

HOLLOW FIBER POROUS MEMBRANE AND METHOD OF FABRICATING THE SAME

Technical Field of the Innovation

[0001] The present invention relates to highly strengthened hollow fiber membranes and methods for fabricating the same.

Background of the Innovation

[0002] Hollow fiber membranes have been mainly used in various fields of filtration and separation processes.

[0003] One known method for fabricating of hollow fiber membranes is the phase inversion technique that includes the following processes: (i) preparing a polymeric dope or spinning solution used to create the membrane by mixing homogeneously a membrane-forming polymeric resin(s), a organic solvent(s), and a pore-forming agent(s) proportionally; (ii) extruding the dope through a spinnerette or a nozzle to form a polymeric precursor article that then enters the coagulation bath; (iii) after diffusing the solvents and pore-forming agents of the polymeric precursor article into the coagulation solution, the resultant polymeric hollow fiber porous membrane is produced due to this phase transfer. The resultant pore size of these hollow fiber membranes can be achieved by controlling composition of spinning solution, parameters of spinning process, post-treatment conditions of membrane and the like.

[0004] The cross section of the hollow fiber membrane fabricated by the solution phase inversion is usually asymmetric. The hollow fiber membrane has a functional separation layer (dense skin layer) on the top of a porous supporting layer (sponge-like and finger-like structures). In order to enhance water flux, it is possible to add various additives such as pore-forming agents and the second solvents in the spinning solution. A few of examples are briefly mentioned hereinafter.

[0005] JP 62-017614 proposes a method for producing hollow fiber membrane by phase inversion technique after polyvinylidene fluoride (PVDF) has mixed with polyethylene glycol (high molecular pore forming agent) and Tween-80 (surfactant). However, the break strength of the membrane formed by this method is not strong enough and water flux of the membrane is low as well. Thus, the product cannot satisfy practical requirements.

[0006] JP 3-071168 discloses a hollow fiber membrane that contains 7.2% of polyethylene glycol as a pore-forming agent. However, the flux is still not high enough.

[0007] CN 1128176A discloses a method for producing hollow fiber membranes that comprise polyvinylidene fluoride (PVDF) which is mixed with a solvent, a polymeric pore forming agent, a nonsolvent and a surfactant. Owing to these agents added proportionally, their property complementation and synergistic effect make the water flux of hollow fiber membrane formed to be high.

[0008] CN 1265048A discloses a hollow fiber membrane that comprises PVDF that has mixed with organic liquids and inorganic particles and then melted to produce the hollow fiber membrane with larger inner diameter. The product can be used for treating high viscosity media.

[0009] All above-mentioned contents are hereby cited as references. However, the strength of the external pressure hollow fiber porous membrane by the above techniques, in particular, tensile strength and breaking tenacity resistance, is not strong enough to be used for separation process in heavily polluted media. The fiber is broken easily off when air agitation is applied to clean the membrane.

[00010] In order to improve the strength of membranes, US 5,472,607 and 6,354,444 disclose a method to produce an external pressure fine tubular membrane, where a polymeric solution is coated onto a tubular support that is a woven or knitted braid. However, the external pressure fine tubular membrane brings in new shortcomings: (i) it has large external diameter so that it has a decreased loading density in the unit capacity of the membrane in comparison with hollow fiber membrane; (ii) its porous membrane can be peeled away easily from the braid when inversely cleaning the polluted membrane, due to weaker bonding force between the tubular support braid and porous polymeric membrane materials; (iii) the breakage and peeling of the membrane occur

easily in bonding area of the root of tubular membrane with epoxy resins owing to membrane fatigue when air agitation is applied to clean the membrane; (iv) it has low productivity; and etc.

Summary of the Invention

[00011] One embodiment of the present invention provides a hollow fiber membrane bundle comprises a plurality of single hollow fiber membrane strands.

[00012] In another embodiment of the hollow fiber membrane bundle, it further comprises a reinforce support strand, wherein the hollow fiber membrane strands are surrounding the reinforce support strand.

[00013] In another embodiment of the hollow fiber membrane bundle, it further comprises a reinforce support tubule, wherein the hollow fiber membrane strands are surrounding the reinforce support tubule.

[00014] In another embodiment of the hollow fiber membrane bundle, the plurality of single hollow fiber membrane strands are 2-8.

[00015] In another embodiment of the hollow fiber membrane bundle, the bundle has following features: outer diameter 0.3 - 3 mm, wall thickness 0.05 - 1 mm, porosity 50 - 90%, pore size 0.01 - 1 mm, the tensile strength at break of bundled hollow fiber membranes 0.2 - 10.0 Kg/bundle, and pure water flux 600-10,000 L/m² h@0.1MPa, 25°C.

[00016] Another embodiment of the present invention provides a method for producing hollow fiber membrane bundles comprising a plurality of single hollow fiber membrane strands, wherein the bundle has following features: outer diameter 0.3 - 3 mm, wall thickness 0.05 - 1 mm, porosity 50 - 90%, pore size 0.01 - 1 mm, the tensile strength at break of bundled hollow fiber membranes 0.2 - 10.0 Kg/bundle, and pure water flux 600-10,000 L/m² h@0.1MPa, 25°C. The method comprises the following steps: providing a spinning solution comprising a membrane forming polymer, pore forming agents, solvents, and surfactants; extruding the spinning solution into a coagulation solution through a nozzle having a plurality of orifices suitably configured as to enable the extruded spinning solutions to form the bundle in the coagulation solution; and

removing the pore forming agents; thereby the hollow fiber membrane bundle is obtained.

[00017] In another embodiment of the method, the plurality of hollow fiber membrane strands comprises 2-8 single hollow fiber membranes.

[00018] In another embodiment of the method, the hollow fiber membrane bundle further comprises a reinforce fiber that is surrounded by the plurality of hollow fiber membranes; and wherein the nozzle comprises a central bore so that the reinforce fiber can be extruded from the nozzle via the central bore with the spinning solution together.

[00019] In another embodiment of the method, the hollow fiber membrane bundle further comprises a reinforce tubule that is surrounded by the plurality of hollow fiber membranes; and wherein the nozzle comprises a central bore so that the reinforce tubule can be extruded from the nozzle via the central bore with the spinning solution together.

[00020] In another embodiment of the method, in the step of extruding, the extrusion is a dry-wet spinning process during which the spinning solution together with a core solution is concurrently extruded through the nozzle to form precursor hollow fibers, subsequently to form a bundle before dropping to the coagulation bath, and finally enter the coagulation solution to form a hollow fiber membrane bundle.

[00021] In another embodiment of the method, the hollow fiber membrane bundle further comprises a reinforce tubule that is surrounded by the plurality of hollow fiber membranes; and wherein the nozzle comprises a central bore so that the reinforce tubule can be extruded from the nozzle via the central bore with the spinning solution together.

[00022] The objectives of and advantages of the invention will become apparent from the following detailed description of preferred embodiments thereof in connection with the accompanying drawings.

Brief Description of the Drawings

[00023] Preferred embodiments according to the present invention will now be described with reference to the Figures, in which like reference numerals denote like elements.

[00024] FIG 1 shows exemplary cross-sectional views of hollow fiber membrane bundles in accordance with one embodiment of the present invention.

[00025] FIG 2 shows exemplary cross-sectional views of hollow fiber membrane bundles in accordance with one embodiment of the present invention.

[00026] FIG 3 shows exemplary cross-sectional views of hollow fiber membrane bundles in accordance with one embodiment of the present invention.

[00027] FIG 4 shows an exemplary cross-sectional view of hollow fiber membrane bundles in accordance with one embodiment of the present invention.

[00028] FIG 5 shows two exemplary bottom plan views of nozzles for producing hollow fiber membrane bundles in accordance with one embodiment of the present invention.

[00029] FIG 6 is a schematic diagram of a spinning apparatus and its process for producing hollow fiber membrane bundles in accordance with one embodiment of the present invention.

Detailed Description of the Innovation

[00030] One object of the present invention is to provide a product of the reinforced hollow fiber membrane and methods for fabricating the same.

[00031] Referring to FIG 1, there are provided exemplary cross-sectional views of hollow fiber membrane bundles in accordance with one embodiment of the present invention. The hollow fiber membrane bundles comprise a plurality of hollow fiber membranes that are bundled together to form a single product. In one embodiment, the hollow fiber membrane bundles can be formed in the spinning process. For example, the dope can be extruded through a nozzle with 2 – 8 annular extrusion orifices together and then enter a coagulation bath so as to produce hollow fiber membranes bundles with 2-8 hollow fiber membranes, having high stability, proper pore size, high water flux and high mechanical strengths. The amalgamation circle of hollow fiber membranes bundles can be adjusted by (i) adjusting the entry distance from the exits of annular extrusion orifices of the nozzle to the solution surface of the coagulation bath, and (ii) selecting the optimal central distance between the exits of annular extrusion orifices of the nozzle. The entry

distance from the dope exits of annular extrusion orifices of the nozzle to the solution surface of the coagulation bath is preferably 1 - 1000 mm and central distance between the dope exits of annular extrusion orifices of the nozzle is preferably 1 - 20 mm. For a single hollow fiber membrane strand before being bundled, its outer diameter is 0.2 - 3.0 mm and wall thickness 0.05 - 1.0 mm.

[00032] Referring to FIG 2, there are provided exemplary cross-sectional views of hollow fiber membrane bundles in accordance with one embodiment of the present invention. Each hollow fiber membrane bundle comprises a plurality of hollow fiber membranes and a reinforce support strand **100** that are bundled together to form a single product. In one embodiment, the hollow fiber membrane bundles can be formed in the spinning process. For example, using a nozzle with 2 – 8 annular extrusion orifices surrounding a central bore, a single reinforce support strand via the central bore can be extruded with the dope through the nozzle into a coagulation bath to form hollow fiber membrane bundles where each bundle comprises 2-8 hollow fiber membranes surrounding a reinforce support strand. Such internally reinforced hollow fiber membranes bundles have high stability, proper pore size, high water flux and excellent mechanical strengths. The amalgamation circle of hollow fiber membranes bundles can be adjusted by (i) adjusting the entry distance from the exits of annular extrusion orifices of the nozzle to the solution surface of the coagulation bath, and (ii) selecting the optimal central distance between the exits of annular extrusion orifices of the nozzle. By selecting the tensile strength resistance and suppleness of the reinforce support strand, such hollow fiber membranes bundles will have high tensile strength and breaking tenacity resistance. The reinforce support stand can be any suitable material that has the desired properties. For example, the reinforce support strands are organic polymeric fibers including cotton thread, woven nylon, polyimide, aromatic polyamide, polypropylene, polyethylene and the like. In addition, the reinforce support strands are inorganic fibers including carbon fiber, glassy fiber, and their braids. Furthermore, by enhancing bonding force between the reinforce support strand materials and membrane materials, the peeling resistance can be increased.

[00033] Referring to FIG 3, there are provided exemplary cross-sectional views of hollow fiber membrane bundles in accordance with one embodiment of the present

invention. Each hollow fiber membrane bundle comprises a plurality of hollow fiber membranes and a woven reinforce tubule that are bundled together to form a single product. In one embodiment, the hollow fiber membrane bundles can be formed in the spinning process. For example, using a nozzle with 2 – 8 annular extrusion orifices surrounding a central bore, a woven reinforce tubule via the central bore is extruded with the dope through the nozzle into a coagulation bath to form a hollow fiber membrane bundle where 2-8 hollow fiber membranes are surrounding one woven reinforce tubule. Such internally reinforced hollow fiber membrane bundles have high stability, proper pore size, high water flux and high mechanical strengths. The amalgamation circle of hollow fiber membranes bundled can be adjusted by (i) adjusting the entry distance from the exits of annular extrusion orifices of the nozzle to the solution surface of the coagulation bath, and (ii) selecting the optimal central distance between the exits of annular extrusion orifices of the nozzle. By selecting the tensile strength resistance and suppleness of the woven reinforce tubule, such hollow fiber membrane bundles will have high tensile strength and breaking tenacity resistance. The woven reinforce tubule can be any suitable material that has the desired properties. For example, the reinforce tubules are organic polymeric fibers including woven nylon, Dacron (polyester fiber), polypropylene, viscose yarn, and the like. Furthermore, by enhancing bonding force between the reinforce tubule materials and membrane materials, the peeling resistance can be increased.

[00034] Referring to FIG 4, there is provided an exemplary cross-sectional view of hollow fiber membrane bundles in accordance with one embodiment of the present invention. Each hollow fiber membrane bundle comprises a plurality of hollow fiber membranes and a tubular support that are bundled together to form a single product. In one embodiment, the hollow fiber membrane bundles can be formed in the spinning process. For example, using a nozzle with 2 – 20 annular extrusion orifices surrounding a central bore, a tubular support via the central bore is extruded with a dope through the nozzle into a coagulation bath to form hollow fiber membrane bundles where each bundle comprises 2-20 hollow fiber membranes surrounding a tubular support. Such internally reinforced hollow fiber membrane bundles have high stability, proper pore size, high water flux and high mechanical strengths. The amalgamation circle of hollow fiber

membranes bundled can be adjusted by (i) adjusting the entry distance from the exits of annular extrusion orifices of the nozzle to the solution surface of the coagulation bath, and (ii) selecting the optimal central distance between the exits of annular extrusion orifices of the nozzle. By selecting the tensile strength resistance and suppleness of the tubular support, such hollow fiber membrane bundles will have high tensile strength and breaking tenacity resistance. The tubular support can be any suitable material with desired properties. For example, the tubular supports are organic polymeric fibers including woven nylon, polyimide, aromatic polyamide, polypropylene, polyethylene, and the like. In addition, the tubular supports are inorganic braids including carbon fiber, glassy fiber, and the like. Furthermore, by enhancing bonding force between the tubular support materials and membrane materials, the peeling resistance can be increased.

[00035] The diameter of reinforce strands adopted in the present invention is preferably 0.01 – 3 mm. The materials are filaments or short fibers including nylon, Dacron (polyester fiber), polypropylene, polyimide, aromatic polyamide, polyethylene, and the like with linear density 50 – 500 dtex / 10 - 500 f; or the yarns twisted from chemical fibers mentioned above; or the woven or knitted strands made from yarns mentioned above; or sewing threads made from chemical fibers mentioned above (specification: 20 – 100 S / 2 - 4 twine); or cotton rope; or inorganic fibers such as carbon fiber, glassy fiber or the like, and their woven strands; or fishing threads made from nylon and polyvinylidene fluoride. The preferred materials are Dacron and polyvinylidene fluoride and the preferred types are sewing and fishing threads.

[00036] When the outer diameter of a single hollow fiber before being bundled is designated as d ; the number of hollow fibers in a bundle as N ; the surface areas of a single hollow fiber membrane before and after being bundled as S_0 , S respectively; and the external diameter of circle of hollow fiber membranes bundled as D ; the ratio (S_0/S) of surface areas of hollow fiber membranes before and after being bundled can be calculated by the following equation (1):

$$[00037] \quad S/S_0 = \frac{1}{\sqrt{N}} \quad D = \sqrt{N} \times d \quad (1)$$

[00038] The effective surface areas of hollow fiber membranes are critical for their functions. It is expected that the effective surface areas of hollow fiber membranes would decrease after being bundled. The results summarized in Table 1 below are

consistent with the expectation. Furthermore, the more the numbers of hollow fiber membrane are in a bundle, the less the effective surface areas of hollow fiber membranes are. Thus, it is important to control the entry distance from the exits of annular extrusion orifices of the nozzle to the solution surface of the coagulation bath and the central distance between the exits of annular extrusion orifices of the nozzle to form an appearance of incomplete amalgamation circle of hollow fiber membrane bundles. The external surface areas of hollow fiber membrane bundles with incomplete circle are larger than those of hollow fiber membranes bundled with complete circle. In the present invention, the numbers of hollow fiber membranes in a bundle is preferably 2 - 8, more preferably 3 - 6.

[00039] Table 1. The external diameter and effective surface area of complete amalgamation circle of the hollow fiber membranes bundled.

[00040]

N (No. of HFM)	d (mm)			S/S ₀
	1.0	1.1	1.2	
	D (mm)			
2	1.41	1.56	1.70	0.71
3	1.73	1.91	2.08	0.58
4	2.00	2.20	2.40	0.50
5	2.24	2.46	2.68	0.45
6	2.45	2.69	2.94	0.41

[00041] When the diameter of a single hollow fiber membrane is small, its breaking tenacity resistance is weak. When the diameter of a single hollow fiber membrane is big, it has the self-supporting property so that its wall thickness has to be increased to maintain certain compression resistance. Thus, this is not only increases production cost but also has a limitation in enhancing its mechanical strengths. The method of the present invention can increase the tensile strength resistance of hollow fiber membranes by increasing the diameter of hollow fiber membrane bundles. However, the wall

thickness of the single hollow fiber membrane can still be kept relatively thin so as to reduce membrane resistance and lower production cost.

[00042] In comparison with using solid rods as reinforce support, the present invention utilizes soft strands ropes or twined chemical fiber yarns as reinforce. Soft materials are helpful for the oscillation of hollow fiber membranes so as to increase membrane cleaning efficiency and reduce the amount of gas usage when air agitation is applied to clean membranes. The suppleness of PVDF hollow fiber membranes is superior to polyethersulfone (PES), but for the breaking tenancy resistance PVDF is inferior to PES. Thus, the method used in the present invention not only shows PVDF suppleness but also increases greatly the breaking tenancy resistance so as to satisfy different application demands.

[00043] In comparison with the method in which the short fibers are added to the spinning solution, the present invention provides that several single hollow fiber membranes are bundled with a reinforced support during spinning process so that the mechanical strength of hollow fiber membrane depends completely on the reinforce support. By selecting the reinforce support with high strength, the mechanical strength of resultant hollow fiber membrane is much stronger than that of hollow fiber membrane in the method in which the short fibers are added to the spinning solution.

[00044] In comparison with the method that the polymeric solution is coated onto a tubular support, which is a woven or knitted braid, to produce the external pressure fine tubular membrane, the method in the present invention eliminates following shortcomings: (i) a tubular polymeric membrane with large external diameter and a decrease in loading density in the unit capacity of the membrane in comparison with hollow fiber membrane; (ii) the porous membrane peeling away easily from the braid when inversely cleaning the polluted membrane due to weaker bonding force between the tubular braid support and the porous polymeric membrane materials; (iii) the breakage and the peeling of the membrane easily in bonding area of the root of tubular membrane with epoxy resins owing to membrane fatigue when air agitation is applied to clean the membrane; (iv) low productivity.

[00045] Progresses in the development of hollow fiber membranes in the fields of water treatment applications are summarized in Table 2 below.

[00046] Table 2. Progress in the development of hollow fiber membranes in the fields of water treatment applications

[00047]

	Generation 1	Generation 2		Generation 3			Generation 4
Principle of membrane formation	Phase inversion	Melt kneading drawing		Phase inversion	Phase inversion / supporting tubule	Thermally induced phase separation	Phase inversion / the reinforced supports
Membrane materials	CA	PP	PE	PVDF	PVDF	PVDF	PVDF
		Phase inversion					
		PS, PAN	PES				
Advantages	Good hydrophilicity	Melt kneading drawing PP and PE membranes with high tensile strength resistance		Asymmetric membrane structure good fouling endurance	High mechanical strengths	Medium mechanical strengths	Asymmetric membrane structure good fouling endurance, high mechanical strengths and low production costs
Shortcomings	Poor chemical stability	Poor fouling endurance and oxidation resistance		Poor mechanical strengths	Fatigue peeling of supporting tubule and high production costs	Symmetric membrane structure and poorer fouling resistance	

[00048] The hollow fiber membranes with high strengths produced by the method of the present invention can be used vertically or horizontally.

[00049] Now referring to FIG 5, there are provided two exemplary bottom plan views of nozzles for producing hollow fiber membrane bundles in accordance with one embodiment of the present invention. As shown in FIG 5(a), the nozzle has 3 annular extrusion orifices surrounding a central bore to form hollow fiber membrane bundles with three hollow fiber membranes surrounding a single support article. FIG 5(b) shows a nozzle that has six modules where each module has the structure as shown in FIG 5(a). It is apparent that other configurations are suitable for the present invention.

[00050] Now referring to FIG 6, there is provided a schematic diagram of a spinning apparatus and its process for producing hollow fiber membrane bundles in accordance with one embodiment of the present invention. The reel **30** of the reinforce strand **31** keeps certain tensile strength. After it goes through a nozzle, the reinforce strand, twined with hollow fiber membranes, enters a coagulation bath **27** and then is drawn to wind onto a reeling wheel **23** via a guiding wheel **22** to produce the reinforced hollow fiber porous membranes with the reinforce strand. The twined reinforced hollow fiber porous membranes are produced without adding a supporting strand. The supporting tubular reinforced hollow fiber porous membranes are produced when a tubular support is added.

[00051] As shown in FIG 6, when several spinning reactors are adopted, the continuous production can be realized. The process has following features in (i) designing a group of dope tanks **1** & **2**, wherein their entry and exit have a three-way valve **10** & **11** respectively for the connection. The process is suitable for continuous spinning production alternately by one tank for spinning and the other for degassing; (ii) designing a group of inner coagulation solution tanks **3** & **4**, connecting up and down pipes **5** with switching valves **17** & **18**. One tank is used as a working tank and the other as a spare tank to continuously replenish inner coagulation solution to the working tank; (iii) installing one pipe **7** for replenishing solution to the coagulation bath **21** and the other pipe **6** for overflowing solution from the coagulation bath **21**. When the dope **26** is extruded through the nozzle **9** into the coagulation solution **27** in the coagulation bath **21**, the high concentration of spinning solvents and additives is formed in the partial area of the coagulation solution. The method, where the solution above is discharged out of the

coagulation bath via a nearby overflowing pipe 6, can effectively avoid a negative effect on the stability of hollow fiber membranes owing to spinning solvents and additives with high concentration in the coagulation bath. Meanwhile, the replenishing solution pipe 7 is located in the position in which the polymeric precursor article enters the coagulation bath. It makes the spinning solvents and additives in the polymeric precursor article to be exchanged and extracted as completely as possible in the coagulation bath so as to produce the hollow fiber membranes with high stable quality. The present innovation can be used for a nozzle with orifices in continuous volume spinning production with high productivity, low cost and good quality.

[00052] The materials for being used as reinforce supporting strand include filaments or short fibers such as nylon, Dacron (polyester fiber), polypropylene, polyimide, aromatic polyamide, polyethylene, or the like; the yarns twisted from chemical fibers mentioned above; the woven or knitted strands made from yarns mentioned above; sewing threads made from chemical fibers mentioned above; or cotton rope; inorganic fiber strands woven from carbon fiber and glass fiber; or fishing threads made from nylon and polyvinylidene fluoride. As shown in FIG 6, filaments or short fibers can be used directly as reinforced supporting strands, or filaments or short fibers, after being twisted in a twisting machine, enter directly a nozzle, or woven strands made from the yarns mentioned above, after being woven or knitting, enter directly a nozzle.

[00053] The principle of formation of the hollow fiber membranes by phase inversion technique is described in following processes: (i) preparing a polymeric dope, alternatively called spinning solution used to create the membrane, by mixing homogeneously a membrane-forming polymeric resin(s), a organic solvent(s), and a pore-forming agent(s) proportionally; (ii) extruding the dope through a spinnerette, alternatively called a nozzle, to form the polymeric precursor article and then enter the coagulation bath; (iii) after diffusing solvents and pore-forming agents of polymeric precursor article into the coagulation solution, the resultant polymeric hollow fiber porous membrane is produced due to this phase transfer. The pore size of these hollow fiber separation membranes can be controlled by composition of spinning solution, parameters of spinning process and post-treatment conditions of membrane.

[00054] The Organic polymeric pore-forming agents can improve the fluidity of spinning solution, porous forming performance and membrane hydrophilicity. The Organic polymeric pore-forming agents can mainly play role in thickening and dispersion of the composition (spinning solution), but have low ability of diffusion and emulsion because of the low surface tension of polymer. Hence, the interface of spinning solution and coagulating solution cannot be fully wetted in order to make the two solutions diffuse each other. In addition, organic polymer pore forming agents are dissolved in the solvents and dispersed in the spinning solution in the molecular form, and not easy to form a great amount of through holes during coagulation. In order to form more through holes, a large amount of pore forming agents is needed. However, the large amount of organic polymer pore forming agents causes the high density of pores and reduces the mechanical strength of the hollow fiber membrane.

[00055] The inorganic pore-forming agents are dispersed in the spinning solution heterogeneously. After forming membrane, the trapped inorganic pore forming agents can be removed by acid, base, or solvent from the membrane to form pores. The method can form bigger size pores and through holes on the wall of the hollow fiber membrane even though a small amount of the inorganic pore-forming agents is added, and make the voids of polymeric conglomeration, formed by organic polymeric pore-forming agents during the phase transfer, linking and running-through so as to form more effective and more through holes with low density of pores. Therefore, such hollow fiber membranes have high mechanical strengths and high water flux. However, the excessive addition of inorganic pore-forming agents results in the poor stability of the spinning solution so that it hinders to produce hollow fiber membranes steadily.

[00056] Low molecular surfactants have low ability of thickening in the spinning solution so that it is difficult to add them singly to the spinning solution to make polymeric resins disperse properly. Hence, it is not easy to achieve hollow fiber porous membranes with high water flux. However, low molecular surfactants have high ability of diffusion and emulsion in the spinning solution so as to be able to offset the shortcomings of the polymeric and inorganic pore-forming agents and improve the interfacial compatibility between organic phase and inorganic phase. Hence, by adjusting the sub-stable structure of the polymeric continuous phases and dispersive phase of

inorganic pore-forming agent in the spinning solutions, low molecular surfactants make the dispersive phase of inorganic pore-forming agents distributed evenly and steadily in the spinning solution, and the polymeric fabric structure of differential phase dispersed homogeneously. In addition, by adjusting the mass exchange rate in the interface between the spinning solution and coagulation solution, low molecular surfactants make the pores in the wall of hollow fiber membrane to be even distribution during the membrane formation by phase inversion.

[00057] Therefore, the concurrent addition to the spinning solution of the polymeric pore-forming agent with thickening and dispersion, the surfactant with interfacial wetting, inorganic pore-forming agent with even distribution of differential phase, makes these pore-forming mechanisms working together and having synergistic effects. The combination of these three components can make the spinning solution proper dispersion and stability, control effectively interfacial wetting between the spinning solution and coagulation solution so as to make two solutions easily diffuse each other and affect the polymeric precipitation and coagulation rate in the coagulation solution, and control well the membrane formation by this phase transfer. Hence, the combination of these three components in the spinning solution results in producing the stable and strong hollow fiber membranes with good size of pores and high water flux.

[00058] In the present invention, the additives in the spinning solution mainly consist of one or several composites of inorganic pore-forming agents, organic polymeric pore-forming agents, and surfactants or other additives.

[00059] The weight percentage of various following substances in the composition is calculated by weight of the composition. The sum of weight percentage of various substances in the composition is 100 %.

[00060] The membrane-forming polymer is PVDF or PVDF copolymer or a mixture, which blends one of both with one of the following hydrophilic polymers: polymethyl methacrylate, polyvinyl alcohol, polyvinyl acetate, polyacrylonitrile and polyvinyl butyral etc. PVDF copolymer has at least 60% or more vinylidene fluoride monomer units. The membrane-forming polymer may be also conventional membrane material such as polysulfone, polyethersulfone, polyacrylonitrile and polyvinyl chloride etc. The

membrane-forming polymer is preferably about 10 - 40 % by weight of the composition, or more preferably 15 – 30 %.

[00061] The solvent, used in the composition, is preferably a strong polar compound such as dimethylformamide (DMF), dimethylacetamide (DMAc), 1-methyl-2-pyrrolidone (NMP), triethyl phosphate, sulfolane, dimethyl sulfoxide, and a mixture thereof. The solvent is preferably 50 - 90 % by weight of the composition, more preferably 60 - 80 %. In certain embodiments, the small amount of one or more weak polar compounds including 1, 4-dioxane and 2-butanone as the second solvent is added to the composition. The second solvent is preferably about 1 - 5 % by weight of the composition.

[00062] Inorganic pore-forming agent is one or a mixture of following compounds: lithium nitrate, sodium chloride, calcium chloride, calcium carbonate, calcium nitrate, silicon dioxide, aluminum oxide, kaoline and the like. The total content of inorganic pore-forming agent is preferably 0.5 - 20 % by weight of the composition, more preferably 1 - 10 %. The size of the inorganic pore-forming agent is <10 nm, more preferably nano level.

[00063] Organic pore-forming agent is one or a mixture of following water-soluble high molecular compounds: polyethylene glycol, polyethylene oxide, polyvinylpyrrolidone, polyvinyl alcohol and methylcellulose. In certain embodiment, the molecular weight of polyethylene glycol is preferably between 200 - 20000 Dalton; the molecular weight of polyoxyethylene preferably 100,000 Dalton or more; the molecular weight of polyvinylpyrrolidone preferably 10,000 – 1.2 million Dalton. The organic polymeric pore-forming agent is 2 - 30 % by weight of composition, more preferably 5 - 20 %.

[00064] The surfactant is one or a mixture the following compounds: cationic surfactants, anionic surfactants, amphoteric surfactant, and nonionic surfactant such as dodecyl sodium sulfate, dodecylbenzenesulfonate, hexadecyltrimethylammonium bromide, isooctanol polyoxyethylene ether, sodium dodecyl amino sulphonate, fluo-surfactants, tween-20, tween-80 etc. The total surfactant content is preferably 0.01 - 5 % by weight of the composition, depending on the different type of surfactant used. For examples, nonionic surfactant is preferably 1 - 2 % by weight of the composition, and fluo-sulficant is preferably 0.05 - 0.5 % by weight of the composition.

[00065] In one embodiment, common spinning condition is used by dissolving and mixing homogenously the membrane-forming polymeric resin, inorganic pore-forming agent, organic polymeric pore-forming agent and surfactant in a strong polar solvent. The hollow filaments are made by wet or dry-wet spinning, and followed by extracting pore agents with bases, acids, water or organic solvent. The resultant hydrophilic hollow fiber membranes produced by the phase inversion process, have high mechanical strengths and high water flux.

[00066] In another embodiment, the method described in the present invention produces the reinforced bundled polymeric hollow fiber membranes. A single hollow fiber membrane before being bundled in a bundle had the outer diameter of 0.2 - 3.0 mm, the wall thickness of 0.05 - 1.0 mm, the porosity of 50 - 90 % and breaking strength of 0.3 - 2 MPa. A single bundle of hollow fiber membranes bundled has tensile strength at break 0.2 - 10 Kg / bundle, and water flux 300 - 10,000 L/m² h@0.1MPa, 25 °C.

[00067] In yet another embodiment, the method described in the present invention has no high demands for the strength of base fiber membrane owing to the tensile strength resistance of hollow fiber membrane resulting mainly from the reinforcement of the bundled membranes and even from the reinforcement of the bundled membranes with the reinforced support. Therefore, a larger amount of pore-informing agent can be added according to requirement so that the hollow fiber membrane with much higher water flux can be produced.

[00068] Examples

[00069] The following examples are provided for the sole purpose of further illustrating the principles of the present invention. It by no means limits the scope of the present invention.

[00070] The following examples have used common spinning conditions. The melting index (MI) of PVDF is 2 - 15.

[00071] The membrane-forming polymeric resins, solvents, and additives are warmed and well stirred in a reactor and followed by degassing to form a spinning solution (polymeric dope). The spinning solution together with a core solution (also called inner coagulation solution) is extruded through a spinning nozzle and drops into the coagulation solution to form a hollow porous fiber membrane.

[00072] In one embodiment, 2 – 8 hollow fiber membranes can be spun into a bundle by improving the structure of spinning nozzle and adjusting spinning process and facilities so as to increase greatly the high tensile strength and breaking tenacity resistance of hollow fiber membrane. In another embodiment, in order to further increase the tensile strength and breaking tenacity resistance, a single reinforced support strand with a dope is extruded through a nozzle with 2 – 8 annular extrusion orifices into a coagulation bath to form 2 – 8 hollow fiber membranes surrounding the reinforced support strand in a bundle. Hence, such bundled hollow fiber membranes with an internal reinforced strand have high mechanical strength, high stability, proper pore size, and high water flux. In yet another embodiment, a reinforced tubule with a dope is extruded through a nozzle with 2 – 8 annular extrusion orifices into a coagulation bath to form 2 - 8 hollow fiber membranes surrounding the reinforced tubule in a bundle. Hence, the hollow fiber membranes bundled with a reinforced tubule have high strength. Such reinforced tubule is a woven or knitted braid as well as a homogeneous non-woven tubule.

[00073] Example 1

[00074] 500 g calcium carbonate (2 mm particle size) were stirred vigorously and dispersed evenly in 5 Kg dimethyl acetamide (DMAc); followed by adding 2 Kg more DMAc, 2 Kg PVDF resin, 500 g polyethylene glycol, and 100 g Tween-20, mixing evenly, and finally degassing to form the spinning solution. The spinning solution with 6 strands of Dacron filament was extruded through a nozzle, as shown in FIG 5 (in a bundle with 6 strands where each strand consists of 3 single hollow fiber membranes surrounding a reinforced support Dacron filament), into a coagulation bath with water as coagulation agent to form bundled hollow fiber membranes. Dacron filament initial modulus is 20 - 300 cN/dtex and linear density is 100 - 500 dtex. After using HCl solution to remove calcium carbonate in the hollow fiber membrane, the external pressure PVDF hollow fiber porous membranes were produced and had the inner diameter 0.5 mm and wall thickness 0.15 mm. The appearance showed the incomplete amalgamation circle (petal-like). A single hollow fiber membrane bundle had the tensile strength at break 10.1 Kg, water flux $970 \text{ L/m}^2 \text{ h@0.1MPa}$, 20 °C, pore size 0.10 mm and porosity 72 %.

[00075] Comparative Example 1

[00076] 500 g calcium carbonate (2 mm particle size) were stirred vigorously and dispersed evenly in 5 Kg dimethyl acetamide (DMAc); followed by adding 2 Kg more DMAc, 2 Kg PVDF resin, 500 g polyethylene glycol, and 100 g Tween-20, mixing evenly, and finally degassing to form the spinning solution. The same process was used as Example 1 except a common spinning nozzle was used. After using HCl solution to remove calcium carbonate in the hollow fiber membrane, the external pressure PVDF hollow fiber porous membranes were produced and had the inner diameter 0.5 mm and wall thickness 0.15 mm. A single hollow fiber membrane had the tensile strength at break 0.11 Kg. water flux 970 L/m² h@0.1MPa, 20 °C, pore size 0.10 mm and porosity 72 %.

[00077] Example 2

[00078] 500 g aluminum oxide (Al₂O₃) sized from 20 - 80 nm were stirred vigorously and dispersed evenly in the 7 Kg 1-methyl-2-pyrrolidone, and followed by adding 2 Kg PVDF resin, 500 g poly(vinylpyrrolidone), and 100 g Tween-80, mixing evenly, and finally degassing to form the spinning solution. The spinning solution with 5 strands of polypropylene yarn was extruded through a nozzle, similar to FIG 5 (in a bundle with 5 strands where each strand consists of 5 single hollow fiber membranes surrounding a reinforced support polypropylene yarn), into a coagulation bath with water as coagulation agent to form bundled hollow fiber membranes. Polypropylene yarn linear density is 100 - 500 dtex. After using NaOH solution to remove Al₂O₃ in the hollow fiber membrane, the external pressure PVDF hollow fiber porous membranes were produced and had the inner diameter 0.6 mm and wall thickness 0.15 mm. A single hollow fiber membrane bundle had the tensile strength at break 11.7 Kg. water flux 870 L/m² h@0.1MPa, 20 °C, pore size 0.20 mm and porosity 78 %.

[00079] Comparative Example 2

[00080] 500 g Al₂O₃ sized from 20 - 80 nm were stirred vigorously and dispersed evenly in the 7 Kg 1-methyl-2-pyrrolidone, and followed by adding 2 Kg PVDF resin, 500 g poly(vinylpyrrolidone), and 100 g Tween-80, mixing evenly, and finally degassing to form a spinning solution. The same process was used as Example 2 except a common spinning nozzle was used. After using NaOH solution to remove Al₂O₃ in the hollow fiber membrane, the external pressure PVDF hollow fiber porous membranes were

produced and had the inner diameter 0.6 mm and wall thickness 0.15 mm. A single hollow fiber membrane had the tensile strength at break 0.07 Kg, water flux 870 L/m² h@0.1MPa, 20 °C, pore size 0.20 mm and porosity 78 %.

[00081] Example 3

[00082] 800 g calcium carbonate (2 mm particle size) were stirred vigorously and dispersed evenly in 5 Kg dimethyl acetamide (DMAc); followed by adding 1.8 Kg more DMAc, 1.8 Kg PVDF resin, 780 g poly(vinyl pyrrolidone) and 20 g fluo-surfactant (FC-4), mixing evenly, and finally degassing to form the spinning solution. The spinning solution was extruded through a nozzle with 6 annular extrusion orifices into a coagulation bath with water as coagulation agent to form a hollow fiber membrane bundle with 6 single hollow fiber membranes. After using HCl solution to remove calcium carbonate in the hollow fiber membrane, the external pressure PVDF hollow fiber porous membranes were produced and had the inner diameter 0.6 mm, wall thickness 0.15 mm and breaking strength 0.43 MPa. A single hollow fiber membrane bundle had the tensile strength at break 1.7 Kg, water flux 1210 L/m² h@0.1MPa, 20 °C, and pore size 0.50 mm.

[00083] Comparative Example 3

[00084] 800 g calcium carbonate (2 mm particle size) were stirred vigorously and dispersed evenly in 5 Kg dimethyl acetamide (DMAc); followed by adding 1.8 Kg more DMAc, 1.8 Kg PVDF resin, 780 g poly(vinyl pyrrolidone) and 20 g fluo-surfactant (FC-4), mixing evenly, and finally degassing to form a spinning solution. The same process was used as Example 3 except a common spinning nozzle was used. After using HCl solution to remove calcium carbonate in the hollow fiber membrane, the external pressure PVDF hollow fiber porous membranes were produced and had the inner diameter 0.6 mm, wall thickness 0.15 mm and breaking strength 0.44 MPa. A single hollow fiber membrane had the tensile strength at break 0.2 Kg, water flux 1190 L/m² h@0.1MPa, 20 °C, and pore size 0.50 mm.

[00085] Example 4

[00086] 500 g calcium carbonate (2 mm particle size) were stirred vigorously and dispersed evenly in 5 Kg dimethyl acetamide (DMAc); followed by adding 2 Kg more DMAc, 2 Kg PVDF resin, 500 g polyethylene glycol, and 100 g Tween-20, mixing

evenly, and finally degassing to form the spinning solution. The spinning solution with 6 strands of PVDF fishing thread was extruded through a nozzle, similar to FIG 5 (in a bundle with 6 strands where each strand consists of 4 single hollow fiber membranes surrounding a reinforced support PVDF fishing thread), into a coagulation bath with water as coagulation agent to form bundled hollow fiber membranes. The diameter of fishing thread is 0.3 mm. After using HCl solution to remove calcium carbonate in the hollow fiber membrane, the external pressure PVDF hollow fiber porous membranes were produced and had the inner diameter 0.5 mm and wall thickness 0.15 mm. The appearance showed the incomplete amalgamation circle (petal-like). A single hollow fiber membrane bundle had the tensile strength at break 15.1 Kg, water flux 940 L/m² h@0.1MPa, 20 °C, pore size 0.10 mm and porosity 72 %.

[00087] Example 5

[00088] 500 g calcium carbonate (2 mm particle size) were stirred vigorously and dispersed evenly in 5 Kg dimethyl acetamide (DMAc); followed by adding 2 Kg more DMAc, 2 Kg PVDF resin, 500 g polyethylene glycol, and 100 g Tween-20, mixing evenly, and finally degassing to form the spinning solution. The spinning solution with 6 strands of woven polypropylene thread was extruded through a nozzle, similar to FIG 5 (in a bundle with 6 strands where each strand consists of 4 single hollow fiber membranes surrounding a reinforced support knitted polypropylene tread), into a coagulation bath with water as coagulation agent to form bundled hollow fiber membranes. The diameter of the woven polypropylene thread is 0.5 mm. After using HCl solution to remove calcium carbonate in the hollow fiber membrane, the external pressure PVDF hollow fiber porous membranes were produced and had the inner diameter 0.5 mm and wall thickness 0.15 mm. The appearance showed the incomplete amalgamation circle (petal-like). A single hollow fiber membrane bundle had the tensile strength at break 13.8 Kg, water flux 930 L/m² h@0.1MPa, 20 °C, pore size 0.10 mm and porosity 72 %.

[00089] Example 6

[00090] 500 g calcium carbonate (2 mm particle size) were stirred vigorously and dispersed evenly in 5 Kg dimethyl acetamide (DMAc); followed by adding 2 Kg more DMAc, 2 Kg PVDF resin, 500 g polyethylene glycol, and 100 g Tween-20, mixing

evenly, and finally degassing to form the spinning solution. The spinning solution with 6 strands of the woven polypropylene tubular braid was extruded through a nozzle, similar to FIG 5 (in a bundle with 6 strands where each strand consists of 6 single hollow fiber membranes surrounding a reinforced support knitted polypropylene tubular braid), into a coagulation bath with water as coagulation agent to form bundled hollow fiber membranes. The outer diameter of the woven polypropylene tubular braid is 1.5 mm. After using HCl solution to remove calcium carbonate in the hollow fiber membrane, the external pressure PVDF hollow fiber porous membranes were produced and had the inner diameter 0.5 mm and wall thickness 0.15 mm. The appearance showed the incomplete amalgamation circle (petal-like). A single hollow fiber membrane bundle had the tensile strength at break 23.1 Kg, water flux $980 \text{ L/m}^2 \text{ h@0.1MPa}$, 20°C , pore size 0.10 mm and porosity 72 %.

[00091] Example 7

[00092] 500 g calcium carbonate (2 mm particle size) were stirred vigorously and dispersed evenly in 5 Kg dimethyl acetamide (DMAc); followed by adding 2 Kg more DMAc, 2 Kg PVDF resin, 500 g polyethylene glycol, and 100 g Tween-20, mixing evenly, and finally degassing to form the spinning solution. The spinning solution with a woven polypropylene tubular braid was extruded through a nozzle, similar to FIG 5 (in a bundle with 6 single hollow fiber membranes surrounding a reinforced support knitted polypropylene tubular braid), into a coagulation bath with water as coagulation agent to form bundled hollow fiber membranes. The outer diameter of the woven polypropylene tubular braid is 2.5 mm. After using HCl solution to remove calcium carbonate in the hollow fiber membrane, the external pressure PVDF hollow fiber porous membranes, as shown in FIG 4, were produced and had the inner diameter 0.4 mm and wall thickness 0.10 mm. The appearance showed the incomplete amalgamation circle (petal-like). A single hollow fiber membrane bundle had the tensile strength at break 19.1 Kg, water flux $980 \text{ L/m}^2 \text{ h@0.1MPa}$, 20°C , pore size 0.10 mm and porosity 72 %.

[00093] 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 hollow fiber membrane bundle comprises a plurality of single hollow fiber membrane strands, wherein the hollow fiber membrane bundle is made of a spinning solution and fabricated by extruding the spinning solution into a coagulation solution through a nozzle having a plurality of orifices suitably configured as to enable the extruded spinning solutions to form the bundle in the coagulation solution.
2. The hollow fiber membrane bundle of Claim 1, further comprises a reinforce support strand, wherein the hollow fiber membrane strands are surrounding the reinforce support strand.
3. The hollow fiber membrane bundle of Claim 1, further comprises a reinforce support tubule, wherein the hollow fiber membrane strands are surrounding the reinforce support tubule.
4. The hollow fiber membrane bundle of Claim 1, wherein the plurality of single hollow fiber membrane strands are 2-8.
5. The hollow fiber membrane bundle of Claim 1, where the bundle has following features: outer diameter 0.3 - 3 mm, wall thickness 0.05 - 1 mm, porosity 50 - 90%, pore size 0.01 - 1 mm, the tensile strength at break of bundled hollow fiber membranes 0.2 - 10.0 Kg/bundle, and pure water flux 600-10,000 L/m² h@0.1MPa, 25°C
6. A method for producing hollow fiber membrane bundles comprising a plurality of single hollow fiber membrane strands, wherein the bundle has following features: outer diameter 0.3 - 3 mm, wall thickness 0.05 - 1 mm, porosity 50 - 90%, pore size 0.01 - 1 mm, the tensile strength at break of bundled hollow fiber membranes 0.2 - 10.0

Kg/bundle, and pure water flux 600-10,000 L/m² h@0.1MPa, 25°C; said method comprises the following steps:

providing a spinning solution comprising a membrane forming polymer, pore forming agents, solvents, and surfactants;

extruding the spinning solution into a coagulation solution through a nozzle having a plurality of orifices suitably configured as to enable the extruded spinning solutions to form the bundle in the coagulation solution; and

removing the pore forming agents;

thereby the hollow fiber membrane bundle is obtained.

7. The method of Claim 6, wherein the plurality of hollow fiber membrane strands comprises 2-8 single hollow fiber membranes.

8. The method of Claim 6, wherein the hollow fiber membrane bundle further comprises a reinforce fiber that is surrounded by the plurality of hollow fiber membranes; and wherein the nozzle comprises a central bore so that the reinforce fiber can be extruded from the nozzle via the central bore with the spinning solution together.

9. The method of Claim 6, wherein the hollow fiber membrane bundle further comprises a reinforce tubule that is surrounded by the plurality of hollow fiber membranes; and wherein the nozzle comprises a central bore so that the reinforce tubule can be extruded from the nozzle via the central bore with the spinning solution together.

10. The method of Claim 6, wherein in the step of extruding, the extrusion is a dry-wet spinning process during which the spinning solution together with a core solution is concurrently extruded through the nozzle to form precursor hollow fibers, subsequently to form a bundle before dropping to the coagulation bath, and finally enter the coagulation solution to form a hollow fiber membrane bundle.

11. The method of Claim 6, wherein the hollow fiber membrane bundle further comprises a reinforce tubule that is surrounded by the plurality of hollow fiber

membranes; and wherein the nozzle comprises a central bore so that the reinforce tubule can be extruded from the nozzle via the central bore with the spinning solution together.

12. A hollow fiber membrane bundle comprises a plurality of single hollow fiber membrane strands, where the bundle has following features: outer diameter 0.3 - 3 mm, wall thickness 0.05 - 1 mm, porosity 50 - 90%, pore size 0.01 - 1 mm, the tensile strength at break of bundled hollow fiber membranes 0.2 - 10.0 Kg/bundle, and pure water flux 600-10,000 L/m² h@0.1MPa, 25°C.

13. The hollow fiber membrane bundle of Claim 12, further comprises a reinforce support strand, wherein the hollow fiber membrane strands are surrounding the reinforce support strand.

14. The hollow fiber membrane bundle of Claim 12, further comprises a reinforce support tubule, wherein the hollow fiber membrane strands are surrounding the reinforce support tubule.

15. The hollow fiber membrane bundle of Claim 12, wherein the plurality of single hollow fiber membrane strands are 2-8.