim 33, wherein the organic pore forming agent is a water soluble compound.

45. The method of claim 44, wherein the water soluble compound is selected from the group consisting of polyethylene glycol, polyoxethylene, polyvinylpyrrolidone, polyvinylalcohol, methylcellulose, and a mixture thereof.

46. The method of claim 45, wherein the organic pore forming agent is more preferably 4-20 wt%.

47. The method of claim 33, wherein the surfactant is an organic surfactant selected from the group consisting of cationic surfactants, anionic surfactants, amphoteric surfactants, and nonionic surfactants.

48. The method of claim 33, wherein the surfactant is selected from the group consisting of dodecyl sodium sulphate, dodecyl benzosulphonate, hexadecyltrimethyl ammonium bromide, secocanol polyoxyethylene, dodecyl amino sulphonate, flouro surfactant, Tween-20 and Tween-80, preferably 0.05-3%wt%.