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(54) **NOVEL ENHANCING ELECTROSTATIC SPINNING NANOFIBER MEMBRANE, PRODUCING METHOD THEREOF, AND DEVICE APPLIED TO METHOD**

(57) A method for preparing a reinforced electrospinning nanofiber membrane, which performs alternate blending electrospinning by utilizing several thermoplastic polymer with a melting point at least 20°C lower than that of the other component or thermoplastic polymer with low melting point, and non-thermoplastic polymer. Electrospun jets of several components are arranged along the movement direction of receiving device in forth-and-back, fibers are arranged randomly and alternately. The blending spinning fiber membrane is

post-treated with thermal calendering, and the hot-pressing temperature is slightly higher than that of starting melting temperature of the polymer with low melting point, time is 1~10 min, pressure is 1~20 MPa. After hot-pressing, the thermoplastic polymer with low melting point is partly melt and forms point bonding at the intersection of fibers, without clogging pores. This invention relates to an electrospun nanofiber membrane and a blending electrospinning device.

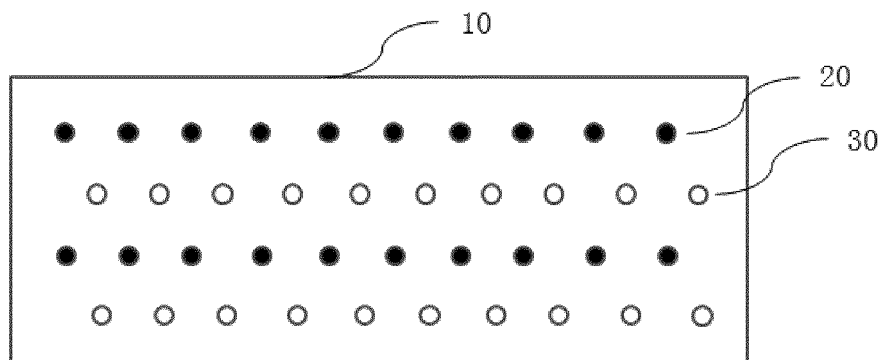


Fig. 1

Description

Technical field

[0001] The present invention relates to the field of electrospun nanofiber membrane, particularly to a novel reinforced electrospun nanofiber membrane, production method thereof and device applied to the method, specifically relates to a method producing electrospun nanofiber membrane through hybrid electrospinning a mixed polymer system containing low-melting point thermoplastic, followed by thermal calendering treatment, realizing the point bonding reinforcement between the nanofibers, and the novel electrospinning device obtained by this method.

Background of the invention

[0002] Electrospinning is a technology that utilizes electrostatic field force to produce nanofiber material, which has been researched widely and extensively throughout the country and abroad in recent years. Nanofiber nonwoven fabrics/membranes (electrospun membrane) prepared by electrospinning technique have many excellent properties, such as flexible optionality of polymer raw material, solution and/or melt electrospinning may be conducted depending on different types of raw materials; thus obtained electrospun membrane has advantageous of high porosity, small and uniformly dispersed pore diameter, adjustable fiber fineness, controllable membrane thickness, as well as isotropy, high efficiency filtration and high barrier property etc., thus which has been researched widely and extensively in the fields of industrial filtration, lithium battery separator, multifunctional film and biomedical. However, the foregoing commercial applications all request electrospun membrane to have a certain mechanical strength to withstand the machining stress during process and meet the strength requirement of the final product. However, the intensity of the ordinary electrospun membrane without reinforcing process is far less than the requirements of industrialized process and final product. The two reasons to explain why electrospinning membrane has low tensile strength are as follows: (1) the electrospinning nanofiber possesses a relative small fiber diameter, a relatively low crystallinity, as well as a relatively low mechanical strength itself; (2) electrospun nanofiber is arranged in stack state on a receiving device, without interweave, cohesion and entanglement between fibers, which has a relatively low cohesive and adhesive force, thus, slippage between fibers occurs easily when external force is performed, which leads to a lower breaking strength.

[0003] The disadvantage on strength of electrospinning nanofiber membrane severely limits the expansion and industrialization of application. Therefore, the study on reinforcement of electrospun membrane has been conducted, with little effect. Although electrospun membrane is one kind of nonwoven fabrics, due to its property

of nanofiber and micro-pores, the reinforcing effect is not satisfied if conventional reinforcement methods for nonwoven such as thermal bonding or thermal calendering bonding with common ES hot-melt fiber, hot-melt powder, hot-melt adhesive are utilized, on the contrary, which may result in clogging pores, losing the property of micropores and micro-pores electrospun membrane. For example, when ES hot-melt fiber was used for performing thermal bonding or thermal calendering bonding, due to the micron magnitude of ES fiber which is larger than the size of nanofiber, after melting, the PE component therein is prone to clog the micro-pores of electrospun membrane, point bonding is not liable to occur, plastic film without pores is prone to be formed, as well as the micropores property of electrospun membranes is lost. When heat treatment (thermal bonding and thermal calendering bonding) is performed to one-component electrospun membrane, the processing window is narrow and the temperature is difficult to be controlled because excessive high temperature would easily melt all fibers to clog the pores along with the loss of electrospun membrane characteristics; while the excessive low temperature cannot sufficiently melt polymer nanofibers, which leading to undesirable bonding and lower strength. If common foam bonding method for nonwoven enhancement was employed, due to that particle size of the adhesive is larger than the diameter of the nanofibers, which serves to little chance of point bonding and then renders the electrospun membrane losing its porous property. Furthermore, the process is complicated and difficult to be controlled.

[0004] Currently, prior art for the reinforcement of electrospun membrane mainly utilizes following methods: (a) Thermal calendering or thermal bonding was directly carried out for mono-component thermoplastic polymer electrospun membrane, the former serves to three-to-four folds increase in tensile breaking strength of the mono-component thermoplastic polymer electrospun membrane (Dongyue *Qi, Master's Thesis of College of Textiles, Tianjin University of Technology, 2013), and the latter serves to about two folds increase (Kun GAO, Doctoral Thesis of Department of Applied Chemistry, Harbin Institute of Technology, 2007); (2) Miscible electrospun membranes are treated with thermal bonding process, which allows the maximum breaking strength of PVDF/PEO bicomponent electrospun membrane to increase from 14.9MPa to 16.1MPa (Kun GAO, Doctoral Thesis of Department of Applied Chemistry Harbin Institute of Technology Thesis, 2007).

[0005] The present invention provides a blending electrospinning - thermal calendering bonding method which is different from the existing bonding techniques for nonwoven fabrics, and it is applied in the reinforcement of electrospinning membrane of all thermoplastic polymers. Ideal structure of point bonding could be obtained, which significantly improves the tensile strength of electrospinning nanofiber membrane without adverse effect on the property of porous and micro-pores thereof, and the ap-

plication fields of electrospun membrane may be expanded, the industrializing production and application process of nanofibers will be accelerated.

Summary of the invention

[0006] Based on the deficiencies of the prior art, the technical problems to be solved by the present invention is to provide a reinforced method comprising that: one or more (two or more) polymers are electrospun from the spinning needles (spinning orifice, orifice, nozzle, spinning head, spinneret) arranged alternatively, interlacing or crossly, respectively, thus obtained several nanofibers are homogeneous dispersed and mixed on the receiving device, followed by thermal calendering process. Several polymers mentioned above comprise thermoplastic polymer, non-thermoplastic polymer or the combination thereof, however, there is at least one kind of thermoplastic polymer with relatively low melting point (the range of relatively low melting point varies according to the end use of the product, if only the difference of melting point between it and other co-spinning polymer can be 20 °C or more), and each polymer have excellent chemical stability. The thermal calendering is conducted after the blending electrospinning; the calendering temperature is slightly higher than that of lower melting point of polymer component. The point bonding occurs at the intersection among nanofibers, which simultaneously improves the cohesive force between fibers and the overall mechanical property of electrospun membrane without blocking micro-pores, it drastically retains the inherent properties of high porosity and micro-pores of electrospun membranes. The technical content of this invention complies with the national environmental requirements, and the process is simple, which is easy to operate and performed for industrialization.

[0007] The technical solution of this invention to solve the technical problem of producing method is to design a reinforcing method for nanofiber nonwoven fabric (electrospun membrane), and the method includes the following process steps:

- (1) Preparing polymer spinning solution: two or more types thermoplastic polymers with a difference of melting point is 20 °C or more, or multiple polymers comprising a thermoplastic polymer with lower melting point, are dissolved in excellent solvents respectively, and stirred homogeneously, then stand for a while, forming several spinning solutions for backup;
- (2) Blending electrospinning: thus prepared polymer solutions aforesaid are fed into respective spinning system in a certain jet mixing arrangement way to reach the same spinning plate, and blending electrospinning is performed under the same receiving distance, spinning voltage and spinning environment;
- (3) Thermal calendering point bonding: after blending electrospinning, thus obtained multi-component

blending electrospun membranes are thermal calendering bonded under a certain temperature and pressure.

[0008] The technical solution of this invention to solve the technical problem of producing method is to design an arrangement structure for the spinning jets of nanofiber nonwoven fabrics. The spinning jets arrangement structure is suitable for the producing method of nanofiber nonwoven fabrics described by this invention, that is, said spinning jets relate to a multi-jets (multi-needle, multi-orifice, multi-nozzle, multi-spinneret) electrospinning technique. The spinning plate has a special structure design, and the spinning jet on the spinneret presents a state of cross-blending arrangement. The arrangement of needles and orifices on the spinning plate can be circular, ellipsoidal and so on.

[0009] Compared to the prior art, the present invention is a producing method for reinforced electrospun membrane in which various polymers are cross-blending electrospinning, followed by thermal calendering treatment, wherein at least one polymer is thermoplastic polymer with relatively low melting point. The producing method of this invention realizes the reinforcement of point bonding among electrospinning nanofibers under the precondition that original superior characteristic of electrospinning is remained, which improves the overall mechanical property of electrospinning membrane and expands the application field of electrospinning nanofiber membrane. The producing apparatus is easily to be manufactured and operated, which satisfies the low-carbon requirement, and it may be implemented with low cost and easily to be promoted industrially.

[0010] Thermal calendering treatment can utilize existing thermal calendering bonding technology and equipment to realize the continuous production.

[0011] The present invention provides a method to produce reinforced electrospinning nanofiber membrane, comprising the following steps:

- a) Preparing polymer spinning solution: two or more polymers with at least 20 °C difference in melting point are dissolved in proper solvents, respectively;
- b) Blend electrospinning: two or more types of polymer solutions obtained in step a which melt in the proper solvents are blending electrospun, obtaining multi-component blending electrospun membrane;
- c) Thermal calendering bonding: reinforced electrospinning nanofiber membranes are obtained by performing thermal calendering bonding to the multi-component electrospun membrane;

wherein the thermal calendering bonding temperature is higher than the lowest melting point among those of two or more polymers, and lower than the second lower melting point among those of two or more polymers, preferably, the temperature is 2-10 °C higher than the lowest melting point among those of two or more polymers.

[0012] Preferably, the polymer comprises one or more in the group consisting of polystyrene (PS), polysulfone (PSF), polyether sulfone (PES), polyvinylidene fluoride (PVDF), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), poly(vinylidene fluoride-co-chlorotrifluoroethylene) (PVDF-CTFE), polyacrylonitrile (PAN), polyamide (PA), polyvinyl carbazole, cellulose acetate (CA), cellulose, chitosan (PAA), polyaniline, polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polypropylene terephthalate (PTT), polyimide (PI), polyurethane (PU), poly(methyl methacrylate) (PMMA), polyvinyl alcohol (PVA), polycarbonate (PC), polyethylene imine (PEI), poly(ether ether ketone) (PEEK), aliphatic amide, polyvinyl acetate (PVAc), polyoxymethylene (POM), polyvinyl chloride (PVC), nylon-6 (PA-6), nylon-66 (PA-66), polytrifluoroethylene, polychlorotrifluoroethylene, polyvinyl fluoride, poly lactic acid, polyethylene oxide and polyvinyl pyrrolidone.

[0013] Preferably, at least one among two or more polymers aforesaid is thermoplastic polymer. Preferably, the thermoplastic polymer comprises polyvinylidene fluoride (PVDF), polyethylene terephthalate (PET), polyamide 6 (PA6) or polyamide 6,6 (PA6,6), polybutylene succinate (PBS), polyacrylonitrile (PAN), polyimide (PI), polyvinyl alcohol-modified thermoplastic starch, thermoplastic polyurethane (TPU), or polypropylene (PP), polyethylene (PE), polystyrene (PS), polyphenylene sulfide (PPS) which has to form a spinning solutions by melting.

[0014] Preferably, the thermoplastic polymer aforesaid is the thermoplastic polymer in same or different types.

[0015] Preferably, the blending electrospinning is alternate blending electrospinning. More preferably, the alternative blending electrospinning is cross or interlacing blending electrospinning. More preferably, the electrospinning jet is arranged crosswise along the motion direction of receiving device in forth-back, or arranged alternately along the width direction of the products in left-right.

[0016] Preferably, the electrospinning jets of blending electrospinning are present on a blending electrospinning plate, spinning head, spinning plate or spinneret. More preferably, multiple needles, orifices or nozzles of blending electrospinning plate, spinning head or spinneret plate or spinneret are arranged alternately or crossly, or electrospinning head, spinneret or spinning die without needle is arranged alternatively in length-breadth.

[0017] Preferably, different spinning solutions are fed by multiple needles, orifices, nozzles of the blending electrospinning plates, spinning head or spinneret under the way of alternation, interlacing or cross.

[0018] Preferably, the electrospinning head, spinneret or die without needle includes the type of a metal roller, metal wire, spiral, sawtooth, centrifugal, bubble.

[0019] Preferably, the thermal calendering time is 1~10 min. Preferably, the thermal calendering pressure is 1~20 MPa.

[0020] The present invention also provides an electrospun nanofiber membrane, which has a tensile breaking

strength of at least 17.8 MPa, preferably, greater than 26.8 MPa. The electrospinning membrane provided by the present invention has various applications, which can be used for different technical fields such as biomedical, energy chemical, filtration of gas and liquid, windproof and waterproof, windproof to keep warm, perspective and breathability, environmental governance, semiconductor sensors and so on. The electrospinning nanofiber membrane provided by the present invention can be used as a lithium ion battery separator, also can be used for air filter material and preparing fabrics that is waterproof, moisture permeable and breathable.

[0021] The present invention provides a method for electrospinning a polymer with high melting point and polymer with low melting point, respectively, the resulting polymer membranes are composited and then thermal calendered to obtain the electrospinning nanofiber membrane. The production method provided by the present invention has high production efficiency, low energy consumption and is suitable for large-scale industrial production.

[0022] The present invention further provides a blending electrospinning apparatus including two or more electrospinning jet emitting devices. Preferably, the emitting device is spinning plate, spinning head, spinnerets or orifice. More preferably, two or more electrospinning emitting devices are in form of linear arrangement of blending multi-needle, linear arrangement of blending multi-nozzle, linear arrangement of blending multi-orifice, linear arrangement of blending multi-nozzle, circular arrangement of blending multi-needle, or blending roller without needle.

Brief description of the drawings

[0023]

Figure 1 is a schematically illustrated form of a spinning needle arrangement in the electrospinning device with two blended polymers and blending linear arranged multi-needle, which is one embodiment of the producing method of the reinforced electrospinning nanofiber membrane of the present invention. Wherein, 10 - spinneret; 20 - thermoplastic polymer with low (high) melting point; 30 - thermoplastic polymer with high (low) melting temperature.

Figure 2 is a schematically illustrated form of a nozzle arrangement in electrospinning device with two polymer and blending linear arranged multi-nozzle, which is another embodiment of the producing method of the reinforced electrospinning nanofiber membrane of the present invention. Wherein, 10 - spinneret; 20 - polymer component with low (high) melting temperature; 30 - polymer component with high (low) melting temperature.

Figure 3 is a schematically illustrated form of an orifices arrangement in electrospinning apparatus with two polymers and blending linear arranged multi-or-

ifice, which is another embodiment of the production method of the reinforced electrospun nanofiber membrane of the present invention that blend multi-orifice is arrayed linearly with two kinds of polymers. Among them, 10 - spinneret; 20 - polymer component with low (high) melting temperature; 30 - polymer component with high (low) melting temperature. Figure 4 is a schematically illustrated form of a nozzle arrangement in electrospinning device with two polymer and blending linear arranged multi-nozzle, which is another embodiment of the producing method of the reinforced electrospinning nanofiber membrane of the present invention. Wherein, 10 - spinneret; 20 - polymer component with low (high) melting temperature; 30 - polymer component with high (low) melting temperature.

Figure 5 is a schematically illustrated form of a an orifices arrangement in electrospinning apparatus with two polymers and blending linear arranged multi-orifice, which is another embodiment of the production method of the reinforced electrospun nanofiber membrane of the present invention that blend multi-orifice is arrayed linearly with two kinds of polymers. Among them, 10 - spinneret; 20 - polymer component with low (high) melting temperature; 30 - polymer component with high (low) melting temperature.

Figure 6 is a schematically illustrated form of a needles arrangement in electrospinning device with two polymers and blending circular arranged multi-needle, which is one embodiment of the producing method of the reinforced electrospinning nanofiber membrane of the present invention. Wherein, 10 - spinneret; 20 - polymer component with low (high) melting temperature; 30 - polymer component with high (low) melting temperature.

Figure 7 is a schematically illustrated form of a needles arrangement in electrospinning device with two polymers and blending circular arranged multi-needle, which is another embodiment of the producing method of the reinforced electrospinning nanofiber membrane of the present invention. Wherein, 10 - spinneret; 20 - polymer component with low (high) melting temperature; 30 - polymer component with high (low) melting temperature.e.

Figure 8 is a schematically illustrated form of aN arrangement in which the spinning head is arranged alternately along its width direction in the blending needleless electrospinning device with two polymer in one row, which is one embodiment of the producing method of the reinforced electrospun nanofiber membrane of the present invention. Wherein, 10 - spinneret; 20 - polymer component with low (high) melting temperature; 30 - polymer component with high (low) melting temperature.

Figure 9 is a schematically illustrated form of an arrangement in which the spinning head is arranged alternately along its width direction in the blending

needleless electrospinning device with two polymer in multiple rows, which is another embodiment of the producing method of the reinforced electrospun nanofiber membrane of the present invention, wherein, 10 - spinneret; 20 - polymer component with low (high) melting temperature; 30 - polymer component with high (low) melting temperature. Figure 10 is the SEM graph of PAN/PVDF21216 blending electrospinning nanofiber membrane treated by thermal calendering, which is one embodiment of the producing method of reinforced electrospinning nanofiber membrane of the present invention.

Figure 10 is the SEM graph of PAN/PVDF21216 bi-component blending electrospinning nanofiber membrane treated by thermal calendering, which is one embodiment of the producing method of reinforced electrospinning nanofiber membrane of the present invention.

Figure 11 is the SEM graph of PVDF6020/PVDF21216 bi-component blending electrospinning nanofiber membrane treated by thermal calendering, which is another embodiment of the producing method of reinforced electrospinning nanofiber membrane of the present invention. Figure 12 is a curve comparing the stress and strain before or after PVDF21216 electrospinning nanofiber membrane is treated by thermal calendering, which is one embodiment of the producing method of reinforced electrospinning nanofiber membrane of the present invention.

Figure 13 is a curve comparing stress and strain of PAN/PVDF21216 blending electrospinning nanofiber membrane before and after treated by thermal calendering, which is one embodiment of the producing method of reinforced electrospinning nanofiber membrane of the present invention.

Figure 14 is a curve of the stress and strain after PAN/PVDF21216 blending electrospinning nanofiber membrane, as well as PAN and PVDF21216 nanofiber membrane are treated by thermal calendering, respectively, which is one embodiment of the producing method of reinforced electrospun nanofiber membrane of the present invention.

Figure 15 illustrates the stress-strain curve before and after PVDF6020 nanofiber membrane is treated by thermal calendering process, which is one embodiment of the present invention.

Figure 16 is a curve comparing the stress and strain before and after PVDF6020/21216 blending electrospinning reinforced nanofiber membranes are treated by thermal calendering, which is one embodiment of the present invention.

Figure 17 is a curve of the stress and strain after two polymer of PVDF6020/21216 blending electrospinning reinforced nanofiber membrane, as well as the mono-component of PVDF6020 and PVDF21216 are treated by thermal calendering, respectively, which is another embodiment of the producing meth-

od of reinforced electrospun nanofiber membrane of the present invention.

Detailed description of the invention

[0024] Hereinafter, the present invention will be further illustrated in combination with the following embodiments and the accompanying drawings. These embodiments are only intended to further illustrate the invention, without intending to limit the protecting scope of the claims of the present invention.

[0025] The producing method of reinforced electrospinning nanofiber nonwoven (electrospun membrane) (abbreviated as producing method) designed by the present invention (see Figs. 1-17) mainly includes the following process steps:

(1) Preparing polymer spinning solution: multiple different polymers (two or more) and the good solvents thereof are stirred and mixed homogeneously in a blender at an appropriate weight percentage, forming two or more spinning solution for reserve after standing 1-2 hours;

(2) Alternative blending electrospinning: feeding the formulated multi-polymer spinning solution into each spinning system, respectively, and conducting cross blending electrospinning under the same receiving distance, spinning voltage, spinning environment. Spinning jets of these polymers are arranged alternately on a same spinneret which can be from different needles of multi-needle electrospinning apparatus, different orifices of multi-orifice electrospinning apparatus, or different spinning heads of needleless electrospinning apparatus. Multiple polymer spinning solutions are arranged crossly along the movement direction of the receiving device in forth-back, and the electrospinning nanofibers of multiple polymers are arranged randomly interlacing in the fiber web after webs formed.

(3) Thermal calendering bonding: after the alternative blending electrospinning, the formed blending spinning nonwoven membrane of two polymers is thermal calendering bonded at a certain temperature, pressure and time, in which the temperature is slightly higher (2~10 °C) than that of the melting point of the polymer with lower melting temperature. The temperature difference between the upper and lower roller/platen is in a range of 2~10 °C, the thermal calendering time is in a range of 1~10 min and the thermal calendering pressure is in a range of 1~20 MPa, respectively. Thermoplastic polymer with low melting point is partly melt during the process of thermal calendering, and the melting occurs only at the intersection between fibers, without clogging the original apertures and pores of the electrospinning nanofiber membrane.

[0026] In the producing method of the present inven-

tion, the thermoplastic polymer refers to the high-molecular material which can be dissolved in good solvent for electrospinning (including solution electrospinning and molten electrospinning), such as polyvinylidene fluoride (PVDF), polyethylene terephthalate (PET), polyamide 6 (PA 6) or polyamide 6,6 (PA 6, 6), polybutylene succinate (PBS), polyacrylonitrile (PAN), polyimide (PI), polyvinyl alcohol-modified thermoplastic starch, thermoplastic polyurethane (TPU), or thermoplastic polymers of polyethylene (PE), polystyrene (PS) and polyphenylene sulfide (PPS) which are difficult to be dissolved in organic solvents, the spinning solution of which are formed by melting.

[0027] In the producing method of the present invention, good solvent for the thermoplastic polymers refers to the solvent which has strong solubility for high-molecular solutes, including water, ethanol, chloroform, acetone, N,N-dimethylformamide (DMF), dimethylacetamide (DMAc) and formic acid, etc. For example, when the polyvinylidene fluoride (PVDF) serves as the thermoplastic polymer, DMF can be its good solvent. When the polyethylene terephthalate (PET) serves as the thermoplastic polymer, the mixed system of TFA and DCM (weight ratio in a range of 5:1~3:1) can be good solvent. When the polyamide 6 (PA 6) or polyamide 6,6 (PA 66) serves as the thermoplastic polymer, formic acid with the weight percentage of 10% ~ 15% can be its good solvent. When the polybutylene succinate polymer (PBS) serves as the thermoplastic polymer, the mixed system of trichloromethane (chloroform) and isopropanol (IPA) (weight ratio is in a range of 6:3~8:3) can be its good solvent. When the polyacrylonitrile (PAN) serves as the thermoplastic polymer, N,N-dimethyl formamide (DMF) can be its good solvent.

[0028] In the producing method of the present invention, the appropriate weight percentage concentration refers to that under which the polymer solutions can be spun continuously and steadily without the presence of large number of beaded fibers under the effect of high-voltage electric field, mainly depending on the material type, molecular weight, used good solvent and product structure property of the high-molecular polymers.

[0029] In the producing method of the present invention, the alternative blending electrospinning refers to that multiple polymer spinning jets are arranged alternately (cross, interlacing) on a same spinning plate, wherein the spinning jets come from different spinning needles of multi-needle electrospinning device/apparatus, different orifices of multi-orifices (multi-nozzles) electrospinning device/apparatus, or different spinning head of needleless electrospinning device/apparatus. Electrospinning jets of multiple polymers are arranged alternately (interlacing) along the movement direction of receiving device in forth-back, or alternatively arranged along the width direction of the product in left-right, and after webs are formed, electrospun nanofibers of multiple polymer are in random crisscross configuration. For example, in the multi-needle (multi-orifice, multi-nozzle) electrospin-

ning apparatus, multiple different polymer spinning solutions are fed according to certain regulation by needles placed in one row, two different spinning solutions are fed in a forth-back cross (interlacing) way by needles placed in different row. In the needleless electrospinning device/apparatus (such as Elmarco Nanospider Electrospinning device, Chech), different spinning solutions are fed with different spinning head, meanwhile, these spinning heads are arranged alternately or crisscross in forth-back.

[0030] In the producing method of the present invention, the thermal calendering temperature is 2~10 °C slightly higher than the melting point of the polymer with lower melting point, and the temperature difference between the upper and lower of rolls/platen is 2~10 °C. The thermal calendering time is 1~10 min, and the thermal calendering pressure is 1~20 MPa. Polymer with low melting point is partly melt during the process of thermal calendering, and the melt only occurs at the crossing point between fibers, without choking the original aperture and pores of the electrospinning nanofiber membrane. The thermal calendering bonding technology utilizes common device/apparatus.

[0031] The further feature of the producing method of the present invention is that the different polymers used for blending electrospinning may be two polymers, in which the between them is higher than 20 °C, also may be same polymer with a melting point difference between them is higher than 20 °C. Also, three or more polymers can be electrospun, as if there is one polymer with relatively low melting point, and the other polymers of blending electrospinning can be thermoplastic, non-thermoplastic or the combination of the both. For example, blending electrospinning of PVDF/PAN, PVDF6020/PVDF21216, PVDF/PAN/PET, PVDF/silk fibroin, PVDF/cellulose, PVDF/PLA, PVDF/PVA, PVDF/PVP, PVDF/PA blending electrospinning, PVDF/PET, PVDF/PS, PVDF/PPS, PVDF/PP, PVDF/PI etc.

[0032] This method can significantly improve the mechanical strength (tensile strength, bursting/puncture strength, tear strength) of nanofiber nonwoven fabric, and positively effect on the value of anti-static water pressure and windproof performance etc. The tensile strength of the electrospinning nanofiber membrane of the present invention is weighed by the conventional techniques in the art, that is, the measuring method for tensile strength regulated in GB13022-91 (with a sample standard of 20 mm x 150 mm, distance between claps of 50 mm, stretching rate of 10 mm / min).

[0033] According to the producing method of blending nanofiber nonwoven fabric, the present invention also designs the spinning plate/spinning head/spinneret (see Figs. 1-9) of reinforced nanofiber nonwoven fabric. In view of multi-needle/multi-orifice/multi-nozzle electrospinning device/apparatus, the arrangement of the needle/orifice/nozzle on the spinning plate/spinning head/spinneret complies with the alternative/interlac-

ing/cross way aforementioned. In view of the needleless electrospinning device/apparatus, the cross blending electrospinning can be realized by making spinning head/die transversely in series (multi-orifice in a single row), or vertically interlacing in paralleled (multi-orifice in multiple rows). Existing known technologies are used for what has not been described.

[0034] The present invention is further illustrated in combination with the embodiments and accompanying drawings.

PVDF and PVDF-HFP: purchased from Solvay, U.S.A (Solvay 6020, Solvay 21216);

PAN (polyacrylonitrile): purchased from Mitsui Chemicals Inc. & Co. (Mitsui Chemicals 1010);

PVA (polyvinyl alcohol): purchased from Shanghai Petrochemical co., LTD;

PBS: synthesized by Chemistry and Chemical Engineering, Tianjin Polytechnic University.

DMF (dimethylformamide), trichloromethane (chloroform), isopropyl alcohol (IPA), acetone (purity 99.5% CaCl₂), C₂H₅OH, sodium carbonate, polyethylene glycol (PEG-20000, the average molecular weight is 18500 -22000): purchased from Tianjin Kermel Chemical Reagent Co., AR;

Dialysis bag: specification of 3500 Dalton, purchased from Beijing Probe Bioscience Co., Ltd.;

Centrifuge: purchased from Huanyu Scientific Instrument Factory, Huanyu City, Jiangsu Province, Model number YXJ-A;

Deionized water: laboratory homemade;

Magnetic stirrer heated at constant temperature in heat storage form: purchased from Yingyu Yuhua Instrument Factory, Gongyi City, Model Number DF-101S;

Dryer: purchased from Shanghai Boxun Co. Ltd, Model Equipment Factory, Model Number GZX-9070MBE;

Magnetic stirrer: purchased from Yingyu Yuhua Instrument Factory, Gongyi City, Model Number DF-101S;

Dryer: purchased from Shanghai Boxun Co. Ltd, Model Equipment Factory, Model Number GZX-9070MBE;

Electrospinning apparatus: homemade/assembled by Nanofiber Lab, Tianjin Polytechnic University, mainly including fluid feeding system, high voltage power, metallic rotary drum, transverse mechanism, spinning plate, stainless steel needle dispensing adhesive etc., wherein the solution electrospinning device utilizes medical syringe pump as feeding system, and molten electrospinning utilizes screw extruder as feeding system.

Several silk (provided by Tianjin Institute of Medical Equipment);

Hot rolls: purchased from Taicang Wanlong Nonwoven Engineering Co., Ltd.. Model number : double-rollers pressure hot machine with heat transfer oils;

Thickness tester for membrane: Jinan Labthink Electromechanical technique Co., Ltd., Mode number: CHY-C2;
SEM (Scanning Electron Microscope): purchased from Hitachi High-Tech Co., Ltd., Model Number: TM-1000;
Universal strength tester: purchased from American Instron company, Model Number: Instron3369
DSC (Differential Scanning Calorimeter): purchased from Germany NETZSCH Thermal Analysis, Model Number: DSC200F3.

Example 1

[0035] PAN, and PVDF (model number: 21216) produced by Solvay are used as two kinds of polymers for blending electrospinning, Wherein PAN serves as the component with high melting point, which is still stable at the temperature of 220 °C, and the tensile modulus of the resulted electrospun nanofiber membrane is relatively high, however, the breaking elongation and breaking strength are relatively low (see Fig.14). PVDF21216 serves as the thermoplastic polymer component with low melting point whose melting point is 135 °C and the starting melting temperature is 110 °C. The tensile modulus of the fiber membrane obtained by mono-component electrospun is relatively low, however, the breaking elongation and breaking strength are high (see Fig.12).

[0036] PAN and PVDF21216 are pre-dried under the condition of 80 °C, PAN and solvent are weighed at a weight ratio of PAN/acetone/DMF = 15/20/65, and PVDF21216 and solvent are weighed at a weight ratio of PVDF21216/acetone/DMF = 10/20/70, and magnetic stirred at 45°C until the formation of transparent blending solution, and then cooled to ambient temperature to obtain the electrospun solution PAN and PVDF21216.

[0037] The prepared PAN and PVDF21216 electrospun solution is fed into a syringe of 20 mL, and the stainless steel dispensing needle with an inner diameter of 0.8 mm serves as the spinning head. The arrangement of PAN and PVDF21216 spinning jets on the spinning plate of the electrospinning apparatus is shown in Fig. 1, wherein PAN is the component with high melting point and PVDF21216 is the component with low melting point. Voltage is applied to the dispersing needle, with all the voltage applied to needles is 35 kV. Metal rotary drum with a diameter of 15 cm and covered with release paper on its surface serves as the receiving device, and the receiving distance is 20 cm. Under the condition of humidity of 25~40%, electrospun is processed for a period of 30 min, obtaining the nanofiber membrane with randomly and alternatively arranged two polymer fibers.

[0038] Spinning composite nanofiber membrane is clapped with two layers and double-sides release papers and fed into hot-rolls. The temperature of the upper and lower squeeze head is 113 °C and 110 °C, respectively, pre-heating for 30 min, and after the temperature is stabilized at the predetermined temperature, the electro-

pinning nanofiber membrane clapped by double-sides release papers is fed into the hot-rolls, which is hot-rolled for 5 min to obtain the reinforced nanofiber membrane, wherein PVDF21216 is partly melt and forms point bonding with PAN (see Fig. 10). After thermal calendering, the thickness of the membrane is measured to be 18.7μm, which is thinner than the thickness of 40 μm before thermal calendering, which can satisfy the requirements of most application fields except for the biological tissue scaffold.

[0039] Measurements for properties of permeability, porosity, tensile strength and so on is performed to the reinforced nanofiber membrane, the results shows that the permeability and porosity of PAN/PVDF21216 composite reinforced electrospinning nanofiber membrane are still extremely high, which is about 1200m³/m²·kPa·h and 84.4%. The breaking strength of the treated PAN/PVDF21216 composite reinforced electrospinning nanofiber membrane is 17.8 MPa, which is significantly higher than the 4 MPa and 8 MP of electrospinning nanofiber membrane with mono-component PAN and PVDF21216, respectively (see Fig.13), and the breaking elongation is also higher than that of PAN but lower than that of PVDF21216, and the modulus is increased dramatically. The disadvantageous of low strength of mono-component membrane is overcome with each advantageous of PAN and PVD21216 remaining, although after mono-component PVDF21216 electrospinning nanofiber membrane is treated with thermal calendering, the strength of it is increased, however, the increasing proportion of 128% is far more lower than the 908% of the PAN/PVDF21216 composite reinforced electrospinning nanofiber membrane (see Fig.14). It indicates that the combining method of cross blending electrospinning - hot rolling treatment realizes the effective point bonding between fibers (see Fig. 10), which significantly improves the tensile strength of the electrospinning nanofiber membrane, with the original advantages of electrospinning nanofiber membrane remaining at the same time.

Example 2

[0040] Thermoplastic polymers of PVDF6020 and PVDF 21216 (produced by Solvay U.S.) serves as two types of polymer components used for solution blending electrospinning. PVDF6020 acts as the component with high melting point of 175 °C, thus obtained electrospun membrane has large breaking strength and appropriate breaking elongation. PVDF21216 acts as the component with low melting point of 135 °C, and the starting melting temperature is 106 °C. The tensile modulus of fiber membrane obtained by electrospun is relatively low, while the breaking elongation is relatively large (see Figs.12 and 15).

[0041] PAN and PVDF21216 are pre-dried for 2 hours under the condition of 80 °C, PVDF6020 and solvent are weighed at a weight ratio of PVDF6020/acetone/DMF = 10/20/70, and PVDF21216 and solvent are weighed at

a weight ratio of PVDF21216/acetone/DMF = 10/20/70, they are magnetic stirred at 45°C until the formation of transparent blending solution, and then cooled to ambient temperature to obtain the electrospun solution of PVDF6020 and PVDF21216.

[0042] The prepared PVDF6020 and PVDF21216 electrospun solution is fed into a syringe of 20 mL, and the stainless steel dispensing needle with an inner diameter of 0.8 mm serves as the spinning head. The arrangement of PVDF6020 and PVDF21216 spinning jets on the spinning plate of the electrospinning apparatus is shown in Figs.3 and 4, wherein PVDF6020 is the component with high melting point and PVDF21216 is the component with low melting point. Voltage is applied to the dispersing needle, with all the voltage applied to needles is 35 kV. Metal rotary drum with a diameter of 15 cm and covered with release paper on its surface serves as the receiving device, and the receiving distance is 18 cm. Under the condition of humidity of 25~40%, electrospun is processed for a period of 30 min, obtaining the nanofiber membrane with randomly and alternatively arranged two polymer fibers.

[0043] Spinning composite nanofiber membrane is clapped with two layers double-sides release papers and fed into hot-rolls, and the thermal calendering pressure is set to 3 MPa. The temperature of the upper and lower squeeze head is 110 °C and 107 °C, respectively, pre-heating for 30 min, and after the temperature is stabilized at the predetermined temperature, the electrospinning nanofiber membrane clapped by double-sides release papers is fed into it, which is hot-rolled for 5 min to obtain the reinforced nanofiber membrane wherein PVDF21216 is partly melt and forms point bonding with PAN (see Fig. 11). After thermal calendering, the thickness of the membrane is measured to be 21.3 μm which is thinner than the thickness of 46 μm before thermal calendering. It indicates that thermal calendering treatment not only improves the strength of electrospun membrane, and also decrease/control the thickness.

[0044] Measurements for properties of permeability, porosity, tensile strength and so on is performed to the reinforced nanofiber membrane, the results shows that the permeability and porosity of PVDF6020/PVDF21216 composite reinforced electrospinning nanofiber membrane are still extremely high, which is about 960 m³/m²·kPa·h and 79.5%. The breaking strength of the treated PVDF6020/PVDF21216 composite reinforced electrospinning nanofiber membrane is 26.8 MPa, which is significantly higher than the 18 MPa and 8 MPa of electrospinning nanofiber membrane with mono-component PVDF6020 and PVDF21216, respectively (see Figd.15-17), the breaking elongation of which is also lower than those of PVDF6020 and PVDF21216, and the modulus is increased dramatically. It overcomes the disadvantageous of low strength of nomo-component membrane with advantageous of each of PVDF6020 and PVDF21216 remaining, although after mono-component PVDF6020 electrospinning nanofiber membrane is treat-

ed with thermal calendering, the strength of which is increased, the increasing proportion of 414% is far more lower than the 665% of the composite reinforced electrospinning nanofiber membrane with PVDF6020/PVDF21216 (see Fig.16). It indicates that the combining method of cross blending spinning-hot rolling treatment realizes the effective point bonding between adjacent fibers (see Fig.11), which significantly improves the tensile strength of the electrospinning nanofiber membrane.

Example 3

[0045] Thermoplastic polymers of PVDF6020 and PVDF 21216 (produced by Solvay U.S.) serves as two polymer components used for solution blending electrospinning. PVDF6020 acts as the component with high melting point of 175 °C, and the obtained electrospun membrane has large breaking strength and appropriate breaking elongation. PVDF21216 acts as the component with low melting point of 135 °C, and the starting melting temperature is 106 °C. The tensile modulus of fiber membrane obtained by electrospun is relatively low, while the breaking elongation is relatively high.

[0046] DF6020 and PVDF21216 are pre-dried for 2 hours under the condition of 80 °C to obtain dry polymer of DF6020 and PVDF21216. Melt blown device with spinneret in two row arranged alternatively is used to conduct the blending electrospinning. The spinning plate is grounded, and formed a net screen with polyester fiber woven fabric. High voltage of negative direct current of 35 KV is applied on the negative electrode under the net screen, the receiving distance is 15 cm, and the relative humidity is controlled in a range of 20~40%.

[0047] Dried polymers of PVDF6020 and PVDF21216 are fed into feeding hoppers of different screw-extruder, the temperature of feeding region, compressing region and measuring region of each screw-extruder is set according to each melting point, which allows the spinning molten of two PVDF completely melt flowing, and after being calculated and filtrated, reaching the spinning hole in the same spinneret but in different row, to conduct melt extruding spinning. After electrospun for 30 min, nanofiber membrane with two polymer fibers arranged randomly and alternatively is obtained.

[0048] Spinning composite nanofiber membrane is clapped with two layers double-sides release papers, and the thermal calendering pressure is set to 3 MPa. The temperature of the upper and lower squeeze head is 110 °C and 105 °C, respectively, pre-heating for 30 min, and after the temperature is stabilized at the predetermined temperature, the electrospinning nanofiber membrane clapped by double-sides release papers is fed into it, which is hot-rolled for 7 min to obtain the reinforced nanofiber membrane wherein PVDF21216 is partly melt and forms point bonding with PVDF6020. After thermal calendering, the thickness of the membrane is measured to be 30 μm, which is thinner than the thickness of 50

μm before thermal calendering. It indicates that thermal calendering treatment not only improves the strength of electrospun membrane, but also decreases/controls the thickness.

[0049] Measurements for properties of permeability, porosity, tensile strength and so on is performed to the reinforced nanofiber membrane, the results shows that the permeability and porosity of PVDF6020/PVDF21216 composite reinforced electrospinning nanofiber membrane are still extremely high, which is about $930 \text{ m}^3/\text{m}^2\cdot\text{kPa}\cdot\text{h}$ and 76%. After treatment, the breaking strength of the treated PVDF6020/PVDF21216 composite reinforced electrospinning nanofiber membrane is 30 MPa, the breaking elongation of which is also lower than those of one-component PVDF6020 and PVDF21216, and the modulus is increased dramatically. The disadvantageous of low strength of nomo-component membrane is overcome with each advantageous of PVDF6020 and PVD21216 remaining.

Example 4

[0050] Domestic PAN and PVDF 21216 produced by Solvay are used as two kinds of polymers for blending electrospinning, Wherein PAN serves as the component with high melting point, which is still heat-stable at the temperature of 220°C , and the tensile modulus of the resultant electrospun nanofiber membrane is relatively high, however, the breaking elongation and breaking strength are relatively low (see Fig.14). PVDF21216 serves as the thermoplastic polymer component with low melting point of 135°C , the starting melting temperature is 110°C , and the tensile modulus of the fiber membrane obtained by mono-component electrospun is relatively low, however, the breaking elongation and breaking strength are relatively high (see Fig.12).

[0051] PAN and PVDF21216 are pre-dried for 2 hours under the condition of 80°C , PAN and solvent are weighed at a weight ratio of PAN/acetone/DMF = 15/20/65, PVDF21216 and solvent are weighed at a weight ratio of PVDF21216/acetone/DMF = 10/20/70, they are magnetic stirred at 45°C until the formation of transparent blending solution, and then cooled to ambient temperature to obtain the PAN and PVDF21216 electrospun solution.

[0052] The prepared PAN and PVDF21216 electrospun solution is fed into a syringe of 20 mL, and the stainless steel dispensing needle with an inner diameter of 0.8 mm serves as the spinning head. The arrangement of PAN and PVDF21216 spinning jets on the spinning plate of the electrospinning apparatus is shown in Fig.7, wherein PAN is the component with high melting point and PVDF21216 is the component with low melting point. Voltage is applied to the dispersing needle, with all the voltage applied to needles being 50 kV. Metal rotary drum with a diameter of 15 cm and covered with release paper on its surface serves as the receiving device, and the receiving distance is 18 cm. Under the condition of hu-

midity of 25~45%, electrospun is processed for a period of 30 min, obtaining the nanofiber membrane with randomly and alternatively arranged two polymer fibers.

[0053] Spinning composite nanofiber membrane is clapped with two layers double-sides release papers and the thermal calendering pressure is set to 6 MPa. The temperature of the upper and lower squeeze head is 115°C and 110°C , respectively, pre-heating for 30 min, and after the temperature is stabilized at the predetermined temperature, the electrospinning nanofiber membrane clapped by double-sides release papers is fed into it, which is hot-rolled for 6 min to obtain the reinforced nanofiber membrane wherein PVDF21216 is partly melt and forms point bonding with PAN. After thermal calendering, the thickness of the membrane is measured to be $22 \mu\text{m}$ which is thinner than the thickness of $39 \mu\text{m}$ before thermal calendering, which can satisfy the requirements of most application fields, except for the biological tissue scaffold.

[0054] Measurements for properties of permeability, porosity, tensile strength and so on is performed to the reinforced nanofiber membrane, the results shows that the permeability and porosity of PAN/PVDF21216 composite reinforced electrospinning nanofiber membrane are still extremely large, which is about $1190 \text{ m}^3/\text{m}^2\cdot\text{kPa}\cdot\text{h}$ and 82.5%. The breaking strength of the treated PAN/PVDF21216 composite reinforced electrospinning nanofiber membrane is 19.4 MPa, which is significantly higher than the 4 MPa and 8 MPa of electrospinning nanofiber membrane with mono-component PAN and PVDF21216, respectively (see Fig.13), and the breaking elongation is also higher than that of PAN but lower than that of PVDF21216, and the modulus is increased dramatically. The disadvantageous of low strength of nomo-component membrane is overcome with each advantageous of PAN and PVD21216 remaining at the same time. It indicates that the combining method of cross blending spinning-hot rolling treatment realizes the effective point bonding between adjacent fibers (see Fig.11), which significantly improves the tensile strength of the electrospinning nanofiber membrane, for example, extremely high permeability, porosity, and extremely small pore size. In fact, after thermal calendering treatment, the pore size will further decreases, which can satisfy the requirement for extremely small pore size in the related art.

Example 5

[0055] The example relates to the preparation of PBS/(SF/PVA) blending electrospun membrane and thermal calendering reinforcing method.

[0056] First of all, PBS spinning solution is prepared by common technology: PBS (synthesized by Chemistry and Chemical Engineering, Tianjin University of Technology) is dissolved in the mixed system of chloroform (chloroform) and isopropyl alcohol (IPA) (with a weight ratio of 7:3) to prepare a PBS solution with the weight

concentration of 15 %. Then, SF/PVA blending solution is prepared by commone technology: silk supplied by Tianjin Institute of Medical Equipment is degummed with sodium carbonate solution of 0.5% to obtain refined silk, followed by that silk fibroin is dissolved in a ternary solvent of $\text{CaCl}_2/\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ (molar ratio of 1:2:8), to obtain the pure silk fibroin solution after centrifugation and dialysis, which is concentrated again, wherein its weight concentration is 25% by measurement. PVA solution with a weight concentration of 8% is formulated, which comprises that mixing SF solution and PVA solution in a volum ratio of 6:4 (or weight ratio of 5:1) to form the SF/PVA blending solution. PBS solution with a weight concentration of 15% and SF/PVA solution with a weight concentration of 25% are fed into adjacent spinnerets by utilizing self-made apparatus with 20 spinning orifices circularly distributed, during the electrospinning, an alternative arrangement state of PBS and SF/PVA jets may be formed, which can be received to obtain a nonwoven nanofiber membrane wherein three-components are mixed homogeneously.

[0057] The prepared PBS and SF/PVA spinning solutions are fed into a syringe of 20 mL with a spinneret inner diameter of 0.8 mm. The arrangement of these two spinning jets on the circle spinning plate is shown in Fig.7, wherein PBS is the thermoplastic component with low melting point, and its melting point is 114°C, and PBS/PVA is the non-thermoplastic polymer, and three of them all have biological degradation property. During the spinning experiment, receiving electrode is connected with direct current negative high voltage, and the 20 spinnerets circularly distributed is grounded, which forms a potential difference of 45 KV between each spinneret and receiving electrode. Metal rotary drum with a diameter of 15 cm and covered with release paper on its surface serves as the receiving device, and the receiving distance is 18 cm. Under the condition of humidity of 25~45%, electrospun is processed for a period of 30 min, obtaining the nanofiber membrane with randomly and alternatively arranged three polymer fibers. Thus obtained nanofiber has an average diameter of 500 nm, and the distribution of diameter is uniform.

[0058] Spinning composite nanofiber membrane is clapped with two layers double-sides release papers and the thermal calendering pressure is set to 5 MPa. The temperature of the upper and lower squeeze head is 108 °C and 105 °C, respectively, pre-heating for 30 min, and after the temperature is stabilized at the predetermined temperature, the electrospinning nanofiber membrane clapped by double-sides release papers is fed into it, which is hot-rolled for 5 min to obtain the reinforced nanofiber membrane wherein PBS nanofiber is partly melt and forms point bonding with SF/PVA nanofiber. After thermal calendering, the thickness of the membrane is weighed to be 25 μm which is thinner than the thickness of 49 μm before thermal calendering. It indicates that thermal calendering treatment not only improves the strength of electrospun membrane, and also decreases/controls the thickness simultaneously. Measurements for properties of permeability, porosity, tensile strength and so on is performed to the reinforced nanofiber membrane, the results shows that the permeability and porosity of PBS/(SF/PVA) blending reinforced electrospinning nanofiber membrane are still extremely high, which is about 9950 $\text{m}^3/\text{m}^2\cdot\text{kPa}\cdot\text{h}$ and 85%. The tensile breaking strength of the treated PBS/(SF/PVA) blending reinforced electrospinning nanofiber membrane is 25 MPa, and the breaking elongation of which is 2~3 folds higher than that of mono-component electrospun membrane.

es/controls the thickness simultaneously. Measurements for properties of permeability, porosity, tensile strength and so on is performed to the reinforced nanofiber membrane, the results shows that the permeability and porosity of PBS/(SF/PVA) blending reinforced electrospinning nanofiber membrane are still extremely high, which is about 9950 $\text{m}^3/\text{m}^2\cdot\text{kPa}\cdot\text{h}$ and 85%. The tensile breaking strength of the treated PBS/(SF/PVA) blending reinforced electrospinning nanofiber membrane is 25 MPa, and the breaking elongation of which is 2~3 folds higher than that of mono-component electrospun membrane.

Claims

1. A method for producing reinforced electrospinning nanofiber membrane, which comprises following steps:

- Preparing polymer spinning solution comprising two or more types of polymers wherein any two of them have a melting point difference of at least 20 °C are dissolved into respective excellent solvents;
- Blending electrospinning wherein two or more types of polymer which are dissolved into proper solvent as obtained in step (a) are blending electrospun to obtain a multi-components blending electrospun membrane;
- Thermal calendering bonding wherein the multi-component blending electrospun membrane is thermal calendered to obtain a reinforced electrospinning nanofiber membrane;

wherein the temperature of thermal calendering is higher than the melting point of the polymer with the lowest melting point in the two or more polymers, and lower than the melting point of the polymer with the second lower melting point in the two or more polymers, preferably the temperature is 2-10°C higher than the melting point of the polymer with the lowest melting point in the two or more polymers.

2. The method according to claim 1, wherein the polymer comprises one or more of the group consisting of polystyrene (PS), polysulfone (PSF), polyether sulfone (PES), polyvinylidene fluoride (PVDF), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), poly(vinylidene fluoride-co-chlorotrifluoroethylene) (PVDF-CTFE), polyacrylonitrile (PAN), polyamide (PA), polyvinyl carbazole, cellulose acetate (CA), cellulose, chitosan (PAA), polyaniline, polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polypropylene terephthalate (PTT), polyimide (PI), polyurethane (PU), poly(methyl methacrylate) (PMMA), polyvinyl alcohol (PVA), polycarbonate (PC), polyethylene imine

- (PEI), polyether ether ketone (PEEK), aliphatic amides, polyvinyl acetate (PVAc), polyoxymethylene (POM), polyvinyl chloride (PVC), nylon-6 (PA-6), nylon-66 (PA-66), polytrifluoroethylene, polychlorotrifluoroethylene, polyvinyl fluoride, polylactic acid, polyethylene oxide and polyvinyl pyrrolidone.
3. The method according to claim 1, wherein at least one of the two or more polymers is a thermoplastic polymer.
 4. The method according to claim 3, wherein the thermoplastic polymer comprises polyvinylidene fluoride (PVDF), polyethylene terephthalate (PET), polyamide 6 (PA6) or polyamide 6,6 (PA6, 6), polybutylene succinate (PBS), polyacrylonitrile (PAN), polyimide (PI), poly vinyl alcohol-modified thermoplastic starch, thermoplastic polyurethane (TPU), or polypropylene (PP), polyethylene (PE), polystyrene (PS) and polyphenylene sulfide (PPS) whose spinning solutions should be formed by melting.
 5. The method according to claim 3 or 4, wherein the thermoplastic polymers are the same or different types.
 6. The method according to any one of the preceding claims 1-5, wherein the blend electrospinning is alternate blending electrospinning.
 7. The method according to claim 6, wherein the alternate blending electrospinning is cross or interlacing electrospinning.
 8. The method according to any one of the preceding claims, wherein the electrospinning jets of the blending electrospinning are arranged crossly along the forth-and-back movement direction of the receiving device, or arranged alternatively along the left-and-right width direction of the product.
 9. The method according to any one of the preceding claims, wherein the electrospinning jets of the blending electrospinning are present on a blending electrospinning plate, or a spinning head, or a spinneret, or a spinning nozzle.
 10. The method according to claim 9, wherein multiple needles, multiple orifices, multiple nozzles on the blending electrospinning plate or spinning head or spinneret or spinning nozzle are arranged alternately in left-right or arranged crossly in length-breadth, or a electrospinning head, spinning nozzle or spinning die without needle are arranged interlacing in length-breadth.
 11. The method according to claim 9 or 10, wherein the different polymer spinning solutions are fed by the multiple-needle, multiple-orifice, multiple-nozzle on the blending electrospinning plate or spinning head or spinneret or spinning nozzle alternating, interlacing or crossing way.
 12. The method according to any one of claims 9 to 11, wherein the electrospinning head, spinneret or spinning die without needle include the type of metal rotary roller, metal wire, spiral, sawtooth, centrifugation and bubble needleless electrospinning head, spinneret or spinning die.
 13. The method according to claim 1, wherein the thermal calendering time is in the range of 1 to 10 min.
 14. The method according to claim 1, wherein the thermal calendering pressure is in the range of 1 to 20 MPa.
 15. An electrospinning nanofiber membrane, which has a tensile breaking strength of at least 17.8 MPa, preferably greater than 26.8 MPa.
 16. A blending electrospinning apparatus including two or more types of electrospinning jet emitting devices.
 17. The blending electrospinning apparatus according to claim 16, wherein the apparatus is a spinning plate, spinning head, spinneret or spinning nozzle.
 18. The blending electrospinning apparatus according to claim 16 or 17, wherein the two or more types electrospinning emitting devices are in the form of blending multiple-needles arranged in line, a blending multiple-nozzle arranged in line, a blending multiple-orifice arranged in line, blending multiple-needle arranged in circle or blending roller without needle.

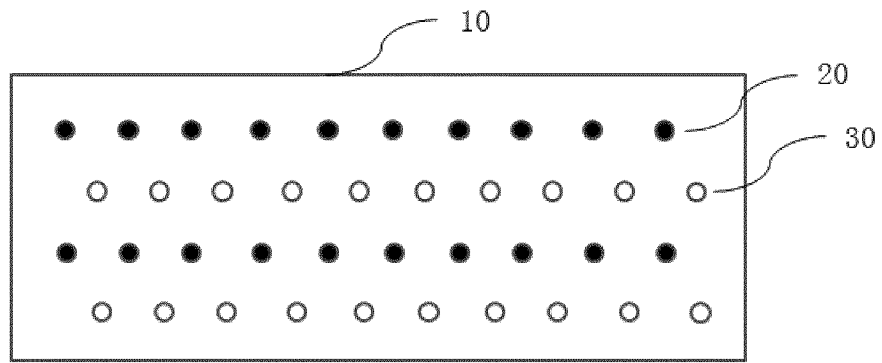


Fig. 1

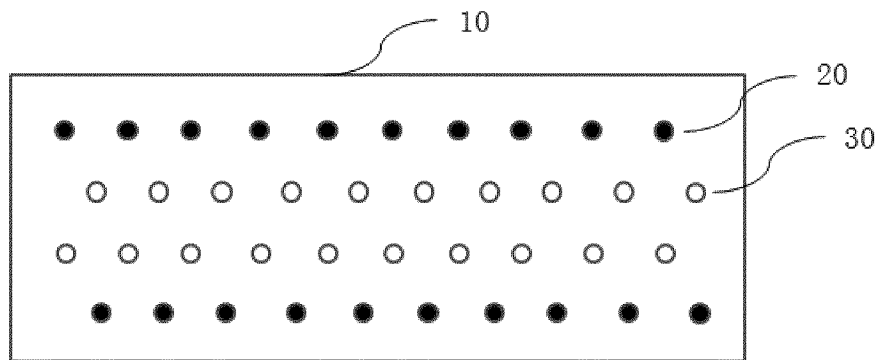


Fig. 2

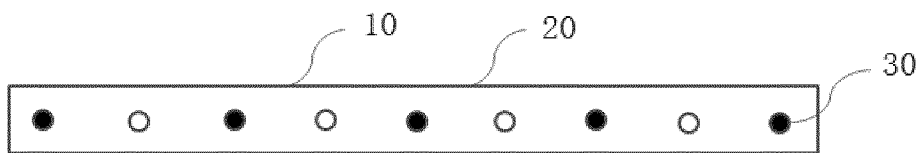


Fig. 3

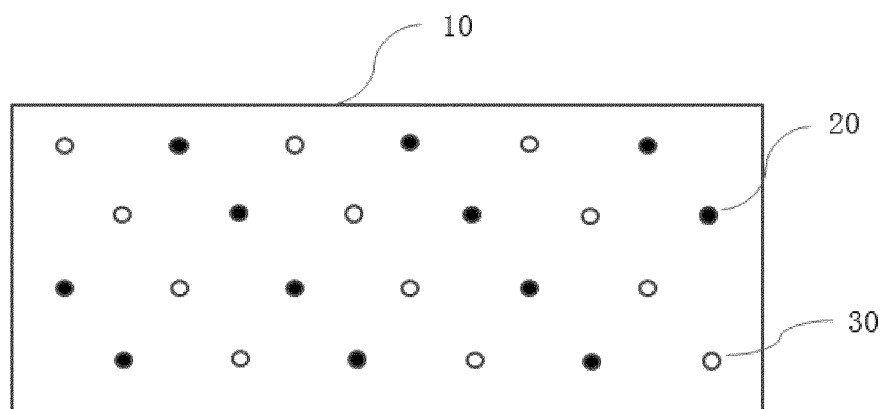


Fig. 4

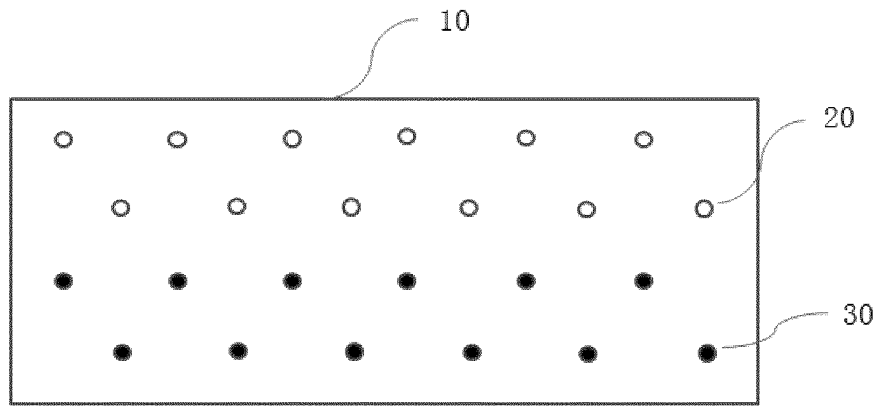


Fig. 5

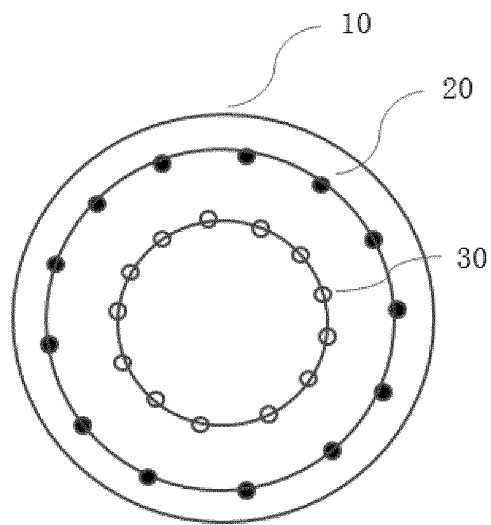


Fig. 6

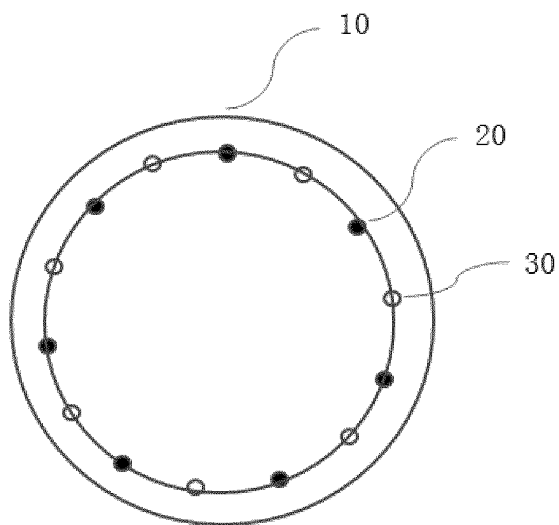


Fig. 7

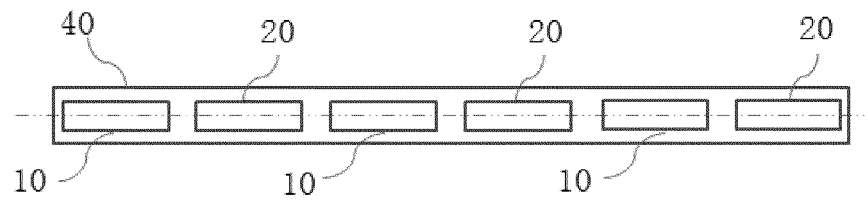


Fig. 8

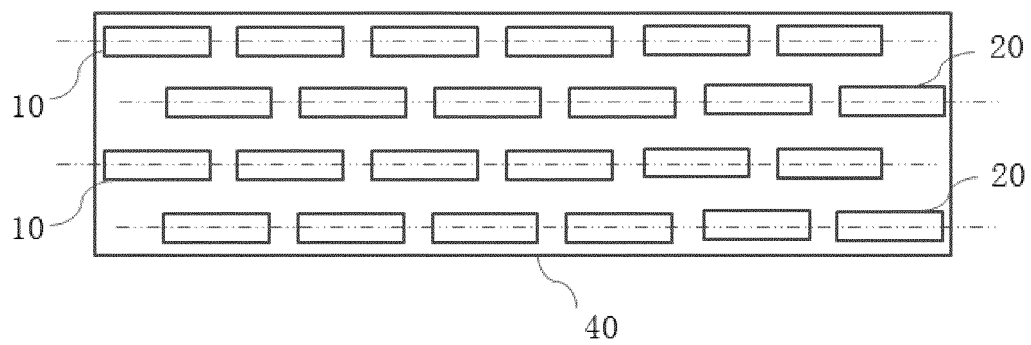


Fig. 9

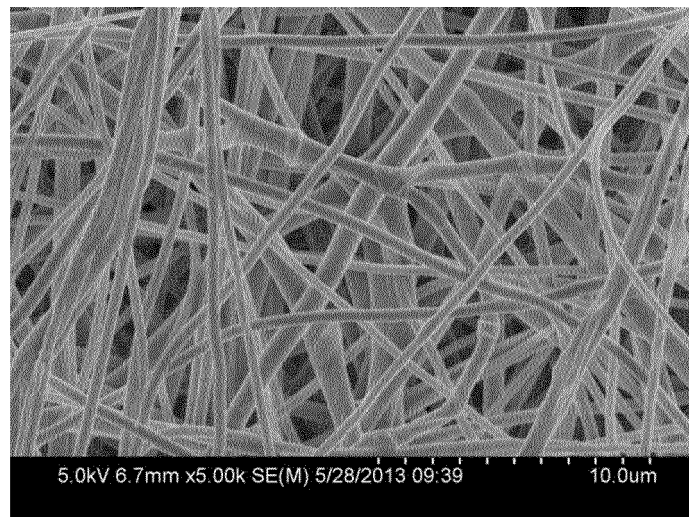


Fig. 10

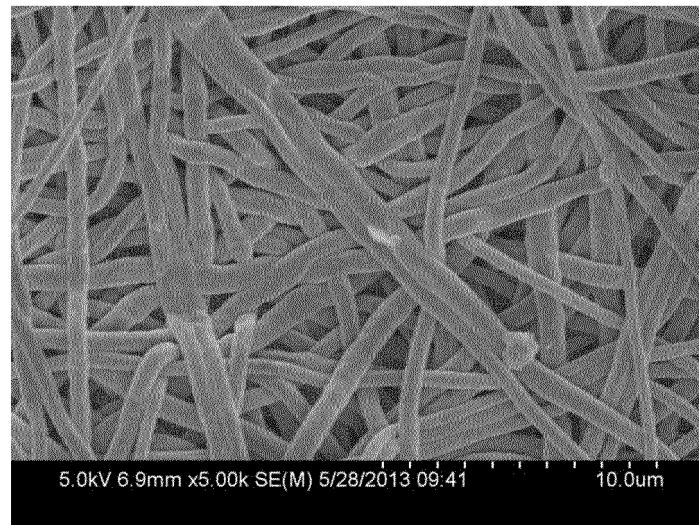


Fig. 11

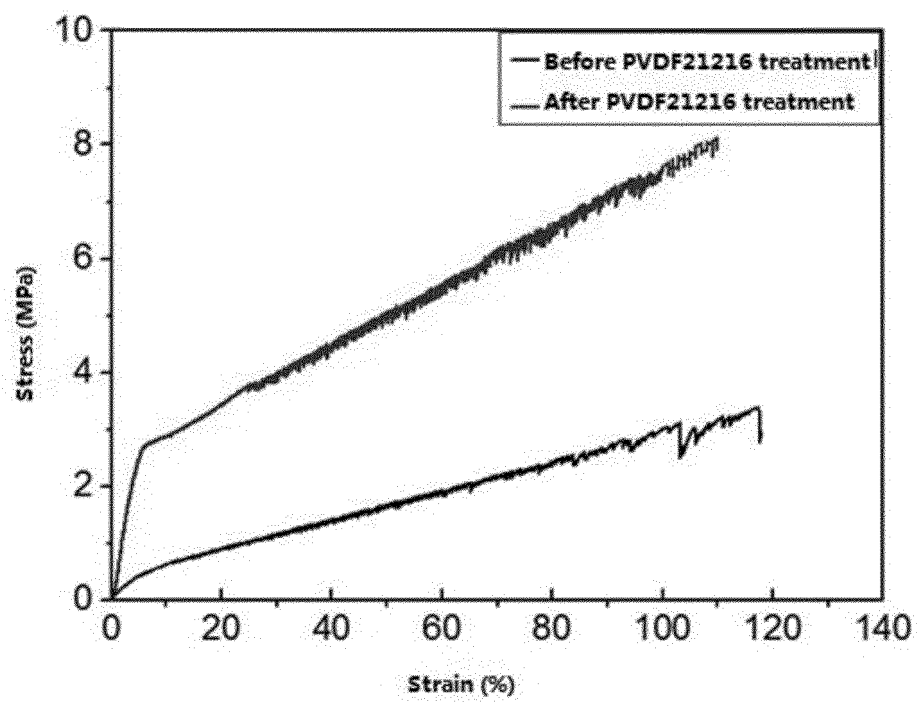


Fig. 12

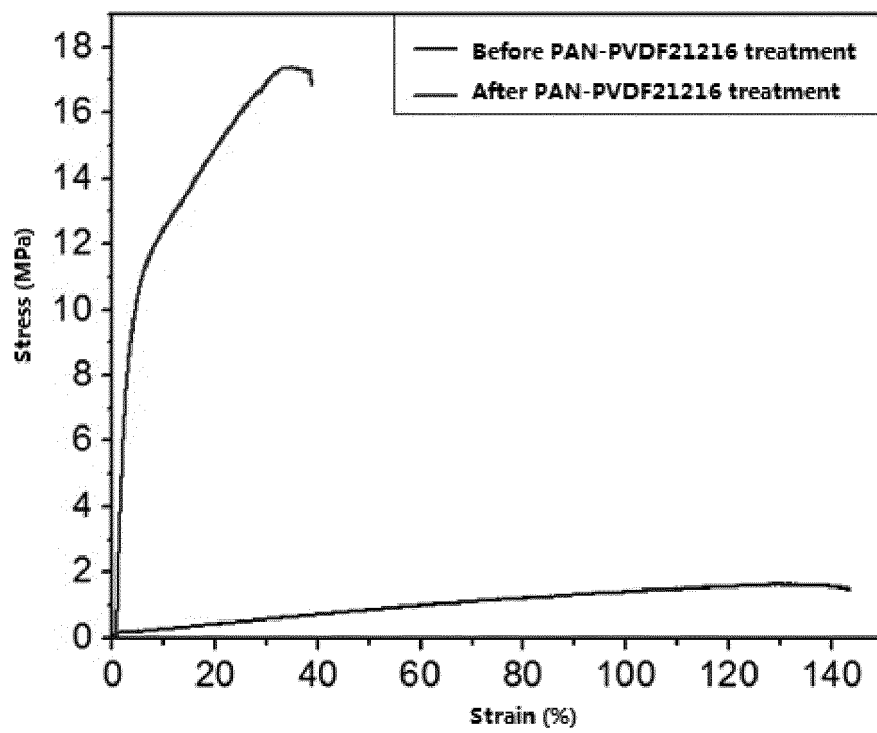


Fig. 13

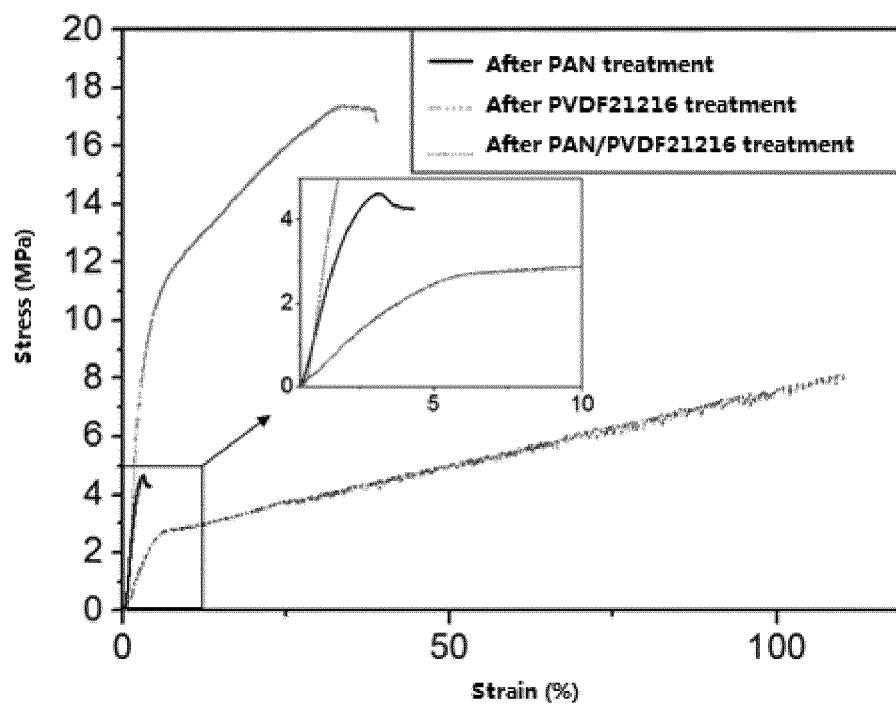


Fig. 14

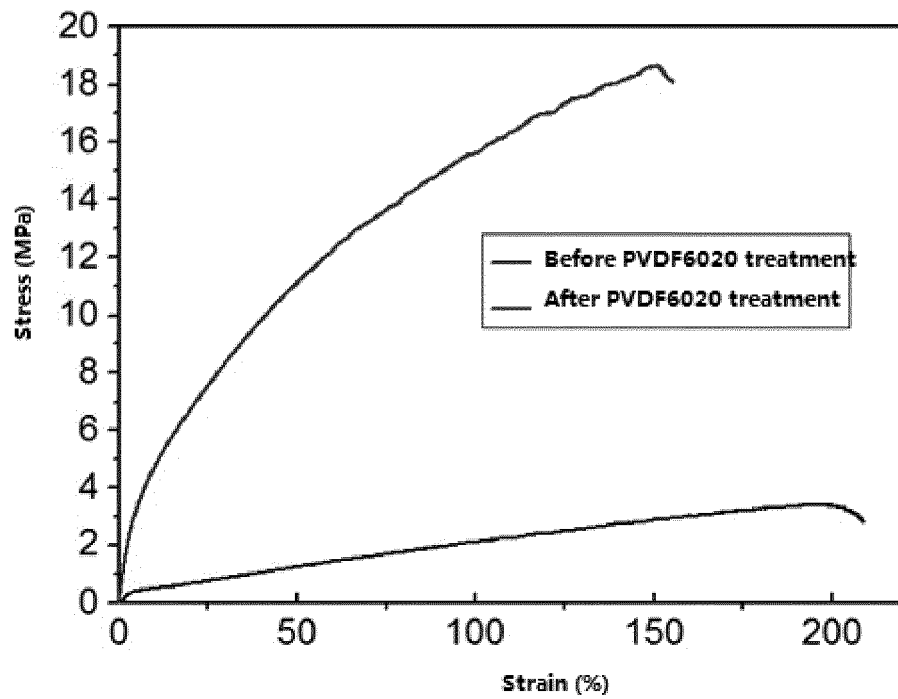


Fig. 15

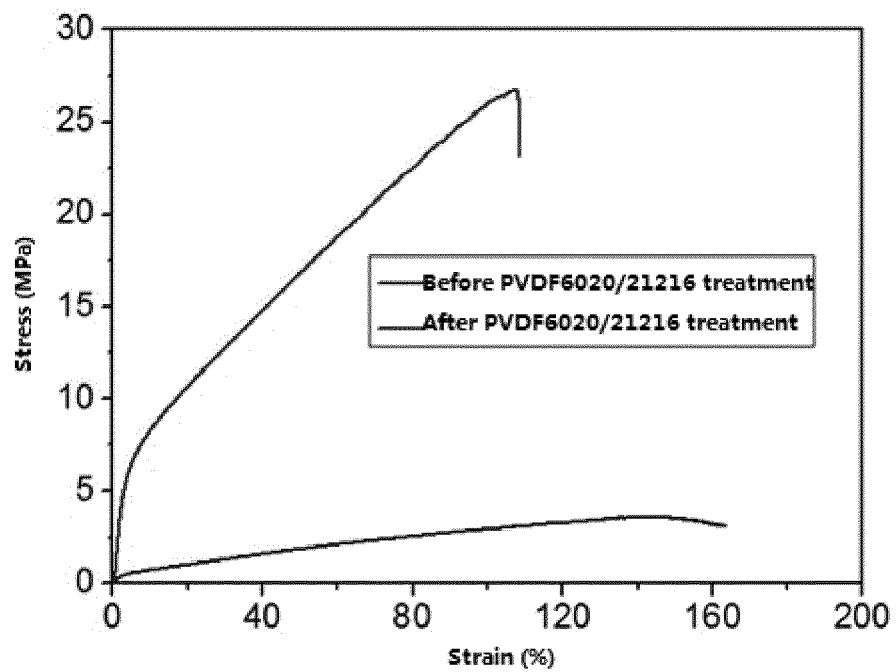


Fig. 16

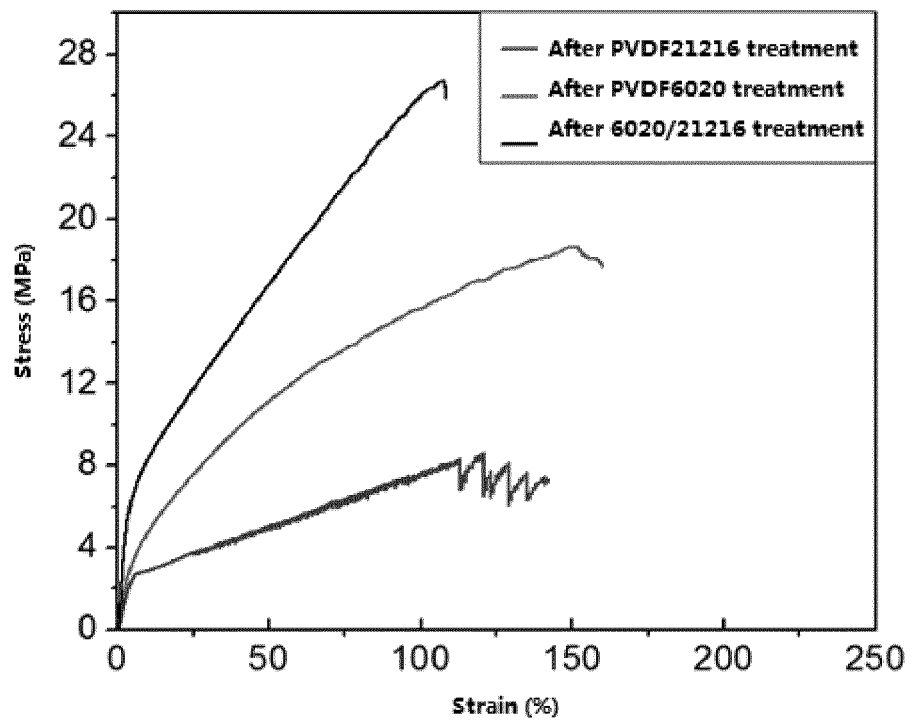


Fig. 17

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2014/082262

A. CLASSIFICATION OF SUBJECT MATTER

D04H 1/541 (2012.01) i; D04H 1/558 (2012.01) n; D04H 1/728 (2012.01) n
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)

D04H, D01D

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CPRSABS; SIPOABS, CNTXT, VEN: nanometre, micrometer, micro-nano, component, induction spinning, hot rolling, adhesion, electrospinning, electrospun, electrostatic, melting point

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	CN 103541149 A (TIANJIN POLYTECHNIC UNIVERSITY), 29 January 2014 (29.01.2014), the whole document	1-18
X	CN 101671853 A (JILIN UNIVERSITY), 17 March 2010 (17.03.2010), description, page 2, paragraph 2 to page 3, paragraph 4, embodiment 10, and figures 1-3	1-15
X	CN 103205818 A (XIAMEN UNIVERSITY), 17 July 2013 (17.07.2013), particular embodiments, and figures 1-2	16-18
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Name and mailing address of the ISA/CN: State Intellectual Property Office of the P. R. China No. 6, Xitucheng Road, Jimenqiao Haidian District, Beijing 100088, China Facsimile No.: (86-10) 62019451	Authorized officer WANG, Han Telephone No.: (86-10) 62085483

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