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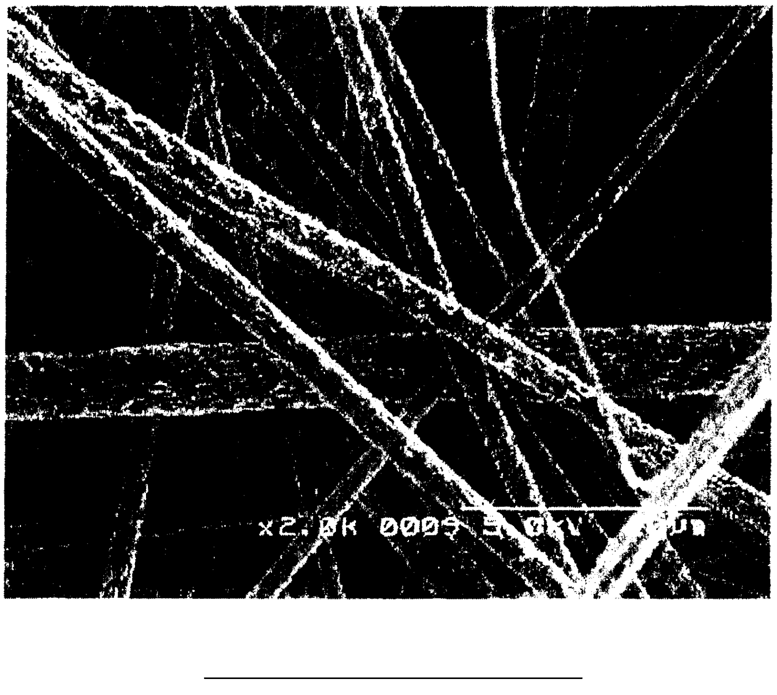
(54) POROUS FIBER, POROUS FIBER STRUCTURE AND METHOD FOR PRODUCTION THEREOF

(57) Provided are porous fibers and fiber structures that have large surface areas and large voids, and controlled hydrophilicity suitable for matrices of cell culture in the field of tissue engineering, and a method for producing the fiber structure including a step in which a solution is produced by dissolving a hydrophobic solvent-soluble polymer and an organic compound having a plurality of hydroxyl groups in a hydrophobic solvent, a step in which the solution is spun by electrospinning, and a step in which a fiber structure accumulated on a collector is obtained.

Fig. 5



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Description

Technical Field

[0001] The present invention relates to a porous fiber produced without needing a coagulating solution, a fiber structure made of the porous fibers, and a method for producing the fiber structure.

[0002] More particularly, the present invention relates to a porous fiber mainly comprising a hydrophobic solvent-soluble polymer and an organic compound containing a plurality of hydroxyl groups, a fiber structure made of the porous fibers, and a method for producing the fiber structure.

Background Art

[0003] In tissue engineering fields, a porous structure is sometimes used as a matrix (scaffold) when cells are cultured. As the porous structure, a freeze dried product of a bioabsorbable organic material, a foamed, and a fiber structure are known (see, for example, non-patent literature 1). These porous structures must have affinity to cells, biodegradability, safety, and so on. Polyglycolic acid, which is used for a surgical suture etc., has excellent biocompatibility, biodegradability, and safety, and a fiber structure made of polyglycolic acid is being studied for using as the matrix (see, for example, non-patent literature 1).

[0004] However, fiber diameters obtained by using conventional methods are too large, and surface areas on which cells can be adhered are not sufficient. In order to increase the surface areas, fiber structures having finer fibers are desired.

[0005] On the other hand, as a manufacturing process for a fiber structure having finer fibers, electrospinning is known (see, for example, patent literature 1 and 2). The process for electrospinning comprises steps introducing a liquid, for example, a solution of a material which form a fibrous structure, into an electric field, drawing the solution toward an electrode by means of the electric force, and forming a fibrous material.

[0006] Usually, the fibrous material is hardened during the solution is drawn. The hardening is performed, for example, by means of cooling (e.g., in cases where the solution to be spun is solid at room temperature), chemical hardening (e.g., a treatment with a hardening vapor), solvent vaporization, and so on.

[0007] Further, the obtained fibrous material is collected on an adequately placed collector from which it can be removed if necessary. Furthermore, electrospinning can obtain a non-woven fibrous material directly, and thereby the operation of the process is simple and easy, that is, there is no need to form fibers once and then to form a fiber structure further.

[0008] It is known to use a fiber structure obtained with electrospinning as a matrix for culturing cells. For example, it is currently under investigation to make a fiber structure from polylactic acid by using electrospinning and to regenerate blood vessels by culturing smooth muscle cells on the fiber structure (see, for example, non-patent literature 2).

[0009] However, the fiber structures obtained by using electrospinning are apt to take a dense structure having short distances between fibers since the fibers have fine diameters. When the fiber structure is used as a cell culture matrix, proliferated cells accumulate on the surfaces of fibers that form the fiber structure, the surfaces of the fiber structure are covered by the cells with progressing culture, and the surfaces are completely covered thick finally. Resultingly, it becomes difficult for a solution containing nutrients etc. to move sufficiently into inner parts of the fiber structure, and this causes a problem in which only sections near the surface can afford to curry out cell culture.

[0010] As a means enabling a solution containing nutrients etc. to move into surfaces of fibers which form the fiber structure during cell culture, it is proposed to make the fibers themselves porous.

[0011] For example, there was a report of electrospinning a fiber structure having regular pores on fiber surfaces from a vaporizable solvent-containing solution (see non-patent literature 3 and patent literature 3). However, by using this method, a fiber structure formed has pores only on fiber surfaces, and it is difficult to make porous so far as the inner fibers.

[0012] Further, a method that forms porous fibers by electrospinning a fiber structure from a solution that contains a hydrophilic polymer and a hydrophobic polymer, and extracts the hydrophilic polymer by immersing the obtained fiber structure into water also has been reported (see non-patent literature 4 and patent literature 3).

[0013] However, the operation of this method is complicated since a water-dipping treatment is needed. Further, the finally obtained porous fibers are substantially composed only of the hydrophobic polymer, and it has a problem that the hydrophilicity of the fiber structure can not be controlled.

[Patent literature 1] JP-A 63-145465 (JP-A means Japanese unexamined patent publication).

[Patent literature 2] JP-A 2002-249966.

[Patent literature 3] The pamphlet of International Publication No. 02/16680,

[Non-patent literature 1] Tissue Engineering, page 258, the translation was supervised by the team represented by Noriya Oono and Masuo Aizawa, NTS INC., January 31, 2002.

[Non-patent literature 2] Joel D. Stitzel, Kristin J. Pawlowski, Gary E. Wnek, David G. Simpson, and Gary L. Bowlin, Journal of Biomaterials Applications 2001, Vol. 16, USA, page 22-33.

[Non-patent literature 3] Michael Bognitzki, Wolfgang Czado, Thomas Frese, Andreas Schaper, Michael Hellwig, Martin Steinhart, Andreas Greiner, and Joechim H. Wendroff, Journal of Advanced Materials 2001, Vol. 13, USA, page 70-72.

[Non-patent literature 4] Michael Bognitzki, Thomas Frese, Martin Steinhart, Andreas Greiner, and Joachim H. Wendroff, Polymer Engineering and Science 2001, Vol. 41, USA, page 982-989.

Disclosure of the Invention

[0014] It is the first object of the present invention to provide a material suitable for a matrix of cell culture in the field of tissue engineering and particularly to provide fibers and a fiber structure made therefrom in which a solution containing nutrients etc. needed for the cell culture can move easily into the whole portion of cells growing on the fiber structure.

[0015] It is the second object of the present invention to provide a production method with which a hydrophilicity-imparted porous fiber structure can be obtained without needing complicated processes such as extraction and the like.

Brief Description of Drawings

[0016]

Figure 1 is a schematic diagram that represents a manufacturing equipment and illustrates one mode of the production method of the present invention.

Figure 2 is a schematic diagram that represents a manufacturing equipment and illustrates one mode of the production method of the present invention.

Figure 3 is an electron micrograph depicting surfaces of a fiber structure obtained with the operation of Example 1 (at a magnification of X2000).

Figure 4 is an electron micrograph depicting a cross-section of a fiber obtained with the operation of Example 1 (at a magnification of X10,000).

Figure 5 is an electron micrograph depicting surfaces of a fiber structure obtained with the operation of Example 2 (at a magnification of X2000).

Figure 6 is an electron micrograph depicting a cross-section of a fiber obtained with the operation of Example 2 (at a magnification of X10,000).

Figure 7 is an electron micrograph depicting surfaces of a fiber structure obtained with the operation of Example 3 (at a magnification of X2000).

Figure 8 is an electron micrograph depicting a cross-section of a fiber obtained with the operation of Example 3 (at a magnification of X10,000).

Figure 9 is an electron micrograph depicting surfaces of a fiber structure obtained with the operation of Example 4 (at a magnification of X2000).

Figure 10 is an electron micrograph depicting a cross-section of a fiber obtained with the operation of Example 4 (at a magnification of X10,000).

Figure 11 is an electron micrograph depicting surfaces of a fiber structure obtained with the operation of Example 5 (at a magnification of X2000).

Figure 12 is an electron micrograph depicting a cross-section of a fiber obtained with the operation of Example 5 (at a magnification of X10,000).

Figure 13 is an electron micrograph depicting surfaces of a fiber structure obtained with the operation of Example 6 (at a magnification of X2000).

Figure 14 is an electron micrograph depicting a cross-section of a fiber obtained with the operation of Example 6 (at a magnification of X10,000).

Figure 15 is an electron micrograph depicting surfaces of a fiber structure obtained with the operation of Example 7 (at a magnification of X2000).

Figure 16 is an electron micrograph depicting a cross-section of a fiber obtained with the operation of Example 7 (at a magnification of X10,000).

Figure 17 is an electron micrograph depicting surfaces of a fiber structure obtained with the operation of Example 8 (at a magnification of X2000).

Figure 18 is an electron micrograph depicting a cross-section of a fiber obtained with the operation of Example 8 (at a magnification of X10,000).

Figure 19 is an electron micrograph depicting surfaces of a fiber structure obtained with the operation of Example 9 (at a magnification of X2000).

Figure 20 is an electron micrograph depicting a cross-section of a fiber obtained with the operation of Example 9 (at a magnification of X10,000).

Figure 21 is an electron micrograph depicting surfaces of a fiber structure obtained with the operation of Reference Example 1 (at a magnification of X2000).

Figure 22 is an electron micrograph depicting a cross-section of a fiber obtained with the operation of Reference Example 1 (at a magnification of X10,000).

Figure 23 is an electron micrograph depicting surfaces of a fiber structure obtained with the operation of Reference Example 2 (at a magnification of X2000).

Figure 24 is an electron micrograph depicting a cross-section of a fiber obtained with the operation of Reference Example 2 (at a magnification of X10,000).

Figure 25 is an electron micrograph depicting surfaces of a fiber structure obtained with the operation of Reference Example 3 (at a magnification of X2000).

Figure 26 is an electron micrograph depicting a cross-section of a fiber obtained with the operation of Reference Example 3 (at a magnification of X10,000).

Best Mode for Carrying Out the Invention

[0017] Hereafter, the present invention will be explained in detail.

[0018] In the present invention, the fiber structure expresses a three-dimensional structure that are formed with heaping, weaving, knitting, or another method from single or a plurality of obtained porous fibers. Concrete forms of the fiber structure include, for example, nonwoven fabrics. Further, tubes, meshes, and the like that are obtained by processing the above mentioned fiber structure can be preferably used in the field of tissue engineering.

[0019] Porous fibers and fiber structures of the present invention contain polymers soluble in hydrophobic solvents.

[0020] The hydrophobic solvent of the present invention expresses an organic substance that can not dissolve water of 5% or more in concentration at room temperature (for example, 27°C) and is liquid at the temperature. As the hydrophobic solvent of the present invention, halogen element-containing hydrocarbons are preferable because they can dissolve polymers well. Examples of more preferable hydrophobic solvents are methylene chloride, chloroform, dichloroethane, tetrachloroethane, trichloroethane, dibromomethane, bromoform, and the like, and methylene chloride is especially preferable.

[0021] Among these solvents, volatile solvents are preferably used. The volatile solvent expresses an organic substance that has a boiling point not higher than 200°C at atmospheric pressure and is liquid at room temperature (for example, 27°C).

[0022] "Soluble" in the present invention means that a solution containing a polymer of 1 wt.% can exist stably at room temperature (for example, at 27°C) without forming precipitates. Examples of polymers soluble in the hydrophobic solvent are polylactic acid, polylactic acid-polyglycolic acid copolymers, aliphatic polyesters such as polycaprolactone, polycarbonates, polystyrene, polyarylates, polymethylmethacrylate, polyethylmethacrylate, cellulose diacetate, cellulose triacetate, polyvinyl acetate, polyvinyl methyl ether, poly(N-vinylpyrrolidone), polybutylene succinate, and polyethylene succinate, and copolymers of these polymers and the like.

[0023] Among these polymers, polylactic acid, polycaprolactone, polycarbonates, polystyrene, and polyarylates are preferable.

[0024] Porous fibers and fiber structures of the present invention may contain one kind, or two or more kinds of polymers soluble in the hydrophobic solvent.

[0025] Porous fibers and fiber structures of the present invention contain an organic compound having a plurality of hydroxyl groups. When an organic compound that does not have a plurality of hydroxyl groups is used, the objective porous fibers can not be obtained, further a fiber structure comprising the porous fibers can not be produced stably, and furthermore, the cell culture using the fiber structure becomes difficult in some cases; and thereby such an organic compound is not preferable.

[0026] It is preferable that a hydroxyl-containing organic compound has a number-average molecular weight not less than 62 nor more than 300. It is not preferable that the organic compound has a number-average molecular weight of more than 300 because the forming of porous fibers becomes difficult.

[0027] Further, an example of the organic compound having a molecular weight of 62 and a plurality of hydroxyl groups is ethylene glycol, and an organic compound having a molecular weight of less than 62 and a plurality of hydroxyl groups does not exist actually. More preferable number-average molecular weights of the organic compound are not less than 62 nor more than 250.

[0028] Examples of organic compounds having a plurality of hydroxyl groups include ethylene glycol, propylene glycol (1,2-propanediol), 1,3-propanediol, diethylene glycol, triethylene glycol, glycerin, pentaerythritol, polyethylene glycol, polypropylene glycol, polyethylene glycol-polypropylene glycol block polymers, and the like.

[0029] In the present invention, polymers or compounds other than hydrophobic solvent-soluble polymers and organic compounds having a plurality of hydroxyl groups can be combinedly used (for example, copolymers of polymers, polymer blends, or compound mixtures) in a range where the purposes are not impaired.

[0030] Porous fibers and fiber structures of the present invention have an average fiber diameter of 0.1-20 μ m. The average fiber diameter of less than 0.1 μ m is not preferable because such porous fibers and fiber structures decompose too quickly in vivo when they are used as cell culture matrices for tissue engineering. Further, the average fiber diameter of larger than 20 μ m is not preferable because the area on which cells can adhere becomes small. A more preferable average fiber diameter is 0.2-15 μ m, and an especially preferable average fiber diameter is 0.2-10 μ m. The fiber diameter expresses the diameter of a fiber cross-section when the cross-section is circler. However, sometimes the shape of a fiber cross-section is oval. The fiber diameter of this case expresses the value calculated by averaging the lengths of the major axis and the minor axis of the oval. Further, when the cross-section of the fiber is not circular nor oval, it is approximated to a circle or an oval, and the cross-section is calculated.

[0031] It is preferable for porous fibers of the present invention to have fiber lengths of 20 μ m or more. When the fiber lengths are less than 20 μ m, the mechanical strengths of the fiber structure obtained from the fibers are insufficient. The fiber lengths are preferably 40 μ m or more, and more preferably 1 mm or more.

[0032] Porous fibers of the present invention express fibers having isolated holes and/or continuous holes on surfaces and in inner parts of fibers. The isolated holes and the continuous holes of the inner parts may form empty bodies so that the fibers may be hollow fibers as a whole.

[0033] Fiber structures of the present invention comprise porous fibers having a void percentage of 5% at least. The void percentage of 5% means that, on a fiber cross-section formed by cutting at an arbitrary position, the sum of the areas of the isolated holes and the continuous holes that reach to the fiber surface, and the areas of the isolated holes and the continuous holes existing in the inner parts of the fiber, that is, the sum of the space areas where fiber forming substances (hydrophobic solvent-soluble polymers, organic compounds having a plurality of hydroxyl groups, and other necessary polymers and compounds) are absent, occupies at least 5% of the whole area of the fiber cross-section including the space areas. A void percentage of less than 5% is not preferable since a solution that contains nutrients and the like does not penetrate sufficiently into the inner parts of the matrix during cell culture. The void percentage is preferably 10% or more.

[0034] That is, a preferable mode of the present invention is porous fibers comprising a hydrophobic solvent-soluble polymer and an organic compound having a plurality of hydroxyl groups, and having an average fiber diameter of 0.1-20 μ m and a void percentage of at least 5%, and fiber structures made therefrom. It is preferable to use an aliphatic polyester, a polycarbonate, polystyrene, or a polyarylate as the hydrophobic solvent-soluble polymer.

[0035] There is no limitation of a method for producing fiber structures of the present invention as long as it can produce fibers and the like having the above-mentioned fiber diameters, but electrospinning is preferable. Hereafter, the fabrication method using electrospinning will be explained in detail.

[0036] In electrospinning used in the present invention, a solution prepared by dissolving a hydrophobic solvent-soluble polymer and an organic compound having a plurality of hydroxyl groups in a hydrophobic solvent is discharged into an electrostatic field generated between electrodes, the solution is drawn toward an electrode, and the formed fibrous material is accumulated on a collector, and thereby a fiber structure can be obtained. That is, when the fibrous material is accumulated, porous fibers of the present invention are already formed. Herein, the fibrous material expresses not only a material having a state of porous fibers and fiber structures in which the solvent of the solution is already evaporated, but also a material having a state in which the solvent of the solution is contained.

[0037] At first, an apparatus to be used in electrospinning will be explained. The electrode to be used in the present invention may be arbitrarily selected from metals, inorganic materials, and organic materials as long as it exhibits conductivity. Further, it may be a body formed by placing a thin film of a metal, an inorganic substance, or an organic substance that shows electroconductivity on an insulator. The electrostatic field of the present invention is formed between a pair of electrodes or among a plurality of electrodes, and a high voltage can be applied on any electrode. This includes the case where three electrodes in total consisting of two electrodes of different high voltages (for example, 15 kV and 10 kV) and an electrode connected to a ground are used, and the case where more than three electrodes are used is also included.

[0038] Next, the fabrication method of the present invention using electrospinning will be explained further in detail. In the first step, a solution is produced by dissolving a hydrophobic solvent-soluble polymer and an organic compound having a plurality of hydroxyl groups in a hydrophobic solvent. In the solution of the fabrication method of the present invention, the concentration of the hydrophobic solvent-soluble polymer is preferably 1-30 wt.%. The concentration of the hydrophobic solvent-soluble polymer of less than 1 wt.% is not preferable because the formation of fiber structures becomes difficult due to extremely low concentration. Further, the concentration of more than 30 wt.% is not preferable because fiber diameters of the obtained fiber structure become large. The concentration of the hydrophobic solvent-soluble polymer is more preferably 2-20 wt.%.

[0039] It is preferable that the concentration of the organic compound having a plurality of hydroxyl groups in the solution of the present invention is 2-50 wt.%. It is not preferable that the concentration of the organic compound having a plurality of hydroxyl groups is less than 2 wt.% since the total areas of the recessed parts and the void parts on fiber cross-sections become small. Further, the concentration of more than 50 wt.% is not preferable since the formation of fiber structures becomes difficult. The concentration of the organic compound having a plurality of hydroxyl groups is more preferably 4-30 wt.%.

[0040] When the boiling point of the organic compound having a plurality of hydroxyl groups of the present invention is low, a part of the compound sometimes evaporates together with a solvent during spinning by means of electrospinning. In the present invention, it is preferable that at least 1 wt.% or more of the hydroxyl-containing organic compound supplied remains in the product. The concentration of the organic compound in the fiber structure is more preferably 5-60 wt.%, and further preferably, 10-60 wt.%.

[0041] In the fabrication method of fiber structures using electrospinning in the presents invention, the hydrophobic solvent can be used alone, or a plurality of the hydrophobic solvents can be used in combination. Further, the hydrophobic solvent can be used in combination with another kind of solvent in a range where the purpose of the present invention is not missed. The concrete examples of the hydrophobic solvent are already shown above.

[0042] Next, the step in which the above mentioned solution is spun by electrospinning will be explained. For discharging the solution into an electrostatic field, an arbitrary method can be used.

[0043] Hereafter, a preferable mode for producing fiber structures of the present invention will be explained further in detail by using Figure 1.

[0044] The solution (2 in Figure 1) is supplied to the nozzle, the solution is placed at a proper position in the electrostatic force, the solution is drawn from the nozzle by means of the electrostatic field, and thereby fibers are formed from the solution. For this purpose, an appropriate apparatus can be used. For example, an appropriate means (e.g., an injection needle-shaped solution ejection nozzle (1 in Figure 1) on which voltage is applied by using a high voltage generator (6 in Figure 1)) is placed at the tip of a cylindrical solution-holding tank (3 in Figure 1) of a syringe, and the solution is guided to the tip.

[0045] The tip of the ejection nozzle (1 in Figure 1) is placed at an appropriate distance from a grounded fibrous material-collection electrode (5 in Figure 1), and when the solution (2 in Figure 1) comes out from the tip of the ejection nozzle (1 in Figure 1), a fibrous material is formed between the tip and the fibrous material-collection electrode (5 in Figure 1).

[0046] Further, fine drops of the solution can be introduced into the electric field with a method known by those in the art, and one preferable mode of the method will be explained by using Figure 2. The only requirement in this mode is that a droplet is held in the electrostatic field apart from the fibrous material-collection electrode (5 in Figure 2) at a distance in which fibers can be formed. For example, an electrode (4 in Figure 2) which directly opposes the fibrous material-collection electrode may be directly inserted into the solution (2 in Figure 2) in a solution-holding tank (3 in Figure 2) having a nozzle (1 in Figure 2).

[0047] When the solution is fed into the electrostatic field from nozzle, a plurality of nozzles can be used so that the production rate of the fibrous material increases. The distance between the electrodes depends on an electrostatic charge level, the size of a nozzle, the flow and the concentration of the solution to be spun, and the like, but the distance of 5-20 cm was appropriate with approximately 10 kV.

[0048] Further, an impressed electrostatic voltage is generally 3-100 kV, preferably 5-50 kV, and more preferably 5-30 kV. The desired electrostatic voltage can be generated by using an appropriate method arbitrarily selected out of known technology.

[0049] The above-mentioned explanation concerns the case where an electrode concurrently works also as a collector; but aside from the electrode, a collector can be additionally placed between electrodes so that a fiber structure is collected on it. In this case, for example, a belt-shaped material is placed between electrodes, and by using the material as the collector, a fiber structure can be produced continuously.

[0050] Finally, a step in which the fiber structure accumulated on a collector is obtained will be explained. In the present invention, while the solution is drawn toward the collector, the solvent evaporates according to conditions, and a fibrous material is formed.

[0051] The solvent normally evaporates completely before the fibrous material is collected on the collector at ordinary room temperature and atmospheric pressure; however, if the evaporation of the solvent is not sufficient, the solution may be drawn under reduced pressure. At the latest, when the fibrous material is collected on the collector, porous fibers of the present invention are formed. Further, the temperature for spinning fibers depends on the evaporation behavior of the solvent and the viscosity of the solution to be spun; however, it is usually 0-50°C. The porous fibers are further accumulated over themselves on the collector, and thereby a fiber structure of the present invention is formed.

[0052] That is, a preferable mode of fabrication methods of the present invention includes a step in which a solution is produced by dissolving a hydrophobic solvent-soluble polymer and an organic compound having a plurality of hydroxyl groups in a hydrophobic solvent, a step in which the solution is spun by using electrospinning, and a step in which a fiber structure accumulated on a collector is obtained; and the fiber structure comprising porous fibers having an average fiber diameter of 0.1-20 μ m and a void percentage of at least 5% is obtained in the preferable mode. In the preferable mode of the present invention, as the hydrophobic solvent-soluble polymer, an aliphatic polyester, a polycarbonate, polystyrene, or a polyarylate is used, and yet it is preferable to use a volatile solvent as the hydrophobic solvent.

[0053] A fiber structure obtained in the present invention can be used alone; however, it may be used in combination with another member with due regard to handleability and other requirements. For example, a nonwoven fabric, a woven fabric, a film, or the like that can serve as a supporting material is used as the collector, and a fiber structure is formed on it; and thereby a member in which a supporting material and the fiber structure are combined can be obtained.

[0054] Uses of fiber structures obtained in the present invention are not limited to cell culture matrices for tissue engineering, but they can be used as various materials such as all sorts of filters, catalyst supporting materials, or the like in which special features of the present invention, that is, dent parts and voids, are used practically.

Examples

[0055] The present invention will be explained further in detail hereafter with examples, while the present invention is not restricted by the examples. Further, evaluations in each of the following examples and reference examples were carried out according to the following methods.

Void percentage:

[0056] Scanning electron micrograph image depicting fiber cross-sections of obtained porous fibers or fiber structures were photographed (at a magnification of

X10,000).

[0057] The whole part of the fiber cross-section was cut out from the photograph paper of the cross-section photograph image, and its weight was measured. Subsequently, the void parts of the fiber were cut out from the photograph paper, and their weights were measured. The void percentage of a fiber was calculated from these weights. This process was repeated five times, and the average value was calculated.

Average fiber diameter:

[0058] Twenty points were randomly selected from a picture of surfaces of obtained porous fibers or fiber structure, photographed with a scanning electron microscope (S-2400, manufactured by Hitachi) (at a magnification of X2,000), the fiber diameter was measured on each point, and the average value (n=20) was calculated for all the fiber diameters, and the value was used as the average fiber diameter.

Existence identification of fibers of less than 20 μ m in fiber length:

[0059] The existence of fibers of less than 20 μ m in fiber length was judged by observing a picture of surfaces of an obtained fiber structure, photographed with a scanning electron microscope (S-2400, manufactured by Hitachi) (at a magnification of X8,000).

Method for determining a hydroxyl-containing organic compound:

[0060] ^{1}H-NMR spectrum of an obtained fiber structure was taken with JNM-EX-270 manufactured by Hitachi at 20 °C using deuterochloroform ($CDCl_3$) as a solvent. The molar ratio between the polymer units and the hydroxyl-containing organic compounds in the fiber structure was determined from the integration ratio of protons which were derived from the chemical structure of the polymer used and that of the hydroxyl-containing organic compound used, and the content (wt.%) of the hydroxyl-containing organic compound was calculated based on the molar ratio.

Example 1

[0061] One pt. wt. of polylactic acid (trade mark "Lacty 9031", manufactured by Shimazu Seisakusyo), 1 pt. wt. of ethylene glycol (special grade chemical, manufactured by Wako Pure Chemical Industries, Ltd.), and 8 pts. wt. of methylene chloride (special grade chemical, manufactured by Wako Pure Chemical Industries, Ltd.) were mixed at room temperature (25°C) to prepare a slightly milky solution.

[0062] The solution was discharged over 5 minutes toward a collector electrode by using an apparatus shown in Figure 2. The inside diameter of the nozzle was 0.8 mm, the voltage was 12 kV, and the distance from the nozzle to the collector electrode was 10 cm. The obtained fiber structure was examined by using a scanning electron microscope (S-2400, manufactured by Hitachi). The average fiber diameter was 3 μ m, and fibers having a fiber diameter of more than 20 μ m were not detected. Fibers having a fiber length of less than 20 μ m were not detected.

[0063] The void percentage was approximately 40%, and the ethylene glycol content in the fiber structure was 18.0 wt.%. Scanning electron micrographs of a surface and a fiber cross section of the fiber structure are shown in Figure 3 and Figure 4.

Example 2

[0064] Except that 1 pt. wt. of diethylene glycol (special grade chemical, manufactured by Wako Pure Chemical Industries, Ltd.) was used in stead of the ethylene glycol, the same operations as Example 1 were curried out. The average fiber diameter was 4 μ m, and fibers having a fiber diameter of more than 20 μ m were not detected. Further, fibers having a fiber length of less than 20 μ m were not detected.

[0065] The void percentage was approximately 15%, and the diethylene glycol content in the fiber structure was 47.9 wt.%. Scanning electron micrographs of a surface and a fiber cross section of the fiber structure are shown in Figure 5 and Figure 6.

Example 3

[0066] Except that 1 pt. wt. of triethylene glycol (special grade chemical, manufactured by Wako Pure Chemical Industries, Ltd.) was used in stead of the ethylene glycol, the same operations as Example 1 were curried out. The average fiber diameter was 3 μ m, and fibers having a fiber diameter of more than 20 μ m were not detected. Further, fibers having a fiber length of less than 20 μ m were not detected. The void percentage was approximately 15%, and the triethylene glycol content in the fiber structure was 46.2 wt.%. Scanning electron micrographs of a surface and a fiber cross section of the fiber structure are shown in Figure 7 and Figure 8.

Example 4

[0067] Except that 1 pt. wt. of polyethylene glycol (average molecular weight of 200, first class chemical, manufactured by Wako Pure Chemical Industries, Ltd.) was used in stead of the ethylene glycol, the same operations as Example 1 were curried out. The average fiber diameter was 2 μ m, and fibers having a fiber diameter of more than 20 μ m were not detected. Further, fibers having a fiber length of less than 20 μ m were not detected. The void percentage was approximately 15%, and the polyethylene glycol content in the fiber structure was 50.0 wt.%. Scanning electron micrographs of a surface and a fiber cross section of the fiber structure are shown in Figure 9 and Figure 10.

Example 5

[0068] Except that 1 pt. wt. of propylene glycol (1,2-propanediol) (special grade chemical, manufactured by Wako Pure Chemical Industries, Ltd.) was used in stead of the ethylene glycol, the same operations as Example 1 were curried out. The average fiber diameter was 4 μ m, and fibers having a fiber diameter of more than 20 μ m were not detected. Further, fibers having a fiber length of less than 20 μ m were not detected. The void percentage was approximately 15%, and the 1,2-propanediol content in the fiber structure was 15.3 wt.%. Scanning electron micrographs of a surface and a fiber cross section of the fiber structure are shown in Figure 11 and Figure 12.

Example 6

[0069] Except that 1 pt. wt. of polycaprolactone (average molecular weight of 70,000-100,000, manufactured by Wako Pure Chemical Industries, Ltd.) was used in stead of the polylactic acid, the same operations as Example 1 were curried out. The average fiber diameter was 4 μ m, and fibers having a fiber diameter of more than 20 μ m were not detected. Further, fibers having a fiber length of less than 20 μ m were not detected. The void percentage was approximately 15%, and the ethylene glycol content in the fiber structure was 16.7 wt. %. Scanning electron micrographs of a surface and a fiber cross section of the fiber structure are shown in Figure 13 and Figure 14.

Example 7

[0070] Except that 1 pt. wt. of polycarbonate (trade mark of "Panlite L1250", manufactured by Teijin Chemicals Ltd.) was used in stead of the polylactic acid, the same operations as Example 1 were curried out. The average fiber diameter was 3 μ m, and fibers having a fiber diameter of more than 20 μ m were not detected. Further, fibers having a fiber length of less than 20 μ m were not detected. The void percentage was approximately 35%, and the ethylene glycol content in the fiber structure was 12.3 wt.%. Scanning electron micrographs of a surface and a fiber cross section of the fiber structure are shown in Figure 15 and Figure 16.

Example 8

[0071] Except that 1 pt. wt. of polystyrene (average molecular weight of 250,000, manufactured by Kanto Chemicals Ltd.) was used in stead of the polylactic acid, the same operations as Example 1 were curried out. The average fiber diameter was 6 μ m, and fibers having a fiber diameter of more than 20 μ m were not detected. Further, fibers having a fiber length of less than 20 μ m were not detected. The void percentage was approximately 35%, and the ethylene glycol content in the fiber structure was 11.2 wt.%. Scanning electron micrographs of a surface and a fiber cross section of the fiber structure are shown in Figure 17 and Figure 18.

Example 9

[0072] Except that 1 pt. wt. of polyarylate (trade mark of "U-polymer U-100", manufactured by Yunitika) was used in stead of the polylactic acid, the same operations as Example 1 were curried out. The average fiber diameter was 3 μ m, and fibers having a fiber diameter of more than 20 μ m were not detected. Further, fibers having a fiber length of less than 20 μ m were not detected. The void percentage was approximately 35%, and the ethylene glycol content in the fiber structure was 12.5 wt.%. Scanning electron micrographs of a surface and a fiber cross section of the fiber structure are shown in Figure 19 and Figure 20.

Co-Example 1

[0073] Except that 1 pt. wt. of methylene chloride was used in stead of the ethylene glycol, the same operations as Example 1 were curried out. The average fiber diameter was 2 μ m, and fibers having a fiber diameter of more than 20 μ m were not detected. Further, fibers having a fiber length of less than 20 μ m were not detected. Dent parts and void parts were not observed in fiber cross-sections, and hence the void percentage was 0%, and the content of the hydroxyl-containing organic compound in the fiber structure was 0 wt.%. Scanning electron micrographs of a surface and a fiber cross section of the fiber structure are shown in Figure 21 and Figure 22.

Co-Example 2

[0074] Except that 1 pt. wt. of polyethylene glycol (average molecular weight of 400, first class chemical, manufactured by Wako Pure Chemical Industries, Ltd.) was used in stead of the ethylene glycol, the same operations as Example 1 were curried out. The average fiber diameter was 3 μ m, and fibers having a fiber diameter of more than 20 μ m were not detected. Further, fibers having a fiber length of less than 20 μ m were not detected. Dent parts and void parts were not observed in fiber cross-sections, and hence the void percentage was 0%, and the content of polyethylene glycol in the fiber structure was 50.0 wt.%. Scanning electron micrographs of a surface and a fiber cross section of the fiber structure are shown in Figure 23 and Figure 24.

Co-Example 3

[0075] Except that 1 pt. wt. of polyethylene glycol (average molecular weight of 600, first class chemical, manufactured by Wako Pure Chemical Industries, Ltd.) was used in stead of the ethylene glycol, the same operations as Example 1 were curried out. The average fiber diameter was 3 μ m, and fibers having a fiber diameter of more than 20 μ m were not detected. Further, fibers having a fiber length of less than 20 μ m were not detected. Dent parts and void parts were not observed in fiber cross-sections, and hence the void percentage was 0%, and the content of polyethylene glycol in the fiber structure was 50.0 wt.%. Scanning electron micrographs of a surface and a fiber cross section of the fiber structure are shown in Figure 25 and Figure 26.

Claims

1. A porous fiber comprising a hydrophobic solvent-soluble polymer and an organic compound having a plurality of hydroxyl groups, and having an average fiber diameter of 0.1-20 μ m and a void percentage of at least 5%.

2. The porous fiber according to Claim 1, wherein the hydrophobic solvent is a halogen element-containing hydrocarbon.

3. The porous fiber according to Claim 2, wherein the halogen element-containing hydrocarbon is selected from the group consisting of methylene chloride, chloroform, dichloroethane, tetrachloroethane, trichloroethane, dibromomethane, and bromoform.

4. The porous fiber according to Claim 1, wherein the hydrophobic solvent-soluble polymer is selected from the group consisting of polylactic acid, polycaprolactone, polycarbonates, polystyrene, and polyarylates.

5. The porous fiber according to Claim 1, wherein the number-average molecular weight of the organic compound having a plurality of hydroxyl groups is not less than 62 nor more than 300.

6. A fiber structure comprising porous fibers that comprise a hydrophobic solvent-soluble polymer and an organic compound having a plurality of hydroxyl groups, and have an average fiber diameter of 0.1-20 μ m and a void percentage of at least 5%.

7. The fiber structure according to Claim 6, wherein the hydrophobic solvent is a halogen element-containing hydrocarbon.

8. The fiber structure according to Claim 7, wherein the halogen element-containing hydrocarbon is selected from the group consisting of methylene chloride, chloroform, dichloroethane, tetrachloroethane, trichloroethane, dibromomethane, and bromoform.

9. The fiber structure according to Claim 6, wherein the number-average molecular weight of the organic compound having a plurality of hydroxyl groups is not less than 62 nor more than 300.

10. The fiber structure according to Claim 6, wherein the hydrophobic solvent-soluble polymer is selected from the group consisting of polylactic acid, polycaprolactone, polycarbonates, polystyrene, and polyarylates.

11. A method for producing a fiber structure comprising porous fibers that have an average fiber diameter of 0.1-20 μ m and a void percentage of at least 5%, including a step in which a solution is produced by dissolving a hydrophobic solvent-soluble polymer and an organic compound having a plurality of hydroxyl groups in a hydrophobic solvent, a step in which the solution is spun by electrospinning, and a step in which a fiber structure accumulated on a collector is obtained.

12. The method for producing the fiber structure according to Claim 11, wherein the hydrophobic solvent is a halogen element-containing hydrocarbon.

13. The method for producing the fiber structure according to Claim 12, wherein the halogen element-containing hydrocarbon is selected from the group consisting of methylene chloride, chloroform, dichloroethane, tetrachloroethane, trichloroethane, dibromomethane, and bromoform.

Fig. 1

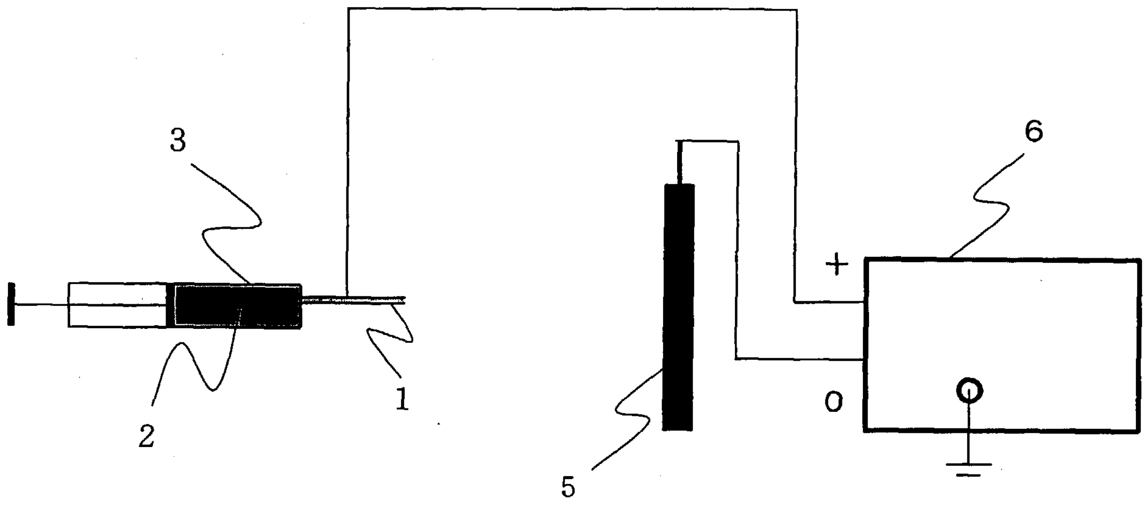


Fig. 2

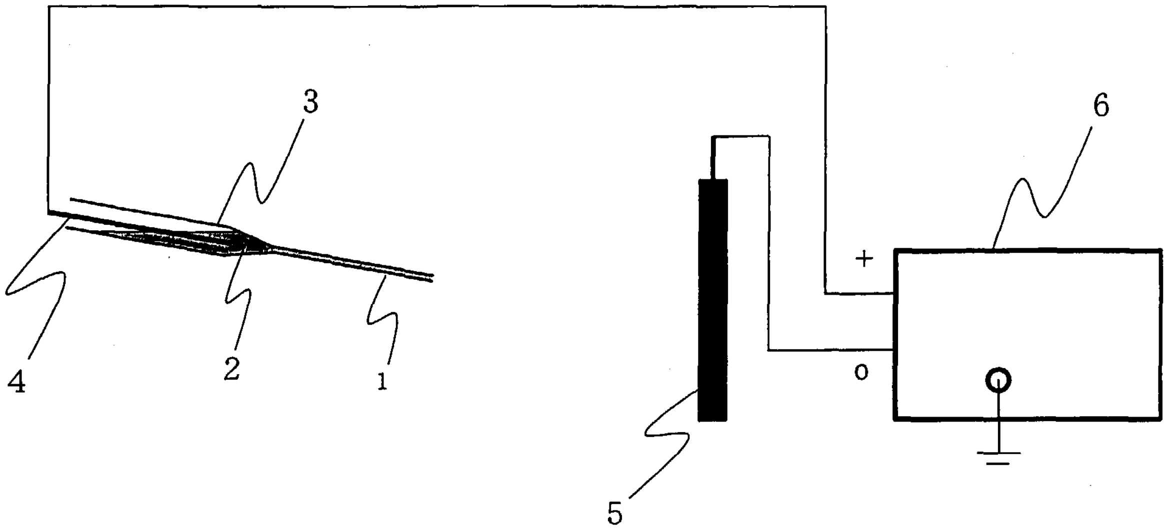


Fig. 3

Fig. 4

Fig. 5

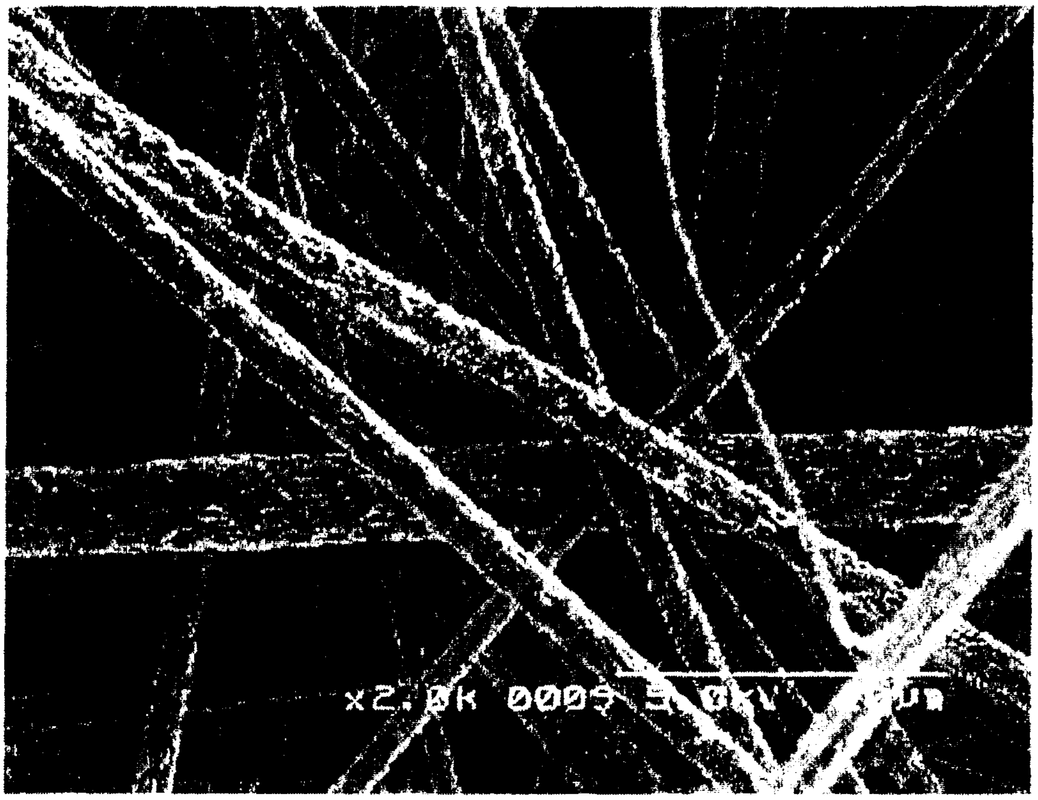


Fig. 6

Fig. 7

Fig. 8

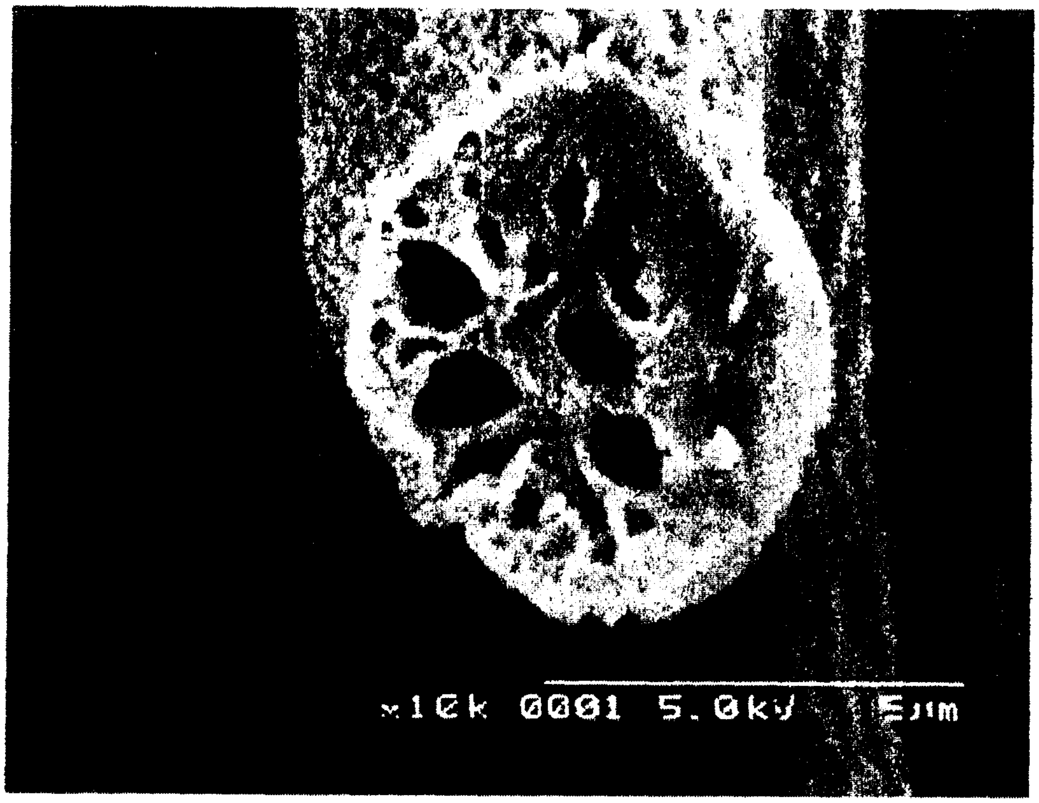


Fig. 9

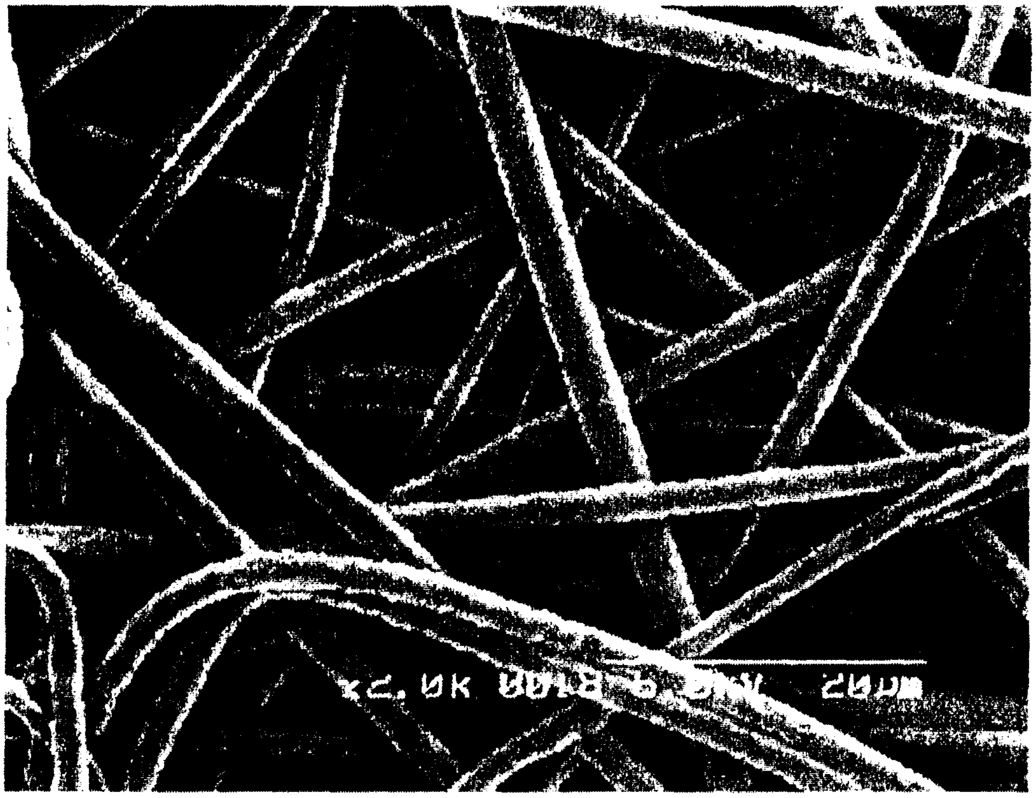


Fig. 10

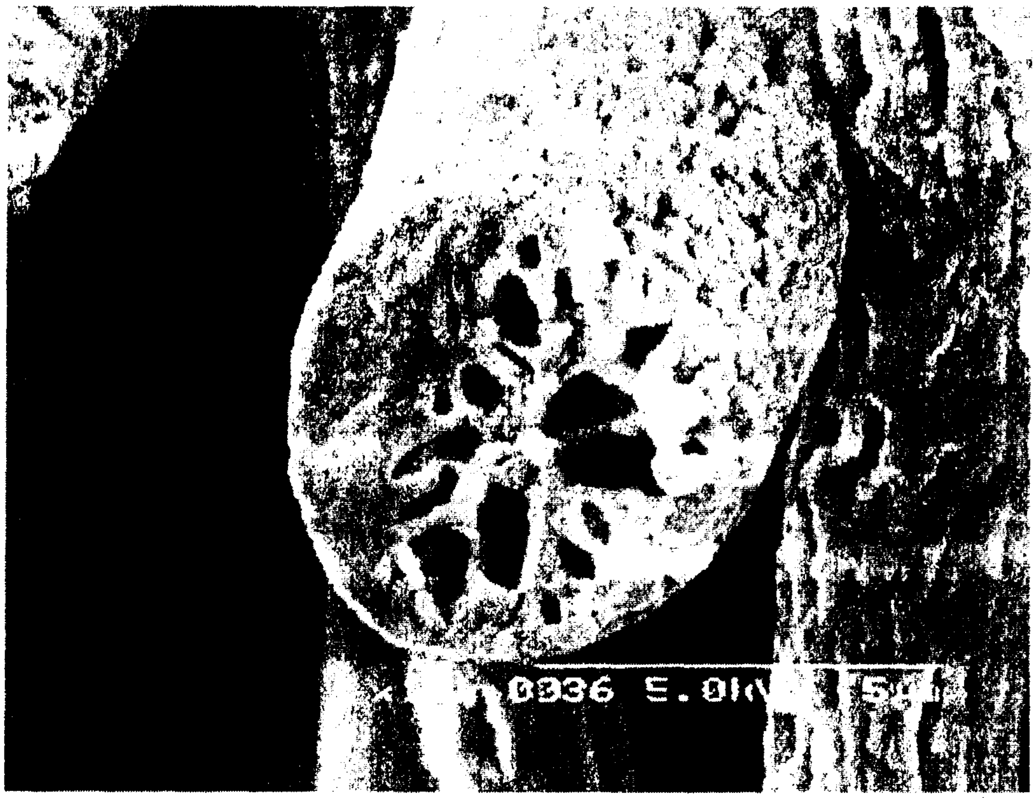
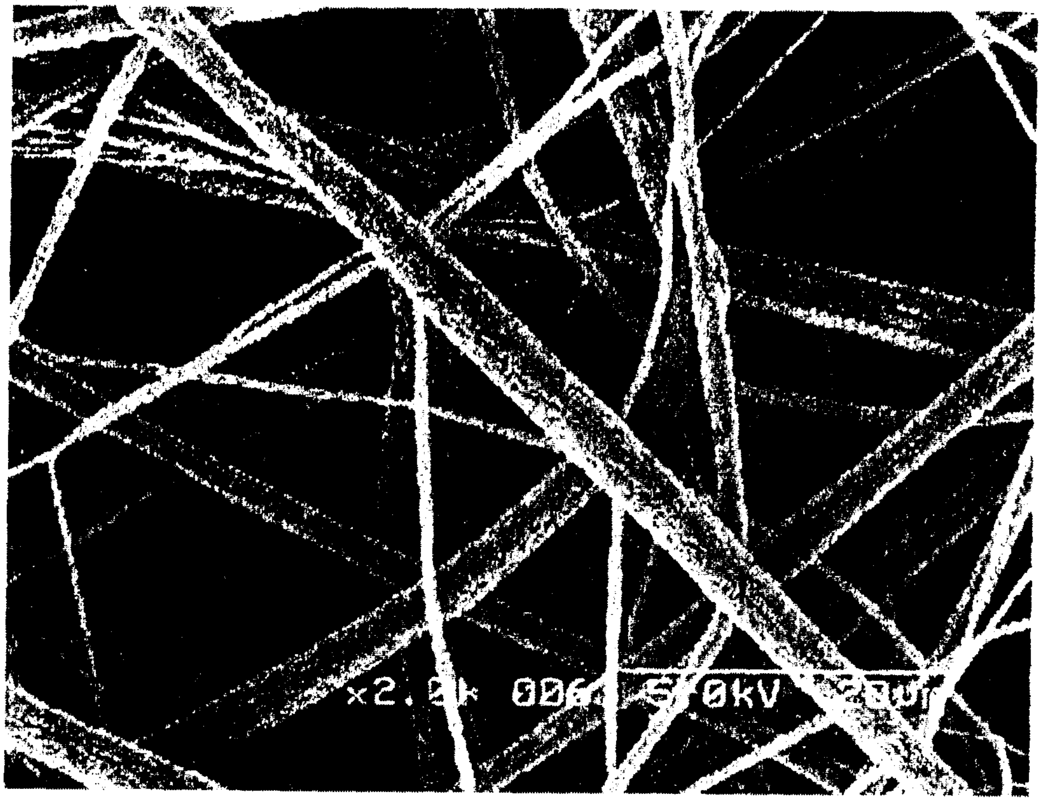


Fig. 11



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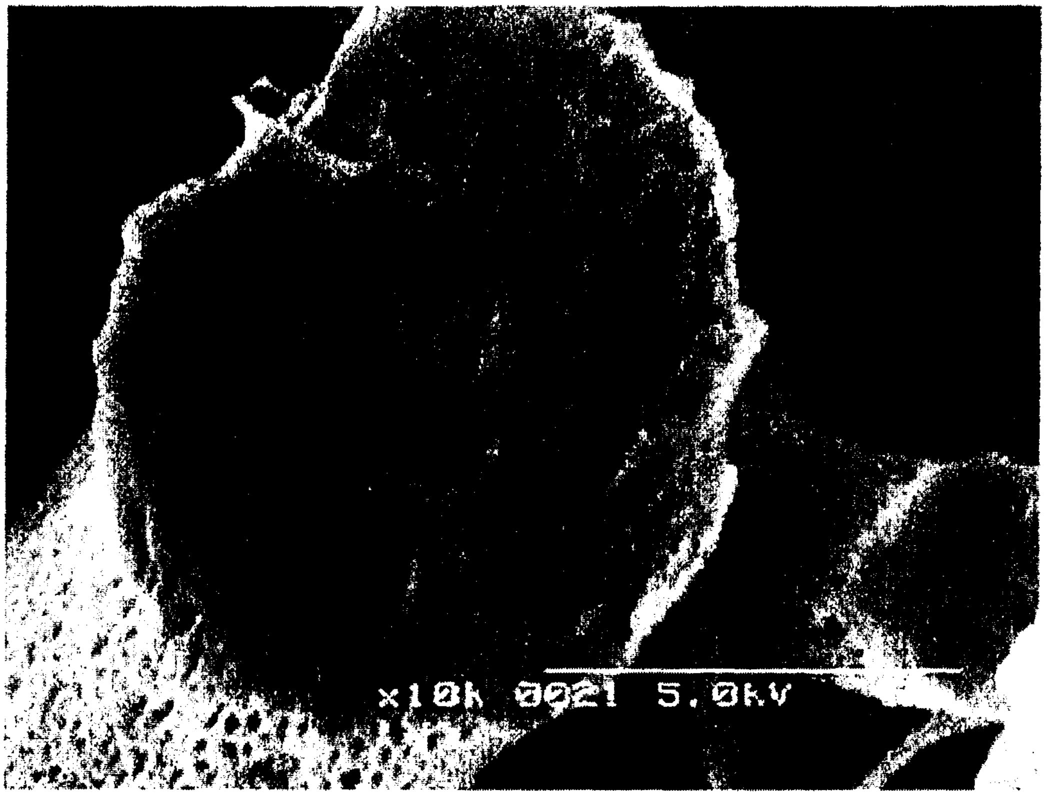

Fig. 13

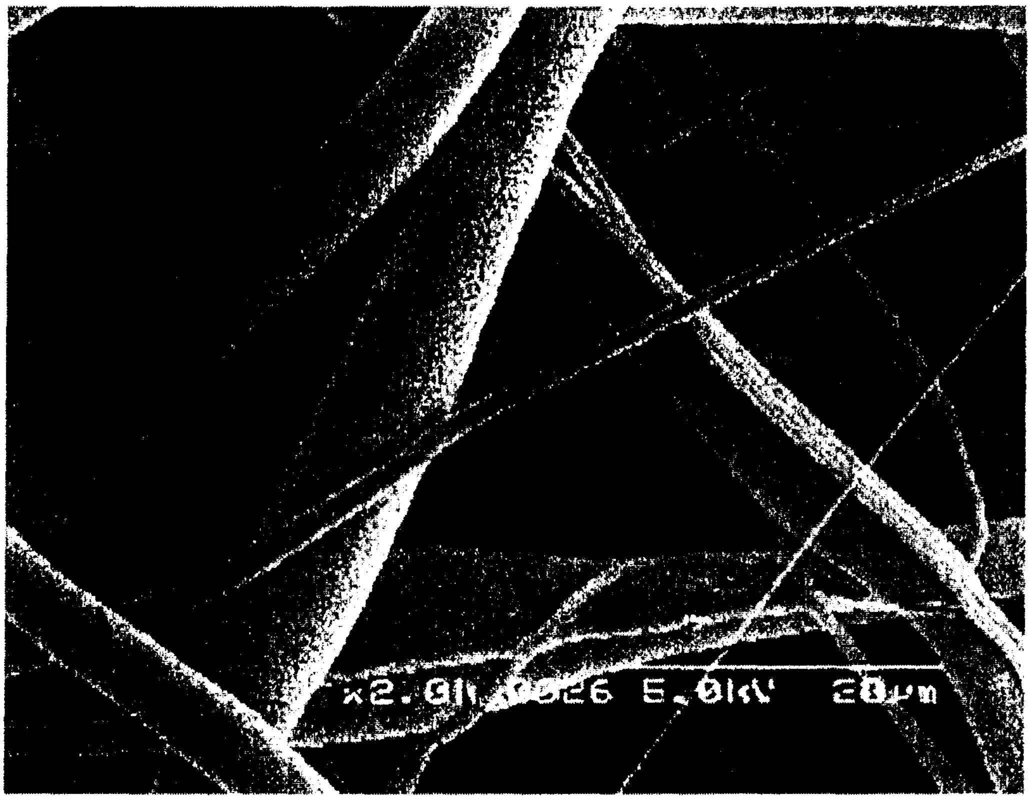

Fig. 14

Fig. 15

Fig. 16

Fig. 17

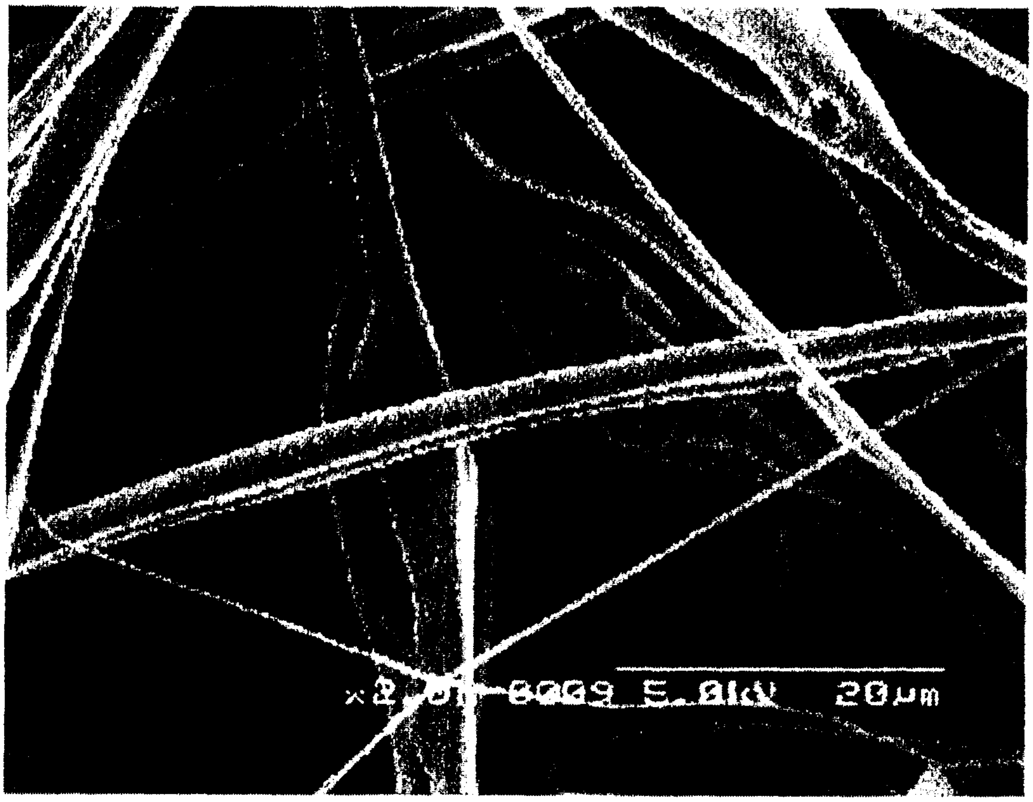

Fig. 18

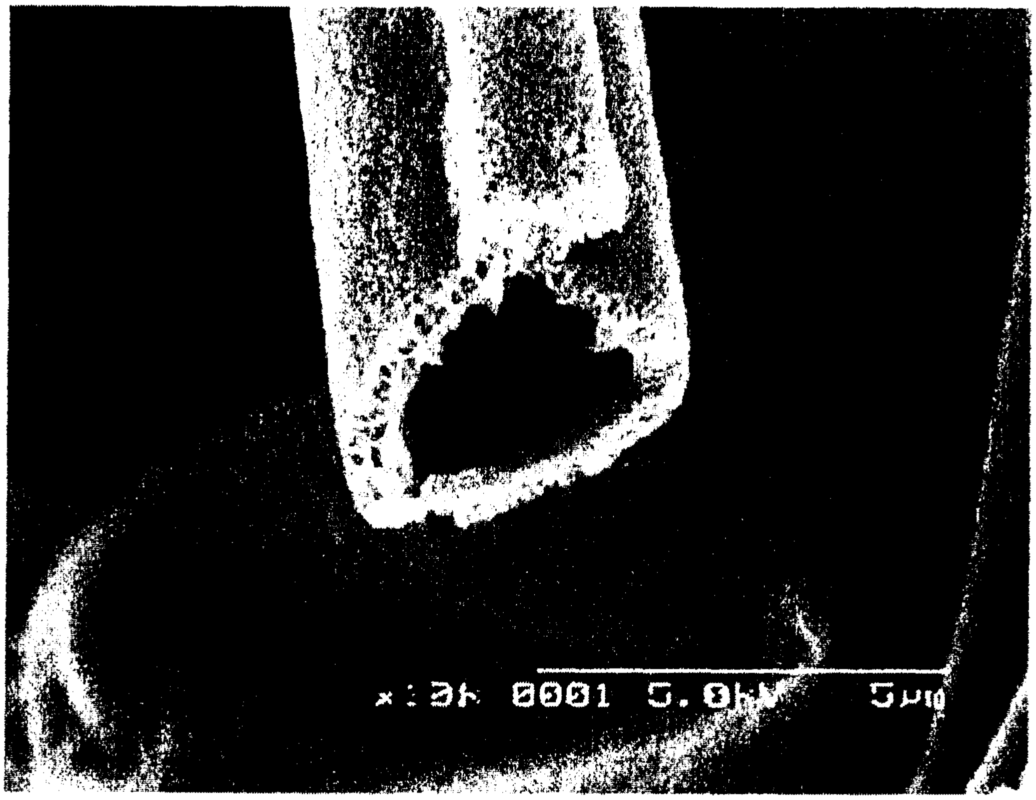

Fig. 19

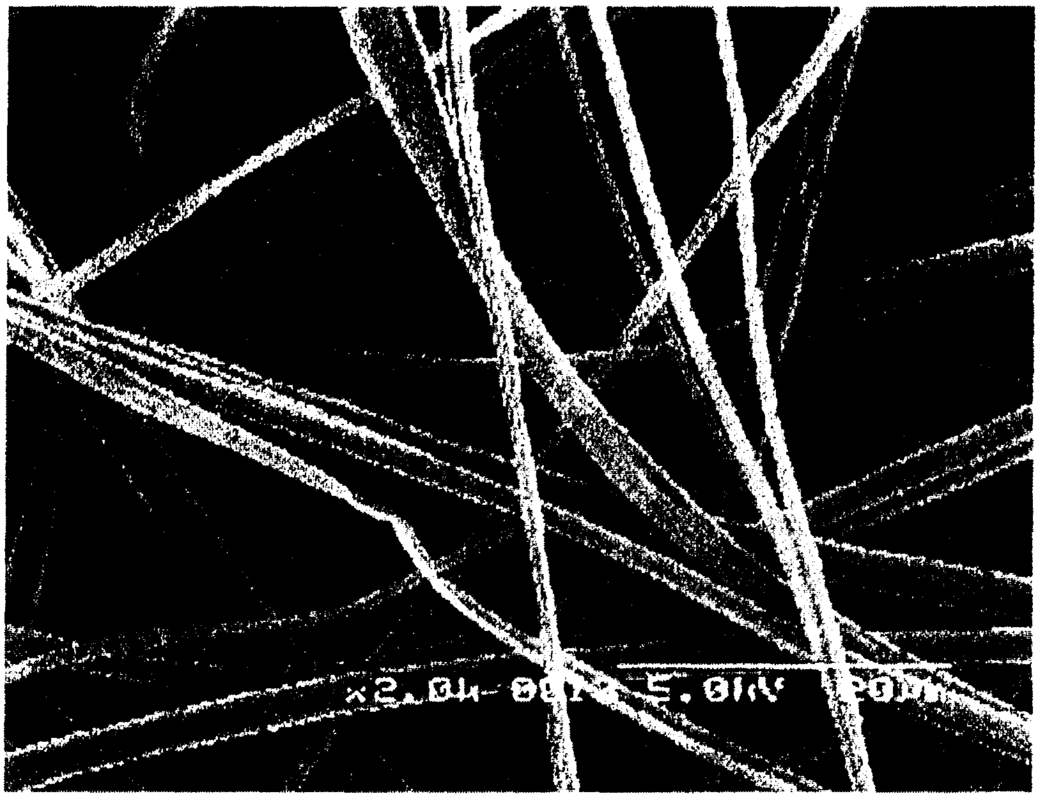

Fig. 20

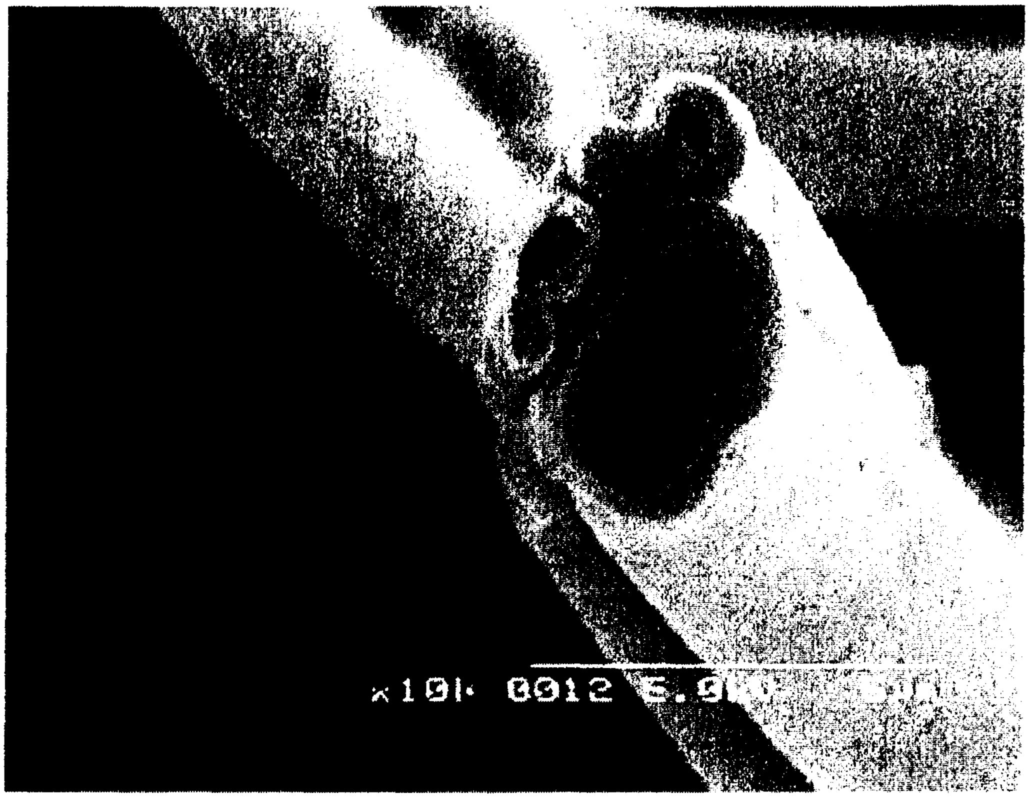

Fig. 21

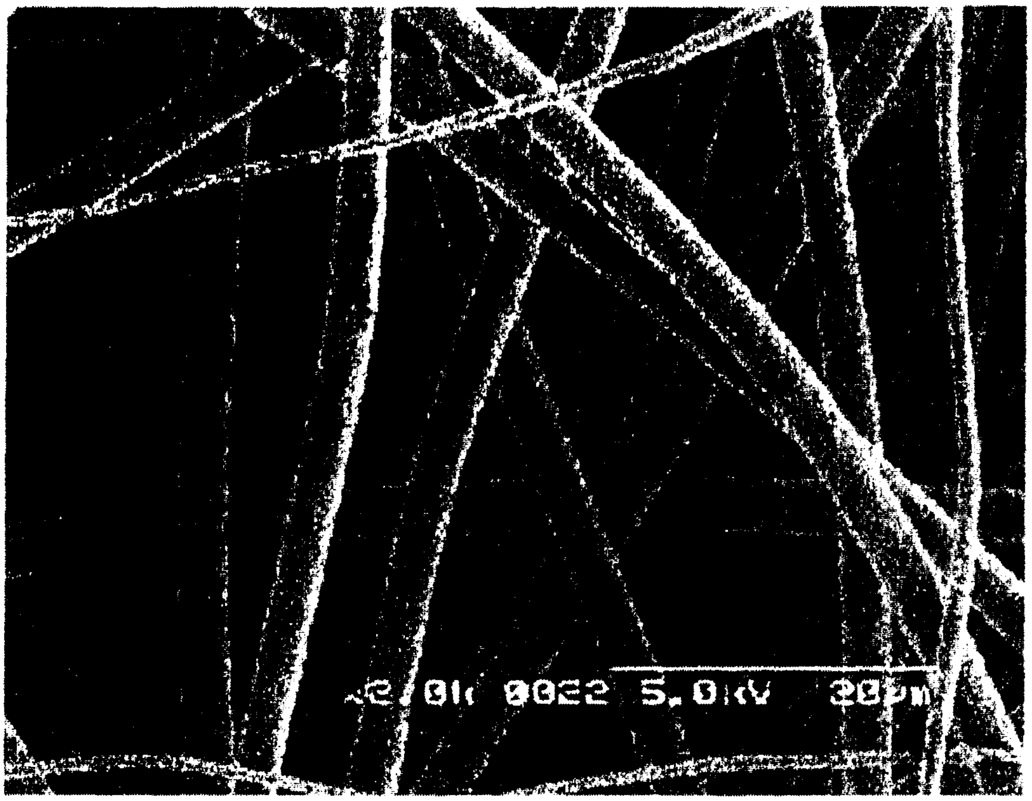

Fig. 22

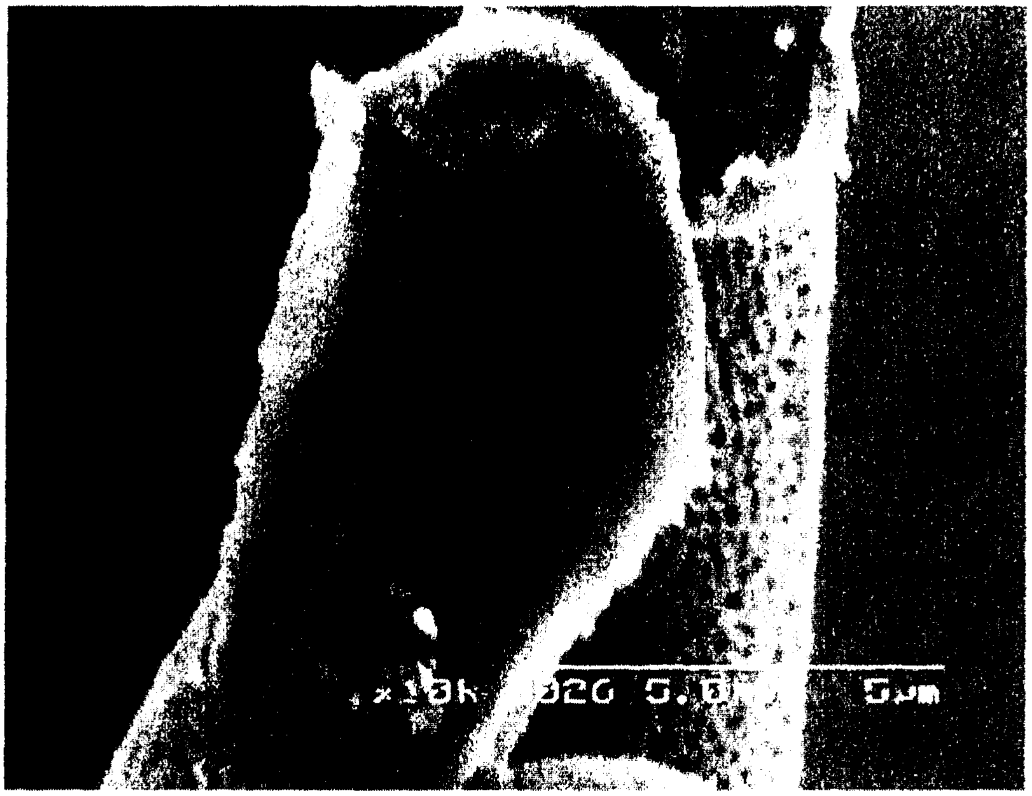

Fig. 23

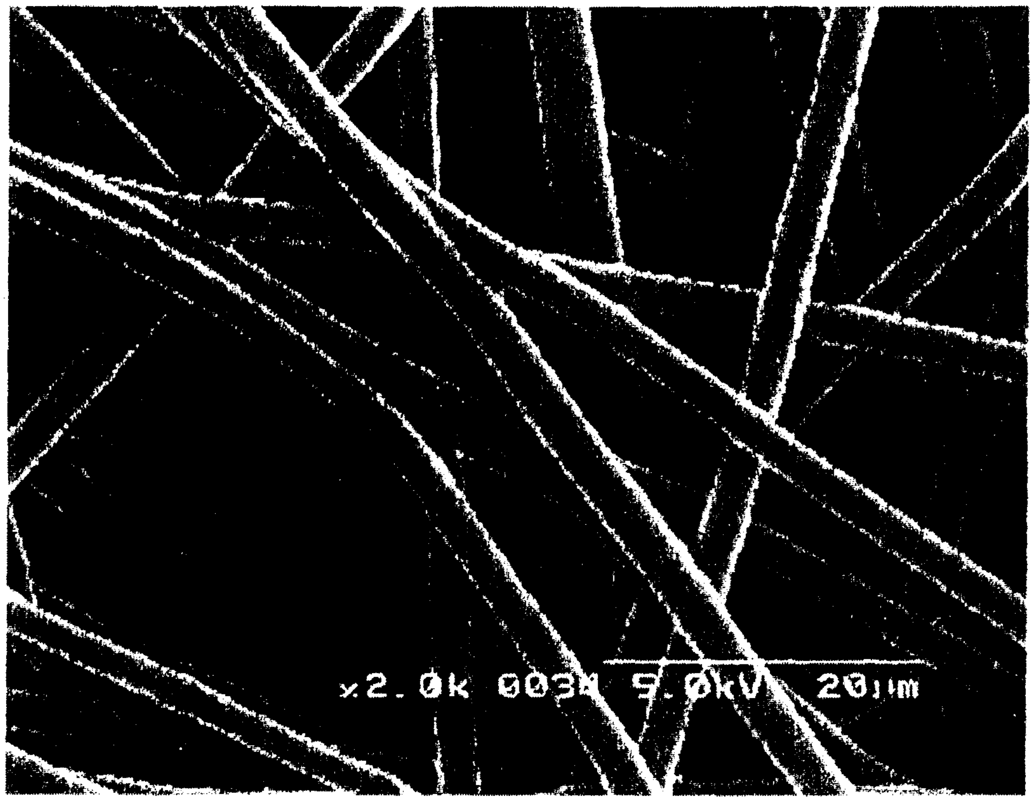

Fig. 24

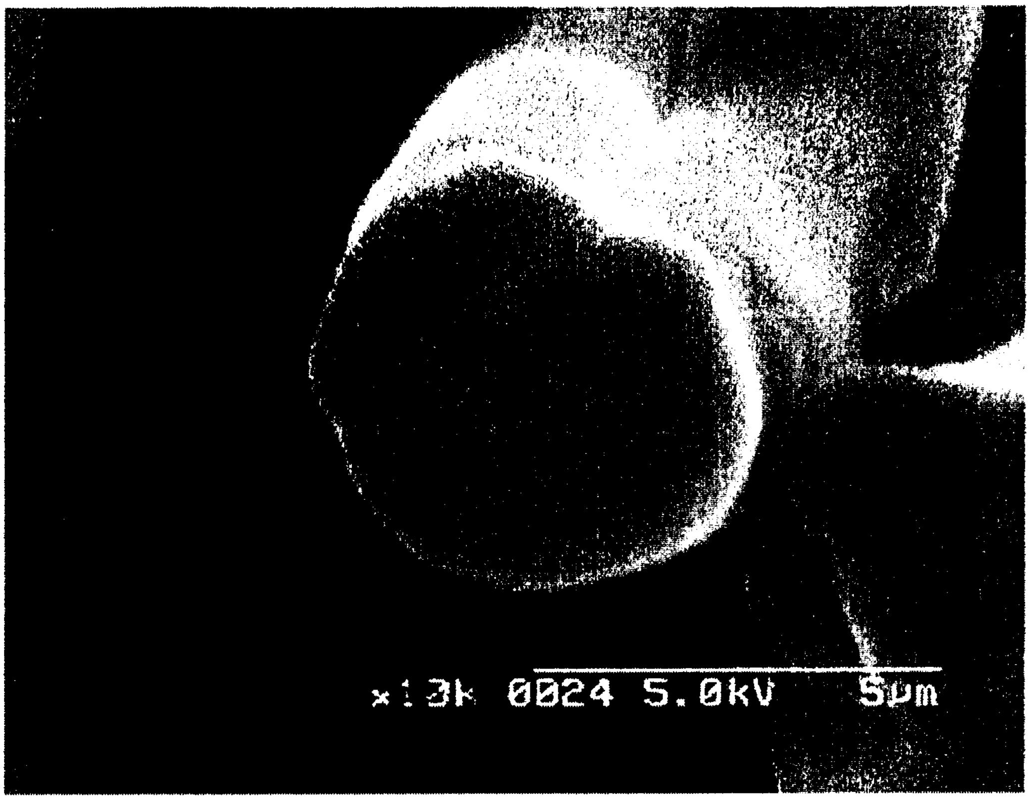

Fig. 25

Fig. 26

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2004/001453

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^7 D01F6/00, 6/56, 6/92, D04H3/00

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)
Int.Cl^7 D01F1/00-9/04, D04H1/00-18/00, D01D1/00-13/02

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

Jitsuyo Shinan Koho	1926-1996	Toroku Jitsuyo Shinan Koho	1994-2004
Kokai Jitsuyo Shinan Koho	1971-2004	Jitsuyo Shinan Toroku Koho	1996-2004

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 57-51809 A (Carl Freudenberg), 26 March, 1982 (26.03.82), Claims & EP 47795 A2 & ZA 8106109 A & CA 1165523 A	1-13
A	WO 02/16680 A1 (CREAVIS GESELLSCHAFT FUR TECHNOLOGIE UND INNOVATION MBH), 28 February, 2002 (28.02.02), ABSTRACT & AU 9375001 A & DE 10040897 A & EP 1311715 A	1-13

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search 10 May, 2004 (10.05.04)	Date of mailing of the international search report 25 May, 2004 (25.05.04)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2004/001453

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 51-40476 A (Imperial Chemical Industries, Ltd.), 05 April, 1976 (05.04.76), Claims; page 4, upper left column, lines 7 to 11; page 10, upper left column; example 1 & SE 7508781 A & DE 2534935 A & FR 2281448 A & US 4043331 A & US 4044404 A & GB 1527592 A & IT 1044659 B & CA 1090071 A & US 4878908 A	1-13
A	JP 3-284326 A (Kuraray Co., Ltd.), 16 December, 1991 (16.12.91), Claims (Family: none)	1-13

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