(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
3 June 2010 (03.06.2010)

PCT

(10) International Publication Number
WO 2010/062016 A2

(51) International Patent Classification:
B32B 27/34 (2006.01) *C08J 5/22* (2006.01)

(21) International Application Number:
PCT/KR2009/001762

(22) International Filing Date:
6 April 2009 (06.04.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10-2008-0119417
28 November 2008 (28.11.2008) KR

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

WO 2010/062016 A2

(54) Title: POLYAMIDE COMPOSITE MEMBRANE HAVING FOULING RESISTANCE AND CHLORINE RESISTANCE AND METHOD THEREOF

(57) Abstract: Provided is a method for preparing a polyamide composite membrane which comprises the steps of: forming a polyamide thin film on a porous supporting layer; coating or crosslinking the polyamide thin film surface with a solution of epoxy-silane compounds and drying the resulted membrane; and washing the dried membrane with a basic aqueous solution. Also provided is a polyamide composite membrane prepared thereby.

Description

POLYAMIDE COMPOSITE MEMBRANE HAVING FOULING RESISTANCE AND CHLORINE RESISTANCE AND METHOD THEREOF

Technical Field

[1] The present invention relates to a polyamide composite membrane and a method for preparing the same. Specifically, the present invention relates to a polyamide composite membrane having both fouling resistance and chlorine resistance at the same time, and a method for preparing the same.

[2]

Background Art

[3] It is known that dissolved substances can be separated from their solvents by use of selective membranes. For example, there are various types of membranes such as microfiltration membranes, ultrafiltration membranes, nanofiltration membranes, reverse osmosis membranes and the like. The reverse osmosis membranes are particularly useful in the desalination of brackish water or sea water. The desalination process of brackish water or sea water using reverse osmosis membranes involves a filtration process for separation by applying pressure to the feed water and forcing the water through the membrane, so that purified water passes through the membrane and the salts or other dissolved substances or molecules are filtered out. During such filtration process, osmotic pressure naturally occurs, and the more concentrated the feed water, the greater the osmotic pressure, which requires higher pressure applied from outside.

[4] Tap water should be treated by chlorination for sterilization. Water for industrial use or desalinated water from sea water should also be treated with chlorine so as to prevent water from being contaminated by bacteria present on a reverse osmosis membrane, and then undergone a dechlorination process. Such dechlorination is generally done by use of activated charcoal or chemical agents, thus having many difficulties in their maintenance.

[5] Reverse osmosis membranes prepared from a porous supporting layer and a polyamide membrane formed on said supporting layer have been widely used. The polyamide membrane can be obtained by interfacial polymerization between polyfunctional amines and polyfunctional acyl halides.

[6] US patent No. 4,277,344 issued to Cadotte, et al., discloses an invention providing an aromatic polyamide thin film obtained by interfacial polymerization between aromatic polyfunctional amine having two primary amine substituents and aromatic acyl halide having three or more acyl halide groups. Although the film has made quite an

achievement in terms of increased flow rate and high salt rejection, to date, various researches to make further improvement in flow rate and salt rejection characteristics still have been made.

[7] US patent No. 4,872,984 issued to Tomashke, proposes a water permeable osmosis membrane prepared by the following steps: (a) coating a microporous supporting layer with an aqueous solution comprising an aromatic polyamine reactant having at least two amine functional groups and an amine salt, to form a liquid layer on said microporous supporting layer; (b) contacting said liquid layer with an organic solvent solution of an aromatic polyfunctional acyl halide or mixture thereof, wherein the aromatic polyfunctional acyl halide has, on the average, at least about 2.2 acyl halide groups which are amine-reactive functional groups; and (c) drying the product of step (b) so as to form a water permeable membrane. Tomashke's membrane preparation method has significantly increased the permeation flow rate by introducing a step of a monomeric amine salt addition, into the Cadotte's membrane preparation method.

[8] US patent No. 5,614,099 issued to Hirose, discloses a technique of adjusting a polyamide surface structure. The invention is to provide a process for preparing a membrane having at least a certain degree of surface roughness, from the finding that the surface roughness is closely related to a flow rate increase, based on the Tomashke's membrane preparation method.

[9] Although these polyamide type reverse osmosis membranes of prior arts show excellent desalination and permeation characteristics, membrane fouling occurred by adsorption of floats or fouling substances dissolved in a solution to the membrane surface cannot be avoided, resulting in decrease in the flow rate. Cleaning agents such as sodium hypochlorite(NaOCl) are used to prevent the membrane fouling. However, the use of cleaning agents poses another problem such as declination of the separation performance caused by residual chlorines which break the polyamide backbone.

[10] To date, techniques to reduce fouling of polyamide membranes generally involve a double-coating process. However, such double coating increases membrane resistance, lowering the permeation property as compared to the water permeability of polyamide composite membrane without double coating.

[11] The present inventors have continued researches to develop polyamide membranes having greater resistance to both chlorine and fouling, and excellent permeation performance. As a result, the present inventors have developed a method for preparing a polyamide composite membrane having both satisfying chlorine resistance and fouling resistance by coating or crosslinking the surface of a polyamide membrane with epoxy-silane compounds.

[12]

Disclosure of Invention

Technical Problem

[13] The present invention is to provide a method for preparing a polyamide composite membrane having both fouling resistance and chlorine resistance at the same time, by coating or crosslinking the polyamide membrane surface with epoxy-silane compounds.

[14] Further, the present invention is to provide a polyamide composite membrane having improved chlorine resistance and fouling resistance prepared by said method.

[15] Moreover, the present invention is to provide a polyamide composite membrane having excellent permeability.

[16] Still further, the present invention is to provide a method for preparing a polyamide composite membrane through a simplified and economical process.

[17]

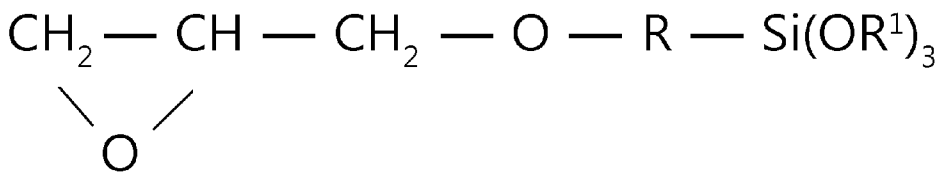
Technical Solution

[18] In one aspect, the present invention provides a method for preparing a polyamide composite membrane, characterized by comprising the steps of: forming a polyamide thin film on a porous supporting layer; coating or crosslinking the polyamide thin film surface with a solution of epoxy-silane compounds and drying the resulted membrane; and washing the dried membrane with a basic aqueous solution.

[19] According to one embodiment of the present invention, the epoxy-silane compounds may be at least one selected from the group consisting of [2,3-epoxypropoxy)alkyl]trialkoxy silane represented by the following chemistry figure 1, glycidylalkyltrialkoxy silane represented by the following chemistry figure 2 and mixtures thereof:

[20] ChemistryFigure 1

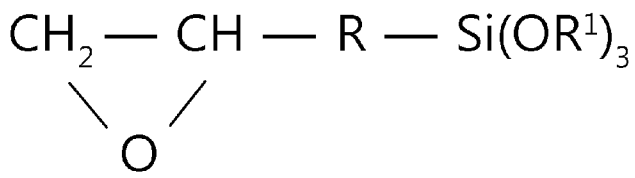
[Chem.1]



[21]

[22] ChemistryFigure 2

[Chem.2]



[23] wherein R is C1~C4 alkylene group, and R' is C1~C4 alkyl group.

[24] The [2,3-epoxypropoxy)alkyl]trialkoxy silane may be at least one selected from the group consisting of [(2,3-epoxypropoxy)methyl]trimethoxy silane, [(2,3-epoxypropoxy)methyl]triethoxy silane, [(2,3-epoxypropoxy)methyl]tripropoxy silane, [(2,3-epoxypropoxy)methyl]tributoxy silane, [2-(2,3-epoxypropoxy)ethyl]trimethoxy silane, [2-(2,3-epoxypropoxy)ethyl]triethoxy silane, [2-(2,3-epoxypropoxy)ethyl]tripropoxy silane, [2-(2,3-epoxypropoxy)ethyl]tributoxy silane, [3-(2,3-epoxypropoxy)propyl]trimethoxy silane, [3-(2,3-epoxypropoxy)propyl]triethoxy silane, [3-(2,3-epoxypropoxy)propyl]tripropoxy silane, [3-(2,3-epoxypropoxy)propyl]tributoxy silane, [4-(2,3-epoxypropoxy)butyl]trimethoxy silane, [4-(2,3-epoxypropoxy)butyl]triethoxy silane, [4-(2,3-epoxypropoxy)butyl]tripropoxy silane, [4-(2,3-epoxypropoxy)butyl]tributoxy silane and mixtures thereof.

[25] The glycidylalkyltrialkoxy silane may be at least one selected from the group consisting of glycidylmethyltrimethoxy silane, glycidylmethyltriethoxy silane, 2-glycidylethyltrimethoxy silane, 2-glycidylethyltriethoxy silane, 3-glycidylpropyltrimethoxy silane, 3-glycidylpropyltriethoxy silane, 3-glycidylpropyltri(methoxyethoxy silane) and mixtures thereof.

[26] According to one embodiment of the present invention, the concentration of said epoxy-silane compounds may be 0.1~5 wt%.

[27] According to another embodiment of the present invention, the method further includes, after coating or crosslinking the polyamide thin film surface with an epoxy-silane compound solution, a step of drying the resulted membrane with hot air at the temperature range of 25~100℃.

[28] In another aspect, the present invention provides a polyamide composite membrane prepared by the foregoing method. Specifically, a polyamide composite membrane is provided, which is comprised of: a porous supporting layer; a polyamide composite membrane formed on the porous supporting layer; and an epoxy-silane compound layer coated or crosslinked on the polyamide composite surface.

[29]

Advantageous Effects

[30] The polyamide composite membrane according to the method of the present invention exhibits excellent fouling resistance and chlorine resistance at the same time as well as good permeation performance, by coating or crosslinking the surface of a polyamide thin film with epoxy-silane compounds. Further, the method of the present invention can produce a polyamide composite layer through a simple process, thus at a

relatively low production cost.

[31]

Mode for the Invention

[32] The method for preparing a polyamide composite membrane of the present invention includes the steps of: forming a polyamide thin film on a porous supporting layer; coating or crosslinking the polyamide thin film surface with a solution of epoxy-silane compounds and drying the resulted membrane; and washing the dried membrane with a basic aqueous solution.

[33]

[34] Hereinafter, the present invention is further illustrated in detail.

[35] The step of forming a polyamide thin film on a porous supporting layer may be carried out by well-known methods in this field of art. The polyamide thin film is generally formed by: spreading an aqueous polyfunctional amine solution over the microporous supporting layer; removing the excess solution therefrom; contacting the resulted surface with an organic solvent containing amine-reactive compounds selected from the group consisting of polyfunctional acylhalide, polyfunctional sulfonylhalide and polyfunctional isocyanate; and carrying out interfacial polymerization.

[36] The porous supporting layer used herein refers to a microporous supporting layer. Any well-known materials and production methods for the porous supporting layer in this field of art may be used herein without being specifically limited. The dimension of a micropore should be large enough for the feed water to permeate, but not too much to hinder the crosslinking of a thin film formed on the micropores. The hole diameter of the porous supporting layer is desirably 1~500 nm, without being specifically limited to this. When the hole diameter of the porous supporting layer is more than 500 nm, the surface membrane obtained from the interfacial polymerization permeates through the holes on the supporting layer, being difficult to form a normal flat membrane.

[37] There is no specific restriction on materials for the microporous supporting layer, any materials generally used in this field of art may be employed. For instance, polymers such as polysulfone, polyether sulfone, polyimide, polyamide, polyether amide, polyacrylonitrile, polymethylmethacrylate, polyethylene, polypropylene, polyvinylidene fluoride and the like may be desirably mentioned. Although thickness of the microporous supporting layer is not specifically limited, 25~130 ㎛ is desirable.

[38] The species of polyfunctional amines are not specifically limited, and any types well-known in this field of art may be used, for example, such as one polyfunctional amine or mixtures thereof. Particularly, examples include aromatic primary diamines of methylphenyldiamine or para-phenyl diamine, or substituted derivatives thereof;

analogues having N-alkyl or aryl substituents; alkane diamines or cycloaliphatic primary amines such as cyclohexane diamine, cycloaliphatic secondary amines such as piperazine and alkyl derivatives thereof; and aromatic secondary diamines. The substituent for the substituted aromatic primary amines includes an alkyl group, an alkoxy group, a hydroxyalkyl group or a halogen atom.

[39] The polyfunctional amine is used in the form of an aqueous solution. The polyfunctional amine may be contained in the aqueous solution at the amount of 0.1~30 wt%. The aqueous solution of the polyfunctional amine has a pH of 7~13. Acid acceptors such as hydroxide, carboxylate, carbonate, borate, alkali metal phosphate, trialkyl amine and the like may be further added to the aqueous solution of the polyfunctional amine, so as to neutralize acids (hydrochloric acid, etc.) generated during the interfacial polymerization.

[40] The polyfunctional amine solution, i.e. aqueous polyamine solution may be used alone or with other additives described in conventional arts. For the improvement in flow rate, a polar protic solvent and a mixture thereof, a mixture of polar protic solvent and polar aprotic solvent may be used. Examples of the polar protic solvent include alcohol, dialcohol, alcohol-ether and the like, and examples of the polar aprotic solvent include diethyleneglycol; ether derivatives such as di(ethylene glycol) tertiary butylmethylether; and sulfoxide derivatives such as dimethylsulfoxide, butylsulfoxide, tetramethylenesulfoxide. Other additives containing monomeric amine salts may be used for increasing the flow rate.

[41] The polyfunctional acyl halide used in the interfacial polymerization is an aromatic compound having 2~3 carboxylic acid halides and for example, trimesoyl chloride, isophthaloyl chloride, terephthaloyl chloride and mixtures thereof may be widely used. The aromatic polyfunctional acylhalide may be used alone or as a mixture, for example such as trimesoyl chloride, a mixture of trimesoyl chloride and isophthaloyl chloride and a mixture of trimesoyl chloride and terephthaloyl chloride. The content of whole carboxylic acid halides in organic solvent may be 0.005~5 wt%.

[42] After forming the polyamide thin film, the surface thereof is coated or crosslinked with a solution of epoxy-silane compounds, and the resulted membrane is dried. The epoxy-silane compounds have both hydrophobic groups and hydrophilic groups. When said functional groups are coated by adhesion on the polyamide surface or crosslinked thereto, chlorine resistance and fouling resistance are improved at the same time. The term 'coating' used herein generally means immobilization of epoxy silane compounds to the polyamide surface by the physical adsorption therebetween. The term 'crosslink' used herein means immobilization of epoxy silane compounds to the polyamide surface by chemical linkages resulted from chemical reactions between nitrogen and oxygen on the polyamide surface and epoxy silane compounds.

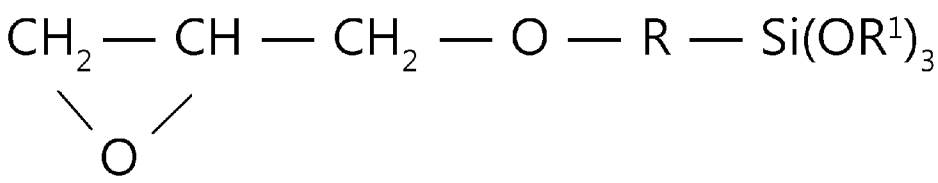
[43] The coating process of the surface of the polyamide thin film with a solution of epoxy-silane compounds involves a reaction of epoxy-silane compounds with polar atoms present on the surface of a polyamide reverse osmosis thin film, via a sol-gel reaction. Specifically, the epoxy-silane compounds may be crosslinked, for example, by Si-O bonds of functional groups such as ethoxy group formed on the polyamide surface, with the result that alkyl groups or epoxy groups can be coated on the membrane surface through a sol-gel method.

[44] As a result of said coating process, polarity of the polyamide thin film surface becomes lowered, leading to homogeneous distribution of water-insoluble polymers over the polyamide thin film surface. It means that during permeation through the polyamide reverse osmosis membrane, permeation of chlorine radicals or substituted chlorine radicals through the reverse osmosis membrane becomes reduced, thereby improving the durability to chlorine-containing solution, i.e. chlorine resistance. At the same time, hydrophilic groups become located on the membrane surface, thereby being possible to reduce fouling on the membrane surface. In this way, the present invention is possible to provide a polyamide composite layer having both satisfying chlorine resistance and fouling resistance through a single coating process.

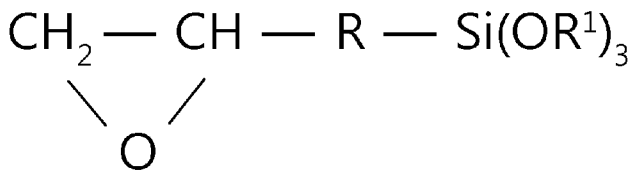
[45] The epoxy-silane compounds may have a structure which contains not more than 3 alkoxy groups bonded with silicon, 1 or more alkyl group and glycidyl group. They may have a structure which contains not more than 3 alkoxy groups bonded with silicon, 1 or more alkyl group, ether group and glycidyl group at the end at the same time. Said compounds may be used alone or as a mixture in the form of a solution.

[46] Particularly, the epoxy-silane compounds may be at least one selected from the group consisting of [2,3-epoxypropoxy)alkyl]trialkoxy silane represented by the following chemistry figure 1, glycidylalkyltrialkoxy silane represented by the following chemistry figure 2 and mixtures thereof:

[47] [Chemistry Figure 1]

[48] 

[49] [Chemistry Figure 2]

[50] 

[51] wherein R is C1~C4 alkylene group, and R' is C1~C4 alkyl group.

[52] The [2,3-epoxypropoxy)alkyl]trialkoxy silane may be selected from [(2,3-epoxypropoxy)methyl]trimethoxy silane, [(2,3-epoxypropoxy)methyl]triethoxy silane, [(2,3-epoxypropoxy)methyl]tripropoxy silane, [(2,3-epoxypropoxy)methyl]tributoxy silane, [2-(2,3-epoxypropoxy)ethyl]trimethoxy silane, [2-(2,3-epoxypropoxy)ethyl]triethoxy silane, [2-(2,3-epoxypropoxy)ethyl]tripropoxy silane, [2-(2,3-epoxypropoxy)ethyl]tributoxy silane, [3-(2,3-epoxypropoxy)propyl]trimethoxy silane, [3-(2,3-epoxypropoxy)propyl]triethoxy silane, [3-(2,3-epoxypropoxy)propyl]tripropoxy silane, [3-(2,3-epoxypropoxy)propyl]tributoxy silane, [4-(2,3-epoxypropoxy)butyl]trimethoxy silane, [4-(2,3-epoxypropoxy)butyl]triethoxy silane, [4-(2,3-epoxypropoxy)butyl]tripropoxy silane, [4-(2,3-epoxypropoxy)butyl]tributoxy silane and mixtures thereof, without being limited to these examples. In the present invention, 3-(2,3-epoxypropoxy)propyltrimethoxy silane or 3-(2,3-epoxypropoxy)propyltriethoxy silane may be preferably used.

[53] The glycidylalkyltrialkoxy silane may be selected from glycidylmethyltrimethoxy silane, glycidylmethyltriethoxy silane, 2-glycidylethyltrimethoxy silane, 2-glycidylethyltriethoxy silane, 3-glycidylpropyltrimethoxy silane, 3-glycidylpropyltriethoxy silane, 3-glycidylpropyltri(methoxyethoxy silane) and mixtures thereof, without being limited to these examples. In the present invention, 3-glycidylpropyltrimethoxy silane or 3-glycidylpropyltriethoxy silane may be preferably used.

[54] The epoxy-silane compounds may be used alone or as a mixture in the form of a solution. The concentration of the epoxy-silane compounds is preferably 0.1-5 wt%. In the meantime, when the concentration is less than 0.1 wt%, the sol-gel reaction of silane occurs so negligibly on the membrane surface that it cannot cover the whole polyamide surface, which would deteriorate the chlorine resistance or fouling resistance properties. When the concentration is more than 5 wt%, the sol-gel reaction of silane on the membrane surface occurs excessively, forming a thick coat, which may cause a significant decrease in the flow rate, making the resulting membrane inefficient, although resistance to chlorine and fouling can be obtained. As for a solvent for the epoxy-silane compound solution, ethanol is mainly used, however a mixed solvent of other polar solvent and water may be used.

[55] According to one embodiment of the present invention, it is desirable to dry a sample by a hot-air or air drying process. The hot-air or air drying process increases the effective concentration of the materials for a sol-gel reaction.

[56] Specifically, the present invention further comprises, after coating or crosslinking the polyamide thin film surface with the solution of epoxy-silane compound, a step of

drying the resulted membrane with hot air at the temperature range of 25~100°C. The hot air drying process effectively fixes the epoxy-silane compounds to the surface of the polyamide thin film. As such hot air drying process is generally well known in this field of art, further detailed description is eliminated herein.

[57] Next, upon completion of the drying process, the resulted polyamide membrane is washed with a basic aqueous solution. Any types of basic aqueous solutions generally used in this field of art may be used without specific restriction. In this specification, a sodium carbonate or sodium hydroxide solution was used.

[58] It has been already explained that the polyamide composite membrane coated (or crosslinked) with epoxy-silane compounds, obtained from the foregoing process, has both hydrophobic groups and hydrophilic groups coated on the polyamide thin film surface at the same time, thus showing fouling resistance and chlorine resistance, simultaneously.

[59] Still another aspect of the present invention provides a polyamide composite membrane prepared by the above-described method. Specifically, the polyamide composite membrane is comprised of: a porous supporting layer; a polyamide thin film formed on the porous supporting layer; and an epoxy-silane compound layer coated or crosslinked on the polyamide thin film surface.

[60] The porous supporting layer, polyamide thin film and epoxy silane compounds are same as in the foregoing description.

[61] Hereinafter, the present invention is further illustrated in detail through the following examples. However, these examples are provided only to illustrate the present invention, without limiting the scope of the present invention.

[62]

[63] **Examples**

[64] The present invention used a disassembled commercial membrane as a substrate to minimize the changes in physical properties in the course of preparing a polyamide membrane, wherein the commercial membrane was originally manufactured as a module. Used was a reverse osmosis membrane for brackish water (CPA2-4040), manufactured by Hydranautics corp. USA, which was formed on a porous supporting layer. The porous supporting layer was a thin film made of polyester unwoven fabric casted with polysulfone, wherein the thickness of the thin film was 100-150 ㎛ and the pore size was 0.01 ㎛. Specifically, the reverse osmosis membrane used herein was a polyamide reverse osmosis membrane for industrial use, made of about 90-95 ㎛ of a reinforcing layer made of polyester unwoven fabric, 40-50 ㎛ of a polysulfone support casted on said reinforcing layer, and about not more than 2 ㎛ of polyamide polymer coated on the polysulfone support.

[65] The initial salt rejection rate and permeation flow rate in the present invention were

measured by using 2,000 ppm of an aqueous NaCl solution. A system used for estimation of a reverse osmosis membrane was comprised of a permeation cell in the form of a flat panel, a high pressure pump, a reservoir and a cooling device. The structure of the permeation cell in the form or a flat panel employs a cross-flow type, having an effective permeation area being 27.01 cm^2. After installing a washed membrane to the permeation cell, warm-up operation of the system for testing a reverse osmosis membrane was carried out sufficiently for about 1 hour until the pressure and water permeation becomes regular. Water permeation degree was determined by measuring the amount of permeated water at an interval of 30 minutes. Salt rejection was determined by analyzing the salt concentration before and after permeation, by using a conductivity meter.

[66] The resistance to chlorine was determined in a mixed aqueous solution of 2,000 ppm of NaCl and 2,000 ppm of NaOCl. In order to exclude the permeation of chlorine and salts through the unwoven fabric that is a porous supporting layer of the reverse osmosis membrane and a polysulfone layer, the mixed solution was allowed to flow through the inside of the system for 10 to 30 seconds and maintained as being a stationary phase so that the salt permeation only occurs through the polyamide surface. Changes in salt rejection and flow rate were practically measured by operating time.

[67] For determination of fouling resistance, an aqueous solution of 2,000 ppm of NaCl and 100 ppm of casein was used. After determination of the initial permeation property, 100 ppm of the aqueous casein solution was directly fed to a tank, and then the permeation property was immediately determined. The changes in water permeation before and after the introduction of the casein-containing solution were plotted, and the slope at the time of change was calculated by using a computer program, determining the level of fouling.

[68]

[69] **Example 1**

[70] The surface of the above-mentioned polyamide membrane (CPA2-4040) was coated with 1.5 wt% of an aqueous solution of 3-(2,3-epoxypropoxy)propyltrimethoxy silane (GPPTMS), wherein ethanol was used as a solvent, and dried with hot air at 70°C for 10 minutes. After drying, the surface was washed with water, and soaked in an aqueous NaOH solution at the pH of 10-11 for 2 hours or more so as to clean it, resulting in a polyamide composite layer. The performance of the resulted composite layer was measured by using 2,000 ppm of an aqueous NaCl solution, under pressure of 225 psi, and the results were represented in Table 1.

[71]

[72] **Comparative example 1**

[73] The polyamide membrane (CPA2-4040) was not subjected to any surface treatment,

but only soaked in distilled water 1 hour or more. Then, its permeation performance was estimated under the same conditions as described in Example 1, and the results were represented in Table 1.

[74]

[75] Table 1

[Table 1]

[Table]

Ð	initial salt rejection (%)	initial permeation flow rate (GFD*)
Example 1	98.09	16.76
Comparative example 1	98.23	22.34

[76] * GFD : gallons/ft^{2}day

[77]

[78] **Examples 2 to 4**

[79] A polyamide composite membrane was prepared as in Example 1, except that the concentration of GPPTMS was changed to 0.1 wt% (Example 2), 1.5 wt% (Example 3) and 3.0 wt% (Example 4), respectively. The system for testing a reverse osmosis membrane was operated with a mixture of 2,000 ppm of an aqueous NaCl solution and 2,000 ppm of an aqueous NaOCl solution, under pressure of 225 psi. Then, the above obtained reverse osmosis membrane was subjected to the system to determine the initial permeation property, and the results were represented in Table 2.

[80]

[81] **Examples 5 and 6**

[82] A polyamide composite membrane was prepared as in Example 1, except that the drying condition for the coat formed by the aqueous GPPTMS solution was changed to 25℃ (Example 5) and 70℃ (Example 6), respectively. The system for testing a reverse osmosis membrane was operated with a mixture of 2,000 ppm of an aqueous NaCl solution and 2,000 ppm of an aqueous NaOCl solution, under pressure of 225 psi. Then, the above obtained reverse osmosis membrane was subjected to the system to determine the initial permeation property, and the results were represented in Table 3.

[83]

[84] Table 2

[Table 2]

[Table]

Đ	initial salt rejection (%)	initial permeation flow rate (GFD)
Example 2	97.74	20.18
Example 3	98.36	18.56
Example 4	98.54	14.85
Comparative example 1	98.23	22.34

[85]

[86] Table 3

[Table 3]

[Table]

Đ	initial salt rejection (%) Đ	initial permeation flow rate (GFD)
Example 3	96.12	23.17
Example 4	98.44	17.62
Comparative example 1	98.23	22.34

[87]

[88] **Example 7**

[89] A polyamide composite membrane was prepared as in Example 1. The system for testing a reverse osmosis membrane was operated with a mixture of 2,000 ppm of an aqueous NaCl solution and 2,000 ppm of an aqueous NaOCl solution, under pressure of 225 psi. Then, the above resulted reverse osmosis membrane was subjected to the system to determine the initial permeation property, and the results were represented in Tables 4 and 5.

[90]

[91] **Comparative example 2**

[92] The polyamide membrane (CPA2-4040) was not subjected to any surface treatment, but only soaked in distilled water 1 hour or more. Then, its permeation performance was estimated under the same conditions as described in Example 2, and the results were represented in Tables 4 and 5.

[93]

[94] **Example 8**

[95] After completion of the estimation as in Example 1, the system for testing a reverse

osmosis membrane was maintained with the permeation cell equipped with said coated membrane for 6 hours under the same conditions as described above, then operated 30 minutes under 225 psi, and the performance of the polyamide reverse osmosis composite membrane was measured. After an elapse of 12 hours, the system was operated 30 minutes under 225 psi again, and then the permeation property of the polyamide reverse osmosis composite membrane was measured. The results showing the changes in performance as time elapsed were represented in Tables 4 and 5.

[96]

[97] **Comparative example 3**

[98] The polyamide membrane (CPA2-4040) was not subjected to any surface treatment, but only soaked in distilled water 1 hour or more. Then, its permeation performance was estimated under the same conditions as described in Example 3, and the results were represented in Tables 4 and 5.

[99]

[100] Table 4

[Table 4]

[Table]

Ð	initial salt rejection (%) after addition of NaOCl	salt rejection (%) after being exposed to NaOCl 6 hours	salt rejection (%) after being exposed to NaOCl 12 hours
Example 7	98.45	-	-
Comparative example 2	98.30	-	-
Example 8	99.00	98.66	98.78
Comparative example 3	98.33	95.48	72.02

[101]

[102] Table 5

[Table 5]

[Table]

Đ	initial flow rate (GFD) after addition of NaOCl	salt rejection (GFD) after being exposed to NaOCl 6 hours	salt rejection (GFD) after being exposed to NaOCl 12 hours
Example 7	13.04	-	-
Comparative example 2	21.35	-	-
Example 8	13.08	18.08	20.53
Comparative example 3	20.31	26.78	35.18

[103]

[104] **Example 9**

[105] The salt rejection and permeation flow rate of the polyamide composite membrane prepared by the method of Example 1 were measured by using a mixed aqueous solution of 2,000 ppm NaCl and 100 ppm casein. The salt rejection and flow rate before and after the introduction of the casen-containing solution were determined and compared. At this time, the permeation flow rate was converted to MFI, an index of membrane fouling, and the results were disclosed in Table 6.

[106]

[107] * Membrane Fouling Index (MFI)

[108] MFI, defined by the following math figure, is mainly used for measuring a fouling level in a microfiltration membrane.

[109] MathFigure 1

[Math.1]

$$\frac{t}{V} = \frac{\eta R_m}{A \Delta P} + \frac{\eta r_c C_b}{2A^2 c_c \Delta P} V$$

$$\therefore MFI = \frac{\eta r_c C_b}{2A^2 c_c \Delta P}$$

[110]

[111] The MFI can be represented by the above math figure, provided that the thickness of

a cake layer formed on the membrane surface (fouling) is in proportion to the filtered amount. To determine the MFI value, the flow rate (Q) is obtained by multiplying the measured permeation flux by the membrane area (A). The resulted value is multiplied by filtration time (t) to obtain the filtered amount (V). By assigning a filtered amount (V) to the horizontal axis (x) and 1/Q to the vertical axis (y), the slope of t/V to V curve is a MFI value. The symbols used in the above math figure refer to the following:

[112] - ΔP (pressure difference before and after passing a membrane) = $\Delta P_m+\Delta P_p+\Delta P_c$

[113] ΔP_m: pressure drop occurred by passing through a membrane

[114] ΔP_p: pressure drop owing to a concentration polarization layer

[115] ΔP_c: pressure drop owing to a cake layer

[116] - R_m: membrane resistance

[117] - A: area of a membrane

[118] - η: absolute viscosity

[119] - C_b: concentration of a bulk layer/ C_c: concentration of a cake layer

[120] - r_c: radius of cake particles

[121]

[122] If MFI is applied to a reverse osmosis membrane process, the change in permeation before and after introduction of fouling materials (reduction in permeation) can be expressed as a change in the slope, helping to understand the level of fouling on the reverse osmosis membrane by comparing the slopes. In other words, according to the definition of MFI, the higher the MFI value of a reverse osmosis membrane, the greater the membrane fouling occurred.

[123]

[124] **Comparative example 4**

[125] The polyamide membrane (CPA2-4040) was not subjected to any surface treatment, but only soaked in distilled water 1 hour or more. Then, its permeation performance was estimated under the same conditions as in Example 4. The change in permeation flow rate represented by MFI was disclosed in Table 6.

[126]

[127] Table 6

[Table 6]

[Table]

Đ	initial salt rejection before addition of casein (%)	salt rejection in 2 hours after addition of casein (%)	initial flow rate before addition of casein (GFD)	flow rate in 2 hours after addition of casein (GFD)	MFI value
Example 9	98.09	98.88	16.76	16.59	8×10^{-6} Đ
Comparative example 4	98.23	98.26	24.18	18.20	0.00215 Đ

[128]

[129] From Tables 1 to 6, it can be seen that the polyamide composite membranes of the present invention exhibit excellent chlorine and fouling resistance at the same time. Therefore, the polyamide composite membranes according to the present invention show strong resistance to cleaning agents such as sodium hypochlorite(NaOCl) that is generally introduced to reduce the membrane fouling, and are capable of reducing fouling of the membrane surface, thereby being advantageously applicable to a sea water desalination system or ultrapure water system.

[130] Additionally, the process of preparing the polyamide composite membrane according to the present invention is simple and economical, since it employs kind of post-treatment of the surface of a polyamide thin film which has already been prepared, with epoxy-silane compounds.

Claims

[1] A method for preparing a polyamide composite membrane, comprising the steps of:

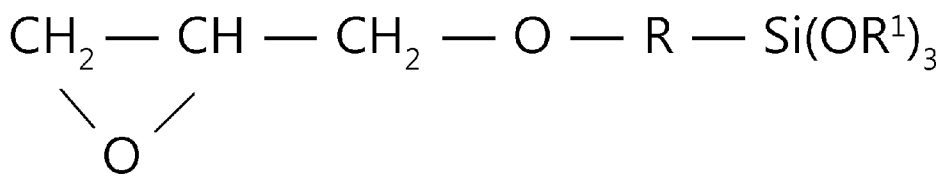
forming a polyamide thin film on a porous supporting layer;

coating or crosslinking the polyamide thin film surface with a solution of epoxy-silane compounds and drying the resulted membrane; and

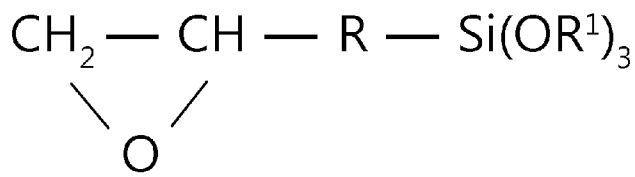
washing the dried membrane with a basic aqueous solution.

[2] The method for preparing a polyamide composite membrane according to claim 1, wherein the epoxy-silane compounds is at least one selected from the group consisting of [2,3-epoxypropoxy)alkyl]trialkoxy silane represented by the following chemistry figure 1, glycidylalkyltrialkoxy silane represented by the following chemistry figure 2 and mixtures thereof:

[Chemistry Figure 1]



[Chemistry Figure 2]



wherein R is C1~C4 alkylene group, and R' is C1~C4 alkyl group.

[3] The method for preparing a polyamide composite membrane according to claim 2, wherein the [2,3-epoxypropoxy)alkyl]trialkoxy silane is at least one selected from the group consisting of [(2,3-epoxypropoxy)methyl]trimethoxy silane,

[(2,3-epoxypropoxy)methyl]triethoxy silane,

[(2,3-epoxypropoxy)methyl]tripropoxy silane,

[(2,3-epoxypropoxy)methyl]tributoxy silane,

[2-(2,3-epoxypropoxy)ethyl]trimethoxy silane,

[2-(2,3-epoxypropoxy)ethyl]triethoxy silane,

[2-(2,3-epoxypropoxy)ethyl]tripropoxy silane,

[2-(2,3-epoxypropoxy)ethyl]tributoxy silane,

[3-(2,3-epoxypropoxy)propyl]trimethoxy silane,

[3-(2,3-epoxypropoxy)propyl]triethoxy silane,

[3-(2,3-epoxypropoxy)propyl]tripropoxy silane,

[3-(2,3-epoxypropoxy)propyl]tributoxy silane,

[4-(2,3-epoxypropoxy)butyl]trimethoxy silane,
[4-(2,3-epoxypropoxy)butyl]triethoxy silane,
[4-(2,3-epoxypropoxy)butyl]tripropoxy silane,
[4-(2,3-epoxypropoxy)butyl]tributoxy silane and mixtures thereof.

[4] The method for preparing a polyamide composite membrane according to claim 2, wherein the glycidylalkyltrialkoxy silane is at least one selected from the group consisting of glycidylmethyltrimethoxy silane, glycidylmethyltriethoxy silane, 2-glycidylethyltrimethoxy silane, 2-glycidylethyltriethoxy silane, 3-glycidylpropyltrimethoxy silane, 3-glycidylpropyltriethoxy silane, 3-glycidylpropyltri(methoxyethoxy silane) and mixtures thereof.

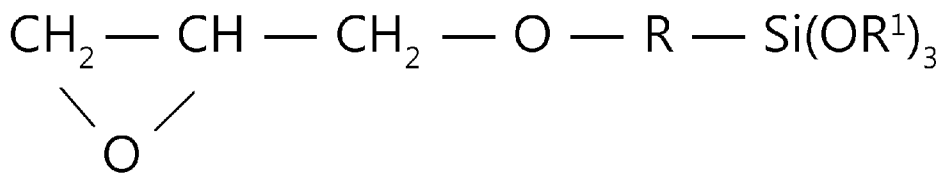
[5] The method for preparing a polyamide composite membrane according to claim 1, wherein the concentration of said epoxy-silane compounds is 0.1~5 wt%.

[6] The method for preparing a polyamide composite membrane according to claim 1, further comprising, after coating or crosslinking the polyamide thin film surface with a solution of epoxy-silane compounds, a step of drying the resulted membrane with hot air at the temperature range of 25~100℃.

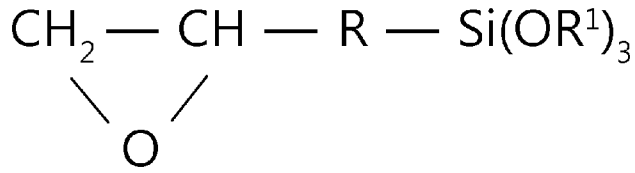
[7] A polyamide composite membrane comprising:
a porous supporting layer;
a polyamide thin film formed on the porous supporting layer; and
an epoxy-silane compound layer coated or crosslinked on the polyamide thin film surface.

[8] The polyamide composite membrane according to claim 7, wherein the epoxy-silane compound is at least one selected from the group consisting of [2,3-epoxypropoxy)alkyl]trialkoxy silane represented by the following chemistry figure 1, glycidylalkyltrialkoxy silane represented by the following chemistry figure 2 and mixtures thereof:

[Chemistry Figure 1]



[Chemistry Figure 2]



wherein R is C1~C4 alkylene group, and R' is C1~C4 alkyl group.

[9] The polyamide composite membrane according to claim 8, wherein the [2,3-epoxypropoxy)alkyl]trialkoxy silane is at least one selected from the group consisting of [(2,3-epoxypropoxy)methyl]trimethoxy silane, [(2,3-epoxypropoxy)methyl]triethoxy silane, [(2,3-epoxypropoxy)methyl]tripropoxy silane, [(2,3-epoxypropoxy)methyl]tributoxy silane, [2-(2,3-epoxypropoxy)ethyl]trimethoxy silane, [2-(2,3-epoxypropoxy)ethyl]triethoxy silane, [2-(2,3-epoxypropoxy)ethyl]tripropoxy silane, [2-(2,3-epoxypropoxy)ethyl]tributoxy silane, [3-(2,3-epoxypropoxy)propyl]trimethoxy silane, [3-(2,3-epoxypropoxy)propyl]triethoxy silane, [3-(2,3-epoxypropoxy)propyl]tripropoxy silane, [3-(2,3-epoxypropoxy)propyl]tributoxy silane, [4-(2,3-epoxypropoxy)butyl]trimethoxy silane, [4-(2,3-epoxypropoxy)butyl]triethoxy silane, [4-(2,3-epoxypropoxy)butyl]tripropoxy silane, [4-(2,3-epoxypropoxy)butyl]tributoxy silane and mixtures thereof.

[10] The polyamide composite membrane according to claim 8, wherein the glycidylalkyltrialkoxy silane is at least one selected from the group consisting of glycidylmethyltrimethoxy silane, glycidylmethyltriethoxy silane, 2-glycidylethyltrimethoxy silane, 2-glycidylethyltriethoxy silane, 3-glycidylpropyltrimethoxy silane, 3-glycidylpropyltriethoxy silane, 3-glycidylpropyltri(methoxyethoxy silane) and mixtures thereof.