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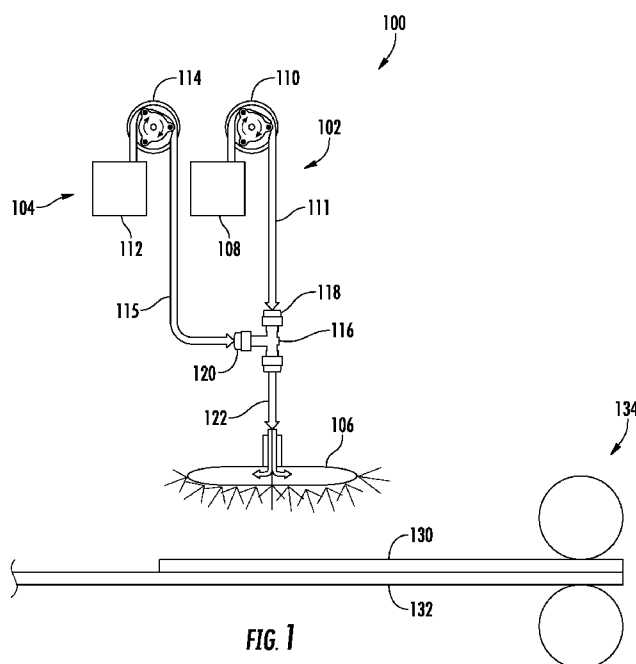
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(57) Abstract: A method of preparing a composite nanofiber layer, which exhibits high internal bond strength by spinning a polymer (from solution) with a melting point of at least 25 deg C higher than that of the other polymer solution with low melting point polymer. The two polymer solutions can be miscible or immiscible. The unique blending of such two polymer solutions are performed just above the spinning head to obtain such composite nanofiber layer with desired final product performance. The nanofiber layer is post-treated with heat of about 100 - 180 deg C along with or without pressure of 40 - 60 psi. After such post-treatment, the low melting temperature polymer partially melts and attaches with adjacent fibers and at intersections just enough to improve the internal bond strength up to 120 psi without affecting the permeability of the porous structure yielding air permeability of at least 1.25 CFM.

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POLYMER / ADHESIVE COMPOSITE FIBERS FOR INTER-FIBER ADHESION**BACKGROUND OF THE INVENTION**

[0001] The applicants have determined that nanofibers will often have inadequate inter-fiber adhesion due to lack of cohesive forces between the fibers such that undesirable delamination can occur between the fibers.

[0002] To prevent delamination, in the past, attempts were made to use heated calender rolls to compress the membrane, use solvent to soften and adhere the fibers, dip the media into adhesive or spray adhesive onto the media to improve the inter-fiber adhesion. However, the heated calender rolls did not help much with the adhesion. The solvent approach caused too many defects in the membrane, which impacted other membrane properties, such as hydrostatic head, negatively. The approach of dipping in adhesive or spraying with adhesive can improve the inter-fiber adhesion but it lowers the air permeability of the membrane significantly. Additionally, it was attempted to mix an adhesive with polymer in the solution and spin the solution into fibers. Unfortunately, this resulted in an unstable solution which resulted in inconsistent fiber spinning.

[0003] Related prior art includes US8231378B2; US20140035177A1; WO2015091187A1; WO2011142726A1; US20160310910A1; WO2011151314A1; and US8642172 B2.

BRIEF SUMMARY OF THE EMBODIMENTS

[0004] New and improved methods of forming a membrane construction and apparatuses for forming such a construction are provided. The methods and/or apparatuses provide membrane constructions that have improved inter-fiber adhesions without reduction or significant reduction in filtering characteristics.

[0005] In an embodiment, a method of forming a membrane construction is provided. The method includes a) flowing a first solution including a first polymer toward a spinneret; b) flowing a second solution including a second polymer, different than the first polymer,

toward the spinneret; c) mixing the first solution and second solution by combining the flow of first solution and flow of second solution to provide a mixture; d) flowing the mixture of the first and second solutions to the spinneret; and e) dispensing, with the spinneret, the mixture to form a nanofiber layer formed from the first and second polymers.

[0006] In one method, the nanofiber layer has inter-fiber adhesions between adjacent fibers formed by the second polymer.

[0007] In one method, flowing the first solution is performed before forming the mixture by a first pump that directly pumps the first solution and flowing the second solution is performed before forming the mixture by a second pump that directly pumps the second solution. As such, none of the first solution flows through the second pump and none of the second solution flows through the first pump.

[0008] In one method, after dispensing the mixture, the method includes processing the nanofiber layer to form the inter-fiber adhesions between the composite fibers.

[0009] In one method, processing the nanofiber layer includes applying heat to the nanofiber layer to melt at least a portion of the nanofiber layer formed from the second polymer.

[0010] In one method, heat is applied for between 60 and 180 seconds.

[0011] In one method, heat is applied for not more than 600 seconds.

[0012] In one method, heat is applied at between 100 and 180 degrees Celsius.

[0013] In one method, heat is applied at between 140 and 160 degrees Celsius.

[0014] In one method, processing the nanofiber layer includes applying both heat and pressure to the nanofiber layer.

[0015] In one method, the heat is applied by calendar rolls, drums or belts.

[0016] In one method, pressure is applied at between greater than 0 PSI and less than or equal to 80 PSI.

[0017] In one method, the first polymer has a melting temperature that is higher than a melting temperature of the second polymer. The step of applying heat is at a temperature higher than the melting temperature of the second polymer. Optionally, the second polymer is raised to a temperature higher than the melting point of the second polymer.

[0018] In one method, the melting temperature of the first polymer is at least 10 degrees Celsius greater than the melting temperature of the second polymer.

[0019] In one method, the melting temperature of the first polymer is between 70 and 300 degrees Celsius and the melting temperature of the second polymer is between 50 and 250 degrees Celsius.

[0020] In one method, the melting temperature of the first polymer is between 200 and 250 degrees Celsius and the melting temperature of the second polymer is between 130 and 150 degrees Celsius.

[0021] In one method, the step of mixing the first solution and second solution occurs in tubing upstream of the spinneret.

[0022] In one method, the mixture of first solution and second solution is formed not more than 3 feet from the spinneret, and in a particular embodiment not more than 3 feet from the outlet nozzles of the spinneret.

[0023] In one method, the mixture of first solution and second solution is formed sufficiently close to the spinneret and the flow of the mixture is such that the mixture can be dispensed before the mixture becomes unstable for immiscible solutions or completely mixed for miscible solutions.

[0024] In one method, the fibers have an average fiber size of between 50 and 1000 nm.

[0025] In one method, the first solution has a viscosity of between 2000 and 4000 cP and wherein the second solution has a viscosity of between 100 and 5000 cP and preferably between 1500 and 2500 cP. Thus, in some embodiments, the first solution has a viscosity that is higher than the viscosity of the second solution.

[0026] In one method, the fibers of the nanofiber layer are nanofibers. At least a portion of the nanofibers are composite fibers formed from both the first and second polymers as the nanofibers are dispensed from the spinneret and prior to forming the nanofiber layer.

[0027] In one method, the mixture of first solution and second solution has, by weight, at least as much first solution as second solution.

[0028] In one method, the step of dispensing, with the spinneret, is performed by forcespinning the mixture and without electrospinning.

[0029] In one method, the first and second solutions are immiscible.

[0030] In one method, the first polymer and second polymer are selected from the group consisting of: polyacetals, polyamides, epoxy, polyesters, polyurethanes, cellulose ethers, cellulose esters, polyalkylene sulfides, polyarylene oxides, polysulfones, modified polysulfone polymers and mixtures thereof. And can further comprise poly(vinylchloride), polymethylmethacrylate, polystyrene, and copolymers thereof, poly(vinylidene fluoride), poly(vinylidene chloride), polyvinylalcohol.

[0031] In one method, the step of dispensing the mixture to form a nanofiber layer includes dispensing the nanofibers onto a substrate. The method further includes removing the nanofiber layer from the substrate prior to the step of applying heat to the nanofiber layer.

[0032] In one method, the first solution may comprise a polymer in the form of polyacetals, polyamides, epoxy, polyesters, polyurethanes, cellulose ethers, cellulose esters, polyalkylene sulfides, polyarylene oxides, polysulfones, modified polysulfone polymers and mixtures thereof and can further comprise poly(vinylchloride), polymethylmethacrylate, polystyrene, and copolymers thereof, poly(vinylidene fluoride), poly(vinylidene chloride),

polyvinylalcohol with the polymer dissolved in anyone of the following: formic acid and/or water, ethanol, chloroform, acetone, N,N- dimethylformamide (DMF), dimethylacetamide (DMAc), formic acid, acetic acid, N-Methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF) and mixture thereof. The second solution may comprise a polymer in the form of polyacetals, polyamides, epoxy, polyesters, polyurethanes, cellulose ethers, cellulose esters, polyalkylene sulfides, polyarylene oxides, polysulfones, modified polysulfone polymers and mixtures thereof and can further comprise poly(vinylchloride), polymethylmethacrylate, polystyrene, and copolymers thereof, poly(vinylidene fluoride), poly(vinylidene chloride), polyvinylalcohol with the polymer dissolved in anyone of the following: formic acid, and/or water, ethanol, chloroform, acetone, N,N- dimethylformamide (DMF), dimethylacetamide (DMAc), formic acid, acetic acid, N-Methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF) etc. and mixtures thereof.

[0033] In one method, the nanofiber layer after heat treatment achieves internal bond strength measured as Z-directional strength between 10 psi and 120 psi.

[0034] In one method, the nanofibers have an average fiber size of between 50 nm and 1000 nm. The nanofiber layer has a hydrostatic head of at least 10000 mm of water (as per AATCC 127) and an air permeability of at least 1.25 cfm (as per ASTM D737) and Z-directional strength of at least 10 psi (as per TAPPI T541-OM-10) and a basis weight of between 5 and 30 grams/square meter.

[0035] In an embodiment, a membrane construction is provided. The membrane construction includes a nanofiber layer formed from a plurality of nanofibers. The plurality of nanofibers are formed from a first polymer and a second polymer. The second polymer is different than the first polymer. The nanofiber layer has a plurality of inter-fiber adhesions formed by the second polymer. The nanofibers have an average fiber size of between 50 nm and 1000 nm and the nanofiber layer has a hydrostatic head of at least 10000 mm of water (as per AATCC 127) and an air permeability of at least 1.25 cfm (as per ASTM D737) and Z-directional strength of at least 10 psi (as per TAPPI T541-OM-10) and a basis weight of between 5 and 30 grams/square meter.

[0036] In one embodiment, the plurality of nanofibers may have some fibers made entirely of the first polymer, some fibers made entirely of the second polymer and some fibers made from a mixture of both the first and second polymers.

[0037] In one embodiment, the nanofibers forming the layer of nanofibers are formed by forcespinning without electrospinning.

[0038] In one embodiment, the ratio-by-weight of the first polymer to the second polymer is between 1 and 10.

[0039] In one embodiment, the ratio-by-weight of the first polymer to the second polymer is between 3 and 5.

[0040] In one embodiment, the first polymer is in a first polymer solution prior to formation of the nanofibers. The second polymer is in a second polymer solution prior to formation of the nanofiber. The first and second polymer solutions are immiscible or miscible.

[0041] In one embodiment, the first polymer is in a first polymer solution prior to formation of the nanofibers. The first polymer solution has a viscosity of between 2000 and 4000 cP. The second polymer is in a second polymer solution prior to formation of the nanofibers. The second solution has a viscosity of between 100 and 5000 cP and preferably between 1500 and 2500 cP.

[0042] In one embodiment, the nanofiber layer has a mean flow pore size of greater than 0.2 μm and less than 5 μm , and more preferably between 0.5 and 1.5 μm , and an average bubble point of greater than 0.5 μm and less than 10 μm , and more preferably between 1 μm and 3 μm .

[0043] In one embodiment, first polymer has a melting temperature that is higher than a melting temperature of the second polymer.

[0044] In an embodiment, a system for forming a membrane is provided. The system includes a) a first solution supply system; b) a second solution supply system; c) a spinneret

downstream of the first and second solution supply systems; and d) a mixing conduit. The mixing conduit is downstream of the second solution supply system and downstream of the first solution supply system. The mixing conduit is upstream of the spinneret. The mixing conduit receives a flow of the first solution from the first solution supply system and receives a flow of the second solution from the second solution supply system. The mixing conduit mixes the flow of first solution with the flow of second solution to form a mixture of the first solution and the second solution upstream of the spinneret. The mixing conduit supplies the mixture to the spinneret.

[0045] In an embodiment, first and second solutions are mixed only while the first and second solutions are flowing from independent storage containers towards the spinneret.

[0046] Embodiments of membrane constructions formed by the processes or apparatus outlined above are provided.

[0047] In an embodiment, the nanofibers has an average fiber size of between 50 and 1000 nm and the nanofiber layer has a hydrostatic head of at least 10000 mm of water (as per AATCC 127) after plasma treatment and an air permeability of at least 1.25 cfm (as per ASTM D737), and Z-directional strength of at least 10 psi (as per TAPPI T541-OM-10).

[0048] In one embodiment, a method for manufacturing a membrane construction is provided. The method includes providing a first solution comprising a polymer A having melting temperature PA_t . The method includes providing a second solution comprising a polymer B having a melting temperature PB_t , where PB_t is less than PA_t . The method includes introducing one solution into the other solution at a location close to a spinneret to form a mixture. The method includes dispensing the mixture through a spinneret as the spinneret is spinning, to form a nanofiber layer. The method includes consolidating the nanofiber layer by thermal bonding at a temperature between PB_t and PA_t using a temperature and optionally, pressure, cycle to form a freely-supported membrane layer.

[0049] In one embodiment, a tube is provided to the spinneret. The first solution and second solution are introduced together into the tube.

[0050] In one embodiment, the first solution and second solution are introduced into the tube not more than 3 feet from the spinneret and particularly not more than 3 feet from outlet ports of the spinneret from which the mixture is dispensed from the spinneret.

[0051] In one embodiment, nanofibers are spun onto a substrate.

[0052] In one embodiment, the substrate is either a filter media or a forming wire.

[0053] In one embodiment, the nanofiber layer is removed from the substrate prior to thermal bonding.

[0054] In one embodiment, the substrate is a filter media. The nanofiber layer is post-heat-treated while on the filter media.

[0055] In one embodiment, Polymer A and Polymer B are selected from the group consisting of: polyacetals, polyamides, epoxy, polyesters, polyurethanes, cellulose ethers, cellulose esters, polyalkylene sulfides, polyarylene oxides, polysulfones, modified polysulfone polymers and mixtures thereof. And can further comprise poly(vinylchloride), polymethylmethacrylate, polystyrene, and copolymers thereof, poly(vinylidene fluoride), poly(vinylidene chloride), polyvinylalcohol.

BRIEF DESCRIPTION OF THE DRAWINGS

[0056] The accompanying drawings incorporated in and forming a part of the specification illustrate several aspects of the present invention and, together with the description, serve to explain the principles of the invention. In the drawings:

[0057] FIG. 1 is a schematic illustration of a system for forming a membrane;

[0058] FIG. 2 is a micrograph image of a nanofiber layer formed from a composite nanoweb prior to treatment in low magnification;

[0059] FIG. 3 is a micrograph image of a nanofiber layer formed from a composite nanoweb after treatment in low magnification;

[0060] FIG. 4 is a micrograph image of a nanofiber layer formed from a composite nanoweb prior to treatment in high magnification; and

[0061] FIG. 5 is a micrograph image of a nanofiber layer formed from a composite nanoweb after treatment in high magnification.

[0062] While the invention will be described in connection with certain preferred embodiments, there is no intent to limit it to those embodiments. On the contrary, the intent is to cover all alternatives, modifications and equivalents as included within the spirit and scope of the invention as defined by the appended claims.

DETAILED DESCRIPTION OF THE INVENTION

[0063] Disclosed embodiments of membranes and methods of manufacturing the membranes will reduce a delamination problem among spun nanofibers and improve the process of forming membranes using spinning techniques for forming the nanofibers into a nanofiber layer, and particularly by way of forcespinning.

[0064] Embodiments will use two separate polymers during the nanofiber formation process. However, to resolve the compatibility issue (i.e. instability issue) between different first and second polymers, a first solution that includes the first polymer is introduced with a second solution that includes the second polymer separately from different containers. The mixing does not occur in a separate container. Instead, the two solutions are mixed in the tubing upstream of the spinneret as the two solutions are flowing towards the spinneret that is used to spin the mixture to form the nanofibers.

[0065] The two solutions are introduced to one another sufficiently close to the spinneret such that the mixture does not become unstable or alternatively become completely mixed. More particularly, the mixture does not have sufficient dwell time to allow for the instability or homogeneity to occur. In some implementations, the two solutions are introduced into a same section of tubing less than or equal to about three feet

before the spinneret that produces the nanofibers. This way, the first polymer and the second can be mixed together without significant instability or homogeneity issues before being made into fibers.

[0066] Polymer solutions with adequate viscoelastic properties exhibit fiber (nano and/or micro) forming characteristics, such as by way of being formed into fibers using a spinneret.

[0067] However, two polymer solutions that are not compatible when mixed can result in phase separation through several mechanisms such as precipitation and/or coagulation. The phase-separated mixture does not form any fibers, resulting in defects such as blobs and shots (spraying) or clogging of the spinneret. On the other hand, two polymer solutions that are miscible can result in a homogeneous solution, which can lead to a nanofiber layer with only one melting temperature instead of fibers with different melting temperatures as used in embodiments of the present application.

[0068] As discussed herein, the lower melting temperature fibers are the target of post formation heat treatment of the nanofiber layer to melt one polymer to bond the nanofibers.

[0069] The problematic unstable and homogenous mixtures do not necessarily occur instantaneously. As such, if the mixture is converted into fibers a small amount of time after the solutions are mixed, the instability and/or homogeneity issues will not present themselves. As such, resulting layers can be made of fibers made from either one of the polymers and/or a mixture of both polymers in a composite fiber.

[0070] Because fibers will be made from both the first and second polymers, these may be referred to as composite fibers.

[0071] Typically, this mixing in the upstream tubing will occur in tubing above the spinneret.

[0072] Following the fiber spinning process, a heat post-treatment process is performed to form inter-fiber adhesion inside the membrane product utilizing heat and, optionally,

pressure. As a result, the level of inter-fiber adhesion required can be obtained without sacrificing the air permeability and hydrostatic head.

[0073] In some embodiments, the first solution may comprise, but is not limited to, a polymer in the form of polyacetals, polyamides, epoxy, polyesters, polyurethanes, cellulose ethers, cellulose esters, polyalkylene sulfides, polyarylene oxides, polysulfones, modified polysulfone polymers and mixtures thereof and can further comprise poly(vinylchloride), polymethylmethacrylate, polystyrene, and copolymers thereof, poly(vinylidene fluoride), poly(vinylidene chloride), polyvinylalcohol with the polymer dissolved in anyone of the following, but not limited to: formic acid and/or water, ethanol, chloroform, acetone, N,N-dimethylformamide (DMF), dimethylacetamide (DMAc), formic acid, acetic acid, N-Methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF) and mixtures thereof.

[0074] The second solution may comprise, but is not limited to, a polymer in the form of polyacetals, polyamides, epoxy, polyesters, polyurethanes, cellulose ethers, cellulose esters, polyalkylene sulfides, polyarylene oxides, polysulfones, modified polysulfone polymers and mixtures thereof and can further comprise poly(vinylchloride), polymethylmethacrylate, polystyrene, and copolymers thereof, poly(vinylidene fluoride), poly(vinylidene chloride), polyvinylalcohol with the polymer dissolved in anyone of the following, but not limited to: formic acid and/or water, ethanol, chloroform, acetone, N,N-dimethylformamide (DMF), dimethylacetamide (DMAc), formic acid, acetic acid, N-Methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF) and mixtures thereof.

[0075] FIG. 1 illustrates a simplified system 100 for forming the membrane. The system includes first and second solution feed systems 102, 104 for flowing first and second solutions, typically polymer solutions, towards a spinneret 106 where the nanofibers will be forcespun. In some implementations, the forcespinning process does not include electrospinning. However, in other implementations other types of spinning may be used to form the nanofibers used to form a nanofiber layer.

[0076] The first solution feed system 102 includes a first solution supply system 108 of the first solution, which may be a container holding the first solution. A first pump 110 directly pumps the first solution towards the spinneret 106 forming a first flow of the first

solution through a first portion of piping 111. It is noted that the second solution does not pass through the first pump 110.

[0077] The second solution feed system 104 includes a second solution supply system 112 of the second solution, which may be a container holding the second solution. A second pump 114 directly pumps the second solution towards the spinneret 106 forming a second flow of the second solution through a second portion of piping 115. It is noted that the first solution does not pass through the second pump 114.

[0078] The first flow of solution through the first portion of piping 111 does not include any of the second solution that is being pumped by the second pump 114. The second flow of solution through the second portion of piping 115 does not include any of the first solution being pumped by the first pump 110.

[0079] The first and second portions of piping 111 and 115 are fluidly connected to a coupling 116 having inlets 118 and 120 for the first and second flows, respectively. The first and second flows of solutions are mixed by combining the two solution flows in a portion of piping formed from coupling and a third portion of piping 122 downstream from coupling 116. This forms a mixture of the first and second solutions that now has both the first and second polymers therein. The coupling and third portion of piping 122 may be referred to as a mixing conduit.

[0080] The third portion of piping 122 is operably in fluid communication with the spinneret 106 through which the mixture is supplied to the spinneret 106. In some embodiments, the portion of piping through which the mixture flows to the spinneret is no more than 3 feet in length. This limits the amount of time that the two solutions remain mixed to avoid instability and homogeneity issues between the two polymer solutions.

[0081] This mixing of the first and second solutions does not occur in a container where the mixed solution is in a non-flowing state, e.g. where two separate solutions are poured into a single container and then the mixed solution is pumped out of the container using a single pump. This situation allows the mixture to dwell and become unstable or homogeneous resulting in a nanofiber layer with issues outlined above and thus becoming susceptible to

potential delamination problems. A container that includes a mixing apparatus that can recirculate or mix the first and second solutions without flowing the mixture towards the spinneret 106 would still be problematic.

[0082] This is particularly true when the first and second polymers/solutions are unstable when being mixed. Similarly, in other situations, this process can not be used with solutions and polymers that are miscible.

[0083] In some implementations when the solutions are fully miscible, the miscibility can be problematic because the polymers in the resulting fibers are not sufficiently distinct to allow the second polymer to maintain a lower melting temperature and to be used as an adhesive by way of forming the inter-fiber adhesions necessary to increase the z-directional strength of the membrane. A short dwell time is also required in these implementations to avoid the formation of a homogeneous mixture.

[0084] In preferred implementations, the spinneret 106 rotates at an excess of 2500 RPM and dispenses the mixture to form a nanofiber layer 130 from the first and second polymers. In some embodiments, the nanofiber layer 130 is formed on a substrate 132. The nanofiber layer 130 is then subjected to post forming processing. In FIG. 1, the nanofiber layer 130 passes through calender rolls 134 where heat and/or pressure is applied to the nanofiber layer 130. It is noted that heat can be provided in other means such as by a heater that is separate from the calender rolls 134 that provides pressure.

[0085] In some embodiments, the nanofiber layer 130 is removed from the substrate 132 prior to any post processing such as the application of heat and/or pressure. In some embodiments, drums or belts could be used to provide heat and/or pressure.

[0086] The substrate could be in the form of forming wire or a filter media. If the substrate is a filter media, this situation may use the process where the nanofiber layer is not removed from the substrate during post processing steps.

[0087] The heat and/or pressure is used to form increased inter-fiber adhesions to improve the strength and reduce delamination of the fibers of the membrane formed from the nanofiber layer.

[0088] The second polymer forms an adhesive that provides the inter-fiber adhesions to increase the strength of the membrane.

[0089] In some embodiments, the first polymer has a melting temperature that is greater than the melting temperature of the second polymer. As such, heat will be applied that will primarily melt the second polymer such that the second polymer can be used as an adhesive to provide improved adhesion between the remaining nanofibers.

[0090] FIGS. 4-5 illustrate the nanofiber layer before and after post forming processing. The images on the left are the nanofiber layer as spun while the images on the right are after thermal treatment. As can be seen in the high magnification image on the right, fiber-to-fiber adhesions and/or fiber intersection bonding is exhibited at a much greater extent after post forming processing.

[0091] When heat is applied, it is typically applied at a temperature above the melting temperature of the second polymer and below the melting temperature of the first polymer. In some embodiments, heat is applied at a temperature of at least 100 degrees Celsius and more preferably at least 140 degrees Celsius. It is noted that heat could be applied that is higher than both the first and second polymers.

[0092] The melting temperature of the first polymer is preferably at least 10 degrees Celsius higher than the second polymer and preferably 25 to 100 degrees Celsius higher.

[0093] The melting temperature of the first polymer may be in the range of between 70 and 300 degrees Celsius and more preferably between 200 and 250 degrees Celsius. The melting temperature of the second polymer may generally be in the range of between 50 and 250 degrees Celsius and more preferably between 130 and 150 degrees Celsius.

[0094] Heat is applied, preferably, for no more than 600 seconds and is typically applied for between 60 and 180 seconds.

[0095] If pressure is applied, pressure will typically be applied on the order of greater than 0 psi and less than or equal to 80 PSI.

[0096] The nanofibers will typically be between 50 and 1000 nm, more preferably between 100 and 500 nm and even more preferably between 200 and 400 nm.

[0097] The viscosity of the first solution is preferably between 2000 and 4000 cP and more preferably between 2800 and 3200 cP. The viscosity of the second solution is preferably between 100 and 5000 cP and preferably between 1500 and 2500 cP and more preferably between 1900 and 2100 cP.

[0098] After formation, the nanofiber layer preferably has a ratio-by-weight of the first polymer to the second polymer of between 1 and 10 and more preferably between 3 and 5. As such, there will typically be more of the first polymer than the second polymer after formation of the nanofiber layer.

[0099] The resulting membrane preferably has a mean flow pore size of greater than 0.2 μm and less than 5 μm and more preferably between 0.5 μm and 1.5 μm .

[0100] The membrane preferably has a bubble point of greater than 0.5 μm and less than 10 μm , and more preferably between 1 μm and 3 μm .

[0101] The membrane preferably has a hydrostatic head of at least 10,000 mm of water as per AATCC 127. This may be reached by post formation plasma treating with a fluorinated polymer.

[0102] The membrane preferably has an air permeability of at least 1.25 cfm as per ASTM D737.

[0103] The membrane preferably has an internal bond strength measured as z-directional strength of at least 10 psi as per TAPPI T541-OM-10. In some embodiments, z-directional strength is between 10 psi and 120 psi and more preferably between 15 and 50 psi, and most preferably between 25 and 35 psi.

[0104] The membrane preferably has a basis weight of between 5 and 30 grams/square meter.

[0105] In a preferred implementation, the first solution is a nylon 6 polymer and the solvent is formic acid.

[0106] All references, including publications, patent applications, and patents cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

[0107] The use of the terms “a” and “an” and “the” and similar referents in the context of describing the invention (especially in the context of the following claims) is to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The terms “comprising,” “having,” “including,” and “containing” are to be construed as open-ended terms (i.e., meaning “including, but not limited to,”) unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., “such as”) provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

[0108] Preferred embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those preferred embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible

variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

WHAT IS CLAIMED IS:

1. A method of forming a membrane construction comprising:
 - a) flowing a first solution including a first polymer toward a spinneret;
 - b) flowing a second solution including a second polymer, different than the first polymer, toward the spinneret;
 - c) mixing the first solution and second solution by combining the flow of first solution and flow of second solution to provide a mixture;
 - d) flowing the mixture of the first and second solutions to the spinneret; and
 - e) dispensing, with the spinneret, the mixture to form a nanofiber layer formed from the first and second polymers.
2. The method of claim 1, wherein the nanofiber layer has inter-fiber adhesions between adjacent fibers formed by the second polymer.
3. The method of claim 1, wherein flowing the first solution is performed before forming the mixture by a first pump that directly pumps the first solution and flowing the second solution is performed before forming the mixture by a second pump that directly pumps the second solution.
4. The method of claim 2, further comprising, after dispensing the mixture, processing the nanofiber layer to form the inter-fiber adhesions between the composite fibers.
5. The method of claim 4, wherein processing the nanofiber layer includes applying heat to the nanofiber layer to melt at least a portion of the nanofiber layer formed from the second polymer to provide inter-fiber adhesions.
6. The method of claim 5, wherein heat is applied for between 60 and 180 seconds.
7. The method of claim 5, wherein heat is applied for not more than 600 seconds.
8. The method of claim 5, wherein heat is applied at between 100 and 180 degrees Celsius.

9. The method of claim 5, wherein heat is applied at between 140 and 160 degrees Celsius.
10. The method of claim 5, wherein processing the nanofiber layer includes applying both heat and pressure to the nanofiber layer.
11. The method of claim 10, wherein the heat is applied by calendar rolls, drums or belts.
12. The method of claim 10, wherein pressure is applied at between greater than 0 PSI and less than or equal to 80 PSI.
13. The method of claim 5, wherein the first polymer has a melting temperature that is higher than a melting temperature of the second polymer, while the step of applying heat is at a temperature higher than the melting temperature of the second polymer.
14. The method of claim 13, wherein the melting temperature of the first polymer is at least 10 degrees Celsius greater than the melting temperature of the second polymer.
15. The method of claim 14, wherein the melting temperature of the first polymer is between 70 and 300 degrees Celsius and the melting temperature of the second polymer is between 50 and 250 degrees Celsius.
16. The method of claim 14, wherein the melting temperature of the first polymer is between 200 and 250 degrees Celsius and the melting temperature of the second polymer is between 130 and 150 degrees Celsius.
17. The method of claim 1, wherein the step of mixing the first solution and second solution occurs in tubing upstream of the spinneret.
18. The method of claim 1, wherein the mixture of first solution and second solution is formed not more than 3 feet from the spinneret.

19. The method of claim 1, wherein the mixture of first solution and second solution is formed sufficiently close to the spinneret and the flow of the mixture is such that the mixture can be dispensed before the mixture becomes unstable for immiscible solutions or completely mixed for miscible solutions.

20. The method of claim 1, wherein the fibers have an average fiber size of between 50 and 1000 nm.

21. The method of claim 1, wherein the first solution has a viscosity of between 2000 and 4000 cP and wherein the second solution has a viscosity of between 100 and 5000 cP and optionally between 1500 and 2500 cP.

22. The method of claim 1, wherein the fibers of the nanofiber layer are nanofibers, at least a portion of the nanofibers being composite fibers formed from both the first and second polymers as the nanofibers are dispensed from the spinneret and prior to forming the nanofiber layer.

23. The method of claim 1, wherein the mixture of first solution and second solution has, by weight, at least as much first solution as second solution.

24. The method of claim 1, wherein the step of dispensing, with the spinneret, is performed by forcespinning the mixture and without electrospinning.

25. The method of claim 1, wherein the first and second solutions are immiscible.

26. The method of claim 1, wherein the first polymer and second polymer are selected from the group consisting of: polyacetals, polyamides, epoxy, polyesters, polyurethanes, cellulose ethers, cellulose esters, polyalkylene sulfides, polyarylene oxides, polysulfones, modified polysulfone polymers and mixtures thereof. And can further comprise poly(vinylchloride), polymethylmethacrylate, polystyrene, and copolymers thereof, poly(vinylidene fluoride), poly(vinylidene chloride), polyvinylalcohol.

27. The method of claim 5, wherein:

the step of dispensing the mixture to form a nanofiber layer includes dispensing the nanofibers onto a substrate; and

the nanofiber layer is removed from the substrate prior to the step of applying heat to the nanofiber layer.

28. The method of claim 1, wherein the first solution may comprise a polymer in the form of polyacetals, polyamides, epoxy, polyesters, polyurethanes, cellulose ethers, cellulose esters, polyalkylene sulfides, polyarylene oxides, polysulfones, modified polysulfone polymers and mixtures thereof and can further comprise poly(vinylchloride), polymethylmethacrylate, polystyrene, and copolymers thereof, poly(vinylidene fluoride), poly(vinylidene chloride), polyvinylalcohol with the polymer dissolved in anyone of the following: formic acid and/or water, ethanol, chloroform, acetone, N,N- dimethylformamide (DMF), dimethylacetamide (DMAc), formic acid, acetic acid, N-Methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF) and mixture thereof;

the second solution may comprise a polymer in the form of polyacetals, polyamides, epoxy, polyesters, polyurethanes, cellulose ethers, cellulose esters, polyalkylene sulfides, polyarylene oxides, polysulfones, modified polysulfone polymers and mixtures thereof and can further comprise poly(vinylchloride), polymethylmethacrylate, polystyrene, and copolymers thereof, poly(vinylidene fluoride), poly(vinylidene chloride), polyvinylalcohol with the polymer dissolved in anyone of the following: formic acid, and/or water, ethanol, chloroform, acetone, N,N- dimethylformamide (DMF), dimethylacetamide (DMAc), formic acid, acetic acid, N-Methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF) etc. and mixtures thereof.

29. The method of claim 1, wherein the nanofiber layer after heat treatment achieves internal bond strength measured as Z-directional strength between 10 psi and 120 psi.

30. The method of claim 1, wherein:

the nanofibers have an average fiber size of between 50 nm and 1000 nm; and

the nanofiber layer has a hydrostatic head of at least 10000 mm of water (as per AATCC 127) and an air permeability of at least 1.25 cfm (as per ASTM D737) and Z-

directional strength of at least 10 psi (as per TAPPI T541-OM-10) and a basis weight of between 5 and 30 grams/square meter.

31. A membrane construction comprising:

a nanofiber layer formed from a plurality of nanofibers, the plurality of nanofibers being formed from a first polymer and a second polymer, the second polymer being different than the first polymer, the nanofiber layer having a plurality of inter-fiber adhesions formed by the second polymer;

wherein the nanofibers have an average fiber size of between 50 nm and 1000 nm and the nanofiber layer has a hydrostatic head of at least 10000 mm of water (as per AATCC 127) and an air permeability of at least 1.25 cfm (as per ASTM D737) and Z-directional strength of at least 10 psi (as per TAPPI T541-OM-10) and a basis weight of between 5 and 30 grams/square meter.

32. The membrane construction of claim 31, wherein the nanofibers forming the layer of nanofibers are formed by forcespinning without electrospinning.

33. The membrane construction of claim 31, wherein the ratio-by-weight of the first polymer to the second polymer is between 1 and 10.

34. The membrane construction of claim 31, wherein the ratio-by-weight of the first polymer to the second polymer is between 3 and 5.

35. The membrane construction of claim 31, wherein:

the first polymer is in a first polymer solution prior to formation of the nanofibers;

the second polymer is in a second polymer solution prior to formation of the nanofibers; and

the first and second polymer solutions are immiscible or miscible.

36. The membrane construction of claim 31, wherein:

the first polymer is in a first polymer solution prior to formation of the nanofibers,

the first polymer solution has a viscosity of between 2000 and 4000 cP; and

the second polymer is in a second polymer solution prior to formation of the nanofibers, the second solution has a viscosity of between 100 and 5000 cP and optionally between 1500 and 2500 cP.

37. The membrane construction of claim 31, wherein the nanofiber layer has a mean flow pore size of greater than 0.2 μm and less than 5 μm , and more preferably between 0.5 and 1.5 μm , and an average bubble point of greater than 0.5 μm and less than 10 μm , and more preferably between 1 μm and 3 μm .

38. The membrane construction of claim 31, wherein the first polymer has a melting temperature that is higher than a melting temperature of the second polymer.

39. A system for forming a membrane comprising:

- a) a first solution supply system;
- b) a second solution supply system;
- c) a spinneret downstream of the first and second solution supply systems; and
- d) a mixing conduit downstream of the second solution supply system and

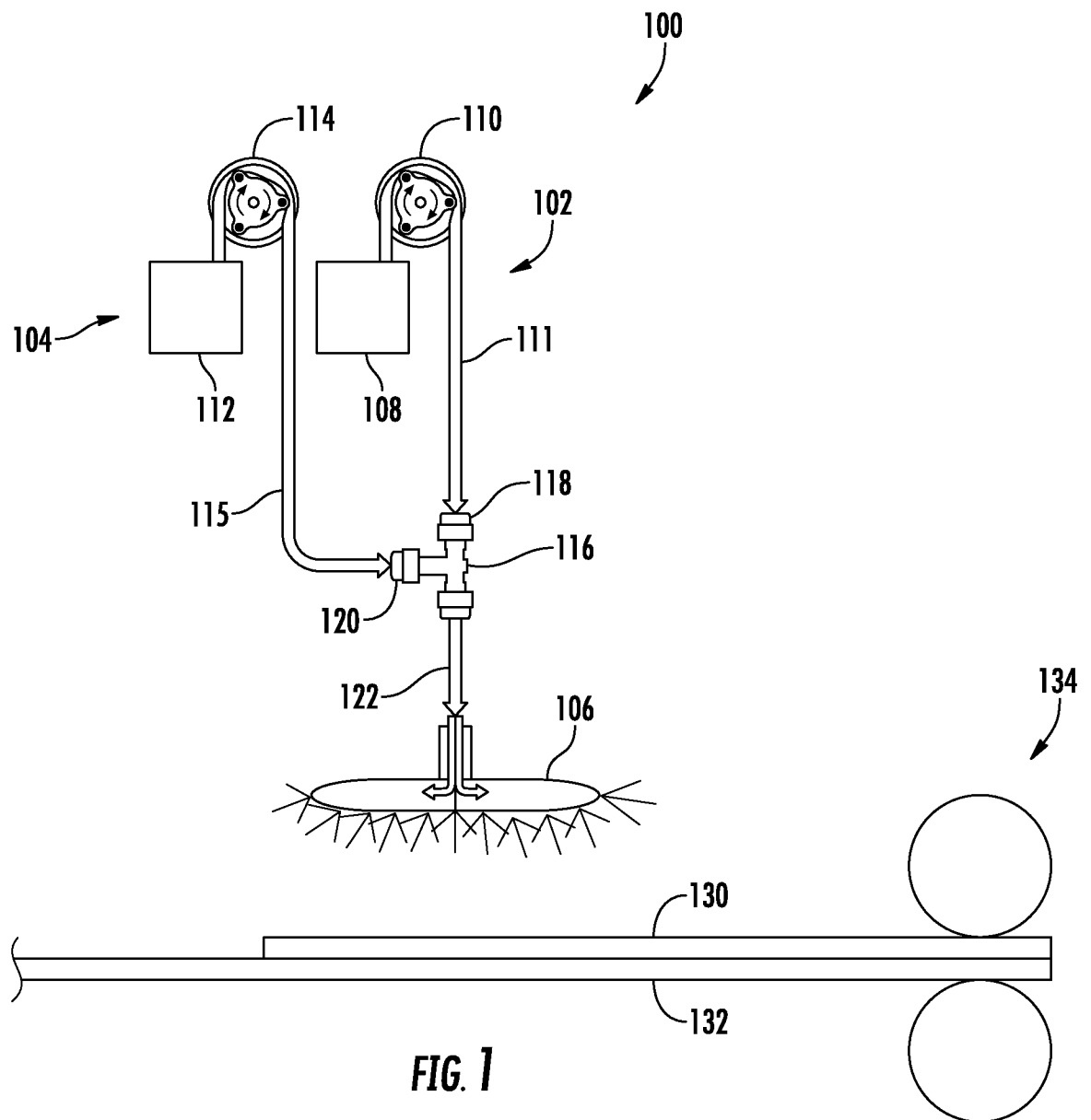
downstream of the first solution supply system, the mixing conduit being upstream of the spinneret, the mixing conduit receiving a flow of the first solution from the first solution supply system and receiving a flow of the second solution from the second solution supply system, the mixing conduit mixing the flow of first solution with the flow of second solution to form a mixture of the first solution and the second solution upstream of the spinneret, the mixing conduit supplying the mixture to the spinneret.

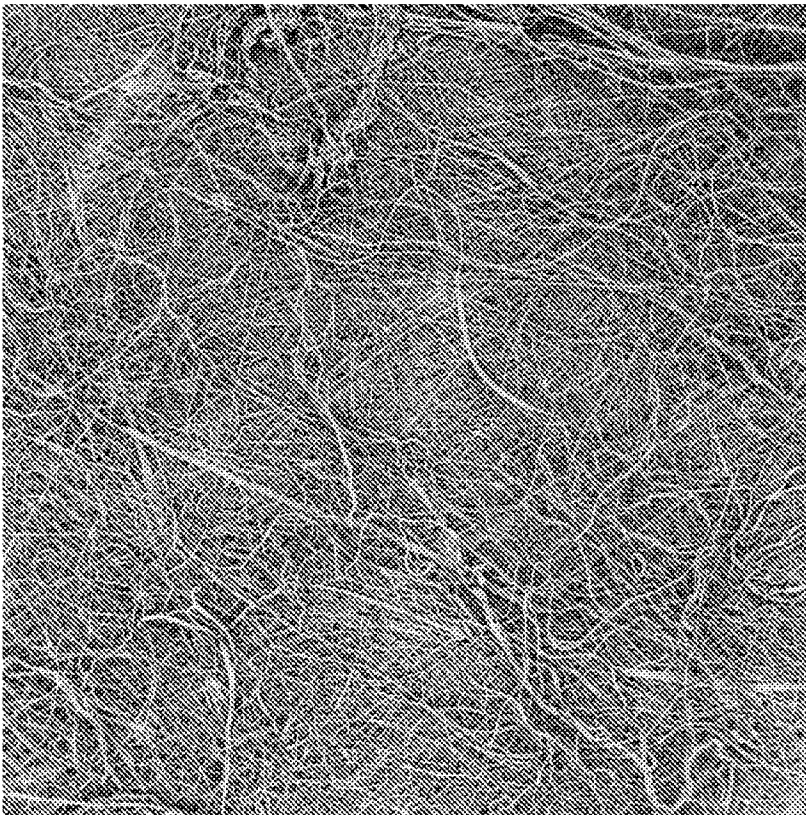
40. A membrane construction formed by the process of any one of claims 1-30.

41. The membrane of claim 40, wherein the nanofibers have an average fiber size of between 50 and 1000 nm and the nanofiber layer has a hydrostatic head of at least 10000 mm of water (as per AATCC 127) after plasma treatment and an air permeability of at least 1.25 cfm (as per ASTM D737), and Z-directional strength of at least 10 psi (as per TAPPI T541-OM-10).

42. A method for manufacturing a membrane construction, comprising the steps of:
- providing a first solution comprising a polymer A having melting temperature PA_t ;
 - providing a second solution comprising a polymer B having a melting temperature PB_t , where PB_t is less than PA_t ;
 - introducing one of the first and second solutions into the other one of the first and second second solution at a location close to a spinneret to form a mixture;
 - dispensing the mixture through a spinneret as the spinneret is spinning, to form a nanofiber layer; and
 - consolidating the nanofiber layer by thermal bonding at a temperature between PB_t and PA_t by means of a temperature and optionally, pressure, cycle to form a freely-supported membrane layer.
43. The method as in claim 42, wherein a tube is provided to the spinneret, and the first solution and second solution are introduced together into the tube.
44. The method as in claim 42, wherein the first solution and second solution are introduced into the tube not more than 3 feet from the spinneret.
45. The method as in claim 42, wherein nanofibers are spun onto a substrate.
46. The method of claim 45, wherein the substrate is either a filter media or a forming wire.
47. The method of claim 46, wherein the nanofiber layer is removed from the substrate prior to thermal bonding.
48. The method of claim 45, wherein the substrate is a filter media, the nanofiber layer is post-heat-treated while on the filter media.
49. The method as in claim 42, wherein Polymer A and Polymer B are selected from the group consisting of: polyacetals, polyamides, epoxy, polyesters, polyurethanes, cellulose

ethers, cellulose esters, polyalkylene sulfides, polyarylene oxides, polysulfones, modified polysulfone polymers and mixtures thereof. And can further comprise poly(vinylchloride), polymethylmethacrylate, polystyrene, and copolymers thereof, poly(vinylidene fluoride), poly(vinylidene chloride), polyvinylalcohol.





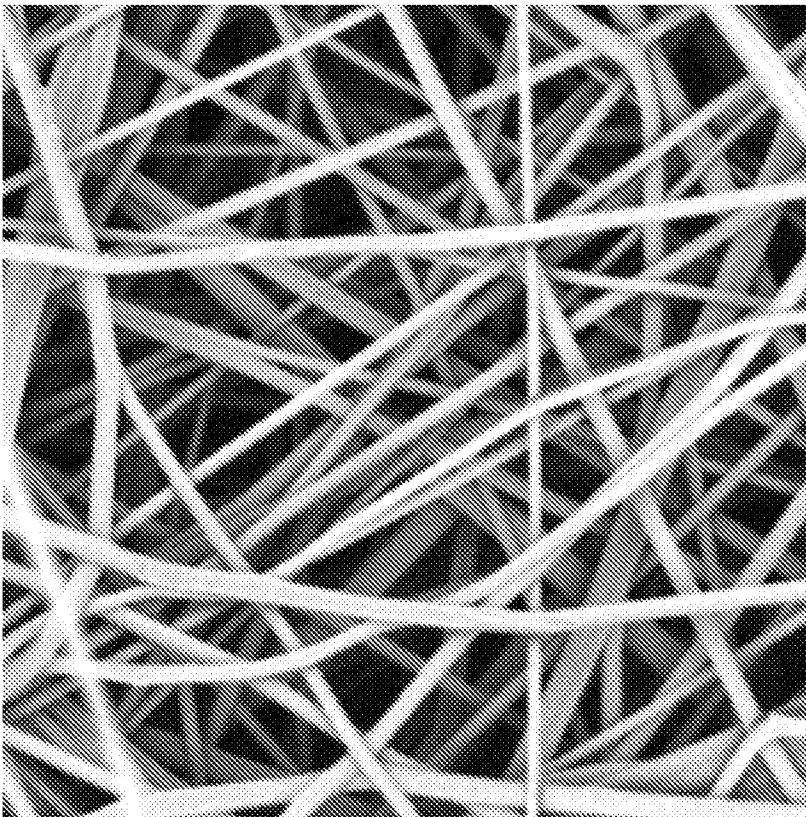
Low Magnification - As Spun

FIG. 2



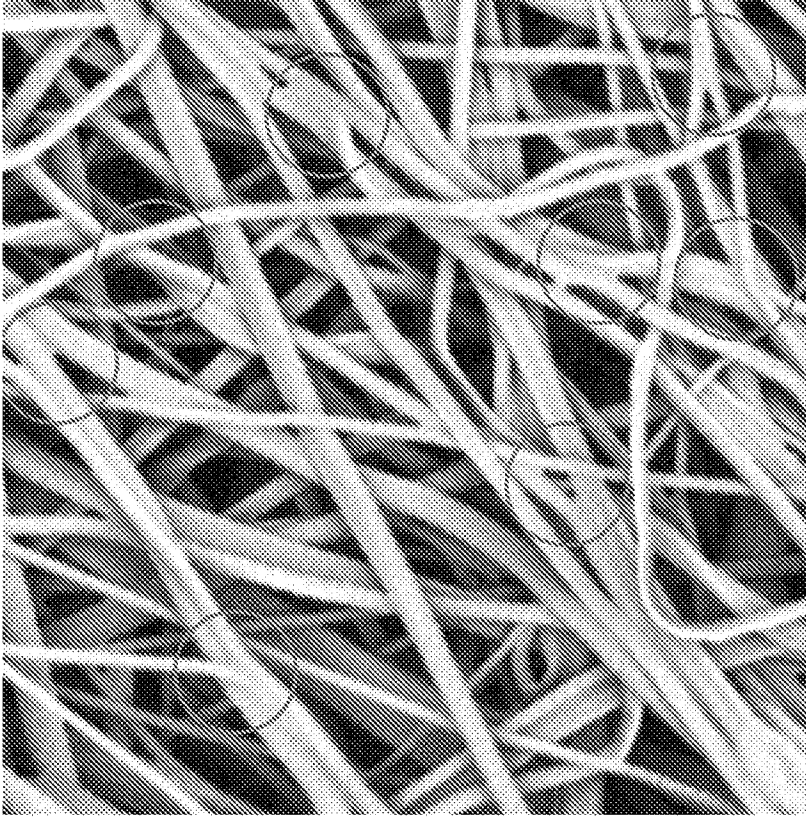
Low Magnification – After Thermal Treatment

FIG. 3



High Magnification - As Spun

FIG. 4



High Magnification – After Thermal Treatment

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2020/023371**A. CLASSIFICATION OF SUBJECT MATTER****B01D 69/12(2006.01)i, B01D 71/06(2006.01)i, B01D 67/00(2006.01)i**

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 69/12; B01D 39/08; B01D 67/00; B01D 71/06; B01D 71/56; B32B 5/26; D01D 13/00; D01D 5/06; D01D 5/18; D04H 1/54; D04H 1/70

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: polymer solution, mixture, spinneret, composite fiber, membrane

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
DX	US 2016-0310910 A1 (DSM IP ASSETS B.V.) 27 October 2016 See paragraphs [0003], [0016]-[0052]; and claims 1-12.	31,33-38
DY		1-30,32,39-49
Y	WO 95-13856 A1 (KIMBERLY-CLARK CORPORATION) 26 May 1995 See page 9, lines 13-29; claim 1; and figure 1.	1-30,39-49
Y	US 2016-0168756 A1 (THE NORTH FACE APPAREL CORP.) 16 June 2016 See claim 1.	24,32
A	CN 202543411 U (WANG JIANMING) 21 November 2012 See the whole document.	1-49
A	WO 2011-142726 A1 (NATIONAL UNIVERSITY OF SINGAPORE et al.) 17 November 2011 See the whole document.	1-49



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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"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

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Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2020/023371

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CN 202543411 U	21/11/2012	None	
WO 2011-142726 A1	17/11/2011	None	