US 20160194796A1

(19) United States

(12) Patent Application Publication

(10) Pub. No.: US 2016/0194796 A1

(43) Pub. Date: Jul. 7, 2016

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(54) **MELT ELECTROSPUN FIBERS CONTAINING MICRO AND NANOLAYERS AND METHOD OF MANUFACTURING**

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(21) Appl. No.: **15/068,945**

(22) Filed: **Mar. 14, 2016**

Related U.S. Application Data

(62) Division of application No. 14/366,323, filed on Jun. 18, 2014, filed as application No. PCT/US2012/069629 on Dec. 14, 2012.

(60) Provisional application No. 61/577,241, filed on Dec. 19, 2011.

Publication Classification

(51) **Int. Cl.**

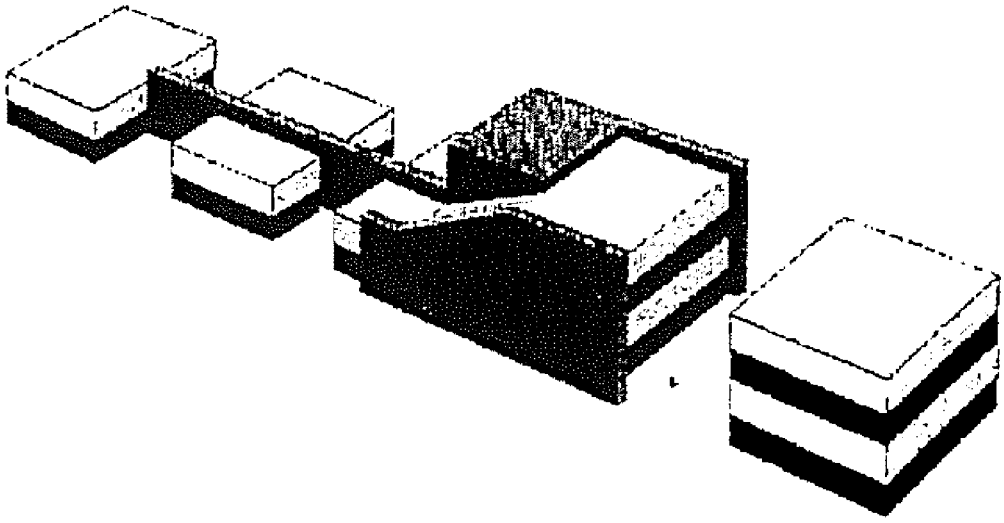
D04H 1/728	(2006.01)
D01F 6/06	(2006.01)
D01F 6/62	(2006.01)
D01F 6/04	(2006.01)

(52) **U.S. Cl.**

CPC ***D04H 1/728*** (2013.01); ***D01F 6/04*** (2013.01); ***D01F 6/06*** (2013.01); ***D01F 6/625*** (2013.01)

(57) **ABSTRACT**

Fibers having two or more alternating polymer layers are formed by co-extrusion followed by electroprocessing. The fibers can be used as a non-woven mat or other substrate for a variety of applications. Delamination of the fibers using ultrasonication yields separated, micro and nanolayer, fiber ribbons which may also be used a non-woven mat or other substrate.



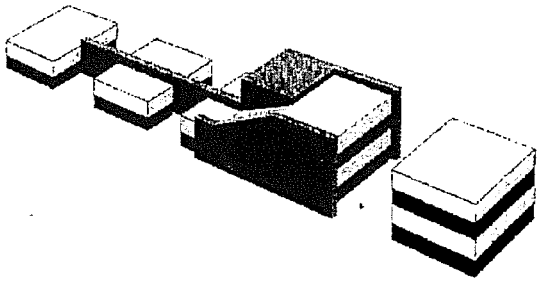


Figure 1a

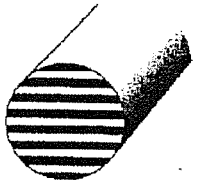


Figure 1b

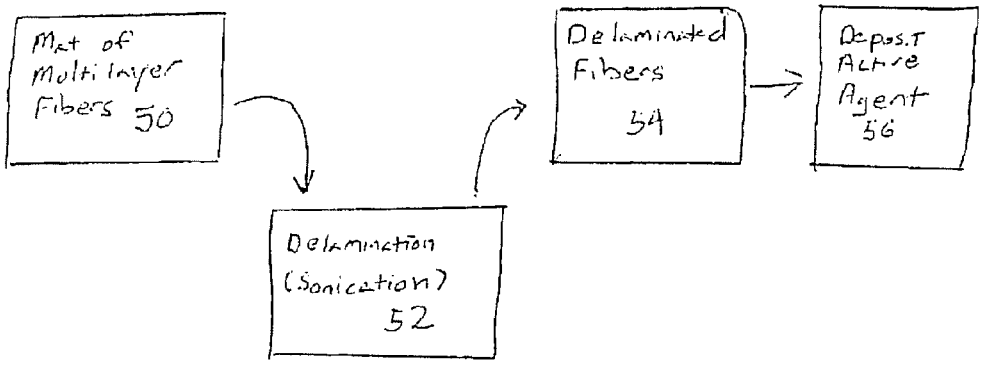


Figure 3

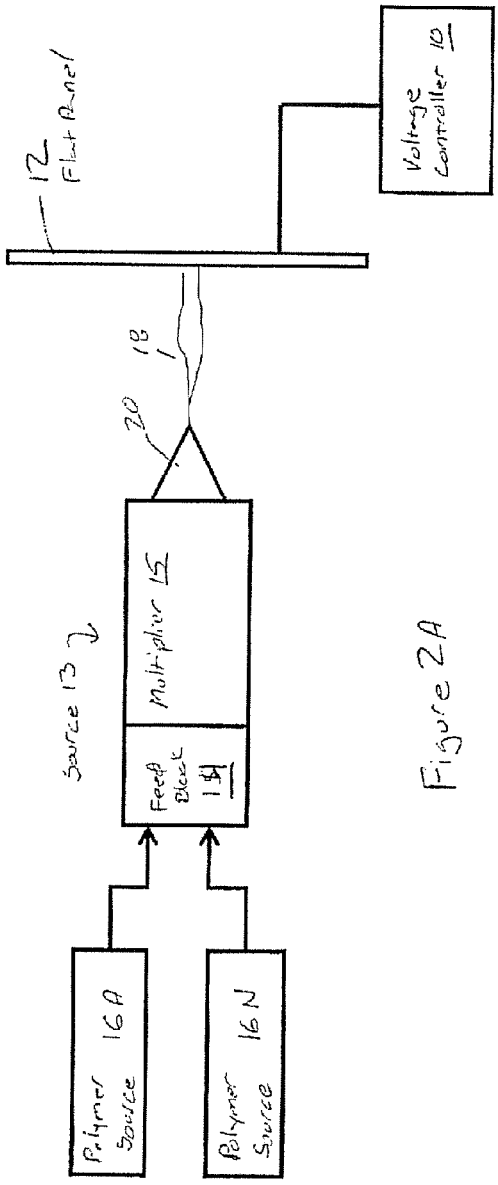


Figure 2A

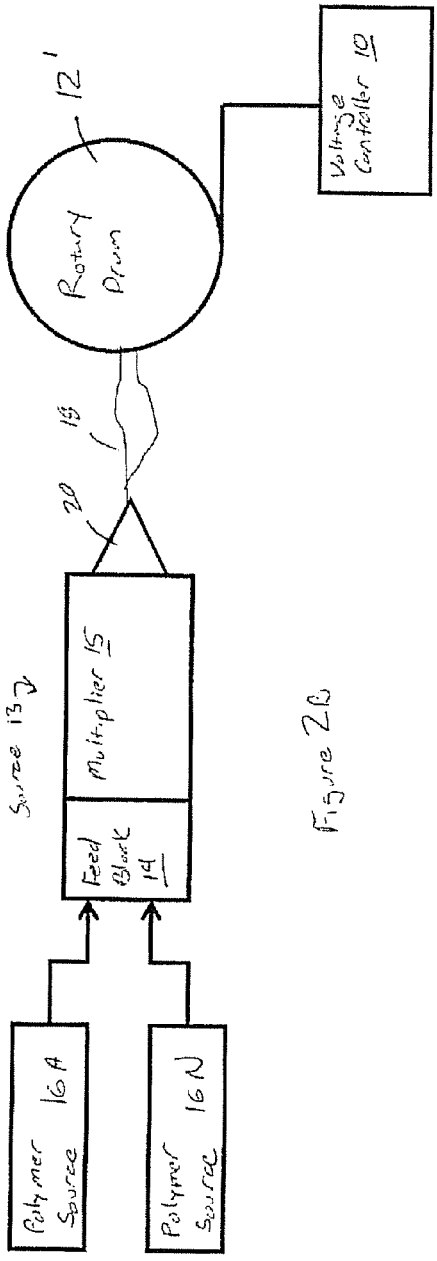
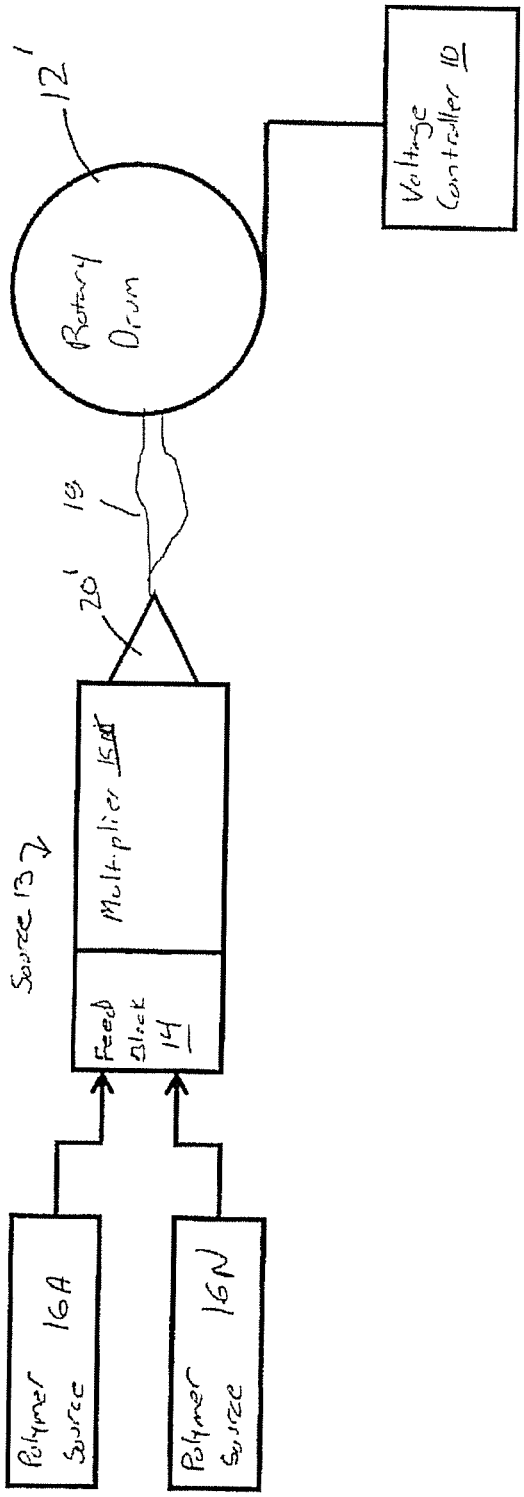


Figure 2B


Voltage Controller 10
12'
Rotary Drum
18
20'
Multiplier Block
Feed Block 14
Source 13
Polymer Source 16A
Polymer Source 16N

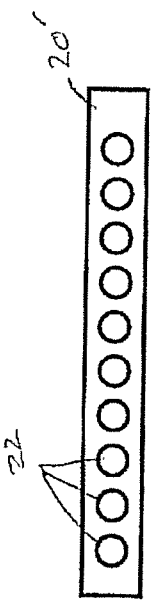

20'
22

Figure 2C

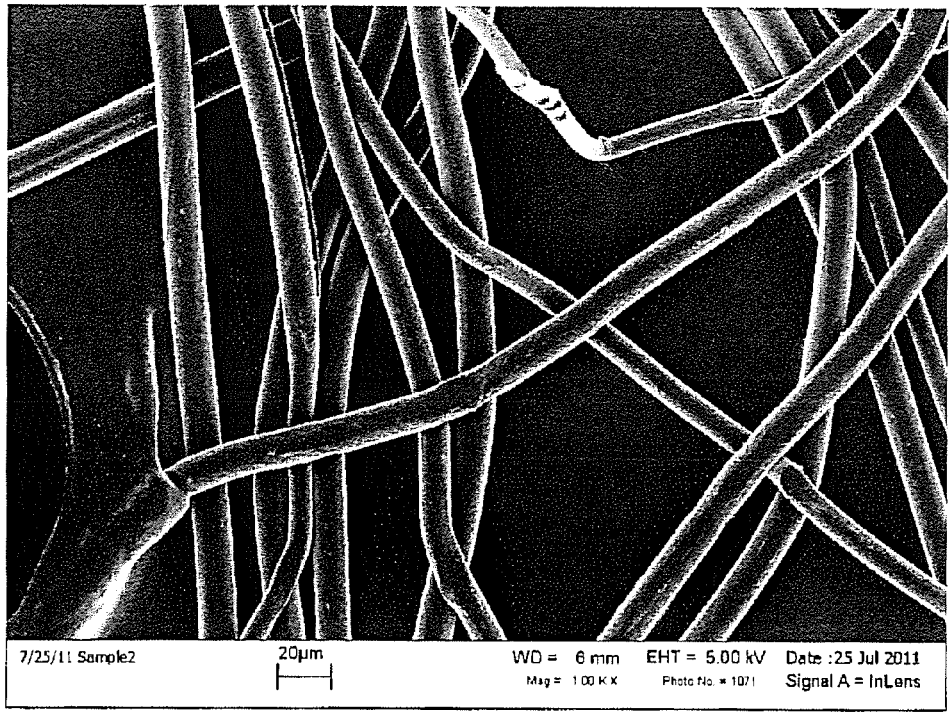


FIGURE 4

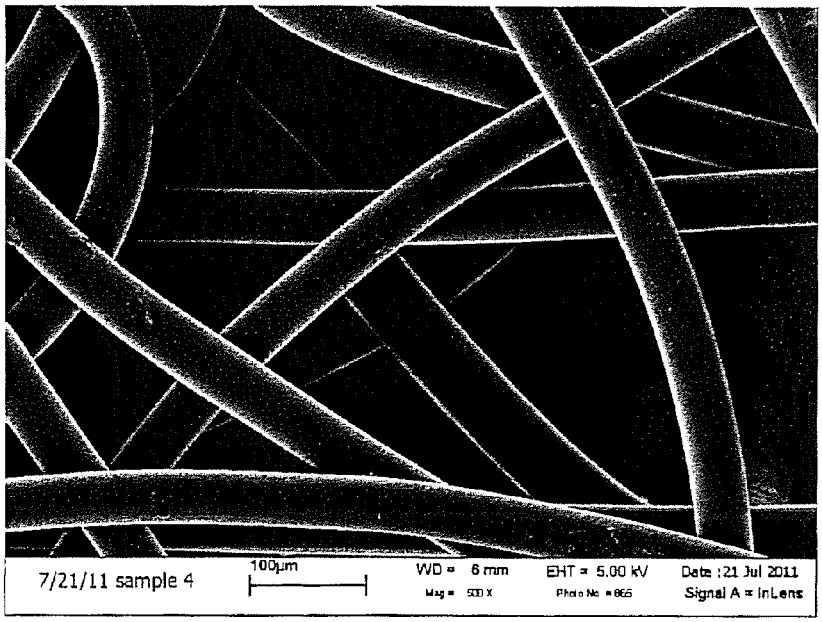


FIGURE 5

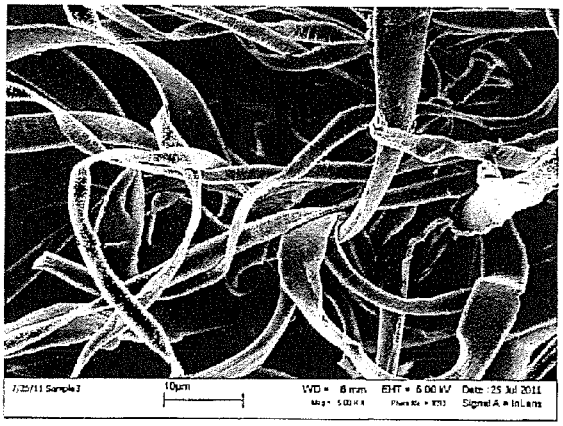


FIGURE 6

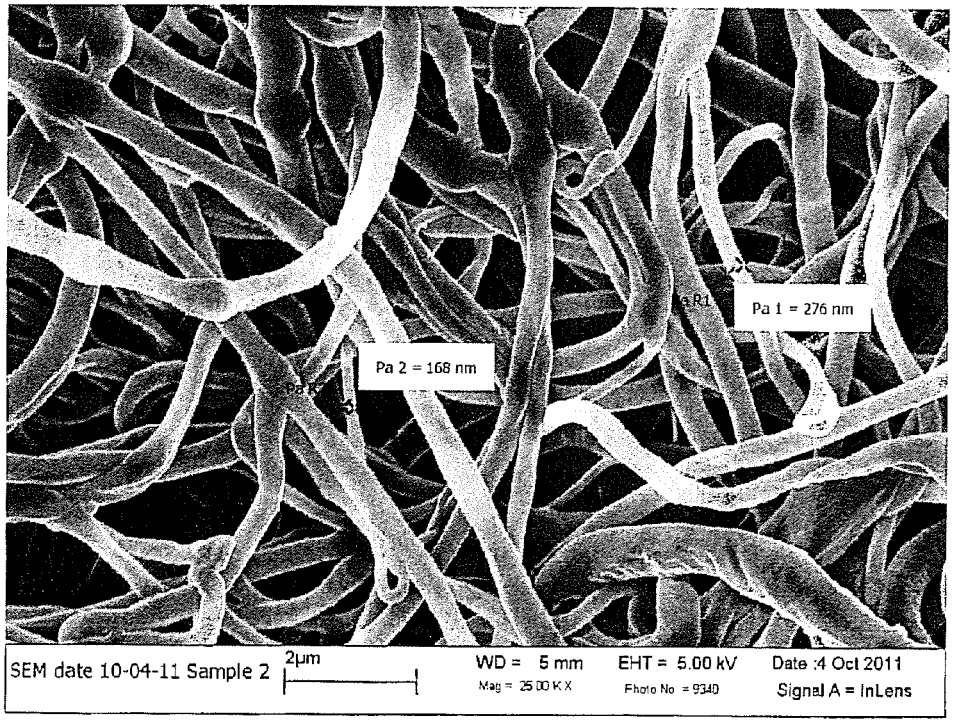


FIGURE 7

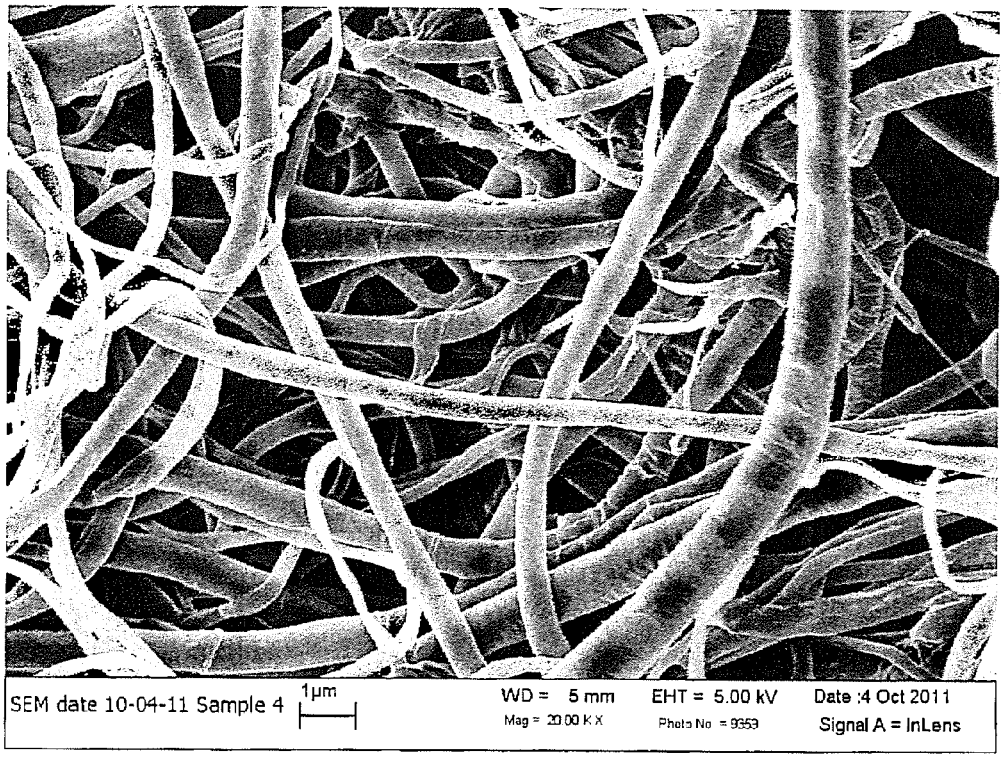

SEM date 10-04-11 Sample 4
1µm
WD = 5 mm
Mag = 20.00 K X
EHT = 5.00 kV
Photo No = 9353
Date :4 Oct 2011
Signal A = InLens

FIGURE 8

MELT ELECTROSPUN FIBERS CONTAINING MICRO AND NANOLAYERS AND METHOD OF MANUFACTURING

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application 61/577,241 filed Dec. 19, 2011, and the complete contents of that application is herein incorporated by reference.

FIELD OF THE INVENTION

[0002] This invention pertains to electrospinning for the production of nanofibers and nanofiber webs, and, more particularly, the invention is focused on producing nanofibers and nanofiber webs from a polymer melt.

BACKGROUND

[0003] Electrospinning is a process that is used to produce nanofibers and nanofiber webs. The nanofibers and nanofiber webs have been evaluated for use in a wide range of applications including without limitation in filtration, protective clothing, drug delivery, tissue engineering, and nanocomposites. Although there is significant research interest in nanofiber development, most of the current work is focused on electrospinning from solutions. Solution electrospinning can pose a significant safety problem during manufacture since most solvents used for synthetic polymers are highly flammable, as well as toxic or carcinogenic. The solvents employed in solution based electrospinning also pose additional concerns such as solvent cost, solvent recovery, low production rates, and limiting limited biomedical applications due to residual toxic solvent. Hence, there is a strong interest in developing solvent-free processes such as melt processes for the manufacture of nanofibers.

SUMMARY

[0004] In an embodiment of the invention, co-extrusion technology is combined with electroprocessing technology to produce nanofibers containing multiple layers of materials.

[0005] In another embodiment of the invention, multilayered nanofibers produced by electroprocessing are effectively "delaminated" (i.e., the layers within the fibers are separated) by sonication or other suitable energy application techniques.

[0006] According to an embodiment of the invention, a "solvent-free" process is used to create fibrous materials that have significantly higher surface areas than currently manufactured nanofibers. Specifically, the process combines coextrusion where two polymer resins in the molten state are arranged to give alternating layers via feed blocks or layer multipliers, with melt electrospinning (or other suitable electroprocessing). By combining the two technologies, nonwoven webs that have hundreds to over a thousand layers within each microfiber can be created. These webs can be subsequently exposed to ultrasonication to create delamination of the layers which result in nanolayer melt electrospun (NME) fibrous webs.

[0007] The multilayer electrospun fibers have been evaluated using electron microscopy both before and after sonication. Experiments have demonstrated that melt electrospun fibers produced according to the invention with 257 alternating layers can be successfully produced and delaminated by ultrasonication.

[0008] The invention includes melt electrospun fibers and matrices, such as non-woven webs, of fibers that contain alternating layers, and their method of production. In addition, the invention includes nanolayer thick fibers (e.g., fiber ribbons) created by delamination of melt electrospun fibers having alternating layers of polymers. Also, the invention includes matrices of these nanolayer thick fibers, in laminated or delaminated form. In some applications, the inventive matrices can have substances of interest deposited on them (e.g., bioactive agents, catalytic agents, fire retardant chemicals, etc.).

[0009] In any exemplary embodiment, two extruders deliver different polymers to a 3 layer feedblock where layering of the melt occurs and this 3 layer melt stream is fed to a single orifice die. A high voltage is applied to a flat plate collector placed at a suitable distance from the die and electrospun fibers are formed and collected on the flat plate. In another exemplary embodiment of this invention, the 3 layer melt stream is fed to a layer multiplying unit where the melt layers are multiplied (multiplying depends on the number of multipliers used). A melt stream with 257 layers, when 7 multipliers are used, is fed to the single orifice die. A high voltage is applied to a flat plate collector placed at a suitable distance and electrospun fibers are collected on the flat plate. In yet another embodiment of the invention, melt electrospun webs that have about 257 alternating layer fibers are exposed to ultrasonication (or other energy application or chemical application) to create nanolayer thick fibers due to delamination of the layers. Delamination can be achieved by other mechanisms such as exposure to chemicals such as chloroform,

DESCRIPTION OF THE DRAWINGS

[0010] FIG. **1**(*a*) is a schematic of the layer multiplying process that occurs when using two layers as input to the layer multiplying process.

[0011] FIG. **1**(*b*) is a schematic of the cross-section of a fiber with multiple layers of two different polymers.

[0012] FIGS. **2**A-C are, respectively, schematic drawings of a system for producing multilayer electrospun fibers according to the invention with a flat plate collector (FIG. **2**A), a rotary drum collector (FIG. **2**B), and a wide width die in combination with a rotary drum collector (FIG. **2**C).

[0013] FIG. **3** illustrates a simplified process for delaminating fibers in a fibrous mat formed by melt electroprocessing multiple polymers according to the invention.

[0014] FIG. **4** is a scanning electron micrograph (SEM) of a melt electrospun fiber described in Example 1 that has 257 alternating layers of polycaopactone (PCL) and polyethylene (PE).

[0015] FIG. **5** is a SEM image of a melt electrospun fiber described in Example 2 that has 257 alternating layers of PCL and PE.

[0016] FIG. **6** is a SEM image of a melt electrospun fiber web described in Example 7 that has 257 alternating layers of PCL and PE after ultarsonication which shows delamination of the layers after sonication.

[0017] FIG. **7** is an SEM image of a melt electrospun fiber web described in Example 8 where PCL and PP layers in the fibers are delaminated by exposure to chloroform with slight agitation.

[0018] FIG. **8** is an SEM image of a melt electrospun fiber web described in Example 9 where PCL and PE layers in the fibers are delaminated by exposure to chloroform with slight agitation.

DETAILED DESCRIPTION

[0019] "Co-extrusion" in the context of the present invention is a process by which two polymer resins in the molten state are arranged via feed blocks or layer multipliers to give alternating layers. The number of layers in the final extruded form (e.g., film or microfiber) can be as low as two or in the hundreds (up to and exceeding a thousand). While feedblock technology is typically used to produce films with approximately 3 to 7 layers, layer-multiplying technology is used to produce hundreds to thousands of layers within 25-50 micron thick films. The layer multiplying process is shown schematically in FIGS. **1***a* and **1***b*.

[0020] With reference to FIG. **1***a* there is shown a two component (AB) co-extrusion system which could include, for example, two single screw extruders each connected by a melt pump to a co-extrusion feedblock. The feedblock combines polymeric material (a) and polymeric material (b) in an (AB) layer configuration (see leftmost portion of FIG. **1***a*). Melt pumps (not shown) control the two melt streams that are combined in the feedblock as two parallel layers. By adjusting the melt pump speed, the relative layer thickness, that is, the ratio of A to B can be varied (as shown, the ratio of the top layer to the bottom layer). From the feedblock, the melt goes through a series of multiplying elements. As shown in FIG. **1***a* a multiplying element first slices the AB structure vertically, and subsequently spreads the melt horizontally. The flowing streams recombine, doubling the number of layers. An assembly of n multiplier elements produces an extrudate with the layer sequence $(AB)_x$ where x is equal to $(2)^n$ and n is the number of multiplying elements to form a multilayer stack (as depicted in the right most portion of FIG. **1***a*). FIG. **1***b* is a cross-sectional view of a fiber with multiple layers produced by co-extrusion (it being recognized that the layers in a co-extruded fiber may not be flat as depicted in FIG. **1***b;* rather, the individual layers may be curved or have other configurations, but will form distinct regions in the fiber).

[0021] Co-extrusion with the use of feedblocks and multipliers is a well understood technique in chemical engineering (see, for example, U.S. Pat. No. 7,936,802, U.S. Pat. No. 7,141,297, U.S. Pat. No. 7,255,928, U.S. Pat. No. 7,052,762, U.S. Pat. No. 3,565,985, and U.S. Pat. No. 3,051,453, each of which are herein incorporated by reference). Layered melt blown fibers made using feed block technology are described in U.S. Pat. No. 5,176,952 and U.S. Pat. No. 5,207,970, both of which are herein incorporated by reference.

[0022] The Examples below show the combination of polyethylene (PE) and polycaprolactone (PCL) being combined as multiple layers in electroprocessed fibers according to the present invention. However, many different polymers can be employed in the practice of the invention including without limitation polyolefins (e.g., polyethylene, polypropylene, etc.), poly(urethanes), poly(siloxanes), poly(vinyl pyrolidone), poly(2-hydroxy ethyl methacrylate), poly(N-vinyl pyrrolidone), poly(methyl methacrylate), poly(vinyl alcohol), poly(acrylic acid), polyacrylamide, poly(ethylene-co-vinyl acetate), poly(ethylene glycol), poly(methacrylic acid), polylactides (PLA), polyplycolides (PGA), poly(lactide-co-glycolides) (PLGA), polyanhydrides, polyorthoesters, styrene-diene block copolymers, and block copolymers with tackifiers. In addition, thermally stable and melt processable natural polymers (e.g., those occurring naturally in a plant or animal) can be employed in the practice of the invention including without limitation plasticized cellulose acetate.

[0023] In the context of the present invention, "electroprocessing" or "electrodeposition" broadly include all methods of electrospinning, electrospraying, electroaerosoling, and electrosputtering of materials, including combinations of two or more of such methods, as well as any other method wherein materials are streamed, sprayed, sputtered, or dripped across an electric field toward a target. A material can be electroprocessed from one or more grounded reservoirs in the direction of a charged substrate or from charged reservoirs toward a grounded target. Electroprocessing can be performed using one or a plurality of nozzles, and, in the case of using multiple nozzles, each nozzle can be connected to a single reservoir or each can be connected to a different reservoir where each reservoir contains the same or a different melt. The size of the nozzles can be varied to provide for increased or decreased flow out of the nozzles, and a pump or a plurality of pumps can be used to control flow from the reservoir(s). Electrospinning is generally defined as a process by which fibers are formed from melt by streaming the melt through an orifice. In an embodiment of this invention, elecrospinning is achieved by applying a voltage to a collector and the melt is streamed from through the orifice to the collector. Other configurations are possible. Electroaerosoling is generally defined as a process by which droplets are formed from a melt by streaming an electrically charged solution or melt through an orifice.

[0024] Electroprocessing techniques are well known in the art. See, for example, U.S. Pat. No. 7,759,082, U.S. Pat. No. 7,615,373, U.S. Pat. No. 7,374,774, U.S. Pat. No. 6,787,357, U.S. Pat. No. 8,282,712, U.S. Pat. No. 6,592,623, U.S. Pat. No. 8,282,712, U.S. Pat. No. 8,277,712, U.S. Pat. No. 8,277,711, U.S. Pat. No. 8,277,706, U.S. Pat. No. 8,262,958, U.S. Pat. No. 8,257,628, U.S. Pat. No. 8,247,335, U.S. Pat. No. 8,246,730, U.S. Pat. No. 8,241,729, U.S. Pat. No. 8,178,199, U.S. Pat. No. 8,240,174, U.S. Pat. No. 8,206,484, U.S. Pat. No. 8,178,199, U.S. Pat. No. 8,178,029, U.S. Pat. No. 8,173,559, U.S. Pat. No. 8,172,092, U.S. Pat. No. 8,168,550, U.S. Pat. No. 8,163,350, U.S. Pat. No. 8,052,407, U.S. Pat. No. 7,757,811, U.S. Pat. No. 7,754,123, U.S. Pat. No. 7,717,975, U.S. Pat. No. 7,691,168, U.S. Pat. No. 7,662,332, U.S. Pat. No. 7,628,941, U.S. Pat. No. 7,618,579, U.S. Pat. No. 7,601,262, U.S. Pat. No. 7,452,835, U.S. Pat. No. 7,291,300, U.S. Pat. No. 7,134,857, U.S. Pat. No. 7,070,640, and U.S. Pat. No. 6,838,005, each of which are herein incorporated by reference. As discussed in these patents, natural fibers (e.g., collagen, fibrin, etc.), and synthetic fibers, and combinations thereof can be produced from solutions by electroprocessing.

[0025] The invention contemplates a co-extruded stream of two or more polymer melts (e.g., polymer blend streams), which can be multiplied or not multiplied, being subject to electroprocessing to produce fibers with a plurality of layers therein. The fibers will have at least two layers (Examples below show co-extruded, electroprocessed fibers with three layers, and show the order of the layers does not impact the ability to form fibers), and possibly 50 to 100 or more layers (Examples below show co-extruded, electroprocessed fibers with 247 layers).

[0026] The fibers produced by co-extrusion and electroprocessing according to the invention are multilayered and have a diameter of 100 μm or less. As shown in the Examples below, fibers of 50 μm or less have been produced, and some

multilayer fibers having diameters as small as 5-10 μm have been produced. Furthermore, on delamination of the multilayer fibers, ribbon shaped fibers which have thicknesses on the order of nanometers have been produced.

[0027] In a preferred embodiment, the electroprocessed materials form a "matrix". Matrices are comprised of multilayer fibers, or blends of multilayer fibers and droplets of any size or shape. Matrices can be single structures or groups of structures, and can be formed through one or more electroprocessing methods using a plurality of materials. Matrices can be engineered to possess specific porosities.

[0028] Substances of interest can be deposited within, anchored to, or placed on matrices. Exemplary substances of interest can include bioactive agents (e.g., proteins, nucleic acids, antibodies, anesthetics, hypnotics, sedatives, sleep inducers, antipsychotics, antidepressants, antiallergics, antianginals, antiarthritics, antiasthmatics, antidiabetics, antidiarrheal drugs, anticonvulsants, antigout drugs, antihistamines, antipruritics, emetics, antiemetics, antispasmondics, appetite suppressants, neuroactive substances, neurotransmitter agonists, antagonists, receptor blockers, reuptake modulators, beta-adrenergic blockers, calcium channel blockers, disulfarim, muscle relaxants, analgesics, antipyretics, stimulants, anticholinesterase agents, parasympathomimetic agents, hormones, anticoagulants, antithrombotics, thrombolytics, immunoglobulins, immunosuppressants, hormone agonists, hormone antagonists, vitamins, antimicrobial agents, antineoplastics, antacids, digestants, laxatives, cathartics, antiseptics, diuretics, disinfectants, fungicides, ectoparasiticides, antiparasitics, heavy metals, heavy metal antagonists, chelating agents, alkaloids, salts, ions, autacoids, digitalis, cardiac glycosides, antiarrhythmics, antihypertensives, vasodilators, vasoconstrictors, antimuscarinics, ganglionic stimulating agents, ganglionic blocking agents, neuromuscular blocking agents, adrenergic nerve inhibitors, antioxidants, anti-inflammatories, wound care products, antithrombogenic agents, antitumoral agents, antithrombogenic agents, antiangiogenic agents, antigenic agents, wound healing agents, plant extracts, growth factors, growth hormones, cytokines, immunoglobulins, osteoblasts, myoblasts, neuroblasts, fibroblasts, glioblasts; germ cells, hepatocytes, chondrocytes, keratinocytes, smooth muscle cells, cardiac muscle cells, connective tissue cells, epithelial cells, endothelial cells, hormone-secreting, cells, neurons, emollients, humectants, anti-rejection drugs, spermicides, conditioners, antibacterial agents, antifungal agents, antiviral agents, antibiotics, tranquilizers, cholesterol-reducing drugs, antitussives, histamine-blocking drugs and monoamine oxidase inhibitors), catalysts (e.g., metals and metal alloys, such as platinum, gold, ruthenium, rhodium, iridium, transition metals and transition metal complexes, nanomaterial catalysts, zeolites, alumina etc.), flame retarding agents, and carbon black

[0029] FIGS. **2**A-C shows schematic drawings of an exemplary electroprocessing configuration where a voltage controller **10** is used to charge a target **12** or **12'**. In FIG. **2**A, the target **12** is a flat panel. In FIGS. **2**B and **2**C, the target **12'** is a mandrel or rotary drum. In FIGS. **2**B and **2**C, the target **12** may be rotated during electroprocessing in order to take up thicker non-woven mats of multilayer fibers. The Target **12** or **12'** can be of many different shapes and sizes to suit the needs of the application.

[0030] Each of FIGS. **2**A-**2**C, show a source **13** having a feedblock **14** and multiplier section **15** that allow combining a plurality of polymers from polymer sources **16***a*-**16***n*. The multiplier section **15** can have zero to a plurality of multipliers (e.g., 2, 3, 7, 10, 20, etc.) depending on the application. With zero multipliers, the feedblock **14** will be used to introduce a layered polymer melt for electroprocessing. However, in some applications, it will be advantageous to have 50 or 100 or more layers in each fiber (the Examples below show formation of fibers with 247 layers). In the present invention, the fibers produced will have at least two different layers of two different polymers (the Examples below show some fibers produced with three different layers having two different polymers, wherein in one Example the outer layers are PE and the inner layer is PCL and in another Example the inner layer is PE and the outer layer is PCL). While the Examples below show combining two polymers into one multilayered fiber, it will be recognized that a plurality of the polymers can be combined by co-extrusion. Thus, fibers having layers of three different polymers, four different polymers, five different polymers, etc. can be made according to the present invention. Thus, FIGS. **2**A-C are depicted with polymer sources **16**A-**16**N, where N equals the number of polymers being combined. Further, the polymers in the polymer sources **16**A-**16**N may themselves be polymer blends.

[0031] For simplicity, FIGS. **2**A-**2**C show a single source **13**. However, it should be recognized that in the practice of the present invention there can be a plurality of sources interacting with a single target **12** or **12'** during electroprocessing, and that the polymers provided by each of the sources can be the same or different. Furthermore, different operational designs can be used for each of the sources to achieve the formation of multilayer fibers of different diameter as well as mixtures of multilayer fibers and multilayer droplets. In the context of the invention, what is required is that the polymers provided by source **13** have at least two different layers of two different polymers. The thickness of each of the layers of polymers in the fiber can be varied by a variety of means including by control of pumps (not shown) from the polymer sources **16**A-**16**N.

[0032] In FIGS. **2**A-**2**C, the stream of polymer **18** emanating from the nozzles or "tips" **20** or **20'** directed towards the target **12** or **12'** can be controlled. For example, source **13** could supply a stream **18** of multilayer fibers or a mixture of multilayer fibers and droplets towards target **12**, or source **13** could supply a stream **22** of multilayer fiber which may include branching. Control of the streams can be achieved by a variety of mechanisms including controlling polymer supply pumps, regulating the nozzle **20** or **20'** sizes in the sources **13**, regulating the charge on the polymer and/or target **12** or **12'**, etc. Ultimately, the target **12** or **12'** will receive a mass of multilayer fibers generally configured as a non-woven mat. The multilayer fibers can have some crosslinking with the polymers in adjacent fibers, and can contain multilayer droplets interspersed with the multilayer fibers. The bottom of FIG. **2**C shows a plan view of the tip **20'** where there are multiple orifices for emitting multiple streams of polymer during electroprocessing. With this design a thick mat can be created over a wide area in a short term.

[0033] FIG. **3** illustrates the process of converting the multilayer fibers created by coextrusion/electroprocessing to ribbon shaped fibers, as shown by Example 7 below. The fibrous mat **50** from the electrospinning target is placed in a delaminating device **52** such as a sonicating bath. The sonicating bath **50** can contain any suitable fluid (e.g., water, solvents, etc.) for permitting ultrasonic energy to interact with the

fibers such as, for example, a mixture of isopropanol and water. Alternatively, delamination may be achieved chemically by, for example, exposure to chloroform, ethyl acetate, or other solvent. Further, chemical and physical techniques may be used in combination, for example, by exposure to chloroform or ethyl acetate which promotes delamination (e.g., by a rinse) in combination with exposure to energy (e.g., sonication). Delamination can be achieved fairly quickly. For example, sonication of a multilayered polyethylene/polycaprolactone fiber of less than 100 μm in diameter achieved delamination in approximately 30 seconds. FIG. **3** shows the delaminated fibers **54** can be retrieved as a mat from the delaminator (sonicating bath) **52**. The delaminated fibers **54** are comprised of a plurality of ribbon shaped fibers, typically on the order of nanometers in thickness where each individual ribbon is of one distinct material. FIG. **3** also shows that active agents **56** (such as biological active agents, catalytic agents, etc.) can be deposited on the delaminated fibers **54**. This can be accomplished by spraying the active agent onto the mat, dipping the mat into a pool of active agents, electroplating the active agent onto the mat, and by many other means recognized by those of skill in the art. In addition, while FIG. **3** shows application of the active agent **56** to the delaminated fibers **54**, in some applications, active agents could simply be applied to the mat of multilayer fibers **50**.

[0034] The fibrous mats produced according to the invention can be used in a wide variety of applications including without limitation filtration, protective clothing, drug delivery, tissue engineering, and nanocomposites. The fibrous materials have significantly higher surface areas than currently manufactured nanofibers, which can provide superior properties in many applications. In addition, the fibrous materials are manufactured in a "solvent free" manner which avoids many of the manufacturing risks and costs encountered in current electrospinning processes.

EXAMPLES

[0035] In the Examples below, the polymeric components are melted in a single screw extruder and transported via gear pumps to a 3 layer feedblock, where the two polymers are formed into a single flow stream of 3 alternating layers. This 3 layer melt stream is delivered to a layer multiplier that has seven multipliers where the 3 layer stream is cut and stacked seven times to have final melt stream that has 257 alternating layers. This melt stream is delivered to a single orifice die and electrospun into fibers by the application of a high voltage to a flat plate collector which is positioned at a suitable distance across from the die.

[0036] The size and structure of the electrospun fibers were obtained using a LEO (Zeiss) 1550 field emission scanning electron microscope (FE-SEM) in the secondary electron mode. Scanning electron microscopy images were obtained at different magnifications and the fiber diameters were measured using image analysis software.

[0037] For delamination, the melt electrospun fibers and webs were immersed in a water/isopropanol (w/w 80/20) mix and exposed to sonication using a Tekmar Sonic Disruptor at different intensities and time periods. These materials were viewed in the SEM to determine if delamination of the layers occurred and to what extent it occurred.

Example 1

[0038] A melt electrospun fiber and web of the present invention was made using polycaprolactone (PCL) resin (CAPA 6250 available from Persorp UK Ltd) and polyethylene (PE) resin (Epolene C-10 available from Westlake Chemical Corporation). The polymer pellets were fed to two extruders connected to gear pumps to control the flow, which fed the melt streams to a 3 layer feedblock. Both extruders and the feedblock were maintained at about 356° F. The feedblock split the two melt streams and arranged them in an alternating fashion into a 3 layer melt stream on exiting the feedblock, with the outer layers being PCL. The PCL PE ratio was maintained at a 50:50 ratio by adjusting the gear pumps and the flow rate of both gear pumps were maintained at 1 revolution per minute (RPM). The layered melt stream was fed to a layer multiplier that had 7 multipliers, which cut and stacked the layered stream 7× and resulted in a melt stream that had 257 layers upon exiting the layer multiplier. The layer multiplier was maintained at about 356° F. This stream with 257 alternating layers was fed to a single orifice die which was maintained at about 356° F., and a voltage of 58 kV was applied to a flat plate collector placed 6 inches away from the die to electrospin a fibrous web. The resulting web had each fiber comprised of 258 alternating PCL/PE layers.

[0039] A scanning electron micrograph (SEM) of the electrospun fiber produced according to this Example 1 is presented in FIG. **4**. The diameter of the fiber is approximately 5-10 μm.

Example 2

[0040] A melt electrospun fiber and web, comprising 257 layer fibers was prepared according to the procedure described in Example 1, except the voltage applied was 42 kV.

[0041] An SEM of the electrospun fibers is presented in FIG. **5**. The fiber diameters are approximately in the 25 to 30 μm range.

Example 3

[0042] A melt electrospun fiber and web, comprising 257 layer fibers was prepared according to the procedure described in Example 1, except the flow rate of both gear pumps were maintained at 2 RPM's, the voltage was 60 kV and the flat plate collector was placed 4 inches away from the die.

Example 4

[0043] A melt electrospun fiber and web of the present invention was made using polycaprolactone (PCL) resin (CAPA 6250 available from Persorp UK Ltd) and polyethylene (PE) resin (Epolene C-10 available from Westlake Chemical Corporation). The polymer pellets were fed to two extruders connected to gear pumps to control the flow, which fed the melt streams to a 3 layer feedblock. Both extruders and the feedblock were maintained at about 320° F. The feedblock split the two melt streams and arranged them in an alternating fashion into a 3 layer melt stream on exiting the feedblock, with the outer layers being PCL. The PCL:PE ratio was maintained at a 50:50 ratio by adjusting the gear pumps and the flow rate of both gear pumps were maintained at 0.5 RPM's. This stream with 3 alternating layers was fed to a single orifice die which was maintained at about 320° F., and a voltage of 60 kV was applied to a flat plate collector placed 4 inches away from the die to electrospin a fibrous web. The resulting web had each fiber comprised of 3 alternating PCL/PE layers.

Example 5

[0044] A melt electrospun fiber and web of the present invention was made using polyethylene (Epolene C-10 available from Westlake Chemical Corporation) and polypropylene (PP) resin (PP 3746G available from Exxon-Mobile Corporation). The polymer pellets and granules were fed to two extruders connected to gear pumps to control the flow, which fed the melt streams to a 3 layer feedblock. Both extruders and the feedblock were maintained at about 392° F. The feedblock split the two melt streams and arranged them in an alternating fashion into a 3 layer melt stream on exiting the feedblock, with the outer layers being PE. The PE:PP ratio was maintained at a 50:50 ratio by adjusting the gear pumps and the flow rate of both gear pumps were maintained at 0.5 RPM. This stream with 3 alternating layers was fed to a single orifice die which was maintained at about 392° F, and a voltage of 60 kV was applied to a flat plate collector placed 3 inches away from the die to electrospin a fibrous web. The resulting web had each fiber comprised of 3 alternating PE/PP layers.

Example 6

[0045] A melt electrospun fiber and web, comprising 3 layer fibers was prepared according to the procedure described in Example 5, except that PCL was substituted for PE, the PCL extruder temperature was maintained at 356° F., the PP extruder and feedblock temperatures were maintained at 428° F., the die temperature was maintained at 536° F., the voltage was 62 kV and the flat plate collector was placed 10 inches away from the die.

Example 7

[0046] A melt electrospun fiber web described in Example 1 was immersed in a water/isopropanol (w/w 90/10) mix and exposed to sonication using a Tekmar Sonic Disruptor at a setting of 3 for 30 minutes. FIG. **6** shows an SEM of the resulting material. Thick, ribbon shaped fibers are observed due to delamination of the layers.

Example 8

[0047] A melt electrospun fiber and web of the present invention was made using polycaprolactone (PCL) resin (CAPA 6250 available from Persorp UK Ltd) and polypropylene (PP) resin (PP 3746G available from Exxon-Mobile Corporation). The polymer pellets and granules were fed to two extruders connected to gear pumps to control the flow, which fed the melt streams to a 3 layer feedblock. Both extruders and the feedblock were maintained at about 356° F. The feedblock split the two melt streams and arranged them in an alternating fashion into a 3 layer melt stream on exiting the feedblock, with the outer layers being PCL. The PCL:PP ratio was maintained at a 50:50 ratio by adjusting the gear pumps and the flow rate of both gear pumps were maintained at 1 revolution per minute (RPM). The layered melt stream was fed to a layer multiplier that had 7 multipliers, which cut and stacked the layered stream 7X and resulted in a melt stream that had 257 layers upon exiting the layer multiplier. The layer multiplier was maintained at about 356° F. This stream with 257 alternating layers was fed to a single orifice die which was maintained at about 356° F., and a voltage of 63 kV was applied to a flat plate collector placed 10 inches away from the die to electrospin a fibrous web. The resulting web had each fiber comprised of 257 alternating PCL/PP layers.

[0048] A melt electrospun fiber web described in this Example 8 was immersed in a beaker of chloroform with a magnetic stirrer and exposed to gentle agitation for 30 minutes. FIG. **7** shows an SEM of the fibrous material where at least a portion of the layers of the multilayer melt electrospun fibers have been delaiminated.

Example 9

[0049] A melt electrospun fiber and web of the present invention was made using polycaprolactone (PCL) resin (CAPA 6250 available from Persorp UK Ltd) and polyethylene (PE) resin (Epolene C-10 available from Westlake Chemical Corporation). The polymer pellets were fed to two extruders connected to gear pumps to control the flow, which fed the melt streams to a 3 layer feedblock. Both extruders and the feedblock were maintained at about 356° F. The feedblock split the two melt streams and arranged them in an alternating fashion into a 3 layer melt stream on exiting the feedblock, with the outer layers being PCL. The PCL:PE ratio was maintained at a 1:2 ratio by adjusting the gear pumps and the flow rate of both gear pumps were maintained at 0.5 and 1.0 revolution per minute (RPM) respectively. The layered melt stream was fed to a layer multiplier that had 7 multipliers, which cut and stacked the layered stream 7× and resulted in a melt stream that had 257 layers upon exiting the layer multiplier. The layer multiplier was maintained at about 356° F. This stream with 257 alternating layers was fed to a single orifice die which was maintained at about 356° F., and a voltage of 65 kV was applied to a flat plate collector placed 10 inches away from the die to electrospin a fibrous web. The resulting web had each fiber comprised of 257 alternating PCL/PE layers.

[0050] A melt electrospun fiber web produced as described in this Example 9 was immersed in a beaker of chloroform with a magnetic stirrer and exposed to gentle agitation for 30 minutes. FIG. **8** shows an SEM of the fibrous material with delamination of at least a portion of the layers.

1-27. (canceled)

28. A method of producing ribbon shaped fibers or a fibrous substrate which includes ribbon shaped fibers, comprising the steps of:

co-extruding two or more polymers;

producing a fiber containing a plurality of alternating layers of two or more different polymers from the co-extruded polymers; and

delaminating the fiber to yield fiber ribbons of individual polymers co-extruded in said co-extruding step.

29. The method of claim **28**, wherein the co-extruded polymers are electroprocessed in said producing step to produce said fiber containing a plurality of alternating layers of two or more different polymers and wherein said fiber has a diameter of 50 μm or less.

30. The method of claim **29**, wherein said electroprocessing and delaminating steps are performed under conditions which produce a fibrous substrate configured as a non-woven.

31. The method of claim **28**, wherein said fiber has a diameter of 10 μm or less.

32. The method of claim **28**, wherein said fiber has at least three layers.

33. The method of claim **28**, wherein said fiber has at least 50 layers.

34. The method of claim **28**, wherein said delaminating step is performed by sonication of said fiber.

35. The method of claim **28**, wherein said delaminating step is performed by chemical exposure of said fiber.

36. The method of claim **28**, wherein said delaminating step is performed by sonication and chemical exposure of said fiber.

37. The method of claim **28**, further comprising depositing a bioactive agent on said fiber ribbons.

38. The method of claim **28**, further comprising depositing a catalytic agent on said fiber ribbons.

39. The method of claim **28**, further comprising depositing a fire or flame retardant on said fiber ribbons.

40. Ribbon shaped fibers or a fibrous substrate which includes ribbon shaped fibers, produced by the process of:

co-extruding two or more polymers;

producing a fiber containing a plurality of alternating layers of two or more different polymers from the co-extruded polymers; and

delaminating the fiber to yield fiber ribbons of individual polymers co-extruded in said co-extruding step.

41. The ribbon shaped fibers or a fibrous substrate which includes ribbon shaped fibers of claim **40**, wherein the co-extruded polymers are electroprocessed in said producing step to produce said fiber containing a plurality of alternating layers of two or more different polymers and wherein said fiber has a diameter of 50 μm or less.

42. The ribbon shaped fibers or a fibrous substrate which includes ribbon shaped fibers of claim **40**, wherein said delaminating step is performed by sonication of said fiber.

43. The ribbon shaped fibers or a fibrous substrate which includes ribbon shaped fibers of claim **40**, wherein said delaminating step is performed by chemical exposure of said fiber.

44. The ribbon shaped fibers or a fibrous substrate which includes ribbon shaped fibers of claim **40**, wherein said delaminating step is performed by sonication and chemical exposure of said fiber.

45. The ribbon shaped fibers or a fibrous substrate which includes ribbon shaped fibers of claim **40** configured as a non-woven.

46. The ribbon shaped fibers or a fibrous substrate which includes ribbon shaped fibers of claim **40** further comprising a bioactive agent deposited on said ribbon shaped fibers or said substrate.

47. The ribbon shaped fibers or a fibrous substrate which includes ribbon shaped fibers of claim **40** further comprising a catalytic agent deposited on said ribbon shaped fibers or said substrate.

48. The ribbon shaped fibers or a fibrous substrate which includes ribbon shaped fibers of claim **40** further comprising a fire or flame retardant deposited on said ribbon shaped fibers or said substrate.

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