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(54) **APPARATUS AND METHOD FOR PRODUCING ELECTROSPUN FIBERS**

**Publication Classification**

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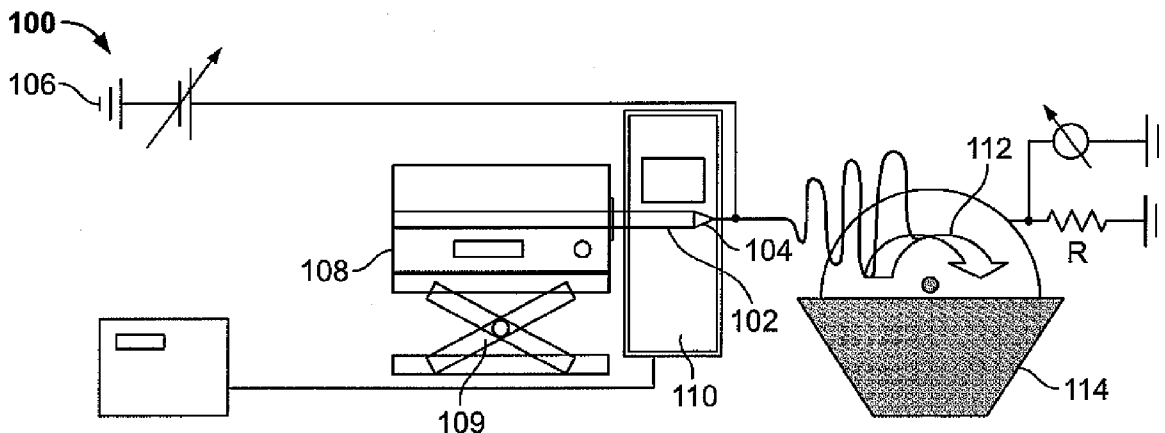
(57) **ABSTRACT**

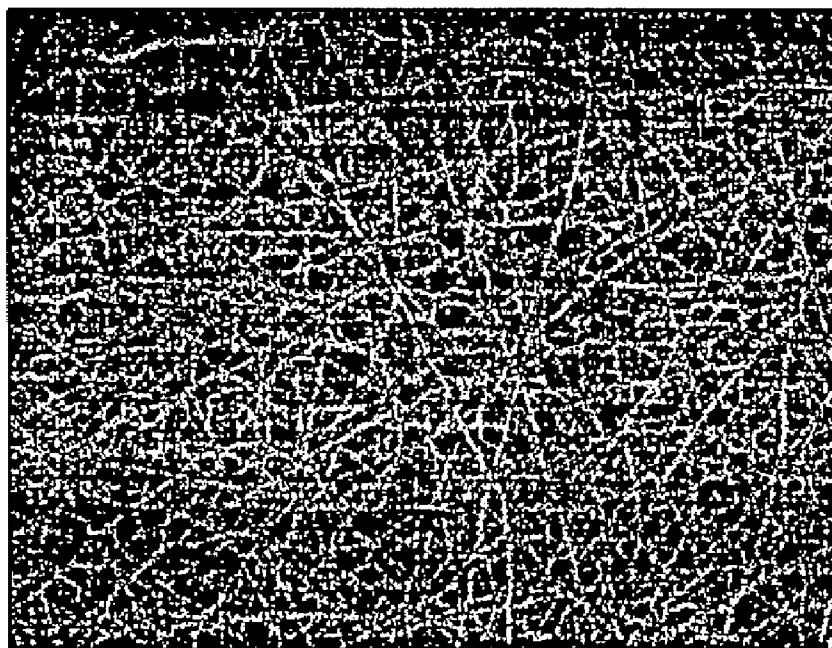
An apparatus for making electrspun fibers comprises a collector that may be submerged in a coagulation bath. The collector may be automatically movable between a first position and a second position, wherein at least a portion of the collected fibers are submerged in a coagulation bath in the first position and spaced apart from the coagulation bath in the second position. The collector may be a rotating collector. A process for making electrospun fibers comprises electrospinning a dispersion and collecting a plurality of electrospun fibers, followed by submerging the collected fibers in a coagulation bath.

**Related U.S. Application Data**

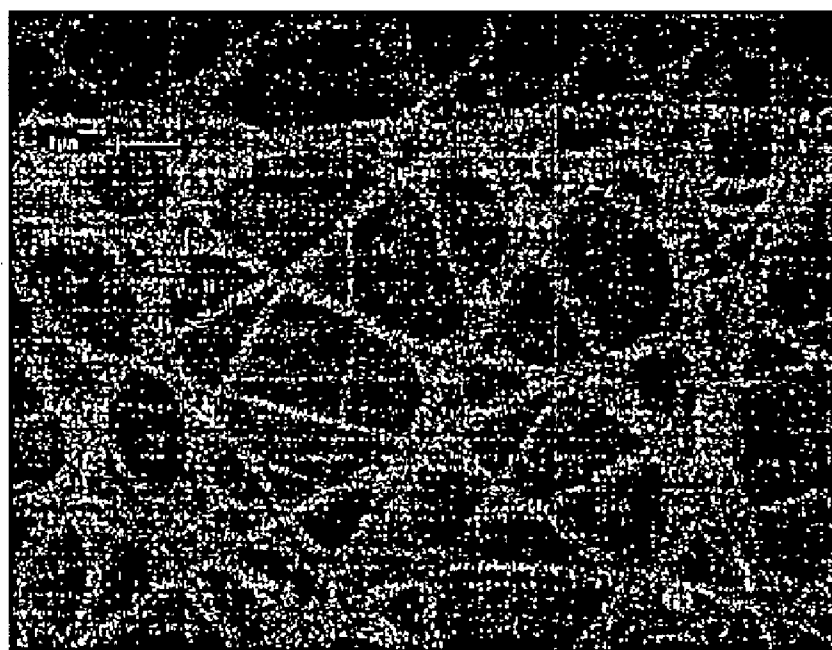
(63) Continuation-in-part of application No. 10/965,813, filed on Oct. 18, 2004, now Pat. No. 7,326,043.

(60) Provisional application No. 60/747,340, filed on May 16, 2006, provisional application No. 60/583,358, filed on Jun. 29, 2004.





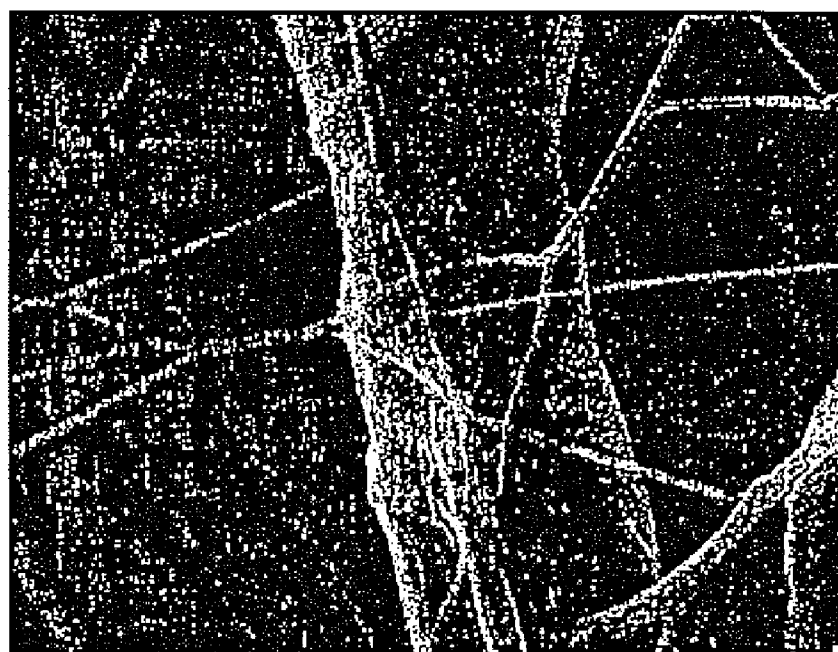
**FIG. 1A**



**FIG. 1B**



**FIG. 2A**



**FIG. 2B**

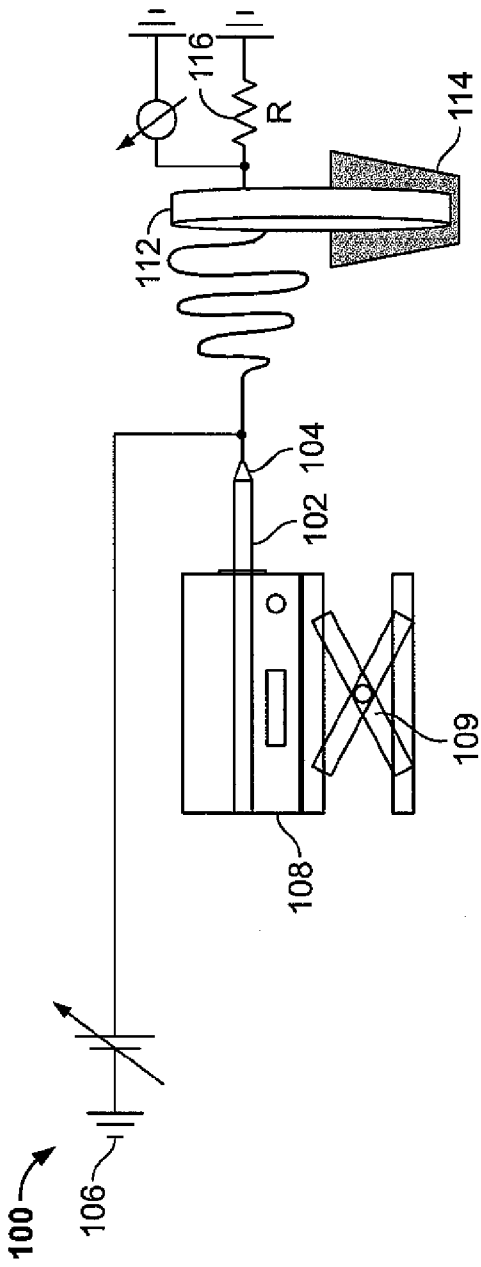


FIG. 3A

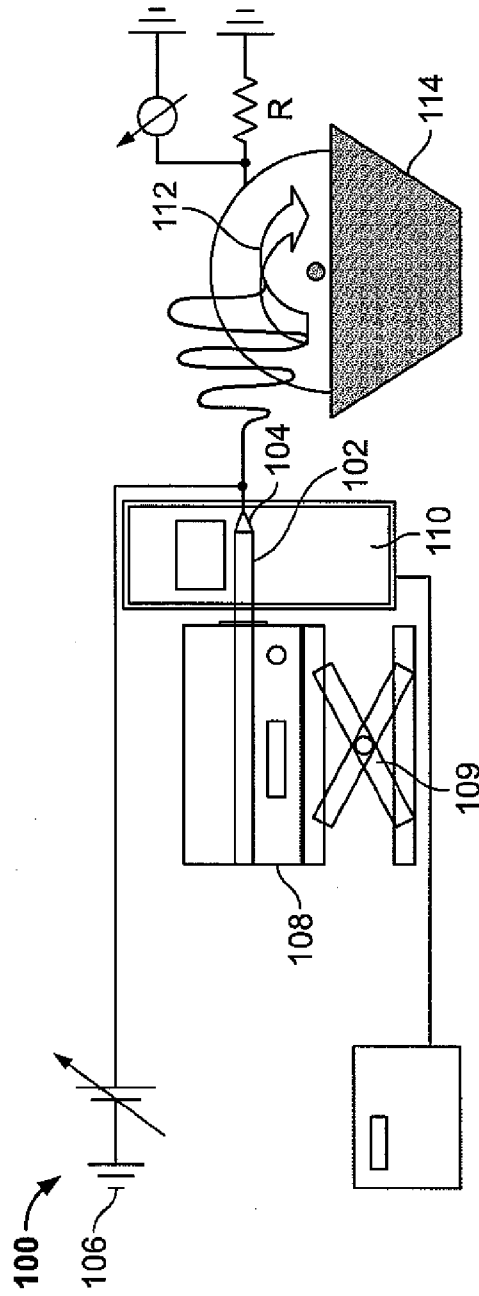


FIG. 3B

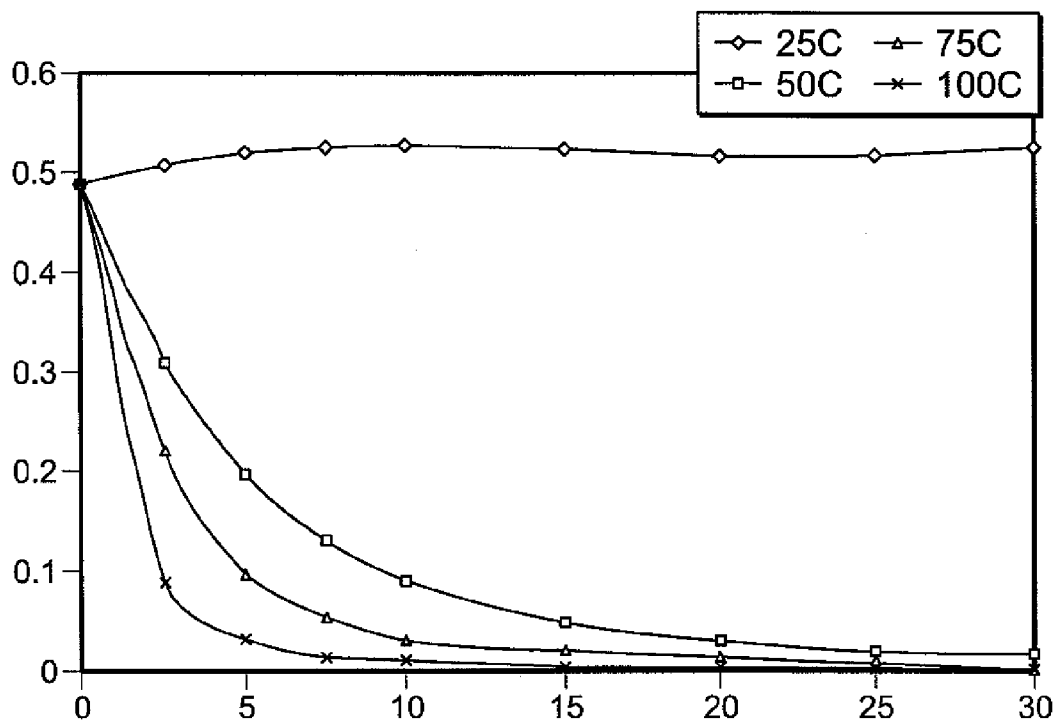


FIG. 4

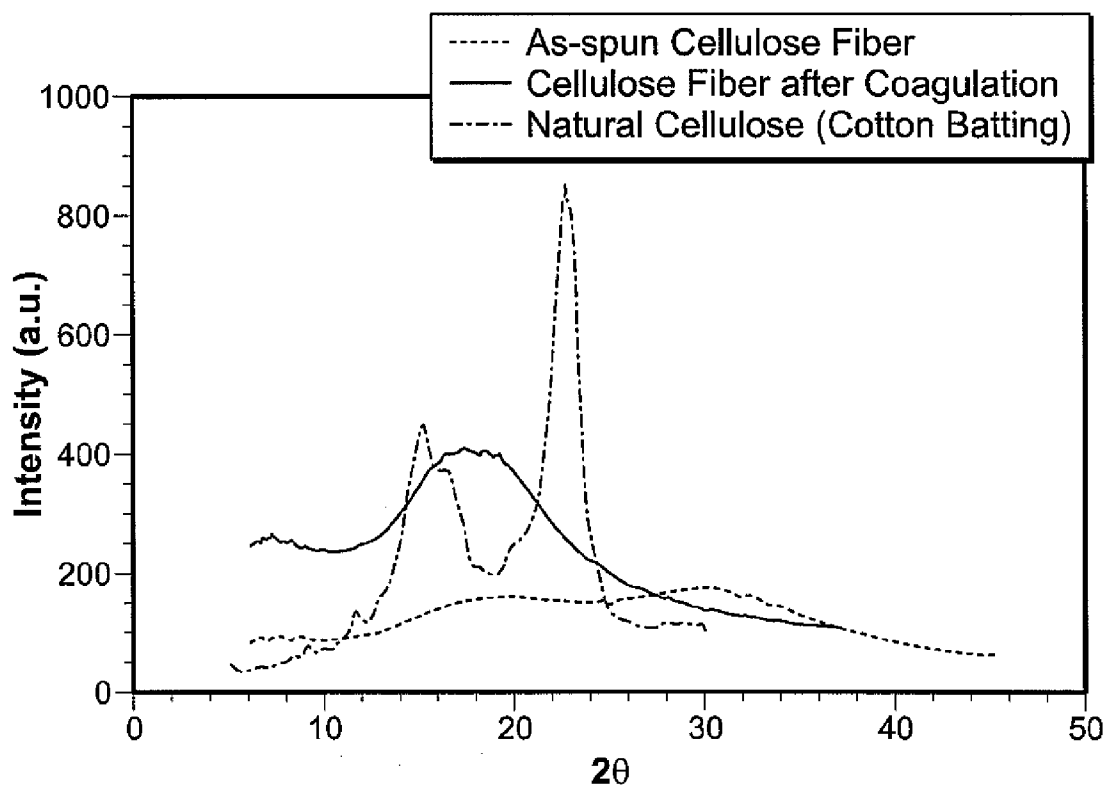


FIG. 5

## APPARATUS AND METHOD FOR PRODUCING ELECTROSPUN FIBERS

### CROSS-REFERENCE TO RELATED APPLICATIONS

**[0001]** The instant application claims the benefit of U.S. Provisional Serial App. No. 60/747,340, which is incorporated by reference herein in its entirety. The instant application further claims the benefit of U.S. patent application Ser. No. 10/965,813, which, in turn, claims the benefit of U.S. Provisional Serial App. No. 60/583,358, both of which are incorporated by reference herein in their entirety.

### FIELD OF INVENTION

**[0002]** The present invention relates to fibers and more particularly to methods for making cellulose nanofibers.

### BACKGROUND

**[0003]** Various naturally occurring polymers are of particular interest due to their abundant availability and biodegradability. Cellulose, for example, is one of the most abundant naturally occurring polymers on earth, and finds use in countless applications. Yet, cellulose has proven difficult to transform into fibers because of its relatively high degree of intermolecular and intermolecular hydrogen bonding, which renders it substantially insoluble in common solvents. The effective manufacture of cellulose fibers, therefore, is an area of interest.

### SUMMARY OF INVENTION

**[0004]** The present invention relates to improved fibers comprising organic polymers and methods for making the same.

**[0005]** In one aspect, a process for making organic fibers comprises electrospinning a dispersion comprising an organic polymer. In one embodiment, the process comprises providing a starting material comprising an organic polymer, dissolving the starting material in a polar solvent to create a dispersion, electrospinning the dispersion by providing an electric charge on droplets of the dispersion to produce a charged jet of polymer and provide a plurality of electrically induced bending instabilities and/or whipping motions, collecting a plurality of the charged jets as fibers and submerging the plurality of fibers into a coagulation bath as they are collected. In another embodiment, the process comprises providing a starting material comprising cellulose, dissolving the starting material in a polar solvent unreactive with cellulose to create a dispersion, electrospinning the dispersion by providing an electric charge on droplets of the dispersion to produce a charged jet of polymer and provide a plurality of electrically induced bending instabilities and/or whipping motions, collecting a plurality of substantially amorphous non-derivatized cellulose nanofibers on a rotating collector and submerging the rotating collector comprising the plurality of substantially amorphous non-derivatized fibers into a coagulation bath on a periodic basis. The collector may, for example, be submerged in regular time intervals between about 1 and about 3.

**[0006]** The above-identified processes may incorporate various additional features and steps. The solvent used in the dissolving step may, for example, be sufficiently volatile to substantially dissolve during the electrospinning step and can comprise lithium chloride and N, N-dimethylacetamide. The

electrospinning step may be carried out in an electric field between about 1.0 kV/cm to about 4.0 kV/cm at a flow rate between about 0.03 ml/min. and about 0.05 ml/min. Further, co-axial electrospinning may be employed. After the collecting step, the recovered fibers may be exposed to at least one of water and alcohol for removing residual solvent without dissolving the fibers or heating at temperatures between about 70° C. and 110° C. Typically, the collected fibers exhibit substantially uniform diameters. The fibers may comprise substantially uniform diameters and a degree of crystallinity between about 1% and about 40%. The fibers may also comprise a substantially amorphous form of cellulose exhibiting an X-ray diffraction pattern comprising at least two 2θ values selected from about 7.0 degrees and about 17.8 degrees. The coagulation bath may comprise at least one of water and alcohol for removing residual solvent without dissolving the fibers.

**[0007]** In another aspect, an apparatus for making fibers comprises a chamber, pump, syringe, voltage supplier and syringe. In one embodiment, the apparatus comprises a chamber for receiving a dispersion, a pump upstream of the chamber for dispensing the dispersion, a syringe for receiving the dispersion from the pump and comprising an opening for providing droplets of the dispersion, a voltage supplier in electrical communication with the syringe and a collector. The voltage supplier provides an electric charge in the droplets emanating from the opening to produce a plurality of charged jets and provide a plurality of electrically induced bending instabilities and/or whipping motions. The collector receives and collects the charged jets as non-woven fibers and automatically moves between a first position and a second position, wherein at least a portion of the collected fibers are submerged in a coagulation bath in the first position and spaced apart from the coagulation bath in the second position. The collector may be a rotating collector.

**[0008]** The apparatus may further comprise a heating chamber constructed of an electrically and thermally insulating material, shielded from the voltage supplier. Additionally or alternatively, a heating gun for heating the collector may be employed.

### BRIEF DESCRIPTION OF THE DRAWINGS

**[0009]** Certain embodiments of the present invention are illustrated by the accompanying figures. It should be understood that the figures are not necessarily to scale and that details not necessary for an understanding of the invention or that render other details difficult to perceive may be omitted. It should be understood, of course, that the invention is not necessarily limited to the particular embodiments illustrated herein.

**[0010]** FIG. 1A is a scanning electron microscope (“SEM”) image of cellulose nanofibers made in accordance with one embodiment of the present invention;

**[0011]** FIG. 1B is an SEM image of FIG. 1A;

**[0012]** FIG. 2B is an SEM image of nanofibers on filter media for dust collection made in accordance with a second embodiment of the present invention;

**[0013]** FIG. 2A is an SEM image of FIG. 2A;

**[0014]** FIG. 3A is a perspective view of one embodiment of an electrospinning apparatus used to prepare the nanofibers of the present invention;

**[0015]** FIG. 3B is a perspective view of an alternate embodiment of the electrospinning apparatus of FIG. 3A;

**[0016]** FIG. 4 is a graph illustrating the volatility of DMAc, with mass measurements plotted as a function of time; and

**[0017]** FIG. 5 is an X-ray diffraction pattern for the cellulose starting material, and cellulose nanofibers made in accordance with the present invention before and after coagulation.

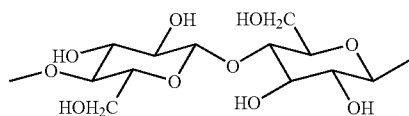
#### DETAILED DESCRIPTION

**[0018]** The nanofibers of the present invention may be made from organic polymeric starting materials. These organic polymeric starting materials are typically mixed with a solvent comprising a relatively high volatility (i.e., the readiness with which a material vaporizes), and then subjected to an electrospinning process. Ideally, the solvent is sufficiently volatile to substantially dissolve during the electrospinning process.

**[0019]** Nanofibers made in accordance with the present invention comprise an organic polymer, and typically exhibit fiber diameters between about 50.0 nm and 1.0 micron, more particularly between about 100.0 nm and 300.0 nm and still more particularly between about 100.0 nm and 200.0 nm. The nanofibers may be relatively amorphous, comprising a degree of crystallinity less than about 60% and more particularly between about 1.0% and 50.0% and still more particularly between about 1.0% and 40.0%. The degree of crystallinity is determined through X-ray diffraction patterns and may be modified by adjustments to the electrospinning process, including spinning distance, flow rate and spinning temperature. The specific surface area of the nanofibers may be between about 1.0 m<sup>2</sup>/g and 50.0 m<sup>2</sup>/g and more particularly between about 5.0 m<sup>2</sup>/g and 10.0 m<sup>2</sup>/g, as measured by the BET surface area testing methodology. The degree of polymerization of the nanofibers may be between about 50 and about 2000 and more particularly about 200 to about 1150.

**[0020]** When the nanofibers are randomly dispersed, with at least some of the nanofibers in physical contact with one another, a nanofiber mat is formed. The nanofiber mat can comprise a plurality of pores or interstices between individual fibers. The pores typically comprise diameters between about 0.5 microns and 3.0 microns.

**[0021]** The nanofibers may be composed of various materials, such as cellulose-based polymers. In one embodiment the nanofibers comprise non-derivatized substantially amorphous cellulose, which comprises the repeat unit:



in random orientations and positions. SEM images of a plurality of cellulose nanofibers made in accordance with certain embodiments of the present invention are shown at FIGS. 1A-2B.

**[0022]** The nanofibers and nanofiber mat of the present invention may be made through a step-wise process. Typically, a starting material is pre-treated and subjected to electrospinning, with heating and an optional coagulation step.

**[0023]** Various starting materials may be employed, including without limitation, organic polymers such as cellulose. The starting materials are often substantially insoluble in common solvents like water. The molecular weight of the starting material may be between about 10,000 and 325,000

g/mol and more particularly between about 30,000 and 200,000 g/mol. The degree of polymerization of the starting material may be between about 50 and about 2,000 and more particularly about 200 to about 1,150. Suitable examples of cellulose starting materials include cotton linter paper, cotton batting, recycled cellulose and purified bast fibers.

**[0024]** The starting material is typically ground into fine particles and soaked in water to break or weaken hydrogen bonding. The starting material may be ground to particle sizes between about 5.0 mesh and 50.0 mesh and more particularly between about 15.0 mesh and 25.0 mesh. The finely divided starting material is placed in water and soaked at room temperature for a period of between about 6.0 hours to about 15.0 hours and more particularly between about 8.0 hours and 12.0 hours. The water may be high performance liquid chromatography water available from Mallinckrodt of Phillipsburg, NJ. The starting material is thereafter dried under vacuum at between about 55° C. and about 65° C.

**[0025]** After the starting material is dried, it may be dissolved in a solvent, comprising a relatively high volatility. Preferably, the solvent does not chemically react with the starting material and is sufficiently volatile to substantially dissolve during the electrospinning process. The term “solvent” as used herein means any compound or substance or mixture of liquid compounds or substances used to dissolve part or all of the starting material.

**[0026]** The solvent may, for example, be a polar solvent used to help weaken or break hydrogen bonding within the organic starting material. The loosening or breakage of hydrogen bonds enhances the solubility of the starting material within the solvent. Polar solvents are beneficial during the electrospinning step because of their relatively high conductivities. In addition, depending on the selection of the solvent, dissolution may proceed without side reactions, leading to a non-derivatized end product. In one embodiment, the solvent comprises DMAc, to which lithium chloride may be added. This solution has been shown to dissolve cellulose from different sources over a large range of concentrations without side reactions. The presence of lithium chloride bridges electrostatic interactions between cellulose and DMAc. In other embodiments, solutions of NMMO/H<sub>2</sub>O may be employed. Dissolution typically proceeds for about 2.0 hours under constant stirring, with mild heating between about 50° C. to about 60° C. The final concentration of starting material in the solution may be between about 1.0% by weight to about 10% by weight and more particularly between about 3.0% by weight to about 6% by weight. The final solution may exhibit a zero shear viscosity between about 2,500 Pa\*s and 3,500 Pa\*s. After dissolution of the starting material in the solvent, the dispersion is subjected to electrospinning.

**[0027]** Electrospinning is a fiber formation process that relies on electrical, rather than mechanical forces to form thin fibers (sub-micron fibers for example). With electrospinning, an electric field is used to draw a solution from the tip of a capillary to a grounded collector. The electric field causes a pendant droplet of the solution at the capillary tip to deform into a conical shape. When the electrical force at the surface of the tip overcomes the surface tension of the solution, a charged jet is ejected and undergoes a series of electrically induced bending instabilities, whereby repulsion of adjacent charged segments generates vigorous whipping motions, which elongate the charged segments into fibers for passage onto a collector. The solvent begins to evaporate after jet formation, causing the deposit of thin fibers on the collector.

To the extent residual solvent remains, the collected fibers may be heated to about 150° C. for removal thereof.

[0028] Referring now to FIGS. 3A and 3B, two embodiments of an electrospinning apparatus 100 for use with the present invention are illustrated. Apparatus 100 comprises syringe 102, tip 104, high voltage supplier 106 positioned at or near tip 104, micropump 108, positioner 109, heating unit 110, rotating collector 112, coagulant bath 114 and motor 116 for driving rotation of collector.

[0029] As shown in FIGS. 3A and 3B, syringe 102 is positioned horizontally on micropump 108 and typically comprises an inner diameter between about 0.10 millimeters to about 0.60 millimeters. The diameter of collected nanofibers may be decreased by decreasing the inner diameter of syringe 102. Micropump 108 may be a PHD 2000 Infusion syringe pump, available from Harvard Apparatus, Inc. of Holliston, Mass. Positioner 109 may be used to control the height of micropump 108.

[0030] Voltage supplier 106 may be set between about 1 OkV to about 30 kV and more particularly between about 15 kV and about 25 kV. Voltage supplier 106 provides an electric field between about 1.0 kV/cm to about 4.0 kV/cm.

[0031] Collector 112 may be mesh or a plate and constructed of a conductive material, such as aluminum, stainless steel or a surface oxidized silicon. Collector 112 may also comprise a flat sheet of non-woven cellulose, mixed with about 10% to about 20% polyester fibers.

[0032] Collector 112 is grounded to create an electric field difference between tip 104 and collector 112, allowing material to move from the high electric field at tip 104, to grounded collector 112. The distance between tip 104 and collector 112 may be between about 5.0 cm and 15.0 cm and more particularly between about 7.0 cm and 12.0 cm. A stepper motor 116 may be connected to collector 112 to provide continuous rotation into coagulant bath 114 at predetermined intervals. The intervals may be between about 1.0 to about 10.0 revolutions per minute and more particularly between about 3.0 to about 5.0 revolutions per minute.

[0033] Once apparatus 100 is assembled, a solution comprising the starting material and solvent is placed into syringe 102, and pumped therethrough at a relatively constant flow rate of about 0.03 milliliters per minute to about 0.05 milliliters per minute. As pumping continues, a charged jet is ejected and elongates as it moves towards collector 112. A plurality of randomly oriented substantially dry non-woven fibers are collected on collector 112. The collected fibers typically exhibit uniform diameters (i.e., substantially all the collected fibers exhibit the same or similar fiber diameters)

[0034] In an alternate embodiment, co-axial electrospinning may be employed. Co-axial electrospinning employs a dual syringe which comprises an internal tube positioned within an external tube. Under this construction, an internal jet within an external jet is ejected from the syringe; the internal jet may comprise organic substances, such as mineral oil, while the external jet comprises the aforementioned solution. When mineral oil is used, hollow nanofibers or nanotubes emerge. The term nanofiber, as used herein, is intended to cover nanotubes.

[0035] The presence of residual solvent in the collected nanofibers can lead to unwanted clumps or film-like structures on nanofiber surfaces. There are various ways to decrease residual solvent.

[0036] To enhance evaporation of solvent during processing, a heating step may be employed. The heating step causes

vaporization of the relatively volatile solvent, while leaving the starting material substantially intact. As shown in FIG. 4, for example, DMAc evaporates rapidly at temperatures beyond 50° C.

[0037] Heating may be carried out through heating unit 110 or electric heating guns. Heating unit 110, the features of which are described in co-pending co-owned U.S. patent application Ser. No. 10/965,813, heats the solution as it travels through syringe. Heating unit 110, typically comprises an electrically and thermally insulating material and may be shielded from high voltage supplier 106 to prevent induced voltage in the heating source. A Faraday cage or screen, comprising an enclosure made of metal mesh, may serve as the shield. Heating unit 110 is typically used for cellulose mixed with solutions of NMMO/water at temperatures ranging between about 70.0° C. and about 110.0° C. for about one hour. Alternatively or additionally, collector 112 may be heated to between about 90.0° C. and about 120.0° C. and more particularly between about 100.0° C. to about 110.0° C. Commercially available electric heating guns may be utilized for this purpose. Such electric heating guns are often used in connection with cellulose solutions comprising DMAc and LiCl. By applying heat to collector 112 rather than the system as a whole, the viscoelastic properties of the solution up to formation of jet are conserved. Heating in this manner also does not significantly degrade the starting material because of the relatively rapid evaporation of the more volatile solvent at elevated temperatures.

[0038] Coagulation bath 114 may also be used to remove solvent from the electrospun fibers. In the DMAc/LiCl system, the presence of hygroscopic salt causes localized moisture absorption, which leads to the formation of water droplets on the intersection of the collected fibers and unwanted fiber swelling. Coagulation bath 114 helps remove residual LiCl by dissolving it. X-ray diffraction patterns, shown at FIG. 5, confirms the removal of salt from the collected fibers, as the characteristic peak of salt, at  $2\theta=30.09$ , is only observed in the untreated fibers and essentially disappears after coagulation. With the NMMO/water system, residual NMMO is exchanged with the contents of coagulation bath 114.

[0039] Coagulation bath 114 may comprise any substance or solution that removes residual solvent but does not dissolve the starting material within the collected fibers. Suitable examples include analytical grade water or alcohol. Exposure to coagulation bath may occur about 1.0 to 3.0 seconds after the substantially dry fibers have been electrospun onto collector 112. This 1.0 to 3.0 second interval is automatically maintained by controlling the rotation speed of rotating collector to between about 1.0 to about 10.0 revolutions per minute and more particularly to between about 3.0 to about 5.0 revolutions per minute. Collected fibers may be exposed to coagulation bath 114 for about 30.0 to 40.0 minutes.

[0040] It bears noting that in the case of cellulose based fibers, collector 112 may comprise cellulose filter media. Under these circumstances, the surrounding cellulose filter media is adapted to distribute moisture absorption uniformly throughout the electrospun fibers, thereby preventing formation of large droplets of water that lead to swelling of the fibers.

[0041] Practice of the above-described methods yields nanofiber mats comprising a plurality of nanofibers typically constructed of a non-derivatized organic polymer. The term non-derivatized, as used herein, means that although residual



solvent may be physically entrapped within the matrix, the atoms or elements of the starting material have not been substituted or replaced with the atoms or elements of another material. For example, a non-derivatized cellulose nanofiber comprises the structure of the repeat unit for cellulose shown above, without substitution or replacement of atoms.

**[0042]** The present invention may be used in a variety of different ways, including, without limitation, in sensing and filtering applications. For instance, nanofibers made in accordance with the present invention may be used for filtration of sub-micron dust particles. The collection efficiency of the nanofibers is relatively high, with collection of about 30% to about 50% of dust passed through a filter comprising the nanofibers of the present invention is typical. The nanofibers are also useful in medical applications. The nanofibers may be used as a hemostatic wound dress, to mimic the formation of fibrin to aid in blood clotting at wound surfaces. In addition, the nanofibers may be used as a barrier after surgery. Since the nanofibers with small fiber dimension can comprise amorphous cellulose, they typically degrade faster than conventional, thick cellulose membranes. With fibers of the present invention, the degradation process within the body occurs in about three to five days. Additionally, the need to dispose of conventional crystalline cellulose in landfills and the like is substantially decreased.

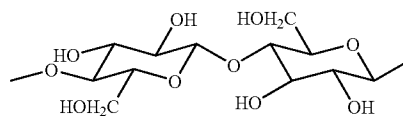
**[0043]** While certain embodiments of the present invention have been shown and described, it will be obvious to those skilled in the art that changes and modifications may be made without departing from the spirit and scope of the invention. The matter set forth in the foregoing description and accompanying drawings is offered by way of illustration only and not as a limitation. The actual scope of the invention is intended to be defined in the following claims.

What is claimed is:

1. A process for making fibers comprising:
  - providing a starting material comprising an organic polymer;
  - dissolving the starting material in a polar solvent to create a dispersion;
  - electrospinning the dispersion by providing an electric charge on droplets of the dispersion to produce a jet of polymer and provide a plurality of electrically induced bending instabilities and/or whipping motions;
  - collecting a plurality of the jets as fibers; and
  - submerging the plurality of fibers into a coagulation bath as they are collected.
2. The process of claim 1, wherein the organic polymer used in the providing step is cellulose.
3. The process of claim 1, wherein the polar solvent used in the dissolving step comprises lithium chloride and N,N-dimethylacetamide.
4. The process of claim 1, wherein the polar solvent is sufficiently volatile to substantially dissolve during the electrospinning step.
5. The process of claim 1, wherein the electrospinning step is carried out in an electric field between about 1.0 kV/cm to about 4.0 kV/cm at a flow rate between about 0.03 ml/min. and about 0.05 ml/min.
6. The process of claim 1, wherein the fibers are nanofibers comprising diameters between about 100 nm and 300 nm.
7. The process of claim 1, wherein the fibers comprise a degree of crystallinity between about 1% and about 40%.
8. The process of claim 1, wherein the fibers comprise a substantially amorphous form of cellulose exhibiting an

X-ray diffraction pattern comprising at least two 2θ values selected from about 7.0 degrees and about 17.8 degrees.

9. The process of claim 1, wherein the fibers comprise a repeat unit conforming to the general formula:



in random positions and orientations.

10. The process of claim 1, wherein the coagulation bath comprises at least one of water and alcohol for removing residual solvent without dissolving the fibers.

11. The process of claim 1, wherein the fibers are collected on a rotating collector and the rotating collector is submerged into a coagulation bath on a periodic basis.

12. The process of claim 1, further comprising heating the rotating collector to temperatures ranging between about 70° C. and 110° C.

13. The process of claim 12, further comprising shielding a voltage collector for supplying an electric charge from heating.

14. The process of claim 1, wherein the collector comprises a cellulose filter media.

15. A process for making cellulose nanofibers comprising: providing a starting material comprising cellulose; dissolving the starting material in a polar solvent unreactive with cellulose to create a dispersion; electrospinning the dispersion by providing an electric charge on droplets of the dispersion to produce a charged jet of polymer and provide a plurality of electrically induced bending instabilities and/or whipping motions; collecting a plurality of the charged jets as substantially amorphous non-derivatized cellulose nanofibers on a rotating collector; and submerging the rotating collector comprising the plurality of substantially amorphous non-derivatized fibers into a coagulation bath on a periodic basis.

16. The process of claim 15, wherein the fibers are submerged in the coagulation bath at regular intervals between about 1 and about 3 seconds.

17. An apparatus for making fibers through electrospinning comprising:
 

- a chamber for receiving a dispersion;
- a pump upstream of the chamber for dispensing the dispersion;
- a syringe for receiving the dispersion from the pump, the syringe comprising an opening sized to providing droplets of the dispersion;
- a voltage supplier in electrical communication with the syringe to provide an electric charge in the droplets emanating from the opening to produce a plurality of charged jets and provide a plurality of electrically induced bending instabilities and/or whipping motions;
- a collector for receiving and collecting the charged jets as non-woven fibers, the collector automatically movable between a first position and a second position, wherein at least a portion of the collected fibers are submerged in a coagulation bath in the first position and spaced apart from the coagulation bath in the second position.

**18.** The apparatus of claim **17**, wherein the collector comprises a rotating collector.

**19.** The apparatus of claim **18**, wherein the rotating collector is submerged in the coagulation bath on a periodic basis.

**20.** The apparatus of claim **17**, further comprising a heating chamber constructed of an electrically and thermally insulating material, the heating chamber positioned to heat the dispersion as it travels through the syringe.

**21.** The apparatus of claim **20**, wherein the heating chamber is shielded from the voltage supplier.

**22.** The apparatus of claim **17**, further comprising a heating gun for heating the collector.

**23.** The apparatus of claim **17**, further comprising a motor for driving the collector.

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