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(54) Title: COATED MICROPOROUS MATERIALS HAVING FILTRATION AND ADSORPTION PROPERTIES AND THEIR USE IN FLUID PURIFICATION PROCESSES

(57) **Abstract**: The present invention is directed to microfiltration and ultrafiltration membranes comprising a microporous material. The microporous material comprises: (a) a polyolefin matrix present in an amount of at least 2 percent by weight, (b) finely divided, particulate, substantially water-insoluble silica filler distributed throughout said matrix, said filler constituting from about 10 percent to about 90 percent by weight of said coated microporous material substrate, (c) at least 20 percent by volume of a network of interconnecting pores communicating throughout the coated microporous material, and (d) at least one coating composition applied to at least one surface of the membrane to adjust the surface energy of the membrane.

COATED MICROPOROUS MATERIALS HAVING FILTRATION AND ADSORPTION PROPERTIES AND THEIR USE IN FLUID PURIFICATION PROCESSES

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to United States Application Serial Number 14/077,741, filed on November 12, 2013, which is a continuation-in-part of United States Patent Application Serial Number 13/599,221, filed on August 30, 2012, which in turn claims the benefit of United States Provisional Patent Application number 61/555,500, filed on November 4, 2011, all of which are incorporated herein by reference in their entireties.

FIELD OF THE INVENTION

[0002] The present invention relates to coated microporous materials useful in filtration and adsorption membranes and their use in fluid purification processes.

BACKGROUND OF THE INVENTION

[0003] Accessibility to clean and potable water is a concern throughout the world, particularly in developing countries. The search for low-cost, effective filtration materials and processes is ongoing. Filtration media that can remove both macroscopic, particulate contaminants and molecular contaminants are particularly desired, including those that can remove both hydrophilic and hydrophobic contaminants at low cost and high flux rate.

[0004] It would be desirable to provide novel membranes suitable for use on liquid or gaseous streams that serve to remove contaminants via both chemisorption and physisorption.

SUMMARY OF THE INVENTION

[0005] The present invention is directed to microfiltration and ultrafiltration membranes comprising a microporous material. The microporous material comprises:

(a) a polyolefin matrix present in an amount of at least 2 percent by weight,

(b) finely divided, particulate, substantially water-insoluble silica filler distributed throughout said matrix, said filler constituting from about 10 percent to about 90 percent by weight of said coated microporous material substrate,

(c) at least 20 percent by volume of a network of interconnecting pores communicating throughout the coated microporous material, and

(d) at least one coating composition applied to at least one surface of the membrane to adjust the surface energy of the membrane.

DETAILED DESCRIPTION OF THE INVENTION

[0006] Other than in any operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0007] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[0008] Also, it should be understood that any numerical range recited herein is intended to include all sub-ranges subsumed therein. For example, a range of "1 to 10" is intended to include all sub-ranges between (and including) the recited minimum value of 1 and the recited maximum value of 10, that is, having a minimum value equal to or greater than 1 and a maximum value of equal to or less than 10.

[0009] As used in this specification and the appended claims, the articles "a," "an," and "the" include plural referents unless expressly and unequivocally limited to one referent.

[0010] The various embodiments and examples of the present invention as presented herein are each understood to be non-limiting with respect to the scope of the invention.

[0011] As used in the following description and claims, the following terms have the meanings indicated below:

[0012] By "polymer" is meant a polymer including homopolymers and copolymers, and oligomers. By "composite material" is meant a combination of two or more differing materials.

[0013] As used herein, "formed from" denotes open, e.g., "comprising," claim language. As such, it is intended that a composition "formed from" a list of recited components be a composition comprising at least these recited components, and can further comprise other, nonrecited components, during the composition's formation.

[0014] As used herein, the term "polymeric inorganic material" means a polymeric material having a backbone repeat unit based on an element or elements other than carbon. For more information see James Mark et al., Inorganic Polymers, Prentice Hall Polymer Science and Engineering Series, (1992) at page 5, which is specifically incorporated by reference herein. Moreover, as used herein, the term "polymeric organic materials" means synthetic polymeric materials, semisynthetic polymeric materials and natural polymeric materials, all of which have a backbone repeat unit based on carbon.

[0015] An "organic material," as used herein, means carbon containing compounds wherein the carbon is typically bonded to itself and to hydrogen, and often to other elements as well, and excludes binary compounds such as the carbon oxides, the carbides, carbon disulfide, etc.; such ternary compounds as the metallic cyanides, metallic carbonyls, phosgene, carbonyl sulfide, etc.; and carbon-containing ionic compounds such as metallic carbonates, for example calcium carbonate and sodium carbonate. See R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at pages 761-762, and M. Silberberg, Chemistry The Molecular Nature of Matter and Change (1996) at page 586, which are specifically incorporated by reference herein.

[0016] As used herein, the term "inorganic material" means any material that is not an organic material.

[0017] As used herein, a "thermoplastic" material is a material that softens when exposed to heat and returns to its original condition when cooled to room temperature. As used herein, a "thermoset" material is a material that solidifies or "sets" irreversibly when heated.

[0018] As used herein, "microporous material" or "microporous sheet material" means a material having a network of interconnecting pores, wherein, on a coating-free,

printing ink-free, impregnant-free, and pre-bonding basis, the pores have a volume average diameter ranging from 0.001 to 0.5 micrometer, and constitute at least 5 percent by volume of the material as discussed herein below.

[0019] By "plastomer" is meant a polymer exhibiting both plastic and elastomeric properties.

[0020] As noted above, the present invention is directed to microfiltration and ultrafiltration membranes comprising a microporous material. Microporous materials used in the membranes of the present invention comprise a polyolefin matrix (a). The polyolefin matrix is present in the microporous material in an amount of at least 2 percent by weight. Polyolefins are polymers derived from at least one ethylenically unsaturated monomer. In certain embodiments of the present invention, the matrix comprises a plastomer. For example, the matrix may comprise a plastomer derived from butene, hexene, and/or octene. Suitable plastomers are available from ExxonMobil Chemical under the tradename "EXACT".

[0021] In certain embodiments of the present invention, the matrix comprises a different polymer derived from at least one ethylenically unsaturated monomer, which may be used in place of or in combination with the plastomer. Examples include polymers derived from ethylene, propylene, and/or butene, such as polyethylene, polypropylene, and polybutene. High density and/or ultrahigh molecular weight polyolefins such as high density polyethylene are also suitable.

[0022] In a particular embodiment of the present invention, the polyolefin matrix comprises a copolymer of ethylene and butene.

[0023] Non-limiting examples of ultrahigh molecular weight (UHMW) polyolefin can include essentially linear UHMW polyethylene or polypropylene. Inasmuch as UHMW polyolefins are not thermoset polymers having an infinite molecular weight, they are technically classified as thermoplastic materials.

[0024] The ultrahigh molecular weight polypropylene can comprise essentially linear ultrahigh molecular weight isotactic polypropylene. Often the degree of isotacticity of such polymer is at least 95 percent, e.g., at least 98 percent.

[0025] While there is no particular restriction on the upper limit of the intrinsic viscosity of the UHMW polyethylene, in one non-limiting example, the intrinsic viscosity can range from 18 to 39 deciliters/gram, e.g., from 18 to 32 deciliters/gram. While there is no particular restriction on the upper limit of the intrinsic viscosity of the UHMW

polypropylene, in one non-limiting example, the intrinsic viscosity can range from 6 to 18 deciliters/gram, e.g., from 7 to 16 deciliters/gram.

[0026] For purposes of the present invention, intrinsic viscosity is determined by extrapolating to zero concentration the reduced viscosities or the inherent viscosities of several dilute solutions of the UHMW polyolefin where the solvent is freshly distilled decahydronaphthalene to which 0.2 percent by weight, 3,5-di-tert-butyl-4-hydroxyhydrocinnamic acid, neopentanetetrayl ester [CAS Registry No. 6683-19-8] has been added. The reduced viscosities or the inherent viscosities of the UHMW polyolefin are ascertained from relative viscosities obtained at 135 °C using an Ubbelohde No. 1 viscometer in accordance with the general procedures of ASTM D 4020-81, except that several dilute solutions of differing concentration are employed.

[0027] The nominal molecular weight of UHMW polyethylene is empirically related to the intrinsic viscosity of the polymer in accordance with the following equation:

$$M=5.37 \times 10^4 [ή]^{1.37}$$

[0028] wherein M is the nominal molecular weight and [ή] is the intrinsic viscosity of the UHMW polyethylene expressed in deciliters/gram. Similarly, the nominal molecular weight of UHMW polypropylene is empirically related to the intrinsic viscosity of the polymer according to the following equation:

$$M=8.88 \times 10^4 [ή]^{1.25}$$

wherein M is the nominal molecular weight and [ή] is the intrinsic viscosity of the UHMW polypropylene expressed in deciliters/gram.

[0029] A mixture of substantially linear ultrahigh molecular weight polyethylene and lower molecular weight polyethylene can be used. In certain embodiments, the UHMW polyethylene has an intrinsic viscosity of at least 10 deciliters/gram, and the lower molecular weight polyethylene has an ASTM D 1238-86 Condition E melt index of less than 50 grams/10 minutes, e.g., less than 25 grams/10 minutes, such as less than 15 grams/10 minutes, and an ASTM D 1238-86 Condition F melt index of at least 0.1 gram/10 minutes, e.g., at least 0.5 gram/10 minutes, such as at least 1.0 gram/10 minutes. The amount of UHMW polyethylene used (as weight percent) in this embodiment is described in column 1, line 52 to column 2, line 18 of U.S. Patent 5,196,262, which disclosure is incorporated herein by reference. More particularly,

the weight percent of UHMW polyethylene used is described in relation to Figure 6 of U.S. 5,196,262; namely, with reference to the polygons ABCDEF, GHCI or JHCK of Figure 6, which Figure is incorporated herein by reference.

[0030] The nominal molecular weight of the lower molecular weight polyethylene (LMWPE) is lower than that of the UHMW polyethylene. LMWPE is a thermoplastic material and many different types are known. One method of classification is by density, expressed in grams/cubic centimeter and rounded to the nearest thousandth, in accordance with ASTM D 1248-84 (Reapproved 1989). Non-limiting examples of the densities of LMWPE are found in the following Table 1.

TABLE 1

Type	Abbreviation	Density, g/cm^3
Low Density Polyethylene	LDPE	0.910-0.925
Medium Density Polyethylene	MDPE	0.926-0.940
High Density Polyethylene	HDPE	0.941-0.965

[0031] Any or all of the polyethylenes listed in Table 1 above may be used as the LMWPE in the matrix of the microporous material. HDPE may be used because it can be more linear than MDPE or LDPE. Processes for making the various LMWPE's are well known and well documented. They include the high pressure process, the Phillips Petroleum Company process, the Standard Oil Company (Indiana) process, and the Ziegler process. The ASTM D 1238-86 Condition E (that is, 190° C. and 2.16 kilogram load) melt index of the LMWPE is less than about 50 grams/10 minutes. Often the Condition E melt index is less than about 25 grams/10 minutes. The Condition E melt index can be less than about 15 grams/10 minutes. The ASTM D 1238-86 Condition F (that is, 190° C. and 21.6 kilogram load) melt index of the LMWPE is at least 0.1 gram/10 minutes. In many cases the Condition F melt index is at least 0.5 gram/10 minutes such as at least 1.0 gram/10 minutes.

[0032] The UHMWPE and the LMWPE may together constitute at least 65 percent by weight, e.g., at least 85 percent by weight, of the polyolefin polymer of the microporous

material. Also, the UHMWPE and LMWPE together may constitute substantially 100 percent by weight of the polyolefin polymer of the microporous material.

[0033] In a particular embodiment of the present invention, the microporous material can comprise a polyolefin comprising ultrahigh molecular weight polyethylene, ultrahigh molecular weight polypropylene, high density polyethylene, high density polypropylene, or mixtures thereof.

[0034] If desired, other thermoplastic organic polymers also may be present in the matrix of the microporous material provided that their presence does not materially affect the properties of the microporous material substrate in an adverse manner. The amount of the other thermoplastic polymer which may be present depends upon the nature of such polymer. In general, a greater amount of other thermoplastic organic polymer may be used if the molecular structure contains little branching, few long side chains, and few bulky side groups, than when there is a large amount of branching, many long side chains, or many bulky side groups. Non-limiting examples of thermoplastic organic polymers that optionally may be present in the matrix of the microporous material include low density polyethylene, high density polyethylene, poly(tetrafluoroethylene), polypropylene, copolymers of ethylene and propylene, copolymers of ethylene and acrylic acid, and copolymers of ethylene and methacrylic acid. If desired. all or a portion of the carboxyl groups of carboxyl-containing copolymers can be neutralized with sodium, zinc or the like. Generally, the microporous material comprises at least 70 percent by weight of UHMW polyolefin, based on the weight of the matrix. In a non-limiting embodiment, the above-described other thermoplastic organic polymer are substantially absent from the matrix of the microporous material.

[0035] The microporous materials used in the membranes of the present invention further comprise finely divided, particulate, substantially water-insoluble silica filler (b) distributed throughout the matrix.

[0036] The particulate filler typically comprises precipitated silica particles. It is important to distinguish precipitated silica from silica gel inasmuch as these different materials have different properties. Reference in this regard is made to R. K. Iler, The Chemistry of Silica, John Wiley & Sons, New York (1979). Library of Congress Catalog No. QD 181.S6144, the entire disclosure of which is incorporate herein by reference. Note especially pages 15-29, 172-176, 218-233, 364-365, 462-465, 554-564, and 578-

579. Silica gel is usually produced commercially at low pH by acidifying an aqueous solution of a soluble metal silicate, typically sodium silicate, with acid. The acid employed is generally a strong mineral acid such as sulfuric acid or hydrochloric acid although carbon dioxide is sometimes used. Inasmuch as there is essentially no difference in density between gel phase and the surrounding liquid phase while the viscosity is low, the gel phase does not settle out, that is to say, it does not precipitate. Silica gel, then, may be described as a nonprecipitated, coherent, rigid, three-dimensional network of contiguous particles of colloidal amorphous silica. The state of subdivision ranges from large, solid masses to submicroscopic particles, and the degree of hydration from almost anhydrous silica to soft gelatinous masses containing on the order of 100 parts of water per part of silica by weight.

[0037] Precipitated silica is usually produced commercially by combining an aqueous solution of a soluble metal silicate, ordinarily alkali metal silicate such as sodium silicate, and an acid so that colloidal particles will grow in weakly alkaline solution and be coagulated by the alkali metal ions of the resulting soluble alkali metal salt. Various acids may be used, including the mineral acids, but the preferred acid is carbon dioxide. In the absence of a coagulant, silica is not precipitated from solution at any pH. The coagulant used to effect precipitation may be the soluble alkali metal salt produced during formation of the colloidal silica particles, it may be added electrolyte such as a soluble inorganic or organic salt, or it may be a combination of both.

[0038] Precipitated silica, then, may be described as precipitated aggregates of ultimate particles of colloidal amorphous silica that have not at any point existed as macroscopic gel during the preparation. The sizes of the aggregates and the degree of hydration may vary widely.

[0039] Precipitated silica powders differ from silica gels that have been pulverized in ordinarily having a more open structure, that is, a higher specific pore volume. However, the specific surface area of precipitated silica as measured by the Brunauer, Emmet, Teller (BET) method using nitrogen as the adsorbate, is often lower than that of silica gel.

[0040] Many different precipitated silicas may be employed in the present invention, but the preferred precipitated silicas are those obtained by precipitation from an aqueous solution of sodium silicate using a suitable acid such as sulfuric acid, hydrochloric acid, or carbon dioxide. Such precipitated silicas are themselves known

and processes for producing them are described in detail in the U.S. Pat. No. 2,940,830 and in West German Offenlegungsschrift No. 35 45 615, the entire disclosures of which are incorporated herein by reference, including especially the processes for making precipitated silicas and the properties of the products.

[0041] The precipitated silicas used in the present invention can be produced by a process involving the following successive steps:

(a) an initial stock solution of aqueous alkali metal silicate having the desired alkalinity is prepared and added to (or prepared in) a reactor equipped with means for heating the contents of the reactor,

(b) the initial stock solution within the reactor is heated to the desired reaction temperature,

(c) acidifying agent and additional alkali metal silicate solution are simultaneously added with agitation to the reactor while maintaining the alkalinity value and temperature of the contents of the reactor at the desired values,

(d) the addition of alkali metal silicate to the reactor is stopped, and additional acidifying agent is added to adjust the pH of the resulting suspension of precipitated silica to a desired acid value,

(e) the precipitated silica in the reactor is separated from the reaction mixture, washed to remove by-product salts, and

(f) dried to form the precipitated silica.

[0042] The washed silica solids are then dried using conventional drying techniques. Non-limiting examples of such techniques include oven drying, vacuum oven drying, rotary dryers, spray drying or spin flash drying. Non-limiting examples of spray dryers include rotary atomizers and nozzle spray dryers. Spray drying can be carried out using any suitable type of atomizer, in particular a turbine, nozzle, liquid-pressure or twin-fluid atomizer.

[0043] The washed silica solids may not be in a condition that is suitable for spray drying. For example, the washed silica solids may be too thick to be spray dried. In one aspect of the above-described process, the washed silica solids, e.g., the washed filter cake, are mixed with water to form a liquid suspension and the pH of the suspension adjusted, if required, with dilute acid or dilute alkali, e.g., sodium hydroxide, to from 6 to 7, e.g., 6.5, and then fed to the inlet nozzle of the spray dryer.

[0044] The temperature at which the silica is dried can vary widely but will be below the fusion temperature of the silica. Typically, the drying temperature will range from above 50 °C to less than 700 °C, e.g., from above 100 °C, e.g., 200 °C, to 500 °C. In one aspect of the above-described process, the silica solids are dried in a spray dryer having an inlet temperature of approximately 400 °C and an outlet temperature of approximately 105 °C. The free water content of the dried silica can vary, but is usually in the range of from approximately 1 to 10 wt.%, e.g., from 4 to 7 wt.%. As used herein, the term free water means water that can be removed from the silica by heating it for 24 hours at from 100 °C to 200 °C, e.g., 105 °C.

[0045] In one aspect of the process described herein, the dried silica is forwarded directly to a granulator where it is compacted and granulated to obtain a granular product. Dried silica can also be subjected to conventional size reduction techniques, e.g., as exemplified by grinding and pulverizing. Fluid energy milling using air or superheated steam as the working fluid can also be used. The precipitated silica obtained is usually in the form of a powder.

[0046] Most often, the precipitated silica is rotary dried or spray dried. Rotary dried silica particles have been observed to demonstrate greater structural integrity than spray dried silica particles. They are less likely to break into smaller particles during extrusion and other subsequent processing during production of the microporous material than are spray dried particles. Particle size distribution of rotary dried particles does not change as significantly as does that of spray dried particles during processing. Spray dried silica particles are more friable than rotary dried, often providing smaller particles during processing. It is possible to use a spray dried silica of a particular particle size such that the final particle size distribution in the membrane does not have a detrimental effect on water flux. In certain embodiments, the silica is reinforced; i.e., has a structural integrity such that porosity is preserved after extrusion. More preferred is a precipitated silica in which the initial number of silica particles and the initial silica particle size distribution is mostly unchanged by stresses applied during membrane fabrication. Most preferred is a silica reinforced such that a broad particle size distribution is present in the finished membrane. Blends of different types of dried silica and different sizes of silica may be used to provide unique properties to the membrane. For example, a blend of silicas with a bimodal distribution of particle sizes may be particularly suitable for certain separation processes. It is expected that

external forces applied to silica of any type may be used to influence and tailor the particle size distribution, providing unique properties to the final membrane.

[0047] The surface of the particle can be modified in any manner well known in the art, including, but not limited to, chemically or physically changing its surface characteristics using techniques known in the art. For example, the silica may be surface treated with an anti-fouling moiety such as polyethylene glycol, carboxybetaine, sulfobetaine and polymers thereof, mixed valence molecules, oligomers and polymers thereof and mixtures thereof. Another embodiment may be a blend of silicas in which one silica has been treated with a positively charged moiety and the other silica has been treated with a negatively charged moiety. The silica may also be surface modified with functional groups that allow for targeted removal of specific contaminants in a fluid stream to be purified using the microfiltration membrane of the present invention. Untreated particles may also be used. Silica particles coated with hydrophilic coatings reduce fouling and may eliminate pre-wetting processing. Silica particles coated with hydrophobic coatings also reduce fouling and may aid degassing and venting of a system.

[0048] Precipitated silica typically has an average ultimate particle size of 1 to 100 nanometers.

[0049] The surface area of the silica particles, both external and internal due to pores, can have an impact on performance. High surface area fillers are materials of very small particle size, materials having a high degree of porosity or materials exhibiting both characteristics. Usually the surface area of the filler itself is in the range of from about 125 to about 700 square meters per gram (m^2/g) as determined by the Brunauer, Emmett, Teller (BET) method according to ASTM C 819-77 using nitrogen as the adsorbate but modified by outgassing the system and the sample for one hour at 130°C. Often the BET surface area is in the range of from about 190 to 350 m^2/g, more often, the silica demonstrates a BET surface area of 351 to 700 m^2/g.

[0050] The BET/CTAB quotient is the ratio of the overall precipitated silica surface area including the surface area contained in pores only accessible to smaller molecules, such as nitrogen (BET), to the external surface area (CTAB). This ratio is typically referred to as a measure of microporosity. A high microporosity value, i.e., a high BET/CTAB quotient number, is a high proportion of internal surface – accessible

to the small nitrogen molecule (BET surface area) but not to larger particles - to the external surface (CTAB).

[0051] It has been suggested that the structure, i.e., pores, formed within the precipitated silica during its preparation can have an impact on performance. Two measurements of this structure are the BET/CTAB surface area ratio of the precipitated silica noted above, and the relative breadth (γ) of the pore size distribution of the precipitated silica. The relative breadth (γ) of pore size distribution is an indication of how broadly the pore sizes are distributed within the precipitated silica particle. The lower the γ value, the narrower is the pore size distribution of the pores within the precipitated silica particle.

[0052] The silica CTAB values may be determined using a CTAB solution and the hereinafter described method. The analysis is performed using a Metrohm 751 Titrino automatic titrator, equipped with a Metrohm Interchangeable "Snap-In" 50 milliliter buret and a Brinkmann Probe Colorimeter Model PC 910 equipped with a 550 nm filter. In addition, a Mettler Toledo HB43 or equivalent is used to determine the 105 °C moisture loss of the silica and a Fisher Scientific Centrific™ Centrifuge Model 225 may be used for separating the silica and the residual CTAB solution. The excess CTAB can be determined by auto titration with a solution of Aerosol OT® until maximum turbidity is attained, which can be detected with the probe colorimeter. The maximum turbidity point is taken as corresponding to a millivolt reading of 150. Knowing the quantity of CTAB adsorbed for a given weight of silica and the space occupied by the CTAB molecule, the external specific surface area of the silica is calculated and reported as square meters per gram on a dry-weight basis.

[0053] Solutions required for testing and preparation include a buffer of pH 9.6, cetyl [hexadecyl] trimethyl ammonium bromide (CTAB), dioctyl sodium sulfosuccinate (Aerosol OT) and 1N sodium hydroxide. The buffer solution of pH 9.6 can be prepared by dissolving 3.101 g of orthoboric acid (99%; Fisher Scientific, Inc., technical grade, crystalline) in a one-liter volumetric flask, containing 500 milliliters of deionized water and 3.708 grams of potassium chloride solids (Fisher Scientific, Inc., technical grade, crystalline). Using a buret, 36.85 milliliters of the 1N sodium hydroxide solution was added. The solution is mixed and diluted to volume.

[0054] The CTAB solution is prepared using 11.0 g ± 0.005 g of powdered CTAB (cetyl trimethyl ammonium bromide, also known as hexadecyl trimethyl ammonium

bromide, Fisher Scientific Inc., technical grade) onto a weighing dish. The CTAB powder is transferred to a 2-liter beaker and the weighing dish rinsed with deionized water. Approximately 700 milliliters of the pH 9.6 buffer solution and 1000 milliliters of distilled or deionized water is added to the 2-liter beaker and stirred with a magnetic stir bar. The beaker may be covered and stirred at room temperature until the CTAB powder is totally dissolved. The solution is transferred to a 2-liter volumetric flask, rinsing the beaker and stir bar with deionized water. The bubbles are allowed to dissipate, and the solution diluted to volume with deionized water. A large stir bar can be added and the solution mixed on a magnetic stirrer for approximately 10 hours. The CTAB solution can be used after 24 hours and for only 15 days. The Aerosol OT® (dioctyl sodium sulfosuccinate, Fisher Scientific Inc., 100% solid) solution may be prepared using 3.46 g ± 0.005 g, which is placed onto a weighing dish. The Aerosol OT on the weighing dish is rinsed into a 2- liter beaker, which contains about 1500 milliliter deionized water and a large stir bar. The Aerosol OT solution is dissolved and rinsed into a 2-liter volumetric flask. The solution is diluted to the 2-liter volume mark in the volumetric flask. The Aerosol OT® solution is allowed to age for a minimum of 12 days prior to use. The shelf life of the Aerosol OT solution is 2 months from the preparation date.

[0055] Prior to surface area sample preparation, the pH of the CTAB solution should be verified and adjusted as necessary to a pH of 9.6 ± 0.1 using 1N sodium hydroxide solution. For test calculations a blank sample should be prepared and analyzed. 5 milliliters of the CTAB solution are pipetted and 55 milliliters deionized water added into a 150-milliliter beaker and analyzed on a Metrohm 751 Titrino automatic titrator. The automatic titrator is programmed for determination of the blank and the samples with the following parameters: Measuring point density = 2, Signal drift = 20, Equilibrium time = 20 seconds, Start volume = 0 ml, Stop volume = 35 ml, and Fixed endpoint = 150 mV. The buret tip and the colorimeter probe are placed just below the surface of the solution, positioned such that the tip and the photo probe path length are completely submerged. Both the tip and photo probe should be essentially equidistant from the bottom of the beaker and not touching one another. With minimum stirring (setting of 1 on the Metrohm 728 stirrer) the colorimeter is set to 100 %T prior to every blank and sample determination and titration initiated with the

Aerosol OT® solution. The end point can be recorded as the volume (ml) of titrant at 150 mV.

[0056] For test sample preparation, approximately 0.30 grams of powdered silica was weighed into a 50-milliliter container containing a stir bar. Granulated silica samples, were riffled (prior to grinding and weighing) to obtain a representative sub-sample. A coffee mill style grinder was used to grind granulated materials. Then 30 milliliters of the pH adjusted CTAB solution was pipetted into the sample container containing the 0.30 grams of powdered silica. The silica and CTAB solution was then mixed on a stirrer for 35 minutes. When mixing was completed, the silica and CTAB solution were centrifuged for 20 minutes to separate the silica and excess CTAB solution. When centrifuging was completed, the CTAB solution was pipetted into a clean container minus the separated solids, referred to as the "centrifugate". For sample analysis, 50 milliliters of deionized water was placed into a 150-milliliter beaker containing a stir bar. Then 10 milliliters of the sample centrifugate was pipetted for analysis into the same beaker. The sample was analyzed using the same technique and programmed procedure as used for the blank solution.

[0057] For determination of the moisture content, approximately 0.2 grams of silica was weighed onto the Mettler Toledo HB43 while determining the CTAB value. The moisture analyzer was programmed to 105 ° C with the shut-off 5 drying criteria. The moisture loss was recorded to the nearest + 0.1%.

[0058] The external surface area is calculated using the following equation,

$$\text{CTAB Surface Area (dried basis) } [m^2/g] = \frac{(2V_o - V) \times (4774)}{(V_o W) \times (100 - \text{Vol})}$$

wherein,

V_o = Volume in ml of Aerosol OT® used in the blank titration.

V = Volume in ml of Aerosol OT® used in the sample titration.

W = sample weight in grams.

Vol = % moisture loss (Vol represents "volatiles").

[0059] Typically, the CTAB surface area of the silica particles used in the present invention ranges from 120 to 500 m^2/g. Often, the silica demonstrates a CTAB surface area of 170-280 m^2/g. More often, the silica demonstrates a CTAB surface area of 281-500 m^2/g.

[0060] In certain embodiments of the present invention, the BET value of the precipitated silica will be a value such that the quotient of the BET surface area in square meters per gram to the CTAB surface area in square meters per gram is equal to or greater than 1.0. Often, the BET to CTAB ratio is 1.0-1.5. More often, the BET to CTAB ratio is 1.5-2.0.

[0061] The BET surface area values reported in the examples of this application were determined in accordance with the Brunauer-Emmet-Teller (BET) method in accordance with ASTM D1993-03. The BET surface area can be determined by fitting five relative-pressure points from a nitrogen sorption isotherm measurement made with a Micromeritics TriStar 3000™ instrument. A flow Prep-060™ station provides heat and a continuous gas flow to prepare samples for analysis. Prior to nitrogen sorption, the silica samples are dried by heating to a temperature of 160 °C in flowing nitrogen (P5 grade) for at least one (1) hour.

[0062] The filler particles can constitute from 10 to 90 percent by weight of the microporous material. For example, such filler particles can constitute from 25 to 90 percent by weight of the microporous material, such as from 30 percent to 90 percent by weight of the microporous material, or from 40 to 90 percent by weight of the microporous material, or from 50 to 90 percent by weight of the microporous material and even from 60 percent to 90 percent by weight of the microporous material. The filler is typically present in the microporous material of the present invention in an amount of 50 percent to about 85 percent by weight of the microporous material. Often the weight ratio of silica to polyolefin in the microporous material is 0.5:1 to 10:1, such as 1.7:1 to 3.5:1. Alternatively the weight ratio of filler to polyolefin in the microporous material may be greater than 4:1.

[0063] The microporous material used in the membrane of the present invention further comprises a network of interconnecting pores (c) communicating throughout the microporous material.

[0064] On an impregnant-free basis, such pores can comprise at least 15 percent by volume, e.g. from at least 20 to 95 percent by volume, or from at least 25 to 95 percent by volume, or from 35 to 70 percent by volume of the microporous material. Often the pores comprise at least 35 percent by volume, or even at least 45 percent by volume of the microporous material. Such high porosity provides higher surface area

throughout the microporous material, which in turn facilitates removal of contaminants from a fluid stream and higher flux rates of a fluid stream through the membrane.

[0065] As used herein and in the claims, the porosity (also known as void volume) of the microporous material, expressed as percent by volume, is determined according to the following equation:

$$\text{Porosity} = 100[1 - d_1 / d_2]$$

wherein d_1 is the density of the sample, which is determined from the sample weight and the sample volume as ascertained from measurements of the sample dimensions, and d_2 is the density of the solid portion of the sample, which is determined from the sample weight and the volume of the solid portion of the sample. The volume of the solid portion of the same is determined using a Quantachrome stereopycnometer (Quantachrome Corp.) in accordance with the accompanying operating manual.

[0066] The volume average diameter of the pores of the microporous material can be determined by mercury porosimetry using an Autopore III porosimeter (Micromeretics, Inc.) in accordance with the accompanying operating manual. The volume average pore radius for a single scan is automatically determined by the porosimeter. In operating the porosimeter, a scan is made in the high pressure range (from 138 kilopascals absolute to 227 megapascals absolute). If approximately 2 percent or less of the total intruded volume occurs at the low end (from 138 to 250 kilopascals absolute) of the high pressure range, the volume average pore diameter is taken as twice the volume average pore radius determined by the porosimeter. Otherwise, an additional scan is made in the low pressure range (from 7 to 165 kilopascals absolute) and the volume average pore diameter is calculated according to the equation:

$$d = 2 [v_1 r_1 / w_1 + v_2 r_2 / w_2] / [v_1 / w_1 + v_2 / w_2]$$

wherein d is the volume average pore diameter, v_1 is the total volume of mercury intruded in the high pressure range, v_2 is the total volume of mercury intruded in the low pressure range, r_1 is the volume average pore radius determined from the high pressure scan, r_2 is the volume average pore radius determined from the low pressure scan, w_1 is the weight of the sample subjected to the high pressure scan, and w_2 is the weight of the sample subjected to the low pressure scan. For ultrafiltration membranes, the volume average diameter of the pores (mean pore size) is typically

less than 0.1 micrometers (microns), and can be in the range of from 0.001 to 0.70 micrometers, e.g., from 0.30 to 0.70 micrometers. For microfiltration membranes, the mean pore size is typically greater than 0.1 micrometers (microns),

[0067] In the course of determining the volume average pore diameter of the above procedure, the maximum pore radius detected is sometimes noted. This is taken from the low pressure range scan, if run; otherwise it is taken from the high pressure range scan. The maximum pore diameter is twice the maximum pore radius. Inasmuch as some production or treatment steps, e.g., coating processes, printing processes, impregnation processes and/or bonding processes, can result in the filling of at least some of the pores of the microporous material, and since some of these processes irreversibly compress the microporous material, the parameters in respect of porosity, volume average diameter of the pores, and maximum pore diameter are determined for the microporous material prior to the application of one or more of such production or treatment steps.

[0068] To prepare the microporous materials of the present invention, filler, polymer powder (polyolefin polymer), processing plasticizer, and minor amounts of lubricant and antioxidant are mixed until a substantially uniform mixture is obtained. The weight ratio of filler to polymer powder employed in forming the mixture is essentially the same as that of the microporous material substrate to be produced. The mixture, together with additional processing plasticizer, is introduced to the heated barrel of a screw extruder. Attached to the extruder is a die, such as a sheeting die, to form the desired end shape.

[0069] In an exemplary manufacturing process, when the material is formed into a sheet or film, a continuous sheet or film formed by a die is forwarded to a pair of heated calender rolls acting cooperatively to form continuous sheet of lesser thickness than the continuous sheet exiting from the die. The final thickness may depend on the desired end-use application. The microporous material may have a thickness ranging from 0.7 to 18 mil (17.8 to 457.2 microns), such as 0.7 to 15 mil (17.8 to 381 microns), or 1 to 10 mil (25.4 to 254 microns), or 5 to 10 mil (127 to 254 microns), and demonstrates a bubble point of 10 to 80 psi based on ethanol.

[0070] Optionally, the sheet exiting the calendar rolls may then be stretched in at least one stretching direction above the elastic limit, depending on whether the membrane being formed is to be for microfiltration or ultrafiltration. Stretching may alternatively

take place during or immediately after exiting from the sheeting die or during calendaring, or multiple times, but it is typically done prior to extraction. Stretched microporous material substrate may be produced by stretching the intermediate product in at least one stretching direction above the elastic limit. Usually the stretch ratio is at least about 1.5. In many cases the stretch ratio is at least about 1.7. Preferably it is at least about 2. Frequently the stretch ratio is in the range of from about 1.5 to about 15. Often the stretch ratio is in the range of from about 1.7 to about 10. Usually the stretch ratio is in the range of from about 2 to about 6. However, care should be taken that stretching does not result in pore sizes too large for ultrafiltration.

[0071] The temperatures at which stretching is accomplished may vary widely. Stretching may be accomplished at about ambient room temperature, but usually elevated temperatures are employed. The intermediate product may be heated by any of a wide variety of techniques prior to, during, and/or after stretching. Examples of these techniques include radiative heating such as that provided by electrically heated or gas fired infrared heaters. convective heating such as that provided by recirculating hot air, and conductive heating such as that provided by contact with heated rolls. The temperatures which are measured for temperature control purposes may vary according to the apparatus used and personal preference. For example, temperature-measuring devices may be placed to ascertain the temperatures of the surfaces of infrared heaters, the interiors of infrared heaters, the air temperatures of points between the infrared heaters and the intermediate product, the temperatures of circulating hot air at points within the apparatus, the temperature of hot air entering or leaving the apparatus, the temperatures of the surfaces of rolls used in the stretching process, the temperature of heat transfer fluid entering or leaving such rolls, or film surface temperatures. In general, the temperature or temperatures are controlled such that the intermediate product is stretched about evenly so that the variations, if any, in film thickness of the stretched microporous material are within acceptable limits and so that the amount of stretched microporous material outside of those limits is acceptably low. It will be apparent that the temperatures used for control purposes may or may not be close to those of the intermediate product itself since they depend upon the nature of the apparatus used, the locations of the temperature-measuring devices, and the identities of the substances or objects whose temperatures are being measured.

[0072] In view of the locations of the heating devices and the line speeds usually employed during stretching, gradients of varying temperatures may or may not be present through the thickness of the intermediate product. Also because of such line speeds, it is impracticable to measure these temperature gradients. The presence of gradients of varying temperatures, when they occur, makes it unreasonable to refer to a singular film temperature. Accordingly, film surface temperatures, which can be measured, are best used for characterizing the thermal condition of the intermediate product.

[0073] These are ordinarily about the same across the width of the intermediate product during stretching although they may be intentionally varied, as for example, to compensate for intermediate product having a wedge-shaped cross-section across the sheet. Film surface temperatures along the length of the sheet may be about the same or they may be different during stretching.

[0074] The film surface temperatures at which stretching is accomplished may vary widely, but in general they are such that the intermediate product is stretched about evenly, as explained above. In most cases, the film surface temperatures during stretching are in the range of from about 20°C to about 220°C. Often such temperatures are in the range of from about 50°C to about 200°C. From about 75°C to about 180°C is preferred.

[0075] Stretching may be accomplished in a single step or a plurality of steps as desired. For example, when the intermediate product is to be stretched in a single direction (uniaxial stretching), the stretching may be accomplished by a single stretching step or a sequence of stretching steps until the desired final stretch ratio is attained. Similarly, when the intermediate product is to be stretched in two directions (biaxial stretching), the stretching can be conducted by a single biaxial stretching step or a sequence of biaxial stretching steps until the desired final stretch ratios are attained. Biaxial stretching may also be accomplished by a sequence of one of more uniaxial stretching steps in one direction and one or more uniaxial stretching steps in another direction. Biaxial stretching steps where the intermediate product is stretched simultaneously in two directions and uniaxial stretching steps may be conducted in sequence in any order. Stretching in more than two directions is within contemplation. It may be seen that the various permutationes of steps are quite numerous. Other

steps, such as cooling, heating, sintering, annealing, reeling, unreeling, and the like, may optionally be included in the overall process as desired.

[0076] Various types of stretching apparatus are well known and may be used to accomplish stretching of the intermediate product. Uniaxial stretching is usually accomplished by stretching between two rollers wherein the second or downstream roller rotates at a greater peripheral speed than the first or upstream roller. Uniaxial stretching can also be accomplished on a standard tentering machine. Biaxial stretching may be accomplished by simultaneously stretching in two different directions on a tentering machine. More commonly, however, biaxial stretching is accomplished by first uniaxially stretching between two differentially rotating rollers as described above, followed by either uniaxially stretching in a different direction using a tenter machine or by biaxially stretching using a tenter machine. The most common type of biaxial stretching is where the two stretching directions are approximately at right angles to each other. In most cases where continuous sheet is being stretched, one stretching direction is at least approximately parallel to the long axis of the sheet (machine direction) and the other stretching direction is at least approximately perpendicular to the machine direction and is in the plane of the sheet (transverse direction).

[0077] Stretching the sheets prior to extraction of the processing plasticizer allows for larger pore sizes than in microporous materials conventionally processed, thus making the microporous material particularly suitable for use in the microfiltration membranes of the present invention. It is also believed that stretching of the sheets prior to extraction of the processing plasticizer minimizes thermal shrinkage after processing.

[0078] The product passes to a first extraction zone where the processing plasticizer is substantially removed by extraction with an organic liquid which is a good solvent for the processing plasticizer, a poor solvent for the organic polymer, and more volatile than the processing plasticizer. Usually, but not necessarily, both the processing plasticizer and the organic extraction liquid are substantially immiscible with water. The product then passes to a second extraction zone where the residual organic extraction liquid is substantially removed by steam and/or water. The product is then passed through a forced air dryer for substantial removal of residual water and remaining residual organic extraction liquid. From the dryer the microporous material may be passed to a take-up roll, when it is in the form of a sheet.

[0079] The processing plasticizer has little solvating effect on the thermoplastic organic polymer at 60°C, only a moderate solvating effect at elevated temperatures on the order of about 100°C, and a significant solvating effect at elevated temperatures on the order of about 200°C. It is a liquid at room temperature and usually it is processing oil such as paraffinic oil, naphthenic oil, or aromatic oil. Suitable processing oils include those meeting the requirements of ASTM D 2226-82, Types 103 and 104. Those oils which have a pour point of less than 22°C, or less than 10°C, according to ASTM D 97-66 (reapproved 1978) are used most often. Examples of suitable oils include Shellflex® 412 and Shellflex® 371 oil (Shell Oil Co.) which are solvent refined and hydrotreated oils derived from naphthenic crude. It is expected that other materials, including the phthalate ester plasticizers such as dibutyl phthalate, bis(2-ethylhexyl) phthalate, diisodecyl phthalate, dicyclohexyl phthalate, butyl benzyl phthalate, and ditridecyl phthalate will function satisfactorily as processing plasticizers.

[0080] There are many organic extraction liquids that can be used. Examples of suitable organic extraction liquids include 1,1,2-trichloroethylene, perchloroethylene, 1,2-dichloroethane. 1,1,1-trichloroethane, 1,1,2-trichloroethane, methylene chloride, chloroform, isopropyl alcohol, diethyl ether and acetone.

[0081] In the above described process for producing microporous material substrate, extrusion and calendering are facilitated when the filler carries much of the processing plasticizer. The capacity of the filler particles to absorb and hold the processing plasticizer is a function of the surface area of the filler. Therefore the filler typically has a high surface area as discussed above. Inasmuch as it is desirable to essentially retain the filler in the microporous material substrate, the filler should be substantially insoluble in the processing plasticizer and substantially insoluble in the organic extraction liquid when microporous material substrate is produced by the above process.

[0082] The residual processing plasticizer content is usually less than 15 percent by weight of the resulting microporous material and this may be reduced even further to levels such as less than 5 percent by weight, by additional extractions using the same or a different organic extraction liquid.

[0083] The resulting microporous materials may be further processed depending on the desired application. In the present invention, a hydrophilic coating may be applied to the surface of the microporous material to adjust the surface energy of the material.

Though not intending to be bound by theory, it is believed that components of the coating interact with the silica particles in the filler of the microporous material and adjust the surface energy, affecting wettability. Application of the coating may occur before, during, or after the stretching step described above, but is usually done simultaneously with stretching to maximize coating coverage on additional surface area created during the stretching process.

[0084] Hydrophilic coatings may comprise one or more of a polyoxazoline, including polyalkyloxazolines such as poly(2-ethyl-2-oxazoline), poly(2-methyl-2-oxazoline), and poly(2-methyl/ethyl-2-oxazoline); triblock copolymers based on poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol); polyethyleneimine; polyamide; oxidized polyethylene or its derivatives; polyethyleneoxide; polyethyleneglycol; polyvinylpyrrolidone; polyacrylic acid; polymethacrylic acid; polyethylene glycol derivatives; polypropylene oxide or its derivatives; a copolymer of poly(ethylene glycol) and polyethyleneoxide; polyvinyl alcohol; ethylene vinyl acetate; cellulose or its derivatives; polyimide; hydrogels such as collagen, polypeptides, guar and pectin; polypeptoids; poly(meth)acrylates such as poly(2-hydroxyethylmethacrylate); poly(meth)acrylamide; polysaccharides; zwitterionic polymers such as poly(phosphorylcholine) derivatives, polysulfobetaines, and polycarbobetaines; polyampholytes, and polyethylenimine. The hydrophilic coating preferably comprises at least one polymer having tertiary amine functional groups, such as poly(2-ethyl-2-oxazoline).

[0085] In certain embodiments, the coating compositions used in the methods of the present invention comprise one or more suitable surfactants to reduce surface tension. Surfactants include materials otherwise known as wetting agents, anti-foaming agents, emulsifiers, dispersing agents, leveling agents etc. Surfactants can be anionic, cationic and nonionic, and many surfactants of each type are available commercially. Some coating compositions include at least a wetting agent. Still other coating compositions may have additional surfactants to perform additional effects.

[0086] Other suitable surfactants may also be selected. The amount and number of surfactants added to the coating compositions will depend on the particular surfactant(s) selected, but should be limited to the minimum amount of surfactant that is necessary to achieve wetting of the substrate while not compromising the performance of the dried coating. In certain embodiments, the coating compositions

comprise 0.01 up to 10 percent by weight of surfactant, in some embodiments, 0.05 up to 5 percent by weight, or, in yet other embodiments, 0.1 up to 3 percent by weight of surfactant. The amount of surfactant present in the coating compositions can range between any combination of these values inclusive of the recited values. The use of coating compositions in the membranes of the present invention allows for their use in separation systems without the need for pre-wetting of the membrane such as with isopropanol.

[0087] The microporous material may be adhered to a support layer such as a fiberglass layer to provide additional structural integrity, depending on the particular end use. Additional optional stretching of the continuous sheet in at least one stretching direction may also be done during or immediately after any of the steps upon extrusion in step (ii). For example, in the production of an ultrafiltration membrane of the present invention, preparation of the microporous material may include stretching of the continuous sheet during calendering, to allow for pore sizes in the upper range of ultrafiltration. Typically, however, in the production of an ultrafiltration membrane of the present invention, preparation of the microporous material does not include stretching steps.

[0088] The microporous materials prepared as described above are suitable for use in the microfiltration and ultrafiltration membranes of the present invention, capable of removing particulates from a fluid stream ranging in size from 0.005 to 0.1 microns (ultrafiltration) and capable of removing particulates from a fluid stream ranging in size from 0.05 to 1.5 microns (microfiltration). The membranes also serve to remove molecular contaminants from a fluid stream by adsorption or by physical rejection due to molecular size.

[0089] The membranes of the present invention may be used in a method of separating suspended or dissolved materials from a fluid stream, such as removing one or more contaminants from a fluid (liquid or gaseous) stream, or concentrating desired components in a depleted stream. The method comprises contacting the stream with the membrane, typically by passing the stream through the membrane. Examples of contaminants include toxins, such as neurotoxins; heavy metal; hydrocarbons; oils; dyes; neurotoxins; pharmaceuticals; and/or pesticides. The fluid stream (such as a water stream, but it may be liquid or gas) is usually passed through the membrane at a flux rate of at least 1, for example, 1 to 10000 gal/(ft^2 day) (GFD),

at 25 psi, without the use of pre-wetting agents. Ultrafiltration membranes may demonstrate a water flux rate of greater than 100 GFD, preferably greater than 150 GFD, and a molecular weight cut-off of 100 to 500,000, while microfiltration membranes may demonstrate a water flux rate of greater than 300 GFD, preferably greater than 500 GFD. The membranes of the present invention demonstrate a Gurley number of less than 2000 seconds.

[0090] Coated membranes comprising microporous material coated with hydrophilic coating compositions demonstrate a water contact angle less than 70°, often less than 30°, more often less than 10°.

EXAMPLES

In Part I of the following examples, the materials and methods used to prepare the microporous sheet materials are described. In Part II, the methods and conditions used to stretch the microporous sheet materials are described. Part III describes the coating formulations and methods used to coat the microporous sheet materials. The physical properties of the Examples (coated) and Comparative Examples (uncoated) are presented in Part IV.

Part I – Preparation of Microporous Sheet Materials

The dry ingredients of Example 1 were separately weighed into a FM-130D Littleford plough blade mixer with one high intensity chopper style mixing blade in the order and amounts specified in Table 1. The dry ingredients were premixed for 15 seconds using the plough blades only. The process oil was then pumped in via a double diaphragm pump through a spray nozzle at the top of the mixer over a period of about 45-60 seconds, with only the plough blades running. The high intensity chopper blade was then turned on, along with the plough blades, and mixing continued for 30 seconds. The mixer was shut off and the internal sides of the mixer were scraped down to ensure all ingredients were evenly mixed. The mixer was turned back on with both the high intensity chopper and plough blades in use, and the mixing continued for an additional 30 seconds. The resulting mixture of dry ingredients was extruded and calendered into sheet form as follows. A gravimetric loss in weight feed system (K-tron model # K2MLT35D5) was used to feed the mix into a 27 millimeter twin screw extruder (Leistritz Micro-27 mm). The extruder barrel was comprised of eight temperature zones and a heated adaptor to the sheet die. The extrusion mixture feed port was located just prior to the first temperature zone.

An atmospheric vent was located in the third temperature zone. A vacuum vent was located in the seventh temperature zone.

The mixture was fed into the extruder at a rate of 90 grams/minute. Additional processing oil also was injected at the first temperature zone, as required, to achieve the desired total oil content in the extruded sheet.

Examples 2 and 3 were prepared, extruded and calendered into final sheet form using an extrusion system that was production sized. The version of the system is similar to the equipment and procedures described above for Example 1 except for the size of the equipment. The oil contained in the extruded sheet (extrudate) being discharged from the extruder is referenced herein as the extrudate oil weight fraction, which is based on the total weight of the sample. The arithmetic average of the extrudate oil weight fraction for all of the samples was 0.57.Residual oil in each of Examples 1, 2 and 3 was removed using a 1,1,2-trichloroethylene oil extraction process.

Table 1: Formulation of the microporous membrane sheet

Ingredient	Example 1	Example 2	Example 3
GUR® 4150[1]	1.44	144	136
FINA® 1288[2]	1.44	144	136
Hi-Sil® 135[3]	5.00	500	500
SYNPRO® 1580[4]	0.05	4	4
IRGANOX® B215[5]	0.03	4	4
TUFFLO® 6056[6]	8.39	835	835

[1]An Ultra High Molecular Weight Polyethylene (UHMWPE), obtained commercially from Ticona Corp and reported to have a molecular weight of about 9.2 million grams per mole.
[2]A High Density Polyethylene (HDPE), obtained commercially from Total Petrochemicals.
[3]A precipitated silica available from PPG Industries, Inc.
[4]Reported to be a calcium-zinc stearate lubricant, obtained commercially from Ferro
[5]A processing and thermal stabilizing blend of antioxidants, obtained commercially from BASF.
[6]A process oil, obtained commercially from PPC Lubricants.

Part II – Preparation of Stretched Sheet Microporous Materials

Stretching was conducted by Parkinson Technologies, Inc. using the Marshall and Williams Biaxial Orientation Plastic Processing System. The Machine Direction Oriented (MDO) stretching of the material from Part II was accomplished by heating the microporous sheet of Examples 2 and 3 and stretching it in the machine direction over a series of rollers maintained at the temperatures listed in Table 2.

Transverse Direction Orientation (TDO) stretching was conducted after MDO stretching by heating the resultant sheets according to the temperature conditions listed in Table 2, and stretching in the transverse (or cross) direction on a tenter frame, consisting of two horizontal chain tracks, on which clip and chain assemblies held the material in place. The combination of MDO and TDO conditions provided biaxial stretching of the material.

Table 2: Microporous sheet stretching conditions:

Example		4	5	6
Microporous sheet material		Ex. 2	Ex. 3	Ex. 3
MCO	Stretch roll (°C)	132	132	132
	Anneal roll (°C)	141	141	141
	Cooling (°C)	25	25	25
	Slow draw speed, FPM	10.4	10.4	10.4
	Fast Roll Speed, FPM	35	35	40
TDO	Stretch ratio	2	3	NA
	Preheat (°C)	132	132	NA
	Stretching (°C)	132	132	NA
	Anneal (°C)	141	141	NA

Part III – Hydrophilic coating formulations:

a) Preparation of hydrophilic coatings:

The hydrophilic coating Examples A, B and C were prepared according to the ingredients and quantities listed in Table 3. The first ingredient of the corresponding Example was dissolved in the specified quantity of deionized water with vigorous stirring. Upon complete dissolution, Pluronic 17R2 was added, followed by butoxyethanol. The coating solutions were stirred gently for a minimum of 30 minutes before proceeding.

Table 3: Hydrophilic coating formulation

Example	A	B	C
Polyethyleneoxazoline[1] (g)	7.5		
Chitosan[2] (g)		10	
PVP-K90[3] (g)			5
Deionized Water (g)	457	480	480
PLURONIC® 17R2[4] (g)	5	5	5
Butoxyethanol (g)	30	5	10

[1]Molecular weight 50,000, available from SigmaAldrich.
[2]Chitosan from shrimp shells, practial grade, available from SigmaAldrich.
[3]Polyvinylpyrrolidone with average Mw 360,000, available from SigmaAldrich.
[4]Block copolymer surfactant, available from BASF Corporation.

b) Procedure for coating microporous materials:

The microporous materials described in the previous Examples were cut into sheets 12 inches square. The hydrophilic coating compositions were applied by dipping the microporous materials of the previous examples into a Pyrex dish containing sufficient hydrophilic coating to completely submerge the sheet. The sheet was submerged in the hydrophilic coating for about 5 minutes. The sheet was then removed from the solution and excess coating solution was allowed to drip off. The coated microporous material was then clamped in an aluminum frame which was fitted with a gasket to prevent the film from shrinking during drying. The frame with film then was dried in an oven at 95°C for 15 minutes. The stretched microporous material of Example 4 was coated with each of the coating solutions of Examples A, B and C in this manner. The stretched microporous materials of Examples 5 and 6 and the unstretched microporous material of Example 1 were coated with the coating formulation of Example A.

Part IV – Properties:

The stretched microporous materials of Examples 4, 5 and 6 and the unstretched microporous material of Example 1 were tested for properties and water permeability with and without a hydrophilic coating applied.

Table 6 demonstrates the differences between the microporous material of Example 4 with and without a hydrophilic coating composition. Tables 7 and 8 illustrate the water permeability of various microporous materials with and without a

hydrophilic coating composition. Properties were determined using the methods described below:

a) Thickness was determined by using an Ono Sokki thickness gauge EG-225. The thickness reported is the average of 9 measurements.

b) Porosity was determined using a Gurley Precision Densometer, model 4340, manufactured by GPI Gurley Precision Instruments of Troy, New York.

c) The maximum elongation or tensile energy to break the samples was determined following the procedure of ASTM D-882-02. Samples were tested oriented such that the stress was applied in the machine direction ("MD") and the transverse direction ("TD") as described in Part II.

d) Contact angle was measured on a VCA 2500XE video contact angle system, available from AST Products, Inc. using 1 microliter of ultrapure water.

e) Water flux testing was carried out on a Sepa CF II cross flow test cell apparatus provided by Sterlitech Corp, Kent WA at 20 psi and 25°C, with an effective membrane area of 140cm^2.

f) Water intrusion pressure was determined on a circular sample with an area of 90cm^2. The sample was sandwiched in a dead end filter provided by Sterlitech Corp, Kent WA. 100mL of water was placed on top of the sample. Pressure was applied in 5 psi increments, holding 15 minutes between pressure increments. The test pressure was recorded when the first drop water was visible passing through the sample.

g) Pore volume: The pore volume, expressed as percent by volume, is determined according to the following equation

$$Porosity = 100(1 - \frac{d1}{d2})$$

Where, d_1 is the density of the sample, which is determined from the same weight and the sample dimensions, and d_2 is the density of the solid portion of the sample, which is determined from the sample weight and the volume of the solid portion of the sample. The volume of the solid portion of the same is determined using a Stereopycnometer (Quantachrome Corp.) in accordance with the accompanying operating manual.

Table 6: Physical properties of uncoated and hydrophilically coated microporous material

Example	CE-4	4A
Microporous Material	Example 4	Example 4
Hydrophilic coating	None	Example A
Thickness (micron)	110	115
Gurley (sec)	36	35
Contact angle	>100°	<20°
MD Maximum elongation	15	14
MD Maximum tension	3550	2970
TD Maximum elongation	63	85
TD Maximum tension	279	175

Table 7: Water permeability of uncoated microporous materials:

Comparative Example	CE-1	CE-4	CE-5	CE-6
Microporous Material	Ex. 1	Ex. 4	Ex. 5	Ex. 6
Water flux @ 20psi (GFD)	<1*	<1*	<1*	<1*
Water intrusion pressure (psi)	>60	>40	>40	>45
Pore volume (%)	>60	>80	>80	>80

* No detectable volume observed after 30 minutes @ 20psi.

Table 8: Water permeability of microporous materials with hydrophilic coating:

Example	1A	4A	4B	4C	5A	6A
Microporous Material	Ex. 1	Ex. 4	Ex. 4	Ex. 4	Ex. 5	Ex. 6
Hydrophilic Coating	Ex. A	Ex. A	Ex. B	Ex. C	Ex. A	Ex. A
Water flux @ 20psi (GFD)	283	884	990	1060	1308	707

Water intrusion pressure (psi)	<5	<5	<5	<5	<5	<5
Water wetable time (sec)	<5	<5	<5	<5	<5	<5
Pore Volume (%)	>60	>80	>80	>80	>80	>80

[0091] Whereas particular embodiments of this invention have been described above for purposes of illustration, it will be evident to those skilled in the art that numerous variations of the details of the present invention may be made without departing from the scope of the invention as defined in the appended claims.

What is claimed is:

1. A coated filtration membrane comprising a coated microporous material, said coated microporous material comprising:

(a) a polyolefin matrix present in an amount of at least 2 percent by weight,

(b) finely divided, particulate, substantially water-insoluble silica filler distributed throughout said matrix, said filler constituting from about 10 percent to about 90 percent by weight of said coated microporous material substrate,

(c) at least 20 percent by volume of a network of interconnecting pores communicating throughout the coated microporous material, and

(d) at least one coating composition applied to at least one surface of the membrane to adjust the surface energy of the membrane; wherein the coated membrane demonstrates a water contact angle less than 70°.

2. The membrane of claim 1, wherein the coated membrane demonstrates a water contact angle less than 30°.

3. The membrane of claim 1, wherein the coated membrane demonstrates an initial water flux of at least 1 GFD at 25 psi without any applied pre-wetting agent.

4. The membrane of claim 1, wherein the polyolefin matrix comprises essentially linear ultrahigh molecular weight polyolefin which is essentially linear ultrahigh molecular weight polyethylene having an intrinsic viscosity of at least about 18 deciliters/gram, essentially linear ultrahigh molecular weight polypropylene having an intrinsic viscosity of at least about 6 deciliters/gram, or a mixture thereof.

5. The membrane of claim 4 wherein the matrix further comprises high density polyethylene and/or low density polyethylene.

6. The membrane of claim 1 wherein the membrane is an ultrafiltration membrane and the mean pore size is less than 0.1 microns.

7. The membrane of claim 6, wherein the coated microporous material demonstrates a molecular weight cut-off of 100-500,000.

8. The membrane of claim 1 wherein the membrane is a microfiltration membrane and the mean pore size is greater than 0.1 microns.

9. The membrane of claim 1 wherein the coated microporous material has a thickness ranging from 0.7 mil to 18 mil (17.8 to 457.2 microns).

10. The membrane of claim 1, wherein the coating applied to the surface of the material comprises a hydrophilic coating.

11. The membrane of claim 10 wherein the hydrophilic coating comprises one or more of a polyoxazoline, triblock copolymers based on poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol), polyethyleneimine, polyamide, oxidized polyethylene or its derivatives, polyethyleneoxide, polyethyleneglycol, polyvinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyethylene glycol derivatives, polypropylene oxide or its derivatives, a copolymer of poly(ethylene glycol) and polyethyleneoxide, polyvinyl alcohol, ethylene vinyl acetate, cellulose or its derivatives, collagen, polypeptides, guar, pectin, polyimide, polypeptoid, poly(meth)acrylate, poly(meth)acrylamide, polysaccharides, zwitterionic polymers, polyampholytes, and polyethylenimine.

12. The membrane of claim 10 wherein the hydrophilic coating comprises at least one polymer having tertiary amine functional groups.

13. The membrane of claim 1, wherein the silica (b) has been surface treated with at least one of polyethylene glycol, carboxybetaine, sulfobetaine and polymers thereof, mixed valence molecules, oligomers and polymers thereof, positively charged moieties, and negatively charged moieties.

14. The membrane of claim 1, wherein the silica (b) has been surface modified with functional groups.

15. The membrane of claim 1, further comprising a support layer to which the microporous material is adhered.

16. The membrane of claim 1, wherein the weight ratio of silica to polyolefin is in the range of 0.5:1 to 10:1.

17. The membrane of claim 1, wherein the microporous material demonstrates a Gurley number of < 2000sec.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/061326

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D67/00 B01D69/14 B01D71/08 B01D71/26 B01D71/44
B01D71/58 B01D71/02
ADD. B01D61/14
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 2013/228529 A1 (GUO QUNHUI [US] ET AL) 5 September 2013 (2013-09-05) paragraph [0102]; claims 1,2,8,9,11-12,13-15; tables 1-2	1-10, 13-17 11,12

X Y	WO 2013/066488 A1 (PPG IND OHIO INC [US]) 10 May 2013 (2013-05-10) paragraphs [0052], [0088], [0035]; claims 1, 2,3,9,10,11,14-15,18,; tables 1-2	1-10, 13-17 11,12

X	US 2011/256364 A1 (BOYER JAMES L [US] ET AL) 20 October 2011 (2011-10-20) paragraphs [0061] - [0074], [0134], [0106]; claims 1,17,19,7	1-11, 13-17

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2008 272636 A (ASAHI KASEI CORP) 13 November 2008 (2008-11-13) paragraphs [0019], [0035], [0045], [0065] - [0066], [0068]; claims 1,10-11	11
Y	EP 2 060 316 A1 (MILLIPORE CORP [US]) 20 May 2009 (2009-05-20) paragraphs [0012], [0020] - [0021], [0031]; claims 1-2,5-6; figure 1	12

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2014/061326

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013228529 A1	05-09-2013	CA 2854488 A1	10-05-2013
		CN 103958038 A	30-07-2014
		EP 2773446 A1	10-09-2014
		KR 20140096339 A	05-08-2014
		TW 201330914 A	01-08-2013
		US 2013228529 A1	05-09-2013
		WO 2013066487 A1	10-05-2013
WO 2013066488 A1	10-05-2013	CA 2854261 A1	10-05-2013
		CN 103987448 A	13-08-2014
		EP 2773447 A1	10-09-2014
		KR 20140095082 A	31-07-2014
		TW 201332637 A	16-08-2013
		US 2013228519 A1	05-09-2013
		WO 2013066488 A1	10-05-2013
US 2011256364 A1	20-10-2011	AU 2011241039 A1	08-11-2012
		CA 2796293 A1	20-10-2011
		CN 102933639 A	13-02-2013
		EP 2558520 A1	20-02-2013
		JP 5513676 B2	04-06-2014
		JP 2013527865 A	04-07-2013
		JP 2014095096 A	22-05-2014
		KR 20130030262 A	26-03-2013
		KR 20140097399 A	06-08-2014
		TW 201139543 A	16-11-2011
		US 2011256364 A1	20-10-2011
		US 2012231242 A1	13-09-2012
		WO 2011129928 A1	20-10-2011
JP 2008272636 A	13-11-2008	NONE	
EP 2060316 A1	20-05-2009	AT 552043 T	15-04-2012
		CN 101474552 A	08-07-2009
		EP 2060316 A1	20-05-2009
		ES 2384479 T3	05-07-2012
		JP 2009125071 A	11-06-2009
		JP 2013051970 A	21-03-2013
		SG 152982 A1	29-06-2009
		US 2009130738 A1	21-05-2009
		US 2010323430 A1	23-12-2010

(19)中华人民共和国国家知识产权局

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B01D 61/14(2006.01)

权利要求书1页 说明书17页

(54)发明名称

具有过滤和吸附性能的涂覆的微多孔材料以及它们在流体净化过程中的用途

(57)摘要

本发明涉及微滤和超滤膜包含微多孔材料。该微多孔材料包含：(a)存在量为至少2重量%的聚烯烃基质，(b)分布在整个所述基质中的细粉碎的、粒状的、基本上水不溶性的二氧化硅填料，所述填料占所述涂覆的微多孔材料基底的约10重量%－约90重量%，(c)至少20体积%的在整个所述涂覆的微多孔材料中连通的互连孔网络，和(d)至少一种涂料组合物，其施涂到所述膜的至少一个表面上以调节所述膜的表面能。

CN 105722584 A

1.涂覆的过滤膜，其包含涂覆的微多孔材料，所述涂覆的微多孔材料包含：

(a)存在量为至少2重量%的聚烯烃基质，

(b)分布在整个所述基质中的细粉碎的、粒状的、基本上水不溶性的二氧化硅填料，所述填料占所述涂覆的微多孔材料基底的约10重量%-约90重量%，

(c)至少20体积%的在整个所述涂覆的微多孔材料中连通的互连孔网络，和

(d)至少一种涂料组合物，其施涂到所述膜的至少一个表面上以调节所述膜的表面能；其中所述涂覆的膜表现出低于70°的水接触角。

2.权利要求1所述的膜，其中所述涂覆的膜表现出低于30°的水接触角。

3.权利要求1所述的膜，其中所述涂覆的膜在没有任何施加的预润湿剂的情况下表现出在25psi下至少1GFD的初始水通量。

4.权利要求1所述的膜，其中所述聚烯烃基质包含基本上线性的超高分子量聚烯烃，其为特性粘度为至少约18分升/克的基本上线性的超高分子量聚乙烯，特性粘度为至少约6分升/克的基本上线性的超高分子量聚丙烯，或它们的混合物。

5.权利要求4所述的膜，其中所述基质进一步包含高密度聚乙烯和/或低密度聚乙烯。

6.权利要求1所述的膜，其中所述膜为超滤膜且其平均孔径低于0.1微米。

7.权利要求6所述的膜，其中所述涂覆的微多孔材料表现出100-500,000的分子量截留。

8.权利要求1所述的膜，其中所述膜为微滤膜且其平均孔径大于0.1微米。

9.权利要求1所述的膜，其中所述涂覆的微多孔材料的厚度范围在0.7密耳-18密耳(17.8-457.2微米)。

10.权利要求1所述的膜，其中施涂到所述材料的表面的所述涂料包括亲水性涂料。

11.权利要求10所述的膜，其中所述亲水性涂料包含以下的一种或多种：聚噁唑啉，基于聚(乙二醇)-聚(丙二醇)-聚(乙二醇)的三嵌段共聚物，聚亚乙基亚胺，聚酰胺，氧化的聚乙烯或其衍生物，聚环氧乙烷，聚乙二醇，聚乙烯基吡咯烷酮，聚丙烯酸，聚甲基丙烯酸，聚乙二醇衍生物，聚环氧丙烷或其衍生物，聚(乙二醇)和聚环氧乙烷的共聚物，聚乙烯基醇，乙烯乙酸乙烯酯共聚物，纤维素或其衍生物，胶原，多肽，瓜尔胶，果胶，聚酰亚胺，聚类胨，聚(甲基)丙烯酸酯类，聚(甲基)丙烯酰胺，多糖，两性离子型聚合物，聚两性电解质，和聚乙烯亚胺。

12.权利要求10所述的膜，其中所述亲水性涂料包含至少一种具有叔胺官能团的聚合物。

13.权利要求1所述的膜，其中所述二氧化硅(b)已用以下的至少一种进行了表面处理：聚乙二醇，羧基甜菜碱，磺基甜菜碱及其聚合物，混合价态分子，低聚物及其聚合物，带正电的结构部分，和带负电的结构部分。

14.权利要求1所述的膜，其中所述二氧化硅(b)已用官能团进行表面改性。

15.权利要求1所述的膜，进一步包含支撑层，所述微多孔材料粘附到所述支撑层。

16.权利要求1所述的膜，其中二氧化硅与聚烯烃的重量比范围在0.5:1-10:1。

17.权利要求1所述的膜，其中所述微多孔材料表现出<2000sec的Gurley数。

具有过滤和吸附性能的涂覆的微多孔材料以及它们在流体净化过程中的用途

[0001] 相关申请的交叉引用

[0002] 本申请要求2013年11月12日提交的美国专利申请系列号14/077,741的优先权，该14/077,741申请为2012年8月30日提交的美国专利申请系列号13/599,221的部分继续申请，该13/599,221申请由要求2011年11月4日提交的美国临时专利申请系列号61/555,500的权益，全部这些申请都以它们的全部内容通过引用纳入本申请。

发明领域

[0003] 本发明涉及可用于过滤和吸附膜的涂覆的微多孔材料以及它们在流体净化过程中的用途。

[0004] 发明背景

[0005] 清洁的和适于饮用的水的可获取性是全球关注的，特别是在发展中国家更是如此。正在进行研究来获得低成本的有效的过滤材料和方法。特别期望的是这样的过滤介质，其可以除去宏观的微粒污染物和分子污染物二者，包括可以以低成本和高流量速率除去亲水和疏水污染物二者的那些。

[0006] 令人期望的是提供适用于液态或气态流的新膜，其用于经由化学吸收和物理吸着二者来除去污染物。

[0007] 发明概述

[0008] 本发明涉及微滤和超滤膜包含微多孔材料。该微多孔材料包含：

[0009] (a)存在量为至少2重量%的聚烯烃基质，

[0010] (b)分布在整个所述基质中的细粉碎的、粒状的、基本上水不溶性的二氧化硅填料，所述填料占所述涂覆的微多孔材料基底的约10%-约90重量%，

[0011] (c)至少20体积%的在整个所述涂覆的微多孔材料中连通的互连孔网络，和

[0012] (d)至少一种涂料组合物，其施涂到所述膜的至少一个表面上以调节所述膜的表面能。

具体实施方式

[0013] 除了任何操作实施例或者另有指示之处外，表示说明书和权利要求中所用的成分、反应条件等的量的全部数字被理解为在全部的情况中是用术语“约”修饰。因此，除非有相反的指示，否则下面的说明书和附加的权利要求中阐明的数字参数是近似的，其可以根据本发明所寻求获得的期望的性能而变化。最起码，和并非打算使用等价原则来限制权利要求的范围，每个数字参数应当至少按照所报告的有效数字的数值和通过使用通常的四舍五入技术来解释。

[0014] 虽然阐明本发明宽的范围的数字范围和参数是近似的，但是在具体实施例中所述数值是尽可能精确来报告的。但是任何数值本质上包含了由它们各自的测试测量中存在的标准偏差所必然形成的某些误差。

[0015] 同样，应当理解这里所述任何数字范围目的是包括处于其中的全部的子范围。例如范围“1-10”目的是包括在所述最小值1和所述最大值10之间(并包括其)的全部子范围，即，具有最小值等于或者大于1和最大值等于或者小于10。

[0016] 作为在说明书和附加的权利要求中所用的，冠词“一个”、“一种”和“该”包括复数指代物，除非明确的和不含糊的限制于一个指代物。

[0017] 在此提出的本发明不同的实施方案和实施例每个被理解为不限制本发明的范围。

[0018] 作为下面的说明书和权利要求中所用的，下面的术语具有下面所示的含义：

[0019] “聚合物”表示包括均聚物和共聚物以及低聚物的聚合物。“复合材料”表示两种或更多种不同材料的组合物。

[0020] 作为此处使用的，“由…形成”表示开放的权利要求语言，例如“包含”。同样，“由一列所述组分形成的”组合物是包含至少这些所述组分的组合物，并且在组合物形成过程中可以进一步包含其他的没有描述的组分。

[0021] 作为此处使用的，术语“聚合物无机材料”表示这样的聚合物材料，其具有基于非碳的元素的主链重复单元。更多的信息参见James Mark等人，Inorganic Polymers，Prentice Hall Polymer Science and Engineering Series，(1992)第5页，其明确在此引入作为参考。此外，作为此处使用的，术语“聚合物有机材料”表示合成聚合物材料，半合成聚合物材料和天然聚合物材料，其全部具有基于碳的主链重复单元。

[0022] 作为此处使用的，“有机材料”表示含碳化合物，其中该碳典型的键合到它本身和键合到氢上，经常也键合到其他元素上，并且不包括二元化合物例如碳氧化物，碳化物，二硫化碳等；这样的三元化合物如金属氰化物，羰基金属，光气，羰基硫等；和含碳的离子化合物例如金属碳酸盐，例如碳酸钙和碳酸钠。参见R.Lewis，Sr.，Hawley's Condensed Chemical Dictionary，(第12版，1993)第761-762页，和M.Silberberg，Chemistry The Molecular Nature of Matter and Change(1996)第586页，其明确在此引入作为参考。

[0023] 作为此处使用的，术语“无机材料”表示任何非有机材料的材料。

[0024] 作为此处使用的，“热塑性”材料是这样的材料，其在曝露于热时软化，并且在冷却到室温时返回它的初始条件。作为此处使用的，“热固性”材料是这样的材料，其在加热时不可逆的凝固或者“固着”。

[0025] 作为此处使用的，“微多孔材料”或“微多孔片材料”表示具有互连孔网络的材料，其中在无涂层、无印刷油墨、无浸渍剂、和预先结合的基材上，该孔的体积平均直径是0.001-0.5微米，并且占此下所述材料的至少5体积%。

[0026] 用“塑性体”表示表现出塑性和弹性体性能二者的聚合物。

[0027] 如上所述，本发明涉及微滤和超滤膜包含微多孔材料。本发明隔膜所用的微多孔材料包含聚烯烃基质(a)。该聚烯烃基质在该微多孔材料中的存在量是至少2重量%。聚烯烃是衍生自至少一种烯属不饱和单体的聚合物。在本发明的某些实施方案中，该基质包含塑性体。例如该基质可以包含衍生自丁烯、己烯和/或辛烯的塑性体。合适的塑性体在商标名“EXACT”下获自ExxonMobil Chemical。

[0028] 在本发明的某些实施方案中，该基质包含衍生自至少一种烯属不饱和单体的不同的聚合物，其可以代替或者与塑性体组合使用。例子包括衍生自乙烯、丙烯和/或丁烯的聚合物例如聚乙烯、聚丙烯和聚丁烯。高密度和/或超高分子量聚烯烃例如高密度聚乙烯也是

合适的。

[0029] 在本发明的一种具体的实施方案中，该聚烯烃基质包含乙烯和丁烯的共聚物。

[0030] 超高分子量(UHMW)聚烯烃非限定性例子可以包括基本上线性的UHMW聚乙烯或者聚丙烯。由于UHMW聚烯烃不是具有无限分子量的热固性聚合物，因此它们在技术上归类为热塑性材料。

[0031] 该超高分子量聚丙烯可以包含基本上线性超高分子量全同立构聚丙烯。通常这样的聚合物的全同立构规整度是至少95%，例如至少98%。

[0032] 虽然对于UHMW聚乙烯的特性粘度的上限没有特别的限制，但是在一个非限定性例子中，该特性粘度可以是18-39分升/克，例如18-32分升/克。虽然对于UHMW聚丙烯的特性粘度的上限没有特别的限制，但是在一个非限定性例子中，该特性粘度可以是6-18分升/克，例如7-16分升/克。

[0033] 在本发明中，特性粘度是通过将UHMW聚烯烃的几个稀溶液外推到零浓度的降低的粘度或特性粘度来确定的，这里该溶剂是新蒸馏的十氢化萘，向其中已经加入了0.2重量%的3,5-二叔丁基-4-羟基氢化肉桂酸，新戊烷四基酯[CAS登记号No.6683-19-8]。该UHMW聚烯烃降低的粘度或特性粘度是使用Ubbelohde No.1粘度计，根据ASTM D4020-81的通用程序在135℃所获得的相对粘度来确定的，除了使用几个不同浓度的稀溶液之外。

[0034] UHMW聚乙烯的名义分子量经验上依据下面的等式与聚合物的特性粘度有关：

[0035] $M=5.37 \times 10^4 [\eta]^{1.37}$

[0036] 其中M是名义分子量，和$[\eta]$是UHMW聚乙烯的特性粘度，以分升/克来表示。类似的，UHMW聚丙烯的名义分子量经验上依据下面的等式与聚合物的特性粘度有关：

[0037] $M=8.88 \times 10^4 [\eta]^{1.25}$

[0038] 其中M是名义分子量，和$[\eta]$是UHMW聚丙烯的特性粘度，以分升/克来表示。

[0039] 可以使用基本线性的超高分子量聚乙烯和低分子量聚乙烯的混合物。在某些实施方案中，该UHMW聚乙烯的特性粘度是至少10分升/克，和该低分子量聚乙烯的ASTM D1238-86条件E熔融指数小于50g/10分钟，例如小于25g/10分钟，例如小于15g/10分钟，和ASTM D1238-86条件F熔融指数是至少0.1g/10分钟，例如至少0.5g/10分钟，例如至少1.0g/10分钟。在这种实施方案中UHMW聚乙烯的用量(重量%)描述在美国专利5196262第1栏第52行到第2栏第18行中，该公开文献在此引入作为参考。更具体的，所用的UHMW聚乙烯的重量%是参考US5196262的图6来描述的；即，参考图6的多边形ABCDEF，GHCI或者JHCK，该图在此引入作为参考。

[0040] 低分子量聚乙烯(LMWPE)的名义分子量低于UHMW聚乙烯。LMWPE是热塑性材料和已知许多不同的类型。一种分类方法是通过密度，以g/cm^3来表示，并且四舍五入到千分位，其是根据ASTM D1248-84的(1989重新核准)。LMWPE密度非限定性的例子在下表1中可以找到。

[0041] 表1

[0042]

类型	缩写	密度，g/cm^3
低密度聚乙烯	LDPE	0.910-0.925
中密度聚乙烯	MDPE	0.926-0.940
高密度聚乙烯	HDPE	0.941-0.965

[0043] 上表1所列的任何或全部的聚乙烯可以用作该微多孔材料基质中的LMWPE。可以使用HDPE，因为它的线性会大于MDPE或LDPE。制造不同的LMWPE的方法是公知的和广泛文献记载的。它们包括高压方法，飞利浦石油公司方法，标准石油公司(印第安纳州)方法和齐格勒方法。LMWPE的ASTM D1238-86条件E(即，190℃和2.16kg负荷)熔融指数小于约50g/10分钟。经常的该条件E熔融指数小于约25g/10分钟。该条件E熔融指数可以小于约15g/10分钟。LMWPE的ASTM D1238-86条件F(即，190℃和21.6kg负荷)熔融指数是至少0.1g/10分钟。在许多情况中该条件F熔融指数是至少0.5g/10分钟例如至少1.0g/10分钟。

[0044] UHMWPE和LMWPE可以一起占微多孔材料的聚烯烃聚合物的至少65重量%，例如至少85重量%。同样，UHMWPE和LMWPE一起可以占微多孔材料的聚烯烃聚合物的基本上100重量%。

[0045] 在本发明的一种具体的实施方案中，该微多孔材料可以包含聚烯烃，其包含超高分子量聚乙烯、超高分子量聚丙烯、高密度聚乙烯、高密度聚丙烯或者其混合物。

[0046] 如果期望，其他热塑性有机聚合物也可以存在于该微多孔材料基质中，限定它们的存在不会实质性的以不利方式影响该微多孔材料基材的性能。其他热塑性聚合物可以的存在量取决于这样的聚合物的性质。通常，与存在大量的支化、许多长侧链或者许多大体积侧基相比，如果分子结构包含较少的支化，较短的侧链和较小体积的侧基，则可以使用更大量的其他热塑性有机聚合物。热塑性有机聚合物非限定性的例子(其任选的可以存在于该微多孔材料的基质中)包括低密度聚乙烯，高密度聚乙烯，聚(四氟乙烯)，聚丙烯，乙烯和丙烯的共聚物，乙烯和丙烯酸的共聚物，和乙烯和甲基丙烯酸的共聚物。如果期望，则含羧基的共聚物的全部或者一部分的羧基可以用钠、锌等中和。通常，该微多孔材料包含至少70重量%的UHMW聚烯烃，基于基质的重量。在一种非限定性实施方案中，上述的其他热塑性有机聚合物基本不存在于该微多孔材料的基质中。

[0047] 本发明的隔膜中所用的微多孔材料进一步包含分布在整个基质中的细粉碎的、粒状的、基本不溶于水的二氧化硅填料(b)。

[0048] 该微粒填料典型的包含沉淀二氧化硅粒子。重要的是将沉淀二氧化硅与硅胶区分开，因为这些不同的材料具有不同的性能。关于这点可以参考R.K.Iler,The Chemistry of Silica,John Wiley&Sons,纽约(1979)。Library of Congress Catalog No.QD181.S6144，其整个公开内容在此引入作为参考。特别要注意第15-29,172-176,218-233,364-365,462-465,554-564和578-579页。硅胶通常在低pH，通过用酸来酸化可溶性金属硅酸盐(典型的是硅酸钠)的水溶液来商业生产的。所用的酸通常是强无机酸例如硫酸或者盐酸，虽然有时候也使用二氧化碳。因为凝胶相和周围的液相之间基本上不存在密度差异，而粘度是低的，因此该凝胶相不沉降出来，也就是说，它不沉淀。因此硅胶可以描述为胶体无定形二氧化硅的连续粒子的非沉淀的、粘在一起的、硬质的三维网络。从大的实体到亚微观粒子的细分范围状态，和从几乎无定形二氧化硅到软的凝胶状物质的水合程度，含有100份水的量级，基于

二氧化硅的重量份。

[0049] 沉淀二氧化硅通常是如下来商业生产的：将可溶性金属硅酸盐(通常是碱金属硅酸盐例如硅酸钠)的水溶液和酸合并，以使得胶体粒子将在弱碱性溶液中生长和用碱金属离子凝结所形成的可溶性碱金属盐。可以使用不同的酸，包括无机酸，但是优选的酸是二氧化碳。在不存在凝结剂时，二氧化硅在任何pH时都不从溶液中沉淀。用于进行沉淀的凝结剂可以是在胶体二氧化硅粒子形成过程中所产生的可溶性碱金属盐，它可以是加入的电解质例如可溶性无机或者有机盐，或者它可以是二者的组合。

[0050] 因此沉淀二氧化硅可以描述为胶体无定形二氧化硅的最终粒子的沉淀聚集体，其在制备过程中在任何点都不作为宏观凝胶而存在。该聚集体的尺寸和水合度可以广泛变化。

[0051] 沉淀二氧化硅粉末不同于硅胶之处在于其已经进行了粉化，通常具有更大的开放结构，即，更高的比孔体积。但是，沉淀二氧化硅的比表面积(通过Brunauer，Emmet，Teller(BET)方法使用氮气作为吸附剂来测量)通常低于硅胶。

[0052] 许多不同的沉淀二氧化硅可以用于本发明，但是优选的沉淀二氧化硅是使用合适的酸例如硫酸、盐酸或者二氧化碳从硅酸钠水溶液中沉淀而获得的那些。这样的沉淀二氧化硅本身是已知的，并且生产它们的方法详细描述在美国专利No.2940830和西德专利No.3545615中，其整个公开内容在此引入作为参考，特别是包括制造沉淀二氧化硅的方法和该产品的性能。

[0053] 用于本发明的沉淀二氧化硅可以通过包括下面的连续步骤的方法来生产：

[0054] (a)制备具有期望的碱度的碱金属硅酸盐的初始储备水溶液，并且加入到反应器中(或者在其中制备)，该反应器装备有用于加热反应器内容物的装置，

[0055] (b)将反应器中的初始储液加热到期望的反应温度，

[0056] (c)将酸化剂和另外的碱金属硅酸盐溶液在搅拌下同时加入该反应器中，同时将反应器内容物的碱度值和温度保持在期望的值，

[0057] (d)停止向反应器中添加碱金属硅酸盐，和将另外的酸化剂加入来将所形成的沉淀二氧化硅悬浮液的pH调整到期望的酸值，

[0058] (e)将反应器中的沉淀二氧化硅与反应混合物分离，清洗来除去副产物盐，和

[0059] (f)干燥来形成沉淀二氧化硅。

[0060] 然后将所清洗的二氧化硅固体使用常规干燥技术来干燥。这样的技术非限定性的例子包括炉子干燥，真空炉干燥，旋转干燥机，喷雾干燥或者旋转闪蒸干燥。喷雾干燥机非限定性的例子包括旋转雾化器和喷嘴喷雾干燥机。喷雾干燥可以使用任何合适类型雾化器来进行，特别是涡轮、喷嘴、液压或者双流体雾化器。

[0061] 所清洗的二氧化硅固体可以不处于适于喷雾干燥的条件。例如所清洗的二氧化硅固体可以过稠而不能喷雾干燥。在上述方法的一方面，所清洗的二氧化硅固体例如清洗的滤饼与水混合来形成液体悬浮液，并且如果需要，用稀酸或稀碱例如氢氧化钠来调整该悬浮液的pH，来形成6-7，例如6.5，然后供给到喷雾干燥机的入口喷嘴。

[0062] 二氧化硅干燥的温度可以广泛的变化，但是将低于二氧化硅的熔化温度。典型的，该干燥温度将高于50℃-小于700℃，例如高于100℃例如200℃到500℃。在上述方法的一方面，该二氧化硅固体是在入口温度约400℃和出口温度约105℃的喷雾干燥机中干燥的。该

干燥的二氧化硅的游离水含量可以是变化的，但是通常是约1-10wt%，例如4-7wt%。作为此处使用的，术语游离水表示通过在100℃-200℃，例如105℃加热它24小时可以从二氧化硅中除去的水。

[0063] 在这里所述方法的一方面，将该干燥的二氧化硅直接推进到造粒机，在这里将它压实和粒化来获得粒状产物。干燥的二氧化硅也可以进行常规的尺寸减小技术，例如作为示例的通过研磨和粉化来进行。使用空气或者过热蒸汽作为工作流体的流体能量研磨也可以使用。所获得的沉淀二氧化硅通常处于粉末形式。

[0064] 最经常的，该沉淀二氧化硅是旋转干燥的或者喷雾干燥的。已经观察到旋转干燥的二氧化硅粒子具有比喷雾干燥的二氧化硅粒子更大的结构完整性。与喷雾干燥的粒子相比，它们在该微多孔材料生产过程中，在挤出和随后的加工过程中不太可能破裂成更小的粒子。在加工过程中旋转干燥的粒子的粒度分布的变化没有喷雾干燥的粒子那样大。喷雾干燥的二氧化硅粒子比旋转干燥的粒子更脆，经常在加工过程中提供较小的粒子。可以使用具体粒度的喷雾干燥的二氧化硅，以使得隔膜中最终的粒度分布对于水流通量不具有不利的影响。在某些实施方案中，该二氧化硅是增强的；即，具有结构完整性，以使得孔隙率在挤出后得以保存。更优选的是这样的沉淀二氧化硅，在其中通过在隔膜制作过程中施加的应力，二氧化硅粒子的初始数目和初始二氧化硅粒度分布大部分不变化。最优选的是增强的二氧化硅，以使得在最终的隔膜中存在着宽的粒度分布。不同类型的干燥的二氧化硅和不同尺寸的二氧化硅的共混物可以用于为隔膜提供独特的性能。例如具有双峰分布的粒度的二氧化硅共混物会特别适于某些分离方法。可以预期的是施加到任何类型的二氧化硅上的外力可以用于影响和调节粒度分布，为最终的隔膜提供独特的性能。

[0065] 该粒子的表面可以以本领域公知的任何方式来改性，包括但不限于使用本领域已知的技术来化学的或者物理的改变它的表面特性。例如该二氧化硅可以用抗污部分来处理表面，例如聚乙二醇、羧基甜菜碱、磺化甜菜碱及其聚合物，混合价分子，其低聚物和聚合物及其混合物。另外一种实施方案可以是二氧化硅的共混物，在其中一种二氧化硅已经用带正电的基团进行了处理，并且其他二氧化硅已经用带负电的基团进行了处理。该二氧化硅也可以用官能团来表面改性，其允许使用本发明的微滤隔膜来目标除去待净化的流体流中的特定污染物。也可以使用未处理的粒子。涂覆有亲水涂层的二氧化硅粒子降低了结垢和可以消除预润湿加工。涂覆有疏水涂层的二氧化硅粒子也降低了结垢和可以帮助系统脱气和通风。

[0066] 沉淀二氧化硅典型的平均最终粒度是1-100nm。

[0067] 二氧化硅粒子的表面积(外表面积和由于孔产生的内表面积二者)会影响性能。高表面积填料是非常小粒度的材料，具有高孔隙度的材料或者表现出两种特性的材料。通常该填料本身的表面积是约125-约700平方米/克(m^2/g)，其是通过Brunauer，Emmett，Teller(BET)方法根据ASTM C819-77使用氮气作为吸附剂来测量的，但是变化是将系统和样品在130℃除气1小时。经常的，该BET表面积是约190-350m^2/g，更经常该二氧化硅的BET表面积是351-700m^2/g。

[0068] BET/CTAB商是整个沉淀二氧化硅表面积(包括包含在孔中的，仅仅小分子例如氮气能够接近的表面积)(BET)与外表面积(CTAB)之比。这个比率典型的被称作微多孔隙率的度量。高的微多孔隙率值(即，高的BET/CTAB商值)是内表面(小的氮气分子可接近(BET表面

积),但是较大的粒子不能接近)与表面(CTAB)相比的高比例。

[0069] 已经建议了在沉淀二氧化硅制备过程中在它内所形成的结构(即,孔)会对性能产生影响。这种结构的两个度量是上述的沉淀二氧化硅的BET/CTAB表面积之比,和沉淀二氧化硅的孔尺寸分布的相对宽度(γ)。孔尺寸分布的相对宽度(γ)是孔尺寸在沉淀二氧化硅粒子内分布有多宽的指示。γ值越低,沉淀二氧化硅粒子内孔的孔尺寸分布越窄。

[0070] 二氧化硅CTAB值可以使用CTAB溶液和下文所述方法来测定。该分析是使用Metrohm751 Titrino automatic titrator来进行的,其装备有Metrohm Interchangeable "Snap-In"50毫升滴定管和Brinkmann Probe Colorimeter Model PC910(装备有550nm滤光片)。另外,使用Mettler Toledo HB43或者等价物来测定二氧化硅的105℃含湿量损失,并且可以使用Fisher Scientific Centrific™ Centrifuge Model 225来分离二氧化硅和残留的CTAB溶液。多余的CTAB可以通过用Aerosol OT®溶液自动滴定来测定,直到获得最大浊度为止,其可以用探针色度计来检测。取对应于150的毫伏读数来作为最大浊度点。知道了给定重量的二氧化硅所吸附的CTAB的量和CTAB分子所占据的空间,就能计算该二氧化硅的外部比表面积,并且基于干重,作为平方米/克来报告。

[0071] 测试和制备所需的溶液包括pH9.6的缓冲剂,鲸蜡基[十六烷基]三甲基溴化铵(CTAB),二辛基磺基琥珀酸钠(Aerosol OT)和1N氢氧化钠。pH9.6的缓冲剂溶液可以如下来制备:将3.101g正硼酸(99%;Fisher Scientific,Inc.,工业级,结晶)溶解在1升容量瓶中,该容量瓶含有500毫升去离子水和3.708g的氯化钾固体(Fisher Scientific,Inc.,工业级,结晶)。使用滴定管,加入36.85毫升的1N氢氧化钠溶液。将该溶液混合和稀释到体积。

[0072] 该CTAB溶液是在称重盘上使用11.0g±0.005g的粉末化的CTAB(鲸蜡基三甲基溴化铵,也称作十六烷基三甲基溴化铵,Fisher Scientific Inc.,工业级)来制备的。将该CTAB粉末转移到2升烧杯中,并且将称重盘用去离子水冲洗。将约700毫升的pH9.6的缓冲剂溶液和1000毫升的蒸馏水或去离子水加入该2升烧杯中和用磁搅拌棒来搅拌。盖上该烧杯和在室温搅拌直到CTAB粉末完全溶解。将该溶液转移到2升容量瓶中,用去离子水冲洗该烧杯和搅拌棒。使得气泡消散,和将该溶液用去离子水稀释到体积。可以加入大搅拌棒和将该溶液在磁搅拌器上混合约10小时。该CTAB溶液可以在24小时后使用并且使用仅仅15天。Aerosol OT®(二辛基磺基琥珀酸钠,Fisher Scientific Inc.,100%固体)溶液可以使用3.46g±0.005g来制备,将其置于称重盘上。将称重盘上的Aerosol OT冲洗到2升烧杯,其包含约1500毫升去离子水和大的搅拌棒。将该Aerosol OT溶液溶解和冲洗到2升容量瓶中。将该溶液稀释到该容量瓶的2升体积标记处。在使用前将Aerosol OT®溶液老化最少12天。该Aerosol OT溶液的存储寿命是从制备日起2个月。

[0073] 在表面积样品制备之前,CTAB溶液的pH应当检验和根据需要使用1N氢氧化钠溶液调整到pH9.6±0.1。对于测试计算来说,应当制备和分析空白样品。吸液5毫升的该CTAB溶液和将55毫升去离子水加入到150毫升烧杯中和在Metrohm751 Titrino自动滴定器上分析。该自动滴定器程序化来测定空白和样品,具有下面的参数:测量点密度=2,信号漂移=20,均衡时间=20秒,起始体积=0ml,终止体积=35ml,和固定的终点=150mV。滴定管尖端和色度计探针刚刚置于溶液表面下,这样布置以使得尖端和光探针路径长度完全淹没。尖端和光探针二者应当是从烧杯底部基本上等距的,并且彼此不接触。使用最小的搅拌(在

Metrohm 728搅拌器上设定为1)时，在每个空白和样品测定之前该色度计设定为100%T，并且滴定是用Aerosol OT®溶液开始的。终点可以作为在150mV的滴定剂的体积(ml)来记录。

[0074] 对于测试样品制备，将约0.30g的粉末化的二氧化硅称重到含有搅拌棒的50毫升容器中。将粒化的二氧化硅样品淘洗(在研磨和称重前)来获得代表性的子样品。使用磨咖啡类型的研磨机来研磨该粒化的材料。然后将30毫升的pH调整的CTAB溶液移液到含有0.30g的粉末化的二氧化硅的样品容器中。该二氧化硅和CTAB溶液然后在搅拌器上混合35分钟。当混合完成时，该二氧化硅和CTAB溶液离心分离20分钟来分离该二氧化硅和过量的CTAB溶液。当离心分离完成时，将该CTAB溶液移液到清洁的容器中减去分离的固体，其被称作“离心分离物”。对于样品分析，将50毫升去离子水置于含有搅拌棒的150毫升烧杯中。然后将10毫升的样品离心分离物移液到相同的烧杯中用于分析。该样品是使用与用于空白溶液相同的技术和程序化方法来分析的。

[0075] 为了测定含湿量，将约0.2g的二氧化硅称重到Mettler Toledo HB43上，同时测定CTAB值。该湿气分析仪程序化到105℃，并且具有切断5干燥标准。湿气损失记录到最接近的+0.1%。

[0076] 外表面积是使用下面的等式来计算的，

[0077]
$$\text{CTAB 表面积(干燥基准)}\ [m^2/g] = \frac{(2V_o - V) \times (4774)}{(V_o W) \times (100 - Vol)}$$

[0078] 其中，

[0079] V_o＝用于空白滴定的Aerosol OT®的体积ml。

[0080] V＝用于样品滴定的Aerosol OT®的体积ml。

[0081] W＝样品重量g。

[0082] Vol＝湿气损失%(Vol表示“挥发物”)。

[0083] 典型的，用于本发明的二氧化硅粒子的CTAB表面积是120-500m^2/g。经常的，该二氧化硅的CTAB表面积是170-280m^2/g。更经常的，该二氧化硅的CTAB表面积是281-500m^2/g。

[0084] 在本发明的某些实施方案中，沉淀二氧化硅的BET值将是这样的值，以使得BET表面积(平方米/克)与CTAB表面积(平方米/克)的商等于或大于1.0。经常的，BET与CTAB之比是1.0-1.5。更经常的，BET与CTAB之比是1.5-2.0。

[0085] 在本申请实施例中所报告的BET表面积值是按照Brunauer-Emmet-Teller(BET)方法，根据ASTM D1993-03来测定的。BET表面积可以通过由来自用Micromeritics TriStar 3000™仪器所进行的氮气吸附等温线测量的五个相对压力点拟合来测定的。流动Prep-060™站提供了热和连续气体流动来制备用于分析的样品。在氮气吸附之前，该二氧化硅样品通过在流动氮气(P5等级)中加热到160℃的温度持续至少一(1)小时来干燥。

[0086] 该填料粒子可以占该微多孔材料的10-90重量%。例如这样的填料粒子可以占该微多孔材料的25-90重量%，例如该微多孔材料的30-90重量%，或者该微多孔材料的40-90重量%，或者该微多孔材料的50-90重量%和甚至该微多孔材料的60-90重量%。该填料典型的在本发明的微多孔材料中的存在量是该微多孔材料的50-约85重量%。经常的，该微多孔材料中的二氧化硅与聚烯烃的重量比是0.5:1-10:1，例如1.7-3.5:1。可选择的，该微多孔材料中的填料与聚烯烃的重量比可以大于4:1。

[0087] 用于本发明隔膜中的该微多孔材料进一步包含互连孔网络(c),其在该微多孔材料整个中连通。

[0088] 基于无浸渍剂时,这样的孔可以占该微多孔材料的至少15体积%,例如至少20-95体积%或者至少25-95体积%,或者35-70体积%。经常的,该孔占该微多孔材料的至少35体积%或者甚至至少45体积%。这样的高孔隙率在整个微多孔材料中提供了更高的表面积,其依次促进了从流体流中除去污染物和流体流穿过该隔膜更高的流量速率。

[0089] 作为此处和权利要求使用的,该微多孔材料的孔隙率(也称作空穴体积,以体积%表示)是根据下面的等式来确定的:

[0090] 孔隙率$=100[1-d_1/d_2]$

[0091] 其中d_1是样品密度,其是由样品重量和样品体积来确定的,样品体积是由测量样品尺寸来确定的,和d_2是样品固体部分的密度,其是由样品重量和样品固体部分的体积来确定的。样品固体部分的体积是使用Quantachrome stereopycnometer(Quantachrome Corp.),根据随之的操作手册来测定的。

[0092] 该微多孔材料的孔的体积平均直径可以通过水银孔隙率测量法,使用Autopore III孔隙率计(Micromeretics,Inc.),根据随之的操作手册来测定的。用于单个扫描的体积平均孔半径是通过孔隙率计自动测定的。在孔隙率计运行中,扫描是在高压范围进行的(138绝对千帕到227绝对兆帕)。如果约2%或更少的总侵入体积发生在该高压范围的下端(138-250绝对千帕),则该体积平均孔直径取通过孔隙率计所测量的体积平均孔半径的两倍。否则,在低压范围内(7-165绝对千帕)进行另外的扫描,并且根据下面的等式来计算体积平均孔直径:

[0093] $d=2[v_1r_1/w_1+v_2r_2/w_2]/[v_1/w_1+v_2/w_2]$

[0094] 其中d是体积平均孔直径,v_1是高压范围侵入的水银的总体积,v_2是低压范围侵入的水银的总体积,r_1是从高压扫描所确定的体积平均孔半径,r_2是从低压扫描所确定的体积平均孔半径,w_1是进行高压扫描的样品的重量,和w_2是进行低压扫描的样品的重量。对于超滤膜来说,孔的体积平均直径(平均孔径)典型地低于0.1微米(microns),并且可以范围在0.001-0.70微米,例如0.30-0.70微米。对于微滤膜来说,该平均孔径典型地大于0.1微米(microns)。

[0095] 在上述程序的测定体积平均孔直径的过程中,所测定的最大孔半径有时候是显著的。如果运行,这取自低压范围扫描;否则它取自高压范围扫描。最大孔直径是最大孔半径的两倍。因为一些生产或处理步骤例如涂覆方法,印刷方法,浸渍方法和/或结合方法会导致填充该微多孔材料的至少一些孔,和因为这些方法的一些不可逆的压缩了该微多孔材料,因此在施加一种或多种这样的生产或者处理步骤之前,测定该微多孔材料的孔隙率,孔的体积平均直径和最大孔直径方面的参数。

[0096] 为了制备本发明的微多孔材料,将填料、聚合物粉末(聚烯烃聚合物)、加工增塑剂和少量润滑剂和抗氧化剂混合,直到获得基本均匀的混合物。形成该混合物中所用的填料与聚合物粉末的重量比基本上与生产该微多孔材料基材所用相同。将该混合物与另外的加工增塑剂一起引入到螺杆挤出机的加热的料筒中。连接到该挤出机上的是口模例如片材口模,来形成期望的最终形状。

[0097] 在一种示例性制造方法中,当该材料形成片或膜时,将通过口模形成的连续片材

或膜推进到一对协同作用的加热的压延辊中形成连续片材，该片的厚度小于离开口模的连续片材。最终的厚度会取决于期望的终端应用。该微多孔材料的厚度可以是0.7-18密耳(17.8-457.2微米)，例如0.7-15密耳(17.8-381微米)，或1-10密耳(25.4-254微米)，或5-10密耳(127-254微米)，并且表现出10-80psi的基于乙醇的起泡点。

[0098] 任选的，根据所形成的膜是用于微滤或超滤，离开压延辊的片然后可以在至少一个拉伸方向上高于弹性限度来拉伸。拉伸可以可选择的在离开片材口模之中或者紧随其后发生，或者在压延过程中发生，或者多次发生，但是典型的在萃取之前进行。拉伸的微多孔材料基材可以通过在至少一个拉伸方向上在高于弹性限度上拉伸中间产物来生产的。通常，拉伸比是至少约1.5。在许多情况中，拉伸比是至少约1.7。优选它至少是约2。经常的，该拉伸比是约1.5-约15。经常的，拉伸比是约1.7-约10。通常，拉伸比是约2-约6。但是，要仔细处理，以使得拉伸不导致对于超滤来说孔尺寸过大。

[0099] 完成拉伸的温度可以广泛变化。拉伸可以在约环境室温来完成，但是通常使用高温。在拉伸之前、之中和/或之后，中间产物可以通过任何广泛的多种技术来加热。这些技术的例子包括辐射加热例如通过电加热的或者燃气红外加热器所提供的。对流加热例如通过再循环热空气所提供的，和传导加热例如通过与加热辊接触所提供的。温度(测量其来用于温度控制的目的)可以根据所用设备和个人喜好来变化。例如可以放置温度测量装置来获得红外加热器表面，红外加热器内部的温度，红外加热器和中间产物之间的点的空气温度，设备内部的点上循环热空气的温度，进入或离开设备的热空气的温度，拉伸方法所用辊表面温度，进入或离开这样的辊的传热流体的温度辊，或者膜表面温度。通常，控制所述温度，以使得中间产物是大致均匀拉伸的，以使得拉伸的微多孔材料的膜厚变化(如果有的话)处于可接受的限度内和使得处于那些限度之外的拉伸的微多孔材料的量是可接受的降低。很显然用于控制目的温度可以或者可以不接近于中间产物本身的那些，因为它们取决于所用设备的性质，温度测量装置的位置和要测量它的温度的物质或物体的情况。

[0100] 由于加热装置的位置和拉伸过程中通常使用的线速度，在该中间产物的整个厚度内可以或者可以不存在变化的温度梯度。同样因为这样的线速度，测量这些温度梯度是不可行的。变化的温度梯度的存在，当它们发生时，使得它不合理的表示单个膜温度。因此膜表面温度(其可以测量)最好用于表征该中间产物的热条件。

[0101] 在拉伸过程中它们通常沿着中间产物的宽度是大致相同的，虽然它们可以有意的变化，例如来补偿沿着所述片具有楔形横截面的中间产物。在拉伸过程中，沿着片长度的膜表面温度可以是大致相同的或者它们可以是不同的。

[0102] 拉伸完成时的膜表面温度可以广泛变化，但是通常它们是这样，即，中间产物大致均匀拉伸，如上面所解释的。在大多数情况中，拉伸过程中膜表面温度是约20℃-约220℃。经常的，这样的温度是约50℃-约200℃。约75℃-约180℃是优选的。

[0103] 拉伸可以根据期望在单个步骤或多个步骤中完成。例如当中间产物是在单个方向上拉伸时(单轴拉伸)，该拉伸可以通过单个拉伸步骤或者顺序的拉伸步骤来完成，直到获得了期望的最终拉伸比。类似的，当中间产物是在两个方向上拉伸时(双轴拉伸)，该拉伸可以通过单个双轴拉伸步骤或者顺序的双轴拉伸步骤来进行，直到获得了期望的最终拉伸比。双轴拉伸也可以通过顺序的在一个方向上一个或多个单轴拉伸步骤和在另一方向上的一个或多个单轴拉伸步骤来完成。双轴拉伸步骤(这里中间产物是在两个方向上同时拉伸

的)和单轴拉伸步骤可以以任何次序依次进行。在大于2个方向上的拉伸预期内的。可以看到所述步骤不同的变换是相当众多的。其他步骤例如冷却、加热、烧结、退火、卷绕、解卷等可以任选的根据期望包括在整个方法中。

[0104] 不同类型的拉伸设备是公知的,并且可以用于完成中间产物的拉伸。单轴拉伸通常是通过在两个辊之间拉伸来完成的,其中第二或下游辊以比第一或上游辊更大的圆周速率来旋转。单轴拉伸也可以在常规张布机上来完成。双轴拉伸可以通过在张布机上在两个不同方向上同时拉伸来完成。但是,更通常的,双轴拉伸是如下来完成的:首先如上所述在两个不同旋转的辊子之间单轴拉伸,随后在不同的方向上使用张布机单轴拉伸或者使用张布机双轴拉伸。最普通类型的双轴拉伸是这样,其中两个拉伸方向是大致彼此处于直角。在大多数其中拉伸连续片材的情况中,一个拉伸方向至少大致平行于片的长轴(加工方向)和另一拉伸方向至少大致垂直于加工方向和处于片的平面内(横向)。

[0105] 在萃取加工增塑剂之前拉伸片材能够获得比常规加工的微多孔材料中更大的孔尺寸,由此使微多孔材料特别适用于本发明的微滤膜。还相信,在萃取加工增塑剂之前拉伸片材最小化了加工后的热收缩。

[0106] 将该产物送到第一萃取区,在这里用有机液体(其是加工增塑剂的良溶剂,是有机聚合物的不良溶剂,并且挥发性大于加工增塑剂)萃取来将该加工增塑剂基本除去。通常但非必需的,加工增塑剂和有机萃取液体二者是基本与水不混溶的。该产物然后送到第二萃取区,在这里将残留的有机萃取液体通过蒸汽和/或水基本除去。该产物然后通过强制空气干燥机来基本上除去残留的水和其余的残留的有机萃取液体。当它处于片形式时,该微多孔材料可以从干燥机送到拉紧辊。

[0107] 该加工增塑剂对于60℃的热塑性有机聚合物具有很少的溶剂化效应,在约100℃量级的高温时仅仅具有中等的溶剂化效应,和在约200℃量级的高温时具有明显的溶剂化效应。它在室温是液体和通常它是加工油例如链烷烃油,环烷烃油或者芳烃油。合适的加工油包括满足ASTM D2226-82,类型103和104的要求的那些。那些油(其的倾点小于22℃或者小于10℃,根据ASTM D97-66(1978年重新核准))是最经常使用的。合适的油的例子包括Shellflex®412和Shellflex®371油(Shell油Co.),其是溶剂精炼的和加氢处理的油,来源于环烷基原油。可以预期的其他材料,包括邻苯二甲酸酯增塑剂例如邻苯二甲酸二丁酯,邻苯二甲酸双(2-乙基己基)酯,邻苯二甲酸二异癸基酯,邻苯二甲酸二环己基酯,邻苯二甲酸丁基苄基酯和邻苯二甲酸二(十三烷基)酯将是功能满意的加工增塑剂。

[0108] 存在着许多可以使用的有机萃取液体。合适的有机萃取液体的例子包括1,1,2-三氯乙烯,全氯乙烯,1,2-二氯乙烷。1,1,1-三氯乙烷,1,1,2-三氯乙烷,二氯甲烷,氯仿,异丙醇,二乙醚和丙酮。

[0109] 在上述生产微多孔材料基材的方法中,当填料带有很多的加工增塑剂时,促进了挤出和压延。填料粒子吸收和保持加工增塑剂的能力是填料表面积的函数。所以该填料典型的具有高表面积,如上所述。因为令人期望的是将填料基本上保持在该微多孔材料基材中,因此当微多孔材料基材是通过上述方法生产时,该填料应当基本不溶于该加工增塑剂和基本不溶于有机萃取液体。

[0110] 该残留的加工增塑剂含量通常小于所形成的微多孔材料的15重量%,并且通过使用相同或不同的有机萃取液体另外的萃取,这可以甚至进一步降低到例如小于5重量%的

水平。

[0111] 所得微多孔材料可根据期望的应用而进一步加工。在本发明中，可将亲水性涂料施涂到微多孔材料的表面以调节该材料的表面能。虽然不希望束缚于理论，但相信，涂料的组分与微多孔材料的填料中的二氧化硅颗粒相互作用并调节表面能，影响润湿性。该涂料的施涂可在上述拉伸步骤之前、期间或之后进行，但通常与拉伸步骤同时进行以最大化在拉伸过程期间产生的额外表面上的涂料覆盖。

[0112] 亲水性涂料可包含以下的一种或多种：聚噁唑啉，包括聚烷基噁唑啉，例如聚(2-乙基-2-噁唑啉)，聚(2-甲基-2-噁唑啉)，和聚(2-甲基/乙基-2-噁唑啉)；基于聚(乙二醇)-聚(丙二醇)-聚(乙二醇)的三嵌段共聚物；聚亚乙基亚胺；聚酰胺；氧化的聚乙烯或其衍生物；聚环氧乙烷；聚乙二醇；聚乙烯基吡咯烷酮；聚丙烯酸；聚甲基丙烯酸；聚乙二醇衍生物；聚环氧丙烷或其衍生物；聚(乙二醇)和聚环氧乙烷的共聚物；聚乙烯基醇；乙烯乙酸乙烯酯共聚物；纤维素或其衍生物；聚酰亚胺；水凝胶，例如胶原、多肽、瓜尔胶和果胶；聚类胨；聚(甲基)丙烯酸酯类，例如聚(甲基丙烯酸2-羟乙酯)；聚(甲基)丙烯酰胺；多糖；两性离子型聚合物，例如聚(磷酰胆碱)衍生物，聚磺基甜菜碱，和聚羧基甜菜碱；聚两性电解质，和聚乙烯亚胺。该亲水性涂料优选地包含至少一种具有叔胺官能团的聚合物，例如聚(2-乙基-2-噁唑啉)。

[0113] 在一些实施方案中，本发明的方法中使用的涂料组合物包含一种或多种合适的表面活性剂以降低表面张力。表面活性剂包括也被称为润湿剂、消泡剂、乳化剂、分散剂、均衡剂等的材料。表面活性剂可以为阴离子型的、阳离子型的和非离子型的，每种类型的许多表面活性剂都可商购。一些涂料组合物包含至少润湿剂。再其它的涂料组合物可具有额外的表面活性剂以发挥额外的效果。

[0114] 还可选择其它的表面活性剂。加入涂料组合物的表面活性剂的量和种数将取决于所选择的特定表面活性剂，但应限制为对实现基底润湿同时不妥协干燥涂料的性能的表面活性剂的最小量。在某些实施方案中，涂料组合物包含0.01到10重量%的表面活性剂，在一些实施方案中，0.05到5重量%，或在再其它实施方案中，0.1到3重量%的表面活性剂。涂料组合物中存在的表面活性剂的量可以范围在这些引述的端点值的数值的任何组合的范围之间。在本发明的膜中使用涂料组合物使得该膜能够用于分离系统中而无需对膜进行预润湿，例如用异丙醇。

[0115] 该微多孔材料可以粘附到载体层例如玻璃纤维层上，来提供另外的结构整体性，这取决于具体的最终应用。另外通过在步骤(ii)中挤出，任选的在至少一个拉伸方向上拉伸该连续片材也可以在任何步骤之中或紧随其后进行。例如在本发明的超滤隔膜的生产中，制备该微多孔材料可以包括在压延过程中拉伸该连续片材，来使得孔尺寸处于超滤的上面范围。但是典型的，在本发明的超滤隔膜生产中，制备该微多孔材料不包括拉伸步骤。

[0116] 如上所述制备的微多孔材料适用于本发明的微滤和超滤膜中，能够从流体流除去尺寸范围在0.005-0.1微米的微粒(超滤)并能够从流体流除去尺寸范围在0.05-1.5微米的微粒(微滤)。该隔膜还用于通过吸附或者通过物理截留(依靠分子尺寸)来从流体流中除去分子污染物。

[0117] 本发明的隔膜可以用于从流体流中分离悬浮的或者溶解的材料的方法中，例如从流体(液态或气态)流中除去一种或多种污染物，或者浓缩贫化流中期望的组分。该方法包

含将所述流与隔膜接触，典型的通过将所述流通过该隔膜。污染物的例子包括毒素例如神经毒素；重金属；烃；油；染料；神经毒素；药品；和/或杀虫剂。流体流(例如水流，但它可以是液体或气体)通常以在25psi下至少1，例如，1-10000gal/(ft^2天)(GFD)的通量流过所述膜，并且不需要使用预润湿剂。超滤膜可表现出大于100GFD，优选大于150GFD的水通量，和100-500,000的分子量截留，而微滤膜可表现出大于300GFD，优选大于500GFD的水通量。本发明的膜表现出低于2000秒的Gurley数。

[0118] 包含用亲水性涂料组合物涂覆的微多孔材料的涂覆的膜表现出低于70°的水接触角，通常为低于30°，更通常为低于10°。

[0119] 实施例

[0120] 在以下实施例的部分I中，描述了用于制备微多孔片材材料的材料和方法。在部分II中，描述了用于拉伸微多孔片材材料的方法和条件。部分III描述了用于涂覆微多孔片材材料的涂料配方和方法。实施例(涂覆的)和比较例(未涂覆的)的物理性能在部分IV中给出。

[0121] 部分I-微多孔片材材料的制备

[0122] 将实施例1的干成分以表1中规定的顺序和量分别称重加入FM-130D Littleford犁片混合器，该混合器具有一个高强度切齿型混合叶片。将干成分仅用犁片预混合15秒。然后将加工油经由双隔膜泵通过位于混合器顶部的喷嘴在约45-60秒期间泵入，这时只有犁片运行。然后启动高强度切齿叶片，与犁片一起，继续混合30秒。关闭混合器，刮擦混合器内壁以确保所有成分都被均匀混合。然后再将混合器启动，高强度切齿和犁片都使用，再继续混合30秒。将所得干成分的混合物按如下挤出并压延成片材形式。重量损失重力计量系统(K-tron型号#K2MLT35D5)用于将混合物供如27毫米双螺杆挤出机(Leistritz Micro-27mm)。挤出机机桶包含八个温区和片材口模的加热适配器。挤出混合物供料口位于刚好在第一温区之前。通气口位于第三温区。真空口位于第七温区。

[0123] 将混合物以90克/分钟的速率供如挤出机。根据需要，还将额外的加工油在第一温区注入，从而在挤出的片材中实现期望的总油含量。

[0124] 使用生产规模的挤出系统来制备实施例2和3，挤出并压延成最终片材形式。该系统的版本类似于以上对实施例1所描述的设备和工序，除了设备的尺寸外。从挤出机排出的挤出片材(挤出物)中含有的油在这里被称为挤出物油重量比例，其基于样品的总重量计。所有样品的挤出物油重量比例的算术平均为0.57。实施例1、2和3中每一个的残余油使用1，1，2-三氯乙烯油萃取工艺去除。

[0125] 表1：微多孔膜片材的配方

[0126]

成分	实施例 1	实施例 2	实施例 3
GUR® 4150[1]	1.44	144	136
FINA® 1288[2]	1.44	144	136
Hi-Sil® 135[3]	5.00	500	500
SYNPRO® 1580[4]	0.05	4	4
IRGANOX® B215[5]	0.03	4	4
TUFFLO® 6056[6]	8.39	835	835

[0127] [1]超高分子量聚乙烯(UHMWPE)，商购自Ticona Corp并且报告为分子量为约9.2百万克每摩。

[0128] [2]高密度聚乙烯(HDPE)，商购自Total Petrochemicals。

[0129] [3]沉淀二氧化硅，获自PPG Industries,Inc.。

[0130] [4]报告为硬脂酸钙-锌润滑剂，商购自Ferro

[0131] [5]抗氧化剂的加工和热稳定共混物，商购自BASF。

[0132] [6]加工油，商购自PPC润滑剂。

[0133] 部分II-拉伸的片材微多孔材料的制备

[0134] 通过Parkinson Technologies,Inc.采用Marshall and Williams双轴定向塑料加工系统进行拉伸。部分II的材料的纵向定向的(MDO)拉伸通过加热实施例2和3的微多孔片材并且将其在纵向上在保持在表2中列出的温度下的一系列辊上拉伸来完成。

[0135] 横向定向(TDO)拉伸在MDO拉伸后通过根据表2中列出的温度条件加热所得片材，并且在拉幅机上在横向(或跨越)方向上拉伸来进行，该拉幅机由两个水平履带组成，在该履带上夹具和链组件将材料保持就位。MDO和TDO条件的组合提供了材料的双轴拉伸。

[0136] 表2:微多孔片材拉伸条件：

[0137]

实施例		4	5	6
微多孔片材材料		实施例 2	实施例 3	实施例 3
MCO	拉伸辊 (°C)	132	132	132
	退火辊 (°C)	141	141	141
	冷却 (°C)	25	25	25
	慢拉拔速度, FPM	10.4	10.4	10.4
	快速辊速度, FPM	35	35	40
TDO	拉伸比	2	3	NA
	预热 (°C)	132	132	NA
	拉伸 (°C)	132	132	NA
	退火 (°C)	141	141	NA

[0138] 部分III-亲水性涂料配方：

[0139] a)亲水性涂料的制备：

[0140] 亲水性涂料实施例A、B和C根据表3中列出的成分和量来制备。将对应实施例的第一成分在激烈搅拌下溶于规定量的去离子水中。溶解完成后，加入Pluronic 17R2，然后加入Butoxyethanol。将涂料溶液温和搅拌最少30分钟后再继续下一步。

[0141] 表3：亲水性涂料配方

[0142]

实施例	A	B	C
聚亚乙基噁唑啉[1] (g)	7.5		
壳聚糖[2] (g)		10	
PVP-K90[3] (g)			5
去离子水 (g)	457	480	480
PLURONIC® 17R2[4] (g)	5	5	5
Butoxyethanol (g)	30	5	10

[0143] [1]分子量50,000，获自SigmaAldrich。

[0144] [2]来自虾壳的壳聚糖，实用级，获自SigmaAldrich。

[0145] [3]聚乙烯基吡咯烷酮，平均Mw 360,000，获自SigmaAldrich。

[0146] [4]嵌段共聚物表面活性剂，获自BASF Corporation。

[0147] b)涂覆微多孔材料的工序：

[0148] 将之前实施例中所述的微多孔材料切割成12英寸见方的片材。通过将之前实施例

的微多孔材料浸渍到含有充足亲水性涂料的Pyrex盘中完全浸没片材，从而施涂亲水性涂料组合物。将片材浸没在亲水性涂料中约5分钟。然后将片材从溶液取出，并让多余涂料溶液滴掉。然后将涂覆的微多孔材料夹持在铝框中，该铝框配有垫圈以防止膜在干燥期间收缩。然后将带有膜的框架在95℃的烘箱中干燥15分钟。将实施例4的拉伸的微多孔材料用实施例A、B和C的涂料溶液中的每一个以这样的方式涂覆。将实施例5和6的拉伸的微多孔材料和实施例1的未拉伸的微多孔材料用实施例A的涂料配方涂覆。

[0149] 部分IV-性能：

[0150] 测试实施例4、5和6的拉伸的微多孔材料和实施例1的未拉伸的微多孔材料在施涂和没有施涂亲水性涂料下的性能和水渗透性。

[0151] 表6显示出实施例4的微多孔材料在有和没有亲水性涂料组合物下的差异。表7和8显示了各种微多孔材料在有和没有亲水性涂料组合物下的水渗透性。使用下述方法测量性能：

[0152] a)厚度使用Ono Sokki厚度量规EG-225测定。记录的厚度为9次测量的平均。

[0153] b)孔隙度使用Troy,New York的GPI Gurley Precision Instruments Gurley Precision Densometer,型号4340测定。

[0154] c)最大伸长率或使样品断裂的拉伸能量根据ASTM D-882-02的规程确定。将样品定向的测试，使得应力如部分II中所述在纵向("MD")和横向("TD")上施加。

[0155] d)接触角在获自AST Products,Inc.的VCA 2500XE视频接触角系统上使用1微升超纯水进行。

[0156] e)水通量测试在Sterlitech Corp,Kent WA提供的Sepa CF II跨越流动测试室装置中在20psi和25℃下进行，其中有效膜面积为140cm^2。

[0157] f)渗水压力在面积为90cm^2的圆形样品上确定。将样品夹在Sterlitech Corp,Kent WA提供的死头过滤器之间。将100mL水置于样品上。以5psi递进施加压力，压力递进之间保持15分钟。当看到穿过样品的第一滴水时记录压力。

[0158] g)孔体积：孔体积，以体积%表示，根据以下等式确定

[0159] $$孔隙度=100(1-\frac{d1}{d2})$$

[0160] 其中，d_1为样品的密度，由样品重量和样品尺寸确定，d_2为样品的固体部分的密度，由样品重量和样品的固体部分的体积确定。样品的固体部分的体积使用真密度仪(Quantachrome Corp.)依照随附的操作指南确定。

[0161] 表6：未涂覆的和亲水性涂覆的微多孔材料的物理性能

[0162]

实施例	CE-4	4A
微多孔材料	实施例 4	实施例 4
亲水性涂料	无	实施例 A
厚度(微米)	110	115
Gurley(秒)	36	35
接触角	>100°	<20°

[0163]

MD 最大伸长率	15	14
MD 最大张力	3550	2970
TD 最大伸长率	63	85
TD 最大张力	279	175

[0164] 表7:未涂覆的微多孔材料的水渗透性:

[0165]

比较例	CE-1	CE-4	CE-5	CE-6
微多孔材料	实施例 1	实施例 4	实施例 5	实施例 6
水通量@20psi(GFD)	<1*	<1*	<1*	<1*
渗水压力(psi)	>60	>40	>40	>45
孔体积(%)	>60	>80	>80	>80

[0166] *在30分钟@20psi后没有可检测到的体积。

[0167] 表8:具有亲水性涂料的微多孔材料的水渗透性:

[0168]

实施例	1A	4A	4B	4C	5A	6A
微多孔材料	实施例 1	实施例 4	实施例 4	实施例 4	实施例 5	实施例 6
亲水性涂料	实施例 A	实施例 A	实施例 B	实施例 C	实施例 A	实施例 A
水通量@ 20psi(GFD)	283	884	990	1060	1308	707
渗水压力(psi)	<5	<5	<5	<5	<5	<5
水润湿时间(秒)	<5	<5	<5	<5	<5	<5
孔体积(%)	>60	>80	>80	>80	>80	>80

[0169] 虽然以上已为了说明的目的描述了本发明的特定实施方案中,但本领域技术人员能够知道,可以对本发明细节进行许多变形而不会背离所附权利要求中限定的本发明的范围。