

Title of the Invention: Composite Yarn, Membrane And Method For Producing The Same

Field of the Invention

The invention relates to a composite yarn that may be used to make a
5 supporting structure of a membrane for Microfiltration or Ultrafiltration applications.

Background

A braided reinforced hollow fiber membrane consists of a tubular
macroporous support that is coated with a thin film of polymer on the outer surface
of the braid to form a functional membrane, where a plurality of membranes can be
10 bundled together to form a filtering membrane module, and can be used in
separation and purification process, such as industrial and municipal wastewater
treatment, brackish water treatment, and water purification.

US Patent No. 5,472,607 describes a hollow fiber membrane comprising of a
tubular braided support coated on its outer surface with a thin semipermeable film of
15 polymer. Voids in the braided support are small enough to inhibit substantial
penetration of the dope, wherein less than 33% of the outer portion of the braid's
cross-sectional area is penetrated by the membrane forming dope.

US Patent No. 6,354,444 describes an asymmetric membrane made of
polymer film supported by a tubular braid. The specifications for a braid to make the
20 long-lived membrane for use in microfiltration and ultrafiltration are described.

Braid reinforced membranes are generally bundled to form a filtering module,
and used as immersed membrane products for use in membrane bioreactors.
Although the membranes do not break during harsh operations, the membrane

coating may occasionally peel off from the braided support at high stress points, particularly where the membrane and the resin potting blocks meet.

US Patent No. 9,022,229 describes a filtering membrane with a polymeric membrane layer coated externally on a supporting structure, which comprises of
5 yarns. Some or all of the yarns of the braid are made of bi-component core-sheath PET-PVDF filaments. By using as few as 4% of the yarns in the braid with bi-component filaments, peel strength is improved, thereby enhancing its application in water or wastewater filtration.

When bi-component PVDF-PET filaments yarns, which are costly compared
10 to single component PET filament yarns, are used in the braided support to improve peel strength of the coating as described in US Patent No. 9,022,229, much of the bi-component filaments are embedded within the braided core of the support and are not in contact with the outer polymer layer, diminishing its main function of adherence with the outer polymer coating.

15 It is therefore desirable to provide a solution to use a first yarn that consists of bi-component filaments and a second yarn consisting of homofilaments to form a composite yarn, where such composite yarns, optionally with more of the second yarns, are braided or woven, which provides good adherence with a thin polymer coated externally, which does not peel off, when the membranes are bundled to form
20 a filtering membrane module, when used in harsh conditions.

Summary of the Invention

In a first aspect of the invention, there is provided a composite yarn comprising a first yarn of bi-component filaments and a second yarn of

homofilaments, wherein a majority of the first yarn is in an outer region of the composite yarn. The composite yarn may be prepared as a cowrapped yarn, a cotwisted yarn or a cospined yarn with the first yarn arranged such that it is formed on the outer region of the composite yarn. Advantageously, when the composite yarn is used to prepare a support structure for a membrane, the bi-component filaments may be exposed to the surrounding environment and thus provides greater interaction with a polymeric membrane layer coated on the supporting structure thereby reducing the amount of the costly bi-component filament required.

Preferably, the bi-components filaments of the first yarn are made from a first polymer and a second polymer. The first polymer preferably exhibits high tensile strength. The second polymer has high affinity with the polymeric membrane layer that is coated on a support structure formed from the composite yarn. The second polymer is preferably soluble or partially soluble in the solvent of the polymeric membrane dope solution.

Preferably, the first polymer is selected from the group consisting of cellulose, polyamide, polyacrylonitrile, polyester, polyolefin, polypropylene, polyvinyl chloride, and their derivatives. More preferably, the first polymer is polyethylene terephthalate (PET).

Preferably, the second polymer is selected from the group consisting of polyacrylonitrile, polysulfone, polyvinyl chloride, polyvinylidene difluoride (also known as polyvinylidene fluoride) (PVDF), and their derivatives, wherein the second polymer is selected to be different from the first polymer. More preferably, the second polymer is polyvinylidene difluoride. Advantageously, PVDF has excellent chemical resistance.

The bi-component filament may be produced as a side-by-side filament, a sheath-core filament, a matrix-fibril bicomponent filament, a segmented pie structure filament, a polymer blend filament.

In an embodiment, the bi-component filament is produced as a sheath-core filament. For example, the core-sheath bi-component filament, used in the first yarn, is made of polyethylene terephthalate (PET), a form of polyester, as the core material, and polyvinylidene difluoride (PVDF) as the sheath material. Preferably, a ratio of a first number of filaments in the core to a second number of filaments in the sheath is 1:1 or higher. In other words, the number of the filaments in the core makes up at least half of the bi-component filament and provides sufficient mechanical strength. Advantageously, the load bearing PET core of the bi-component yarns in the braided support provide the high tensile strength required as the braided support of the membrane, while reducing the amount of the costly PVDF polymer used in the braided support.

In an embodiment, the second yarn of homofilaments comprises a third polymer. The third polymer may be selected from the group consisting of cellulose, polyamide, polyacrylonitrile, polyester, polyolefin, polypropylene, polyvinyl chloride, and their derivatives. The third polymer preferably exhibits high tensile strength, and preferably is the same material as the first polymer. More preferably, the third polymer is polyethylene terephthalate (PET). Advantageously, the PET second yarns of the composite yarns provide the high tensile strength required as the braided support of the membrane.

Preferably, the bi-component filaments make up 0 to 100 percent of a total number of filaments in the composite yarn, excluding 0 percent and 100 percent.

More preferably, the bi-component filaments make up at least 1 percent of the total number of filaments in the composite yarn, or 1 to 50 percent of the total number of filaments in the composite yarn.

In a second aspect of the invention, there is provided a membrane comprising
5 a supporting structure and a polymeric membrane layer on the supporting structure. The composite yarns of the first aspect may be braided or woven to form the supporting structure and may be coated externally with a polymeric membrane layer to form a braided or composite braided reinforced membrane. Advantageously, the PVDF sheath of the bi-component filaments of the first yarn in the outer region of the
10 composite yarn in the braided support allows for improved adhesion of the PVDF polymeric membrane layer coated externally on the support structure.

In an embodiment, the composite yarn makes up 0 to 100 percent of a second total number of filaments in the supporting structure, excluding 0 percent and 100 percent. Preferably, the composite yarn makes up 4 to 50 percent of a second total
15 number of filaments in the supporting structure.

Optionally, some of the composite yarns may be substituted with a third yarn of homofilaments, and together with the composite yarns, are braided or woven to form the supporting structure. The third yarn comprises a fourth polymer, which may be selected from the group consisting of cellulose, polyamide, polyacrylonitrile,
20 polyester, polyolefin, polypropylene, polyvinyl chloride, and their derivatives. The fourth polymer preferably exhibits high tensile strength, and further preferably is the same material as the first and third polymer. The fourth polymer is preferably polyethylene terephthalate (PET).

In an embodiment, the polymeric membrane layer is selected from the group consisting of cellulose acetate, cellulose triacetate, polyether ether ketone, polyacrylonitrile, polyamides, polyethylene, polystyrene, polysulfone, polyvinyl chloride, polyvinylidene difluoride (PVDF), derivatives of the preceding polymers, blends of the preceding polymers and co-polymers of the preceding polymers. Preferably, the polymeric membrane layer penetrates partially into the supporting structure. More preferably, the polymeric membrane layer penetrates to about one third to one half of a thickness of the supporting structure.

Preferably, the membrane may be formed as a flat sheet, a tube or a hollow fiber.

The composite braided reinforced membrane may be bundled into a filtering membrane module, and may be used in a separation and purification process, such as industrial and municipal wastewater treatment, brackish water treatment, and water purification.

In a third aspect of the invention, there is provided a filtering membrane module comprising a plurality of membranes, according to the second aspect above, bundled together and potted with a resin.

In a third aspect of the invention, there is provided a method of forming a membrane, the method includes braiding or weaving the composite yarn according to the first aspect above into a support structure; and coating the support structure with a dope solution to form a polymeric membrane layer, the dope solution comprising a membrane forming polymer.

Preferably, the membrane forming polymer is selected from the group consisting of cellulose acetate, cellulose triacetate, polyether ether ketone,

polyacrylonitrile, polyamides, polyethylene, polystyrene, polysulfone, polyvinyl chloride, polyvinylidene difluoride (PVDF), derivatives of the preceding polymers, blends of the preceding polymers and co-polymers of the preceding polymers. More preferably, the membrane forming polymer is polyvinylidene difluoride.

5 Preferably, the dope solution further comprises an additive and a solvent, the additive being able to enhance or control the pore formation or the hydrophilicity of the polymeric membrane layer and the solvent is able to dissolve or partially dissolve the membrane forming polymer.

10 More preferably, the additive is selected from the group consisting of glycerol, polyethylene glycol (PEG), polyvinylpyrrolidone (PVP), water, and combinations thereof.

15 More preferably, the solvent is selected from the group consisting of acetone, chloroform, cyclohexane, dichloroethane, dimethylacetamide (DMAc), dimethylformamide, dimethylsulfoxide, formamide triethylphosphate, hexane, N-methyl-2-pyrrolidone (NMP), tetrahydrofuran, and combinations thereof. A single solvent or a mixture of solvents may be selected and used.

 Preferably, the dope solution comprises 14 to 30 weight percent of the membrane forming polymer, 1 to 20 weight percent of the additive and 55 to 85 weight percent of the solvent.

20 Preferably, coating of the support structure is done at a temperature of 50 to 90°C.

 Preferably, the method further includes allowing the coated support structure to pass through air; and entering a coagulation bath to form the membrane.

Preferably, wherein the coated support structure passes through 30 to 200 mm of air.

Preferably, the coagulation bath is at a temperature of 20°C to 60°C

Preferably, the method further includes passing the membrane through a
5 leaching tank.

In an embodiment, the braided reinforced hollow fiber membrane is prepared by coating the braided support with a dope solution based on PVDF and Dimethylacetamide (DMAc). The PVDF membrane layer penetrates partially into the braided support, and is not peelable from the braided support.

10 In yet another embodiment of the invention, the composite yarn, described above, together with a third yarn, which consists of PET filaments, are braided or woven together to form the composite braided support. The composite braided reinforced hollow fiber membrane is produced by coating the composite braided support with a dope solution based on PVDF and DMAc, as described above. The
15 PVDF membrane layer penetrates partially into the composite braided support and is not peelable from the support structure.

The composite yarn described above advantageously allows for greater interaction between the second polymer in the bi-component filaments and the polymeric membrane layer, and thus allows the polymeric membrane layer to be
20 held more strongly to the support structure with minimal use of the costly bi-component filament.

Detailed Description of Embodiments of the Invention

In the following description, numerous specific details are set forth in order to provide a thorough understanding of various illustrative embodiments of the invention. It will be understood, however, to one skilled in the art, that embodiments of the invention may be practiced without some or all of these specific details. It is
5 understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to limit the scope of the invention.

Embodiments described in the context of one of the systems or methods are analogously valid for the other systems or methods. Similarly, embodiments described in the context of a method are analogously valid for a system, and vice
10 versa.

Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly
15 described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

As used herein, the articles “a”, “an” and “the” as used with regard to a feature
20 or element include a reference to one or more of the features or elements. As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items. As used herein, the terms “first,” “second,” and “third,” etc. are used merely as labels, and are not intended to impose numerical requirements on their objects.

The terms “about”, “approximately”, “substantially” must be read with reference to the context of the application as a whole, and have regard to the meaning a particular technical term qualified by such a word usually has in the field concerned. For example, it may be understood that a certain parameter, function,
5 effect, or result can be performed or obtained within a certain tolerance, and the skilled person in the relevant technical field knows how to obtain the tolerance of such term.

Where a range of values is recited, it is to be understood that each intervening integer value, and each fraction thereof, between the recited upper and lower limits
10 of that range is also specifically disclosed, along with each subrange between such values. The upper and lower limits of any range is included in the disclosure or unless expressly excluded, and each range where either, neither or both limits are included is also encompassed within the invention. Where a value being discussed has inherent limits, for example where a component can be present at a concentration
15 of from 0 to 100%, or where the pH of an aqueous solution can range from 1 to 14, those inherent limits are specifically disclosed. Where a value is explicitly recited, it is to be understood that values which are about the same quantity or amount as the recited value are also within the scope of the invention, as are ranges based thereon.

Embodiments of the invention relates to a braided or composite braided
20 reinforced polymeric membrane, which has high tensile strength. A plurality of membrane fibers may be bundled together and potted with a resin into a filtering membrane module. A resin may be an epoxy resin, or a polyurethane resin, or any other adhesive resin, or a combination thereof, that can securely bundle the membrane fibers into a filtering membrane module. The filtering membrane module

may be used for separation and purification process, such as industrial and municipal wastewater treatment, brackish water treatment, and water purification.

In one embodiment of the invention, bi-component filaments make up a first yarn. The bi-component filaments comprise a first polymer and a second polymer.

5 The first and second polymers are combined to form filaments of desirable properties. Bi-components filaments may be produced as side-by-side filaments, sheath-core filaments, matrix-fibril bicomponent filaments, segmented pie structure filaments, polymer blends filaments. Preferably, sheath-core filaments comprising of a first polymer core and a second polymer sheath are used to form the first yarn.

10 Sheath-core filaments may be produced by extrusion with the second polymer extruded as the sheath surrounding the already formed first polymer, the core, or may be produced by co-extrusion where both the first and second polymers are extruded together to form the sheath-core filament. The methods of producing the bi-components filaments are known.

15 The first polymer is chosen for its tensile strength and other factors including cost. The first polymer may be cellulose, polyamide, polyacrylonitrile, polyester, polyolefin, polypropylene, polyvinyl chloride, and their derivatives. Preferably, the first polymer is polyethylene terephthalate (PET). The second polymer is chosen for its compatibility with the polymeric membrane layer of the membrane, and is soluble

20 or partially soluble in the solvent used in forming the polymeric membrane layer. The second polymer may be polyacrylonitrile, polysulfone, polyvinyl chloride, polyvinylidene difluoride (may also be known as polyvinylidene fluoride) (PVDF), and their derivatives. Preferably the second polymer is PVDF. For example, a sheath-core filament with a PET core and a PVDF sheath may have a core/sheath ratio of

50/50 (1:1) or higher as measured by the number of filaments in the core and sheath regions, such that the filaments, when formed into a first yarn, has got sufficient and comparable mechanical strength when used with a second or third yarn. In other words, the core contains 50% or more of the number of filaments in the sheath-core filament.

A second yarn is made of homofilaments. The homofilaments of the second yarn comprises a third polymer. The third polymer is chosen for its tensile strength and other factors including cost and similar mechanical properties with that of the first polymer in the first yarn. The third polymer may be cellulose, polyamide, polyacrylonitrile, polyester, polyolefin, polypropylene, polyvinyl chloride, and their derivatives. Preferably, the third polymer is PET, and is the same as the first polymer in the bi-component filament

The first yarn and the second yarn are mixed and combined to form a single composite or hybrid yarn. A majority of the first yarn of bicomponent filaments is in an outer region of the composite yarn. For example, at least 50% of the first yarn should be in the outer region of the composite yarn, preferably at least 60%, at least 70%, at least 80% or at least 90% of the first yarn should be in the outer region. The outer region refers to the region of the composite yarn exposed to the surrounding environment. Advantageously, when the hybrid yarn is used to make a support structure for a membrane, the location of the majority of the first yarn in the outer region allows the first yarn bicomponent filaments to easily come into direct contact with the dope solution and polymeric membrane layer formed on the supporting structure. On the other hand, if the bicomponent filaments resides in the 'inner region', the polymer dope solution needs to penetrate through the outer region of the

hybrid yarn before it comes in contact with the bicomponent filaments. Usually, this is not feasible as the penetration is limited by the membrane spinning conditions and the tightness of the braid. A composite yarn may be produced by known methods, for example as a cowrapped yarn, a cospined yarn, or a cotwisted yarn. In an example, the second yarn of homofilaments with no twist is wrapped with continuous bicomponent filaments of the first yarn to form a hybrid yarn (i.e. a cowrapped yarn). In another example, both the first and second yarns are heli-twisted together to form a hybrid yarn (i.e. a cotwisted yarn). A composite yarn may contain 0 to 100% of the first yarn (in terms of the number of filaments) excluding 0 and 100%, preferably containing 1 to 50% of the first yarn. In other words, the number of bicomponent filaments of the first yarn is present in 0 to 100% of the total number of filaments present (excluding 0 and 100%), preferably 1 to 50%, with the homofilaments making up the remainder. The composite yarns are braided or weave to form a support structure of the membrane. For example, the support structure is a braid of the composite yarn.

The braided or composite braided reinforced polymeric membrane may be in the form of flat sheets or tubes or hollow fibers. The cross-section of a finished membrane comprises of two or more regions. In the case of a hollow fiber membrane, it has an outer diameter of about 3.5 mm or less, preferably 2.8 mm or less. The inner most wall of the membrane defines a lumen or bore of the membrane, which may have a diameter of between 0.25 and 2.5 mm, preferably between 0.5 and 2.0 mm. A support structure of the membrane defines the inner most surface of the membrane and an outer surface. The support structure has a thickness of between 0.1 and 0.8 mm, preferably between 0.2 and 0.6 mm. The support structure

has voids or pores or openings, which allows fluid communication from outside to inside and inside to outside. On top of the support structure lies a polymeric membrane layer, which the outer most wall defines the outer diameter of the hollow fiber membrane. The inner most wall of the polymeric membrane layer may meet the
5 outer surface of the support structure. Preferably the polymeric membrane layer may penetrate the support structure and extend through the entire thickness of the support structure. More preferably, the polymeric membrane layer may penetrate the support structure and extend into about one third to one half of the thickness of the support structure. In one embodiment of the invention, the thickness of the uniform
10 polymeric membrane layer that lies above the support structure, is controlled by the membrane preparation method and is typically between 0.03 to 0.2 mm, preferably between 0.05 to 0.12 mm.

The support structure of the membrane comprises of yarns that are braided or woven to form a sheet or tube. In the case of a hollow fiber membrane, the support
15 structure is made in a Diamond or Regular or Hercules braid pattern, preferably a Diamond braid pattern, where one yarn passes above and then below the other yarns. The braid is woven by a tubular braiding machine, and the method and type of machine is known. The braid is preferably woven with 36-44 picks per inch.

A third yarn may optionally be used together with the composite yarn to be
20 woven together to form a composite braid (or a support structure) of the membrane. The third yarn comprises of homofilaments. The homofilaments of the third yarn comprises of a fourth polymer. The fourth polymer is chosen for its tensile strength and other factors including cost and similar mechanical properties with that of the first polymer in the first yarn and third polymer in the second yarn. The fourth polymer

may be cellulose, polyamide, polyacrylonitrile, polyester, polyolefin, polypropylene, polyvinyl chloride, and their derivatives. Preferably, the fourth polymer is PET. The composite braid (in other words the support structure) may comprise of 0 to 100 % (excluding 0 and 100 %) of the composite yarn in terms of the total number of
5 filaments in the composite braid, preferably containing 4 to 50% of the composite yarn in terms of the total number of filaments.

The polymeric membrane layer of the membrane is casted or coated onto the support structure. Generally, the dope solution comprises of a membrane forming polymer and a solvent for the polymer. Optionally, additives may be added to the
10 dope solution. A membrane forming polymer includes cellulose acetate, cellulose triacetate, polyether ether ketone (PEEK), polyacrylonitrile, polyamides, polyethylene, polystyrene, polysulfone, polyvinyl chloride, polyvinylidene difluoride (PVDF) or their derivatives, or blends or co-polymers of the above. Preferably, the membrane forming polymer is PVDF. Solvents includes acetone, chloroform,
15 cyclohexane, dichloroethane, dimethylacetamide (DMAc), dimethylformamide, dimethylsulfoxide, formamide triethylphosphate, hexane, N-methyl-2-pyrrolidone (NMP), tetrahydrofuran, or others that are able to dissolve or partially dissolve the membrane forming polymer, or a combination of the above. Additives may comprise
20 hydrophilic additives that may enhance or control the pore formation or the hydrophilicity of the polymeric membrane layer of the membrane.

The dope solution may comprise 14 to 30 wt% membrane forming polymer, 1 to 20 wt% additives, and 55 to 85 wt% solvent.

In the case of a braided or composite braided reinforced hollow fiber membrane, the general process for the preparation of the membrane is as below. A braided or composite braided support tube is guided and delivered via a set of rollers, which controls the support tube tension, to the spinneret. The support tube is allowed to pass through the innermost bore of the spinneret, which opens into a dope chamber of the spinneret. Herein, a dope solution, with temperature of 50 to 90°C, preferably 50 to 70°C, is fed into the spinneret and flows uniformly by way of connected orifices into the dope chamber of the spinneret. The dope solution coats uniformly on the external surface of the support tube. The dope solution in the dope chamber of the spinneret is preferably allowed to penetrate the support tube and extend through the thickness of the support tube. More preferably, the dope solution is allowed to extend into about one third to one half of the thickness of the support tube. When a braided or composite braided support tube is used, where bi-components filaments are used, the second polymer in the sheath of bi-components filaments, which are soluble or partially soluble in the solvent of the dope solution, allows for higher affinity with the membrane polymer layer in the dope solution, thereby anchoring the polymeric membrane layer and improve adhesion of the layer with that of the support tube. The support tube together with the dope solution coating exit through a sizing orifice or bore to achieve the required polymeric membrane layer thickness. The dope solution coated support tube is allowed to travel a distance, in the range of 30 to 200 mm, in air before entering a coagulation bath, containing water at a controlled temperature in the range of 20 to 60°C, wherein polymer phase inversion, of the dope solution coating, from liquid to solid takes place to form the hollow fiber membrane. The hollow fiber membrane is collected by a

take-up wheel at a rate of 10 to 40 m/min. Optionally, the hollow fiber membrane may be passed through a leaching tank containing water comprising of sodium hypochlorite or just water, via a series of rollers, to further remove solvent and additives.

5 In the following examples, the percentage of the bicomponent filaments refers to the number of bi-component filaments divided by the total number of filaments in the composite yarn, and the ratio of the bi-component filaments refer to the number of the filaments belonging to the first polymer to the number of filaments belonging to the second polymer, which are PET and PVDF respectively in the following
10 examples.

EXAMPLE 1

A composite yarn comprising 1.5% of 50/50 core-sheath PET-PVDF bi-components filaments together with PET homofilaments, are woven to form a braid support tube with inner diameter of 1.00 mm and outer diameter of 1.90 mm. The
15 braid support tube, together with a dope solution at 65°C comprising 20 wt% PVDF, 8 wt% PVP, and 72 wt% DMAc, are fed into a spinneret. The dope solution coats uniformly on the braid support tube and exits the spinneret, traveling through a 100 mm air gap, before entering a coagulation bath controlled at 40°C. Upon coagulation and forming the membrane layer, the hollow fiber membrane is collected by a take-
20 up wheel at a rate of 25 m/min. The braided reinforced hollow fiber membrane has an outer diameter 2.04 mm, a water permeability of 880 L/m²/h at 20°C and 0.1 MPa, and a bubble point of 0.26 MPa. The PVDF membrane layer could not be removed from the support tube via a peel strength test using standard test equipment.

COMPARATIVE EXAMPLE 1

A yarn comprising only PET homofilaments are woven to form a braid support tube with inner diameter of 1.00 mm and outer diameter of 1.89 mm. A dope solution and preparation method analogous to that of Example 1 are used to produce braided reinforced hollow fiber membrane. The braided reinforced hollow fiber membrane has an outer diameter 2.01 mm, a water permeability of 920 L/m²/h at 20°C and 0.1 MPa, and a bubble point of 0.25 MPa. The PVDF membrane layer peel strength is 0.25 N.

EXAMPLE 2

A composite yarn similar to the one used in Example 1, comprises of 4.4% of 50/50 core-sheath PET-PVDF bi-components filaments together with PET homofilaments, are woven to form a braid support tube with inner diameter of 1.00 mm and outer diameter of 1.90 mm. The braid support tube, together with a dope solution at 55°C comprising 16 wt% PVDF, 8 wt% PVP, 8 wt% PEG and 68 wt% DMAc, are fed into a spinneret. The dope solution coats uniformly on the braid support tube and exits the spinneret, traveling through a 50 mm air gap, before entering a coagulation bath controlled at 40°C. Upon coagulation and forming the membrane layer, the hollow fiber membrane is collected by a take-up wheel at a rate of 28 m/min. The braided reinforced hollow fiber membrane has an outer diameter 2.00 mm, a water permeability of 1,130 L/m²/h at 20°C and 0.1 MPa, and a bubble point of 0.23 MPa. The PVDF membrane layer could not be removed from the support tube via a peel strength test using standard test equipment.

EXAMPLE 3

A composite yarn similar to the one used in Example 1, comprises of 50% of 50/50 core-sheath PET-PVDF bi-components filaments together with PET

homofilaments, are woven to form a braid support tube with inner diameter of 1.00 mm and outer diameter of 1.92 mm. The braid support tube, together with a dope solution at 68°C comprising 22 wt% PVDF, 6 wt% PVP, and 72 wt% NMP, are fed into a spinneret. The dope solution coats uniformly on the braid support tube and exits the spinneret, traveling through a 80 mm air gap, before entering a coagulation bath controlled at 40°C. Upon coagulation and forming the membrane layer, the hollow fiber membrane is collected by a take-up wheel at a rate of 20 m/min. The braided reinforced hollow fiber membrane has an outer diameter 2.08 mm, a water permeability of 760 L/m²/h at 20°C and 0.1 MPa, and a bubble point of 0.30 MPa. The PVDF membrane layer could not be removed from the support tube via a peel strength test using standard test equipment.

EXAMPLE 4

Yarns comprise of 100% of 50/50 core-sheath PET-PVDF bi-components filaments, are woven to form a braid support tube with inner diameter of 1.00 mm and outer diameter of 1.92 mm. The braid support tube, together with a dope solution at 65°C comprising 21 wt% PVDF, 3 wt% PVP, 3 wt% Glycerin and 73 wt% DMAc, are fed into a spinneret. The dope solution coats uniformly on the braid support tube and exits the spinneret, traveling through a 120 mm air gap, before entering a coagulation bath controlled at 40°C. Upon coagulation and forming the membrane layer, the hollow fiber membrane is collected by a take-up wheel at a rate of 30 m/min. The braided reinforced hollow fiber membrane has an outer diameter 2.04 mm, a water permeability of 660 L/m²/h at 20°C and 0.1 MPa, and a bubble point of 0.31 MPa. The PVDF membrane layer could not be removed from the support tube via a peel strength test using standard test equipment.

EXAMPLE 5

A composite yarn analogous to the one used in Example 3, are used together with a third yarn of comprising of PET homofilaments only, are woven to form a composite braid support tube with inner diameter of 1.00 mm and outer diameter of 1.90mm. The composite braid support tube comprises of 4.2% of the composite yarn, and support tube effectively comprises of 2.1% of the PET-PVDF bi-component filaments. The braid support tube, together with a dope solution at 50°C comprising 16 wt% PVDF, 4 wt% PVP, and 80 wt% NMP, are fed into a spinneret. The dope solution coats uniformly on the braid support tube and exits the spinneret, traveling through a 50 mm air gap, before entering a coagulation bath controlled at 40°C. Upon coagulation and forming the membrane layer, the hollow fiber membrane is collected by a take-up wheel at a rate of 30 m/min. The braided reinforced hollow fiber membrane has an outer diameter 2.02 mm, a water permeability of 920 L/m²/h at 20°C and 0.1 MPa, and a bubble point of 0.26 MPa. The PVDF membrane layer could not be removed from the support tube via a peel strength test using standard test equipment.

EXAMPLE 6

A composite braid support tube similar to the one used in Example 5, are woven from a 50% composite yarn comprising of 50% of 50/50 core-sheath PET-PVDF bi-components filaments together with PET homofilaments, and further comprises of 50% of a third yarn comprising of PET homofilaments only, wherein the effective PET-PVDF bi-components filaments is 25% of the composite braid support tube. The composite braid support tube has inner diameter of 1.00 mm and outer diameter of 1.92mm. The braid support tube, together with a dope solution at 70°C comprising

24 wt% PVDF, 1 wt% PVP, and 75 wt% DMAc, are fed into a spinneret. The dope solution coats uniformly on the braid support tube and exits the spinneret, traveling through a 50 mm air gap, before entering a coagulation bath controlled at 40°C. Upon coagulation and forming the membrane layer, the hollow fiber membrane is collected by a take-up wheel at a rate of 20 m/min. The braided reinforced hollow fiber membrane has an outer diameter 2.06 mm, a water permeability of 790 L/m²/h at 20°C and 0.1 MPa, and a bubble point of 0.30 MPa. The PVDF membrane layer could not be removed from the support tube via a peel strength test using standard test equipment.

EXAMPLE 7

A composite yarn analogous to the one used in Example 3, are used together with a third yarn comprising of PET homofilaments only, are woven to form a composite braid support tube with inner diameter of 1.00 mm and outer diameter of 1.90mm. The composite braid support tube comprises of 8.4% of the composite yarn, and support tube effectively comprises of 4.2% of the PET-PVDF bi-component filaments. The braid support tube, together with a dope solution at 55°C comprising 20 wt% PVDF, 2 wt% PVP, 8 wt% Glycerin and 70 wt% DMAc, are fed into a spinneret. The dope solution coats uniformly on the braid support tube and exits the spinneret, traveling through a 100 mm air gap, before entering a coagulation bath controlled at 40°C. Upon coagulation and forming the membrane layer, the hollow fiber membrane is collected by a take-up wheel at a rate of 25 m/min. The braided reinforced hollow fiber membrane has an outer diameter 2.06 mm, a water permeability of 1210 L/m²/h at 20°C and 0.1 MPa, and a bubble point of 0.26 MPa.

The PVDF membrane layer could not be removed from the support tube via a peel strength test using standard test equipment.

5 The examples show that as little as 1 percent (or 1.5 percent) of the bi-component filaments in the outer region of the composite yarn is sufficient to provide a support structure which interacts strongly with the polymeric membrane layer and dope solution. Advantageously, this minimises the cost of the support structure and membrane while preventing the removal of the polymeric membrane layer from the support structure and protecting the structural integrity of the membrane.

10 It is to be understood that the embodiments and features described above should be considered exemplary and not restrictive. Many other embodiments will be apparent to those skilled in the art from consideration of the specification and practice of the invention. The scope of the invention should, therefore, be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled. Furthermore, certain terminology has been used for
15 the purposes of descriptive clarity, and not to limit the disclosed embodiments of the invention.

Claims

[Claim 1] A composite yarn comprising a first yarn of bi-component filaments and a second yarn of homofilaments, wherein a majority of the first yarn is in an outer region of the composite yarn.

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[Claim 2] The composite yarn according to claim 1 wherein the bi-component filament comprises a first polymer and a second polymer.

[Claim 3] The composite yarn according to claim 2 wherein the first polymer is
10 selected to have high tensile strength, the second polymer is selected to have high affinity with a polymeric membrane layer.

[Claim 4] The composite yarn according to any one of claims 2 to 3 wherein the first polymer is selected from the group consisting of cellulose, polyamide,
15 polyacrylonitrile, polyester, polyolefin, polypropylene, polyvinyl chloride, and their derivatives.

[Claim 5] The composite yarn according to any one of claims 2 to 4 wherein the first polymer is polyethylene terephthalate.

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[Claim 6] The composite yarn according to any one of claims 2 to 5 wherein the second polymer is selected from the group consisting of polyacrylonitrile, polysulfone, polyvinyl chloride, polyvinylidene difluoride (PVDF), and their derivatives, wherein the second polymer is selected to be different from the first polymer.

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[Claim 7] The composite yarn according to claims 2 to 6 wherein the second polymer is polyvinylidene difluoride.

[Claim 8] The composite yarn according to any one of claims 2 to 7 wherein the
5 bi-component filament is produced as a side-by-side filament, a sheath-core filament, a matrix-fibril bicomponent filament, a segmented pie structure filament, a polymer blend filament.

[Claim 9] The composite yarn according to claim 8 wherein the bi-component
10 filament is produced as the sheath-core filament with a core made of the first polymer and a sheath made of the second polymer.

[Claim 10] The composite yarn according to claim 9 wherein a ratio of a first
15 number of filaments in the core to a second number of filaments in the sheath is 1:1 or higher.

[Claim 11] The composite yarn according to any one of claims 1 to 10 wherein the
second yarn of homofilaments comprises a third polymer, the third polymer is
selected from the group consisting of cellulose, polyamide, polyacrylonitrile,
20 polyester, polyolefin, polypropylene, polyvinyl chloride, and their derivatives.

[Claim 12] The composite yarn according to claim 11 wherein the third polymer is polyethylene terephthalate.

[Claim 13] The composite yarn according to any one of claims 1 to 12 wherein the bi-component filaments make up 0 to 100 percent of a total number of filaments in the composite yarn, excluding 0 percent and 100 percent.

5 [Claim 14] The composite yarn according to claim 13 wherein the bicomponent filaments makes up 1 to 50 percent of the total number of filaments in the composite yarn.

[Claim 15] The composite yarn according to any one of claims 1 to 14 wherein the
10 composite yarn is prepared as a cowrapped yarn, a cotwisted yarn, or a cospined yarn.

[Claim 16] A membrane comprising a supporting structure and a polymeric membrane layer on the supporting structure, wherein the composite yarn according
15 to any one of claims 1 to 15 is braided or woven to form the supporting structure.

[Claim 17] The membrane according to claim 16 wherein a third yarn and the composite yarn is braided or woven to form the supporting structure.

20 [Claim 18] The membrane according to claim 17 wherein the third yarn comprises a fourth polymer, the fourth polymer selected from the group consisting of cellulose, polyamide, polyacrylonitrile, polyester, polyolefin. polypropylene, polyvinyl chloride, and their derivatives.

[Claim 19] The membrane according to any one of claims 17 to 18 wherein the composite yarn makes up 0 to 100 percent of a second total number of filaments in the supporting structure, excluding 0 percent and 100 percent.

- 5 [Claim 20] The membrane according to claim 19 wherein the composite yarn makes up 4 to 50 percent of the second total number of filaments in the supporting structure.

- [Claim 21] The membrane according to any one of claims 16 to 20 wherein the
10 polymeric membrane layer is selected from the group consisting of cellulose acetate, cellulose triacetate, polyether ether ketone, polyacrylonitrile, polyamides, polyethylene, polystyrene, polysulfone, polyvinyl chloride, polyvinylidene difluoride (PVDF), derivatives of the preceding polymers, blends of the preceding polymers and co-polymers of the preceding polymers.

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[Claim 22] The membrane according to any one of claims 16 to 21 wherein at least part of the polymeric membrane layer penetrates the supporting structure.

- [Claim 23] The membrane according to claim 22 wherein the polymeric
20 membrane layer penetrates to about one third to one half of a thickness of the supporting structure.

[Claim 24] The membrane according to any one of claims 16 to 23 wherein the membrane is a flat sheet, a tube, or a hollow fiber.

[Claim 25] A filtering membrane module comprising a plurality of membranes according to any one of claims 16 to 24 bundled together and potted with a resin.

5 [Claim 26] A method of forming a membrane, the method comprising:
braiding or weaving the composite yarn according to any one of claims 1 to 15 into
a support structure; and
coating the support structure with a dope solution to form a polymeric membrane
layer, the dope solution comprising a membrane forming polymer.

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[Claim 27] The method according to claim 26 wherein the membrane forming
polymer is selected from the group consisting of cellulose acetate, cellulose
triacetate, polyether ether ketone, polyacrylonitrile, polyamides, polyethylene,
polystyrene, polysulfone, polyvinyl chloride, polyvinylidene difluoride (PVDF),
15 derivatives of the preceding polymers, blends of the preceding polymers and co-
polymers of the preceding polymers.

[Claim 28] The method according to any one of claims 26 to 27 wherein the dope
solution further comprises an additive and a solvent, the additive being able to
20 enhance or control the pore formation or the hydrophilicity of the polymeric
membrane layer and the solvent is able to dissolve or partially dissolve the
membrane forming polymer.

[Claim 29] The method according to claim 28 wherein the additive is selected from the group consisting of glycerol, polyethylene glycol (PEG), polyvinylpyrrolidone (PVP), water, and combinations thereof.

- 5 [Claim 30] The method according to any one of claims 28 to 29 wherein the solvent is selected from the group consisting of acetone, chloroform, cyclohexane, dichloroethane, dimethylacetamide (DMAc), dimethylformamide, dimethylsulfoxide, formamide triethylphosphate, hexane, N-methyl-2-pyrrolidone (NMP), tetrahydrofuran, and combinations thereof.

10

[Claim 31] The method according to any one of claims 28 to 30 wherein the dope solution comprises 14 to 30 weight percent of the membrane forming polymer, 1 to 20 weight percent of the additive and 55 to 85 weight percent of the solvent.

- 15 [Claim 32] The method according to any one of claims 26 to 31 wherein coating of the support structure is done at a temperature of 50 to 90°C.

[Claim 33] The method according to any one of claims 26 to 32 further comprising allowing the coated support structure to pass through air; and entering a coagulation bath to form the membrane.

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[Claim 34] The method according to claim 33 wherein the coated support structure passes through 30 to 200 mm of air.

[Claim 35] The method according to any one of claims 33 to 34 wherein the coagulation bath is at a temperature of 20°C to 60°C

[Claim 36] The method according to any one of claims 33 to 35 further comprising
5 passing the membrane through a leaching tank.