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A Hollow Fiber Membrane and The Preparation Thereof

Field of the Invention

This invention is related to manufacturing and preparation technique for a hollow fiber membrane, particularly to a hollow fiber membrane with perfect elastic performance and its manufacturing method, of which, the proposed International Patent Classification No. is Int.Cl.B01D 69/00(2006.01)I.

Background of the Invention

Polyurethane is a type of block copolymer formed by alternating connection of soft / rigid segment, of which, the soft segment of perfect resilience can produce excessive elongated deformation in case of tension at high-elasticity status at room temperature; whereas the rigid segment is the node produced for elongated deformation and resilience of the soft segment. Owing to its unique chemical constitution and such characteristics as high elasticity, strength, heat resistance and chemical resistance, polyurethane has wide application in automobile, shoemaking, wire and cable manufacturing industries. In 1970, Bowen proposed to use the polyurethane as selective adsorbent for certain substances. From then on, application of polyurethane to membrane material has drawn increasing attentions from the people. However, as the structure of polyurethane is so dense and difficult for pore formation, polyurethane is mainly used for gas separation, infiltration vaporization and separation of inorganic metal ion, which is seldom used for study of liquid separation membrane. Presently, wet-spinning method is a common technology in manufacturing and preparation of hollow fiber liquid separation membrane, which is characterized by low spinning temperature, easy operation and pore formation. Li Xianfeng and his colleagues have disclosed "A Polyurethane / Inorganic Particle Mixed Composite Membrane and Its Manufacturing Method (Patent No.: ZL02131196X) which aims to produce polyurethane / inorganic particle mixed hollow fiber composite membrane



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characterized by interfacial microvoid with wet spinning method. According to further study, the hollow fiber composite membrane as produced is provided with elastic performance, which manifested by corresponding variation to the aperture of the microvoid of the fiber membrane accompanied by the variation to working pressure (refer to X.F.Li, C.F.Xiao, Structure and properties of Composite Polyurethane Hollow Fiber Membranes, Chinese J. Polym. Sci., 23(2005)203-210). However, such technology has such disadvantages as high consumption of solvent and environmental pollution; furthermore, mechanical property of the fiber membrane produced and profile recovery during pressure response is also unsatisfactory. Conventional melt-spinning methods require no solvent, which are characterized by short technological flow. Nevertheless, structure of fiber membrane as produced is relatively dense, which is unfavorable for pore formation and control of aperture. In particular, it has more stringent requirements for thermal stability of polymer and pore forming agent owing to high spinning temperature and high energy consumption. Therefore, reduction in melt-spinning temperature for the purpose of energy saving, effective control of membrane pore precision and structure and improvement of product performance serve as the key technique on display of advantages of melt-spinning in accommodation with hollow fiber.

Summary of the Invention

In view of deficiencies to prior art, the following two technical problems are to be settled by the invention:

The first technical problem to be settled by the invention is to design a hollow fiber that has strong pressure sensitivity to the separation system and perfect pattern memory, which is provided with abundant microvoid structure in accommodation with industrialized production as well as practical promotion and application.

The second technical problem to be settled by the invention is to design a hollow fiber manufacturing method. Such method aims to manufacture hollow fiber with melt-spinning methods to overcome such disadvantages as high energy consumption and difficulty with control of membrane pore, which is characterized by relatively low spinning temperature, easy control of membrane pore structure, short technological flow, simplified membrane manufacturing technology, excellent product quality, low cost and availability to industrialized mass production. Meanwhile, it can minimize the solvent recovery for wet-spinning method to ensure environmental protection and energy saving, which has promising industrialization prospect.

Technical solution to settlement of the first technical problem in this invention is to design a hollow fiber membrane, which is characterized in that mass percent formula for membrane forming system of such hollow fiber membrane is stated as follows:

Polyurethane	25~45;
Composite pore forming agent	35~60;
Organic low molecular weight liquid	15~20,
sum of all constituents is 100%	

Wherein, aforesaid polyurethane is of fiber grade with mass ratio between soft and rigid segments between 1/1 and 1/5; aforesaid composite pore forming agent serves as the mixture of pore forming agent for interfacial microvoid and non-interfacial microvoid respectively, in which, pore forming agent for interfacial microvoid accounts for 10-30% of total mass of composite pore forming agent; Pore forming agent for interfacial microvoid refers to non-water

soluble inorganic particle incompatible with polyurethane, which is composed of mixture of one or two random proportions between SiO_2 and CaCO_3 with mean diameter up to $0.01 \sim 5\mu\text{m}$; pore forming agent for non-interfacial micrivoird refers to water soluble substance composed of water soluble inorganic particle, water soluble polymer, water or aforesaid water soluble substances of random proportion; aforesaid water soluble inorganic particle is composed of any of LiCl , CaCl_2 , NaCl and KCl with mean diameter up to $0.01 \sim 5\mu\text{m}$; aforesaid water soluble particle includes polyvinyl pyrrolidone or polyethylene glycol; aforesaid organic low molecular weight liquid refers to high boiling point water soluble solvent of polyurethane, including one or more mixture of dimethylformamide, dimethylsulfoxide and dimethylacetamide of random proportion.

Technical solution to settlement of the second technical problem in this invention is to design a hollow fiber manufacturing method, which is characterized by the following melt-spinning process: Firstly, prepare polymer membrane forming system according to requirements for mass percent formula of aforesaid hollow fiber membrane before pouring it into the hybrid cauldron for heated forcible premixing at the heating temperature of $130 \sim 140^\circ\text{C}$; inject the mixture uniformly mixed into the twin screw extruder for dissolution and fusion prior to membrane manufacturing with melt-spinning methods through hollow spinning assembly at the temperature of $130 \sim 155^\circ\text{C}$; moreover, aforesaid hollow fiber membrane can be obtained through extraction-in-water as conventional wet-spinning method.

As compared with prior art, preparation method in this invention aims to integrate advantages of melt-spinning and wet-spinning methods to proceed with melt-spinning through uniform mixing of small quantity of organic low molecular weight liquid with polyurethane and composite pore forming agent, which can effectively reduce the spinning temperature. For instance, melt-spinning temperature of polyurethane membrane is

normally around 160°C; whereas melt-spinning temperature of this invention is only required to be within 130~155°C, which is easy for control. It is applicable to produce hollow fiber membrane of precise pressure response and multiple microvoid structure (including interfacial microvoid and non-interfacial microvoid) through extraction-in-water by selection of appropriate extension ratio for spinneret. This membrane is characterized by excellent elastic recovery, high water flux, varied pressure of separation system, high sensitivity and perfect separation memory, which is applicable to industrialized production and practical application. Moreover, such hollow fiber membrane is manufactured with melt-spinning method at a relatively low fusion temperature. It only requires appropriate yet small quantity of solvent, which is characterized by short spinning flow, easy control of membrane structure, simple membrane manufacturing technique, easy operation, omission of special equipments and high product quality. It can minimize the solvent recovery of wet-spinning method, which is favorable for environmental protection, energy saving and implementation of industrialization.

Brief Description of the Drawings

FIG 1 is a diagram of engineering stress-strain curve for an embodiment (embodiment 4) of hollow fiber membrane of the invention.

FIG 2 is a diagram of pressure response curve for an embodiment (embodiment 6) of hollow fiber membrane of the invention.

Description of the Preferred Embodiment

Further description of the invention in combination with embodiments is stated as follows:

Mass percent formula for membrane forming system of hollow fiber membrane (hereinafter referred to as hollow membrane or membrane) of the invention is stated as follows:

Polyurethane	25~45;
Composite pore forming agent	35~60;
Organic low molecular weight liquid 15~20, sum of all constituents	

is 100%.

Polyurethane according to formula of the invention is of basement membrane material or matrix, of which chemical constitution consists of soft segment and rigid segment; soft segment is dibasic alcohol of low molecular weight or aromatic diisocyanate coupled with diamine; soft segment is of polyether diols or polyester diols. Mass ratio between rigid and soft segments of aforesaid polyurethane is available for selection within the range of 1/1 ~ 1/5. Ideal mass ratio between rigid and soft segments of polyurethane is 1/2. Other physiochemical indicators of polyurethane as selected should be up to fiber grade.

With reference to composite pore forming agent as designed in the formula of the invention, the specified decomposition temperature should be higher than the spinning temperature, which shall not incur any physical or chemical damage to the hollow membrane as obtained. Specifically speaking, aforesaid composite pore forming agent is the mixture of interfacial and non-interfacial pore forming agents, of which, interfacial pore forming agent accounts for 10-30% of the total mass of composite pore forming agent; pore forming agent for interfacial microvoid refers to non-water soluble inorganic particle incompatible with polyurethane, which is composed of mixture of one or two random proportions between SiO_2 and CaCO_3 with mean diameter up to $0.01 \sim 5\mu\text{m}$; pore forming agent for non-interfacial microvoid refers to water soluble substance composed of water soluble inorganic particle, water soluble polymer, water or aforesaid water soluble substances of random proportion; aforesaid water soluble inorganic particle is composed of any of LiCl , CaCl_2 , NaCl and KCl with mean diameter up to $0.01 \sim 5\mu\text{m}$; aforesaid water soluble polymer consists of polyvinyl pyrrolidone (PVP) or polyethylene glycol (PEG). To ensure smooth spinning process, it is applicable to add small quantity of water (normally not over

10% total mass of composite pore forming agent) to facilitate formation of membrane permeability microvoid structure. As shown by the test, it is necessary to use non-interfacial pore forming agent (water soluble constituent) as critical constituent of pore forming agent to ensure permeability of hollow fiber membrane as obtained. Meanwhile, to ensure better mechanical property of fiber membrane following removal of non-interfacial pore forming agent, optimal proportion of interfacial pore forming agent in the total mass of composite pore forming agent shall be within 10-30%. According to general aspect of the invention, water flux of hollow membrane as obtained shall be increased accompanied by increased total mass of composite pore forming agent while the membrane strength is reduced accordingly. Therefore, content of aforesaid composite pore forming agent shall be controlled within 60% of the total mass of membrane manufacturing (forming) system. Nevertheless, ideal content of pore forming agent must be within 35-60%. It is applicable to endow membrane with interfacial microvoid through control of stretching ratio of spinneret after membrane formation; it is also applicable to endow the membrane with non-interfacial microvoid through removal of soluble pore forming agent by means of extraction-in-water, and thereby obtain hollow fiber membrane of perfect permeability as provided with both interfacial and non-interfacial microvoid structures.

Aforesaid formula of the invention is with unique design of appropriate low molecular weight liquid. It is one of the critical technologies of the invention. Aforesaid organic low molecular weight liquid should be good solvent for polyurethane and has high boiling point and water solubility for the purpose of plasticizing polyurethane and composite pore forming agent to ensure adequate mixed extrusion of all constituents at a temperature relatively lower than the melting point of polyurethane and spinnability of membrane manufacturing system. As shown in the test, aforesaid relatively low temperature range is 130-155 °C. As compared with melting point of polyurethane (160 °C as proposed), this temperature range can reduce the energy consumption by 18.75-3.13%, which has obvious

energy saving effect. Other bases as selected by aforesaid liquid of low molecular weight include boiling point and decomposition temperature higher than aforesaid spinning and membrane manufacturing temperature, which shall not incur physical or chemical damages to hollow membrane as obtained finally. According to aforesaid principle, liquid of low molecular weight of the invention consists of one or more of mixture among dimethylformamide (DMF), dimethylsulfoxide (DMAc) and dimethylacetamide (DMSO) at any proportion. Accompanied by increase in content of organic liquid of low molecular weight, spinning temperature can be reduced accordingly. This is favorable for formation of microvoid after extraction and increase in water flux of membrane. However, extremely high content of organic liquid of low molecular weight may result in reduction in stretching strength and durability of the membrane as obtained. Therefore, optimal range for adding of organic liquid of low molecular weight of the invention shall be 15-20% of total mass of membrane manufacturing system. Although matrix of polyurethane in the formula for aforesaid membrane manufacturing system of the invention far exceeds that for membrane manufacturing with wet-spinning method as compared with mass of added organic liquid of low molecular weight, it will not affect the spinning shaping and formation of microvoid structure of fiber membrane. On the contrary, it can minimize the dual diffusion process of solvent-nonsolvent of conventional wet-spinning method, and prevent the formation of membrane pore structure with obvious defects. Furthermore, strength of membrane as obtained is obviously higher than similar membrane as manufactured with conventional wet-spinning method. Moreover, according to corresponding study, aforesaid organic liquid of low molecular weight can play an active role in improvement of permeability of microvoid structure of hollow fiber membrane after extraction despite of the fact that its chief role in plasticization of polymer and improvement of spinnability of membrane forming system. As shown in the test with manufacturing method of the invention, ideal range of aforesaid spinning temperature can be reduced to 130~155°C once organic liquid of low molecular weight in the formula of the invention is selected. Selection of

temperature for embodiment of special process is related to mass percent content of organic liquid of low molecular weight. Manufacturing method of the invention can relatively reduce the spinning temperature, and save the energy to ensure easy spinning operation. Furthermore, heated forcible premixing of membrane forming system in the hybrid cauldron prior to injection into the twin screw extruder following dissolution and melting can improve the fluidity of polymer system, expand the range for selection of pore forming agent, and facilitate industrialized production.

Aforesaid elastic function of hollow membrane of the invention is mainly reflected on the two aspects: Firstly, relatively high breaking elongation and perfect elastic recovery can extend the length of the hollow membrane to 500% of original one under the stretching stress. Once the stress is released, membrane length can be recovered to original one (membrane length can be recovered to 200% of original one once the stretching stress is released at the deformation by 500% approximately). Furthermore, flux can also be recovered to the original one. Such performance can effectively ensure the perfect deformation performance of existing fiber membrane material, which can prevent such problems as inevitable deformation and breakage under the stress during use. Secondly, hollow membrane body may subject to uniform expansion under internal air pressure, which may result in high microvoid aperture on the membrane surface and high porosity. As a result of it, membrane function of "low-pressure filtration-high-pressure cleaning (including washing and backwashing)" can be obtained. Furthermore, internally pressurized membrane assembly obtained thereafter can realize online cleaning (including washing and backwashing) during application of the membrane, and minimize the frequency of conventional chemical cleaning to the extent of extending service life of membrane material.

Meanwhile, the invention is also designed with manufacturing method for aforesaid hollow

fiber membrane (manufacturing method for short). Such method aims to prepare polymer membrane forming system according to mass percent formula for the hollow fiber membrane of the invention, which takes the following melt-spinning process to prepare aforesaid hollow fiber membrane: Firstly, add aforesaid polymer membrane forming system into the hybrid cauldron for heated forcible premixing at the temperature of 130 ~ 140°C; inject the mixture uniformly mixed into the twin screw extruder for dissolution and fusion prior to membrane manufacturing with melt-spinning and wet-spinning methods through hollow spinning assembly at the temperature of 130 ~ 155°C; after that, hollow fiber membrane can be obtained through water extraction with conventional wet-spinning method.

Manufacturing method of the invention aims to uniformly mix appropriate amount of organic liquid of low molecular weight with polyurethane and composite pore forming agent for melt-spinning at a relatively low temperature. It is a new hollow membrane manufacturing method created with integration of advantages of wet-spinning and melt-spinning techniques: Melt-spinning temperature is lower than that of melt-spinning with conventional method; limited amount of necessary solvent for wet-spinning is characterized by short technological flow, simple process, easy control of membrane pore, energy saving, reduced emission and environmental protection.

Extraction-in-water technique of the invention is identical to prior wet-spinning methods. The only difference is that extraction-in-water of conventional wet-spinning process mainly aims to facilitate the dual dispersion of solvent trickle for the purpose of membrane solidification. Extraction-in-water process of the invention is provided with conventional dual dispersion and solidification process as thermally induced phase separation, which can play a role in stabilizing and optimizing porous structure of fiber membrane. Furthermore, it is also available for adequate removal of water soluble pore forming agent during

membrane manufacturing with spinning method. However, membrane manufacturing with conventional melt-spinning method is free of water extraction process.

Another characteristic of preparation method of the invention is that stretching process is prior to the extraction-in-water process during membrane manufacturing with melt-spinning method. Stretching ratio of aforesaid stretching process is 3-5 times; whereas stretching processing temperature is 40-60 °C. Such process can prevent damages to the evenness of microvoid structure of fiber membrane as incurred by post stretching during manufacturing of hollow membrane with conventional melt-spinning method.

Issues not described in the invention are applicable to prior art.

Several preferred embodiments of the invention are listed as follows, which shall not constitute limitations on claims of the invention.

Embodiment 1

Mass percent content of polymer matrix constituted by fiber grade polyether polyurethane at the rigid segment / soft segment mass ratio of 1/2 is 25%; composite pore forming agent is the mixture of 0.01 μ m SiO₂ powder and PVP, accounting for 60% of total mass of the system. The former belongs to interfacial pore forming agent, accounting for 30% of total mass of composite pore forming agent. The later belongs to non-interfacial pore forming agent, accounting for 70% of total mass of composite pore forming agent. DMSO is used as the organic liquid of low molecular weight, of which, mass percent content is 15%. Mixture of the aforesaid three substances shall serve as the membrane forming system for heated forcible premixing in the hybrid cauldron at the temperature of 130 °C. Such membrane forming system shall be added into the twin-screw extruder following the dissolution and melting for membrane manufacturing with melt-spinning method through

hollow spinning assembly. Stretching ratio of spinneret can be selected as 3 or 5 times; whereas processing temperature must be controlled at 130 °C. In this way, aforesaid hollow membrane can be obtained through adequate water extraction.

According to inspection, corresponding value of water flux of hollow membrane as tested with internal pressure method at the stretching ratio of 3 and 5 times, pressure of 0.1MPa and temperature below 25 °C is 690 and 1130 ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) respectively.

Embodiment 2

Adjust the proportion of interfacial pore forming agent and non-interfacial pore forming agent of embodiment 1 to 10% and 90% of total mass of pore forming agent respectively; select stretching ratio of spinneret as 3 with other conditions unchanged to obtain aforesaid hollow membrane.

According to inspection, corresponding value of water flux of hollow membrane of the embodiment as tested with internal pressure method at the pressure 0.1MPa and the temperature below 25 °C is 1090 ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$).

Embodiment 3

Mass percent content of polymer matrix constituted by fiber grade polyether polyurethane at the rigid segment / soft segment mass ratio of 1/2 is 45%; composite pore forming agent is the mixture of 0.01 μm SiO_2 powder 5 μm CaCO_3 powder and PEG, accounting for 60% of total mass of the system. The former two belong to interfacial pore forming agent with mass ratio of 1/1, accounting for 30% of total mass of composite pore forming agent. The later belongs to non-interfacial pore forming agent, accounting for 70% of total mass of composite pore forming agent. DMSO is used as the organic liquid of low molecular weight, of which, mass percent content is 20%. Mixture of the aforesaid three substances

shall serve as the membrane forming system for heated forcible premixing in the hybrid cauldron. Such membrane forming system shall be added into the twin-screw extruder following the dissolution and melting for membrane manufacturing with melt-spinning method through hollow spinning assembly. Stretching ratio of spinneret can be selected as 3 times; whereas processing temperature must be controlled at 155°C. In this way, aforesaid hollow membrane can be obtained through adequate water extraction.

According to inspection, corresponding value of water flux of hollow membrane of the embodiment as tested with internal pressure method at the pressure 0.1MPa and the temperature below 25°C is 920 ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$).

Embodiment 4

Change non-interfacial pore forming agent PVP into 2 μm LiCl, CaCl_2 , NaCl and KCl particles based on the embodiment 2 with other conditions unchanged to obtain hollow membrane of 4 formulas.

According to inspection, corresponding value of water flux of hollow membrane of the embodiment as tested with internal pressure method at the pressure 0.1MPa and the temperature below 25°C is 1520, 1610, 1480 and 1590 ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) respectively.

It is applicable to carry out elasticity test for hollow membrane as obtained through addition of KCl particles to further obtain stretching curve (as shown in FIG 1). Viewing from FIG 1, it can be seen that breaking elongation of fiber membrane under the action of stretching stress is relatively high, which can be up to 500%. Length of fiber membrane can be recovered below 200% of original one once stretching stress is released at the deformation of 500% approximately.

Embodiment 5

It is applicable to obtain hollow membrane by changing organic liquid of low molecular weight of embodiment 1 into DMF and DMAc with other conditions unchanged.

According to inspection, corresponding value of water flux of hollow membrane of the embodiment as tested with internal pressure method at the pressure 0.1MPa and the temperature below 25°C subjects to no obvious change as compared with embodiment 1.

Embodiment 6

It is applicable to obtain pressure response curve (see FIG 2) by testing water flux of CaCl₂ containing hollow membrane of embodiment 4 at the temperature below 25°C under different working pressure.

Normally, Microvoid structure of hollow membrane can be assumed as parallel cylindrical profile of equal aperture. Water flux J passing through such pore can be described with Hagen-Poiseuille equation as follows:

$$J = \frac{\varphi r^2 \Delta p}{8 \eta d}$$

Wherein, φ , r , η , ΔP and d refer to porosity, pore radius, viscosity, working pressure and thickness of separation membrane respectively. If there is no change to the microvoid structure and porosity of the membrane subjecting to pure water test at the different filtration pressure, the water flux shall be directly proportional to the working pressure in linear relationship, namely $J=K\Delta P$. It is obvious that curve variation as shown in FIG 2 is not in compliance with linear relationship. This indicates that body of hollow membrane of the invention becomes expanded under the internal pressure, resulting in expanded microvoid aperture on the membrane surface and high porosity. Membrane diameter has witnessed a significant expansion accompanied by rise of internal pressure.

Claims

1. A hollow fiber membrane, which is characterized in that mass percent formula of its membrane forming system is as follows:

Polyurethane 25~45;

Composite pore forming agent 35~60;

Organic liquid of low molecular weight 15~20, sum of all constituents is 100%

Wherein aforesaid polyurethane is of fiber grade with mass ratio between soft and rigid segments between 1/1 and 1/5; aforesaid composite pore forming agent serves as the mixture of pore forming agent for interfacial microvoid and non-interfacial microvoid respectively, in which, pore forming agent for interfacial microvoid accounts for 10-30% of total mass of composite pore forming agent; Pore forming agent for interfacial microvoid refers to non-water soluble inorganic particle incompatible with polyurethane, which is composed of mixture of one or two random proportions between SiO_2 and CaCO_3 with mean diameter up to $0.01\sim 5\mu\text{m}$; pore forming agent for non-interfacial microvoid refers to water soluble substance composed of water soluble inorganic particle, water soluble polymer, water or aforesaid water soluble substances of random proportion; aforesaid water soluble inorganic particle is composed of any of LiCl , CaCl_2 , NaCl and KCl with mean diameter up to $0.01\sim 5\mu\text{m}$; aforesaid water soluble particle includes polyvinyl pyrrolidone or polyethylene glycol; aforesaid organic low molecular weight liquid refers to good solvent of water soluble polyurethane of high boiling point, including one or more mixture of dimethylformamide, dimethylsulfoxide and dimethylacetamide of random proportion.

2. A hollow fiber membrane according to Claim 1, which is characterized in that mass ratio between rigid and soft segments of aforesaid polyurethane is 1/2.

3. A hollow fiber membrane according to Claim 1, which is characterized in that water with amount no more than 10% total mass of composite pore forming agent is added into

the aforesaid membrane forming system.

4. A hollow fiber membrane manufacturing method, which is characterized in that it takes the following melt-spinning process: Firstly, prepare polymer membrane forming system according to requirements for mass percent formula of hollow fiber membrane according to Claim 1, 2 and 3; pour it into the hybrid cauldron for heated forcible premixing at the heating temperature of $130\sim 140^{\circ}\text{C}$; inject the mixture uniformly mixed into the twin screw extruder for dissolution and fusion prior to membrane manufacturing with melt-spinning methods through hollow spinning assembly at the temperature of $130\sim 155^{\circ}\text{C}$; after that, hollow fiber membrane can be obtained through extraction-in-water as conventional wet-spinning method.

5. A hollow fiber membrane manufacturing method according to Claim 4, which is characterized in that stretching process and extraction-in-water process shall be carried out in proper sequence following membrane manufacturing with melt-spinning methods; stretching ratio of aforesaid stretching process is 3-5 times; whereas stretching processing temperature is $40\sim 60^{\circ}\text{C}$.