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BACTERIAL CELLULOSE-POLY(ETHYLENE OXIDE)-POLY(PROPYLENE OXIDE)-POLY(ETHYLENE OXIDE) BLOCK COPOLYMER COMPOSITE MEMBRANE AND MANUFACTURING METHOD THEREOF

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ABSTRACT

The present invention relates to the technical field of development and modification of bacterial cellulose membrane materials, and in particular to a bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane and a manufacturing method thereof. In the present invention, a wet bacterial cellulose membrane is impregnated in a poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer solution, and a resulting membrane is washed and dried successively to obtain the bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane. According to examples, the bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane manufactured by the present invention has a tensile strength of up to 124.6 MPa, increasing by 110% compared with an uncomposited bacterial cellulose membrane (59.3 MPa); tensile strain increases from 3.95% to 14.10%, and by 257%.

Editorial Note

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There is only nine pages of the description

BACTERIAL CELLULOSE-POLY(ETHYLENE OXIDE)-POLY(PROPYLENE OXIDE)-POLY(ETHYLENE OXIDE) BLOCK COPOLYMER COMPOSITE MEMBRANE AND MANUFACTURING METHOD THEREOF

TECHNICAL FIELD

The present invention relates to the technical field of development and modification of bacterial cellulose membrane materials, and in particular to a bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane and a manufacturing method thereof.

BACKGROUND

Bacterial cellulose, also known as β-1,4 glucan, is a pure cellulose produced by microbes and a branchless straight chain structure of β-D-glucose bonded by a β-1,4-glycosidic bond. Bacterial cellulose, as a novel biomaterial, features high water absorption and retention, high gas and liquid permeability, high wet strength, and *in situ* molding in a wet state due to unique texture structure and "nano effect" thereof. The bacterial cellulose can be used as artificial skin in temporary wound dressing due to excellent biocompatibility, mechanical strength when wet, excellent gas and liquid permeability, and inhibition of skin infection; the bacterial cellulose can serve as food forming agent, thickener, dispersant, anti-melting agent, etc. due to strong hydrophilicity, viscosity, and stability; if bacterial cellulose acetate is added to the pulp, paper strength and durability will be improved to solve a problem of reclamation and recycling of waste paper, where the bacterial cellulose can be used in ordinary pulp to make high-quality special paper. However, strong brittleness and poor flexibility of the bacterial cellulose greatly limit the high value use in promotion of bacterial cellulose membrane material.

U.S. Patent No. US2019022634A1 provides an ion exchange membrane and a method for manufacturing same, where a support fiber mat consisting of a laminate is manufactured by electrospinning. The method can simply control the thickness, electroconductivity and mechanical strength of the membrane, and the diameter/ratio of a pore, etc. to be suitable for use in different ion exchanges. Therefore, the ion exchange membrane manufactured by the method can be utilized as a universal ion exchange membrane which has a large ion exchange capacity, a small electrical resistance, and a small diffusion coefficient as well as excellent mechanical strength and durability. However, the method has such disadvantages as complex operation, relatively high cost, and uneasy mass production; moreover, the flexibility of the membrane should be improved.

U.S. Patent No. US2019022599A1 provides a fluid separation membrane synthesized by an organic polymer layer. The membrane has a fully co-continuous porous structure and high compression strength in the fiber cross-section direction (direction orthogonal to the fiber axis). However, costs of raw materials required in the method are high, the operation is complex, and the

separation membrane lacks of certain flexibility.

Korean Patent No. KR20180124259A discloses a method for manufacturing a conductive nano-fiber membrane having excellent transparency and flexibility. The method obtains a transparent and flexible nanofiber sheet in an environmentally friendly and economical manner. The conductive nanofiber membrane manufactured is excellent in transparency and flexibility, and has excellent electrification performance, thereby being widely used in electronic materials such as solar cells, transistors, displays, biosensors, gas sensors and the like or functional clothing materials and the like. However, the method has such disadvantages as complex operation, metal introduction, relatively high cost, and large ambient pollution burden.

China Patent No. CN107541860A discloses a preparing method and application of a bacterial-cellulose-and-lignin composite fiber membrane. The bacterial-cellulose-and-lignin composite fiber membrane prepared through high-pressure injection with the water needle-steadying method: has the bacterial-cellulose-fiber unique advantages of being high in purity, crystallinity degree and mechanical strength, good in biological compatibility, excellent in water permeability and air permeability and good in liquid keeping performance; also has the stable chemical property after lignin fibers are treated at the high temperature; has nontoxic, tasteless, non-pollution and radioactivity-free excellent qualities; is an environment-friendly product; has the good tenacity and dispersity and the super-high water absorbing capacity; and has the quite-excellent thickening anti-cracking performance. A composite fiber mask prepared in the mode that the prepared composite fiber membrane serves as a mask substrate is thin in thin layer, better in moisturizing gas permeability, and the skin friendly performance and the liquid containing performance are further improved. However, the membrane has poor flexibility.

China Patent No. CN108232085A discloses a bacterial cellulose diaphragm coated with polyionic liquid and a preparation method thereof. Nanofibers of the bacterial cellulose diaphragm is coated with polyionic liquid (imidazolium salt, pyrrolidine salt, piperidine salt, and quaternary ammonium salt) on the surface, a hot press is utilized to press the bacterial cellulose diaphragm to be thin, and after drying, the polyionic liquid-coated bacterial cellulose diaphragm is obtained. The bacterial cellulose diaphragm has the advantages of high mechanical strength, good thermal stability, good lyophilic property, and high porosity; the preparation method thereof is simple and has low requirement on equipment; however, the method costs highly and is not eco-friendly, and the flexibility of the bacterial cellulose diaphragm should be improved.

China Patent No. CN109097418A discloses a method for *in situ* preparation of an antibacterial bacterial cellulose membrane. Folium Mori protein is prepared from the Folium Mori by using an alkaline extraction acid precipitation method, residues are hydrolyzed into monosaccharide by using dilute sulfuric acid, Folium Mori hydrolysate containing an

antimicrobial substance is obtained after mixture, then the Folium Mori hydrolysate is used as carbon and nitrogen source and an antimicrobial raw material, and *Acetobacter xylinum* is inoculated to prepare the antibacterial bacterial cellulose membrane. The method is simple, and the cost is low; the antibacterial property of the bacterial cellulose membrane prepared is stable, and antibacterial substances are not easily lost. However, the bacterial cellulose membrane is less flexible, limiting further use thereof in other fields.

China Patent No. CN107082903A discloses a modification method for a bacterial cellulose membrane. The method firstly mixes bacterial cellulose with epichlorohydrin to perform a substitution reaction to introduce an epoxy group, then carries out grafting with β-cyclodextrin under an alkaline condition, introduces the hydrophilic molecule β-cyclodextrin with hydrophobic inner cavities, and makes the bacterial cellulose with an amphiphilic nature that can both contain hydrophilic small molecules and hydrophobic molecules without damaging original properties of the bacterial cellulose. The method has the advantages that the natural release rate and the transdermal release rate of hydrophobic small molecule vitamin E and tea tree oil are significantly increased, and has great application prospects in the field of skin care products. However, the method is complex to operate, and increases time and reaction costs, with poor controllability of the reaction.

China Patent No. CN104262662A discloses a method for improving the plasticity and flexibility of a bacterial cellulose membrane. In the method, an initial bacterial cellulose wet membrane sample is soaked in alkaline liquor and then soaked and purified in deionized water; the purified bacterial cellulose membrane is soaked into polyether amine salt solutions, followed by oscillating and compounding for 24 h at room temperature. The compounded cellulose membrane is increased by 11.45 times. In the method, polyether amide salt is used as a curing agent, which enhances the elasticity and toughness of the mixture, and as an excellent adhesive, can achieve the plasticity and flexibility of the bacterial cellulose membrane better. The method is simple and easy to operate; however, polyether amide is toxic; meanwhile, hydrochloric acid is further used as an acid solvent in preparing the polyether amine salt, where pollution occurs largely during treatment, with high relative treatment costs.

In conclusion, bacterial cellulose, as an abundant biomass resource, limits the use thereof due to poor flexibility and plasticity thereof. Therefore, a bacterial cellulose membrane with high flexibility, high strength, environmental protection, and low cost will further achieve high value added utilization of the bacterial cellulose.

SUMMARY

An objective of the present invention is to provide a bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane and a

manufacturing method thereof; the bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane manufactured is low-cost, nontoxic, highly flexible, and environmentally friendly.

To achieve the above objective, the present invention provides the following technical solutions.

The present invention provides a method for manufacturing a bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane, including the following steps:

impregnating a wet bacterial cellulose membrane in a poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer solution, washing and drying a resulting membrane successively to obtain the bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane.

Preferably, the wet bacterial cellulose membrane is purified before impregnating the wet bacterial cellulose membrane in the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer solution, and the purification is conducted by soaking in an alkali liquor.

Preferably, the alkali liquor is aqueous sodium hydroxide (NaOH) solution, aqueous potassium hydroxide (KOH) solution, or aqueous calcium hydroxide ($Ca(OH)_2$) solution, and the alkali liquor has a mass concentration of 3-6 g/L.

Preferably, the impregnation is conducted ultrasonically at an ultrasonic frequency of 25-130 kHz.

Preferably, the impregnation is conducted for 0.5-10 h at room temperature.

Preferably, a solvent of the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer is water, and the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer has a mass concentration of 1-20wt%.

Preferably, deionized water is used as a reagent in the washing, and the washing is conducted by flushing.

Preferably, the drying is conducted for 1-2 h at 80-120°C.

The present invention provides a bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane manufactured by the manufacturing method according to the above technical solution.

The present invention provides a method for manufacturing a bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane, including the following steps:

impregnating a wet bacterial cellulose membrane in a poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer solution, washing and drying a resulting membrane

successively to obtain the bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane.

The present invention uses a low-cost biomass wet bacterial cellulose membrane as a raw material, which is abundant and renewable; the present invention selects poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer as a flexible complex additive, which is green, efficient, and environmentally friendly.

The present invention use poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer to adsorb onto and into the wet bacterial cellulose membrane to function as a physical adsorbent; after drying, hydrogen bonding is formed between the block copolymer and cellulose fiber, which increases binding forces between fibers and improves dry membrane strength; meanwhile, poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer covers on the fiber surface, which reduces the brittleness of the bacterial cellulose fiber and thus increases the toughness of the membrane.

The present invention merely uses a simple impregnation method to successfully manufacture a highly flexible and dry bacterial cellulose membrane featuring low cost, high yield, and strong feasibility, increasing the flexibility and tensile strength of the dry bacterial cellulose membrane and facilitating high value added utilization of the bacterial cellulose. According to examples, the bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane manufactured by the present invention has a tensile strength of up to 124.6 MPa, increasing by 110% compared with an uncomposited bacterial cellulose membrane (59.3 MPa); tensile strain increases from 3.95% to 14.10%, and by 257%.

DETAILED DESCRIPTION

The present invention provides a method for manufacturing a bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane, including the following steps:

impregnating a wet bacterial cellulose membrane in a poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer solution, washing and drying a resulting membrane successively to obtain the bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane.

In the present invention, unless otherwise specified, all desired raw materials are commercially available products well known to those skilled in the art.

Preferably, in the present invention, the wet bacterial cellulose membrane is purified before impregnating the wet bacterial cellulose membrane in the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer solution, and the purification is preferably conducted by soaking in an alkali liquor; the alkali liquor is preferably aqueous NaOH solution, aqueous

KOH solution, or aqueous $Ca(OH)_2$ solution; the alkali liquor preferably has a mass concentration of 3-6 g/L, and more preferably 4-5 g/L; the soaking in an alkali liquor preferably lasts for 30-300 min, and more preferably 50-200 min. In the present invention, cells and other impurities are removed from the wet bacterial cellulose membrane by purification.

After the purification is completed, the present invention preferably washes the resulting membrane with deionized water until neutral, and then conducts the impregnation.

In the present invention, the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer solution is preferably aqueous poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer solution, and the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer preferably has a mass concentration of 1-20wt%, and more preferably 5-15wt%. In the present invention, the impregnation is preferably conducted ultrasonically at 25-130 kHz, and more preferably 50-80 kHz; the impregnation is preferably conducted at room temperature; the impregnation preferably lasts for 0.5-10 h, more preferably 1-8 h, and most preferably 3-5 h. During impregnation, the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer is adsorbed onto and into the wet bacterial cellulose membrane to function as a physical adsorbent; after drying, hydrogen bonding is formed between the block copolymer and cellulose fiber, which increases binding forces between fibers and improves dry membrane strength; meanwhile, the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer covers on the fiber surface, which reduces the brittleness of the bacterial cellulose fiber and thus increases the toughness of the membrane.

After the impregnation is completed, the present invention washes and dries the resulting membrane successively. In the present invention, deionized water is preferably used as a reagent in the washing, and the washing is preferably conducted by flushing; the washing preferably lasts for 1-5 min, and more preferably 2-4 min. In the present invention, the drying is preferably conducted at 80-120°C, and more preferably 90-100°C; the drying preferably lasts for 1-2 h, and more preferably 1.2-1.5 h. The drying method is not particularly limited in the present invention, as long as the method used is well known to those skilled in the art.

The present invention provides a bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane manufactured by the manufacturing method according to the above technical solution. The present invention uses a bacterial cellulose as a raw material and poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer as a flexible complex additive. The bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane manufactured by a simple impregnation method has a tensile strength of up to 124.6 MPa,

increasing by 110% compared with the uncomposited bacterial cellulose membrane (59.3 MPa); the tensile strain further increases from 3.95% to 14.10%, and by 257%.

The technical solutions of the present invention will be described below clearly and completely with reference to the examples of the present invention. It is clear that the described examples are only a part of examples of the present invention, not all examples of the present invention. All other examples obtained by persons of ordinary skill in the art based on the example of the present invention without creative efforts shall fall within the scope of the present invention.

Example 1

A wet bacterial cellulose membrane was impregnated in a NaOH solution (4 g/L) for 60 min; a resulting membrane was washed with deionized water until neutral; then, a resulting membrane was impregnated in a 5wt% poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer aqueous solution and sonicated for 1 h at room temperature (at 28 kHz); a resulting composite membrane was flushed with deionized water for 3 min and dried for 1 h at 90°C to obtain a bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane.

Comparative Example 1

Preparation of uncomposited bacterial cellulose membrane: A wet bacterial cellulose membrane was impregnated in a NaOH solution (4.0 g/L) for 60 min; a resulting membrane was washed with deionized water until neutral; a resulting membrane was impregnated in deionized water and sonicated for 1 h at room temperature (at 28 kHz); then, a resulting wet membrane was dried for 1 h at 90°C to obtain an uncomposited bacterial cellulose membrane.

With reference to China National Standard GB/T1040.3-2006, mechanical property tests were performed on bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membranes manufactured in Example 1 and Comparative Example 1. Results showed that the bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane manufactured in Example 1 had a tensile strength of 92.8 MPa and a tensile strain of 9.47%; the uncomposited bacterial cellulose membrane manufactured in Comparative Example 1 had a tensile strength of 59.3 MPa and a tensile strain of 3.95%; compared with both, the tensile strength and tensile strain of the composite membrane manufactured in Example 1 increased by 56.50% and 140%, respectively.

Example 2

A wet bacterial cellulose membrane was impregnated in a KOH solution (4.5 g/L) for 100 min; a resulting membrane was washed with deionized water until neutral; then, a resulting membrane was impregnated in a 5wt% poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer aqueous solution and sonicated for 10 h at room temperature (at 40 kHz);

a resulting composite membrane was flushed with deionized water for 5 min and dried for 2 h at 110°C to obtain a bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane.

With reference to the method of Example 1, the bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane manufactured in Example 2 had a tensile strength of 90.1 MPa, which increased by 51.94% compared with the uncomposited bacterial cellulose membrane manufactured in Comparative Example 1 (59.3 MPa); the bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane had a tensile strain of 9.22%, which increased by 133% compared with the uncomposited bacterial cellulose membrane (3.95%).

Example 3

A wet bacterial cellulose membrane was impregnated in a $Ca(OH)_2$ solution (5.0 g/L) for 240 min; a resulting membrane was washed with deionized water until neutral; then, a resulting membrane was impregnated in a 10wt% poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer aqueous solution and sonicated for 5 h at room temperature (at 120 kHz); a resulting composite membrane was flushed with deionized water for 2 min and dried for 2 h at 80°C to obtain a bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane.

With reference to the method of Example 1, the bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane manufactured in Example 3 had a tensile strength of 124.6 MPa, which increased by 110% compared with the uncomposited bacterial cellulose membrane manufactured in Comparative Example 1 (59.3 MPa); the bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane had a tensile strain of 14.10%, which increased by 257% compared with the uncomposited bacterial cellulose membrane (3.95%).

Example 4

A wet bacterial cellulose membrane was impregnated in a $Ca(OH)_2$ solution (3.5 g/L) for 120 min; a resulting membrane was washed with deionized water until neutral; then, a resulting membrane was impregnated in a 8wt% poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer aqueous solution and sonicated for 8 h at room temperature (at 80 kHz); a resulting composite membrane was flushed with deionized water for 4 min and dried for 1.5 h at 120°C to obtain a bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane.

With reference to the method of Example 1, the bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane

manufactured in Example 4 had a tensile strength of 114.6 MPa, which increased by 93.25% compared with the uncomposited bacterial cellulose membrane manufactured in Comparative Example 1 (59.3 MPa); the tensile strain increased from 3.95% to 12.10%, and by 206%.

Example 5

A wet bacterial cellulose membrane was impregnated in a KOH solution (3.0 g/L) for 150 min; a resulting membrane was washed with deionized water until neutral; then, a resulting membrane was impregnated in a 8wt% poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer aqueous solution and sonicated for 7 h at room temperature (at 100 kHz); a resulting composite membrane was flushed with deionized water for 4 min and dried for 2 h at 100°C to obtain a bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane.

With reference to the method of Example 1, the bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane manufactured in Example 5 had a tensile strength of 110.2 MPa, which increased by 85.83% compared with the uncomposited bacterial cellulose membrane manufactured in Comparative Example 1 (59.3 MPa); the bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane had a tensile strain of 12.21%, which increased by 209% compared with the uncomposited bacterial cellulose membrane (3.95%).

From the above examples, the present invention provides a bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane and a manufacturing method thereof. In the present invention, a highly flexible and dry bacterial cellulose membrane can be successfully manufactured by a simple impregnation method. The bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane manufactured has a tensile strength of up to 124.6 MPa, increasing by 110% compared with the uncomposited bacterial cellulose membrane (59.3 MPa); the tensile strain increases from 3.95% to 14.10%, and by 257%.

The foregoing descriptions is merely preferred examples of the present invention; it should be noted that various modifications and variations can be made by those skilled in the art without departing from the principles of the present invention and are within the scope of the invention.

Editorial Note

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There is only one page of the claim

What is claimed is:

1. A method for manufacturing a bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane, comprising the following steps:

impregnating a wet bacterial cellulose membrane in a poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer solution, washing and drying a resulting membrane successively to obtain the bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane.

2. The manufacturing method according to claim 1, wherein the wet bacterial cellulose membrane is purified before impregnating the wet bacterial cellulose membrane in the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer solution, and the purification is conducted by soaking in an alkali liquor.

3. The manufacturing method according to claim 2, wherein the alkali liquor is aqueous sodium hydroxide (NaOH) solution, aqueous potassium hydroxide (KOH) solution, or aqueous calcium hydroxide ($Ca(OH)_2$) solution, and the alkali liquor has a mass concentration of 3-6 g/L.

4. The manufacturing method according to claim 1, wherein a solvent of the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer is water, and the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer has a mass concentration of 1-20wt%.

5. A bacterial cellulose-poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer composite membrane manufactured by the manufacturing method according to any one of claims 1 to 4.