Controlling the Architecture of Nanofiber-Coated Microfibers Using Electrospinning

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ABSTRACT: This study shows that electrospinning nanofibers onto single microfibers allows for careful tailoring of material properties that may suit a wide variety of applications. The nanofiber-coated microfibers are created by electrospinning nanofibers alongside a microfiber toward a collector that rotates around the microfiber. This force the nanofibers to be collected around the microfiber, creating a hierarchical structure that can be modified at nano scale. In this study, control of nanofiber diameters, nanofiber alignment, and nanofiber loading was evaluated. It was seen that varying polymer concentration affected the nanofiber diameters, collecting the nanofiber-coated microfibers at different speeds changed the degree of alignment of the nanofibers and that changing the polymer feeding rate affected the loading density of the nanofibers collected. The carefully designed nanofiber-coated microfibers have great potential in creation of highly porous materials with tailored properties down to nano scale. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 511–517, 2010

Key words: electrospinning; nanofibers; biopolymers; surfaces; biomaterials

INTRODUCTION

With the rapid progress in the field of nanotechnology, a new arena for the use of textile materials has been found. High surface-to-volume ratios, highly porous structures, and flexibility are some of the advantages of nanofibrous nonwovens. Possibilities of modifying and designing nanofiber materials at a nano scale level open up new doors to creation of highly intricate hierarchical structures for applications in such diverse areas as solar cells, fuel cells, membranes and filters, chemical and biological protection, sensors, drug delivery, and tissue regeneration.[1–6]

Electrospinning is a straightforward method used to produce nanofibers from a wide variety of materials, including polymers, ceramics, and metals.[7–10] It is a very versatile method which allows for the production of fibers with very different morphologies. By varying polymers, solvents, and process parameters, it is possible to create beaded fibers, flat fibers, smooth fibers, porous fibers, core-sheath fibers, hollow fibers, etc.[7,11] Furthermore, apart from the morphology of the fibers themselves, the overall composition and architecture of the nanofibrous structure can be carefully designed in terms of alignment, incorporated particles, porosity, composite structure, etc.[4,7,12,13]

The diameters of the electrospun fibers are often of importance as these affect the available surface area in the electrospun material as well as the material porosity and pore sizes. Modifying the polymer concentration is the most common approach to varying the diameters of electrospun fibers as the diameters of the fibers are strongly related to the viscosity of the polymer solution and thereby also to the polymer molecular weight and concentration.[14–17] A viscosity that is too low results in electrospraying rather than spinning as droplets are formed instead of fibers.[13,16,18] Low solution viscosity also promotes formation of beads.[11] On the other hand, a viscosity that is too high results in clogging of the needle and thereby no fiber formation.[17]

Electrospinning usually results in random matrices; however, it is possible to use patterned collectors to achieve very specific fiber orientations or to use rotating collectors to create highly aligned fibers.[13,19–21] Alignment of electrospun fibers is commonly achieved by using a fast rotating collector which allows the fibers to be collected in a very organized aligned manner, or by using a collector formed as two electrodes placed at some distance, creating a gap between the electrodes, where aligned fibers can be deposited.[7,12,13] The main benefit of an aligned nanofiber matrix is the improved mechanical properties.[7] This has been utilized in vascular tissue

engineering for tubular structures aiming at mimicking native blood vessels.[7,22] Directing cell growth is another application of aligned nanofibers, a concept that has been used, for example, in nerve regeneration applications, where guided axonal growth is crucial.[12,19,22]

To create hierarchical structures, it is important to connect nanoscale features of nanofibers with larger microscale features. One approach may be to combine nanofibers and microfibers. This has been previously explored in the area of tissue engineering for creation of highly porous scaffolds with body-mimicking features. By combining nanofibers and microfibers in a scaffold, it is possible to increase the porosity and pore sizes of the scaffold, thereby enabling more efficient cell infiltration, mass transport, and oxygen delivery.[6,14,23–27]

As mentioned earlier, there are limitations in the span of fiber diameters that can be electrospun. To overcome this limitation, a combination of electrospinning and other technologies for producing fibers can be used. Fiber bonding and electrospinning have been combined to create microfibers and nanofibers, respectively, in a layered scaffold for tissue engineering.[25,28] The authors have previously explored an alternative method to combine nanofibers and microfibers by preparing nanofiber-coated microfibers.[5] The electrospinning setup was modified so that the nanofibers were ejected alongside a melt spun microfiber moving slowly towards a small collector rotating around the microfiber. The rotation of the collector forced the nanofibers to be intertwined with the microfiber, hence creating a nanofiber-coated microfiber. Further, the nanofiber-coated microfibers were packed into scaffolds with porosities over 90%.[5] These scaffolds were seeded with human chondrocytes and cultured for two weeks. When comparing scaffolds of nanofiber-coated microfibers with pure nanofiber scaffolds, it was observed that the infiltration of cells was significantly enhanced in the scaffolds containing both nano- and microstructures. It was furthermore noted that the nanofiber-coated microfiber could be formed into structures of any size, shape, and porosity.

This study continues the investigation of the nanofiber-coated microfibers, focusing on the possibilities of tailoring the structure on nano scale to suit different applications. The control of the alignment of nanofibers is investigated as well as the possibility of varying the loading (g/m) of nanofibers onto each microfiber. Furthermore, the relation between fiber concentration and fiber diameter is investigated. Poly-L-lactic acid (PLLA) nanofibers are electrospun onto single Poly(lactic acid) (PLA) microfibers. PLA is a widely used biocompatible and biodegradable biopolymer that has been previously electrospun.[6] It is concluded that by using the method of nanofiber-coated microfibers, it is possible to create fibers with a wide range of nano scale morphologies. This is a key issue for the development of new nano structured materials as tailoring of the material for different applications will prove to be of great importance.

MATERIALS

Poly(lactic acid) (PLA) (100%) (Terramac, 70,000–10000 g/mol, %D $<$ 3) from Unitika Co. (Tokyo, Japan) was used as microfiber. Two filaments (diameter 15 μm each) from the filament yarn were used, thereby ending up with a microfiber diameter of 30 μm. Before being used, the fibers were washed by swirling in 20 wt % sodium lauryl sulfate (Sigma Aldrich, St Louis, MO) for 2 min and rinsing in pure water. For electrospinning of nanofibers, Poly-L-lactic acid (PLLA) (85.000–160.000 g/mol, Sigma Aldrich, St Louis, MO) was dissolved in 7 : 3 (vol) ratio of chloroform/ethanol.

METHODS

Electrospinning

The effect of polymer concentration on electrospun PLLA nanofiber diameter was initially investigated using traditional electrospinning. Polymer concentrations evaluated were 3, 5, 7.5, 10, 15, and 20 wt %. A syringe capped with a blunt needle (0.6 mm i.d.) was filled with PLLA solution. A 5 × 5 cm aluminium foil was grounded and used as collector. The distance between the needle and the collector was 10 cm and the voltage was set to 20 kV (HV power supply, Gamma High Voltage Research, Ormond Beach, FL). The flow rate of the polymer solution was 0.6 mL/h.

Nanofiber-coated microfibers were electrospun as previously described.[5] Briefly, a syringe capped with a blunt needle (0.6 mm i.d.) was filled with PLLA solution, and the needle was charged with 20 kV (HV power supply, Gamma High Voltage Research). The collector was a 1 × 1 cm copper tape mounted on a disk rotating around the microfiber. The distance between the needle and the collector was 13 cm. The rotating collector, along with a Teflon tube between syringe and collector, was used to force the nanofibers to the microfiber. The nanofiber-coated microfibers were collected on a rotating wheel using a 230 V, 10 rpm motor.

To evaluate the possibilities of controlling the nanofiber loading on each microfiber (mass of nanofibers per unit length of microfiber, g/m), the alignment of the nanofibers and the diameters of the nanofibers, three different electrospinning parameters were varied: polymer feeding rate (0.6, 1, 2,

4, and 6 mL/h), polymer concentration (5, 7.5, 10, and 15 wt %), and collection speed (5×10^{-3}, 11×10^{-3} and 21×10^{-3} m/s) of the microfiber through the spinning process.

The speed of the microfiber through the spinning was controlled by varying the size of the wheel onto which the nanofiber-coated microfibers were collected, a larger wheel yielding a higher collection speed.

All experiments, i.e., electrospinning under each parameter setting, were repeated three times on different days to limit the effects of possible variations in environmental parameters such as temperature and humidity.

After electrospinning, all samples were kept in a fume hood for at least 24 h to allow residual solvent to evaporate.

Fiber characterization

Fiber morphology was evaluated using a scanning electron microscope (SEM), JSM-5300 (JEOL, Tokyo, Japan). The samples were sputter coated with gold prior to SEM analysis using Fine Coat Ion Sputter JFC-1100, JEOL, Tokyo, Japan.

Nanofiber diameters were measured using the software SemAfore, Ver. 4.02. About 10 m of nanofiber-coated microfibers were electrospun from each polymer concentration and 5 samples were randomly taken and imaged from each such fiber. Ten nanofibers per image were measured, i.e., in total, 50 nanofibers per polymer concentration. Means and standard deviations were calculated.

The alignment of nanofibers on the microfiber was measured using the software ImageJ. A reference line was drawn along the orientation of the microfiber, and the angle between the line and each nanofiber was calculated using the software. A total of six images each of the low (5×10^{-3} m/s) and the high (21×10^{-3} m/s) fiber collection speeds were taken. All images were taken from different nanofiber-coated microfibers to avoid a fiber being measured multiple times. The orientation of 20 electrospun fibers on each image was calculated. Resulting orientation angles ranged from 0–90°, with 0° being parallel to the reference line.

Loading of nanofibers onto each microfiber (g/m) was determined by measuring UV absorbance with a Perkin Elmer (Waltham, MA) UV/Vis Spectrophotometer Lamda 14. A known concentration of a methyl red derivative was mixed into the spin solution, and 8 m of nanofiber-coated microfibers were produced at polymer feeding rates at 0.6 and 2 mL/h, respectively. The fibers were diluted in chloroform and absorbance was measured at 433 nm. Loading of nanofibers was determined using a calibration curve.

RESULTS AND DISCUSSION

By electrospinning nanofibers onto single microfibers and forming these nanofiber-coated microfibers into desired three-dimensional matrices, it is possible to create very porous structures with nano features, reaching porosities that are not possible to achieve using traditional electrospinning. As shown in this study, it is possible to tailor the morphology of the fibers with regards to features such as nanofiber diameters, degree of nanofiber alignment, and nanofiber loading, i.e., amount of nanofibers electrospun onto each microfiber (g/m).

Nanofiber diameter

A trend of increasing fiber diameters with increasing polymer concentration was observed, and the fibers were in the same size range, 0.2–2.5 μm, when being produced either by traditional electrospinning or as nanofiber-coated microfibers (Fig. 1). When using traditional electrospinning, fiber diameters obtained were in the range of 0.33 ± 0.07 μm at 5 wt %, 0.65 ± 0.14 μm at 7.5 wt %, 1.00 ± 0.24 μm at 10 wt %, and 1.62 ± 0.33 μm at 15 wt %. For the nanofiber-coated microfibers, diameters were in the range of 0.32 ± 0.06 μm at 5 wt %, 0.68 ± 0.19 μm at 7.5 wt %, 1.58 ± 0.26 μm at 10 wt %, and 1.71 ± 0.33 μm at 15 wt %. It can thereby be observed that at polymer concentrations of 10 wt % and higher, the electrospun fibers are in microscale. To avoid any confusion, the fibers electrospun onto microfibers are however referred to as nanofibers.

The observation on traditional electrospinning confirms results of other research groups.[14,15] The relationship between fiber diameters and polymer
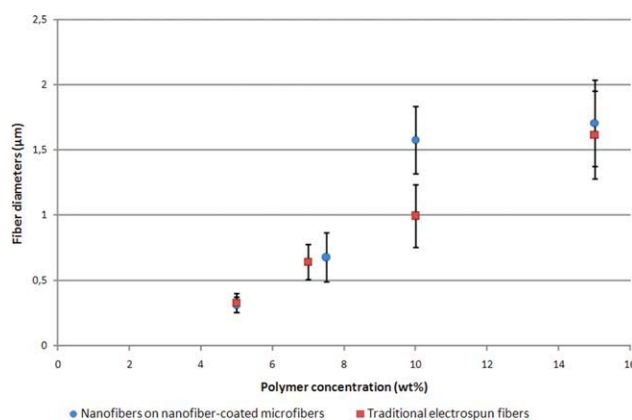

Figure 1 Relationship between diameters of electrospun PLLA fibers and polymer concentration when producing traditional electrospun fibers (■) and nanofiber-coated microfibers (●). Nanofibers (40–50) of each concentration measured and means calculated. Standard deviations are also displayed. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
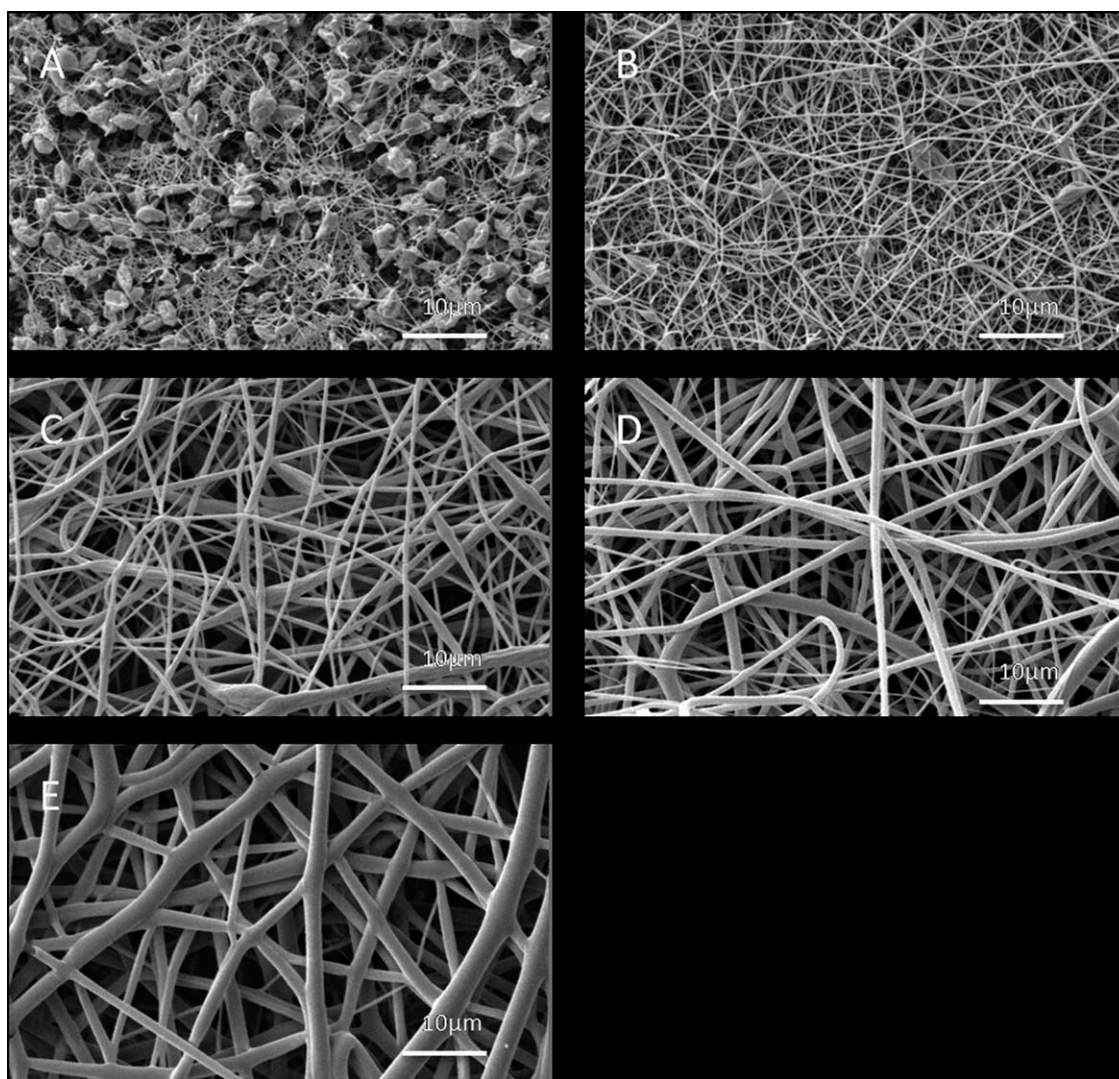
Figure 2   SEM images of PLLA nanofibers electrospun from polymer solutions of (A) 3 wt %, (B) 5 wt %, (C) 7.5 wt %, (D) 10 wt %, and (E) 15 wt %. Solvent used was 7 : 3 (vol) ratio of chloroform/ethanol. The scale bar is 10 µm in all images.

concentration is seen also in the SEM images (Figs. 2 and 3). For traditional electrospinning, PLLA concentrations between 5 and 15 wt % generated smooth fibers (Fig. 2). At a lower concentration, bead formation was extensive, an observation in agreement with the observation of other researchers.[15] At concentrations over 15 wt %, the viscosity of the polymer solution became too high, making electrospinning impossible. Also for the nanofiber-coated microfibers, beaded structures were observed at a low polymer concentration (5 wt %); whereas, increasing the polymer concentration above 5 wt % resulted in a decrease in the number of beads and an increase in fiber diameters (Fig. 3). True nanofibers (<1 µm) without beads are created from polymer concentrations of 5–10 wt %.

Besides polymer concentration, the nanofiber diameter is somewhat affected by the polymer feeding rate and also to some extent the strength of the electric field, as discussed in studies performed by other research groups.[14–17] However, these parameters are not explored further here.

By controlling the diameters of the electrospun fibers, it is possible to control the available surface area in the material. This affects, for example, the release of particles possibly incorporated into the material or the effect of a surface modification. Moreover, for tissue engineering applications, the availability of surfaces for cell adhesion is important.[29,30]

Nanofiber alignment

Using the method for producing nanofiber-coated microfibers, it is possible to create random as well as aligned nanofiber orientations upon the individual
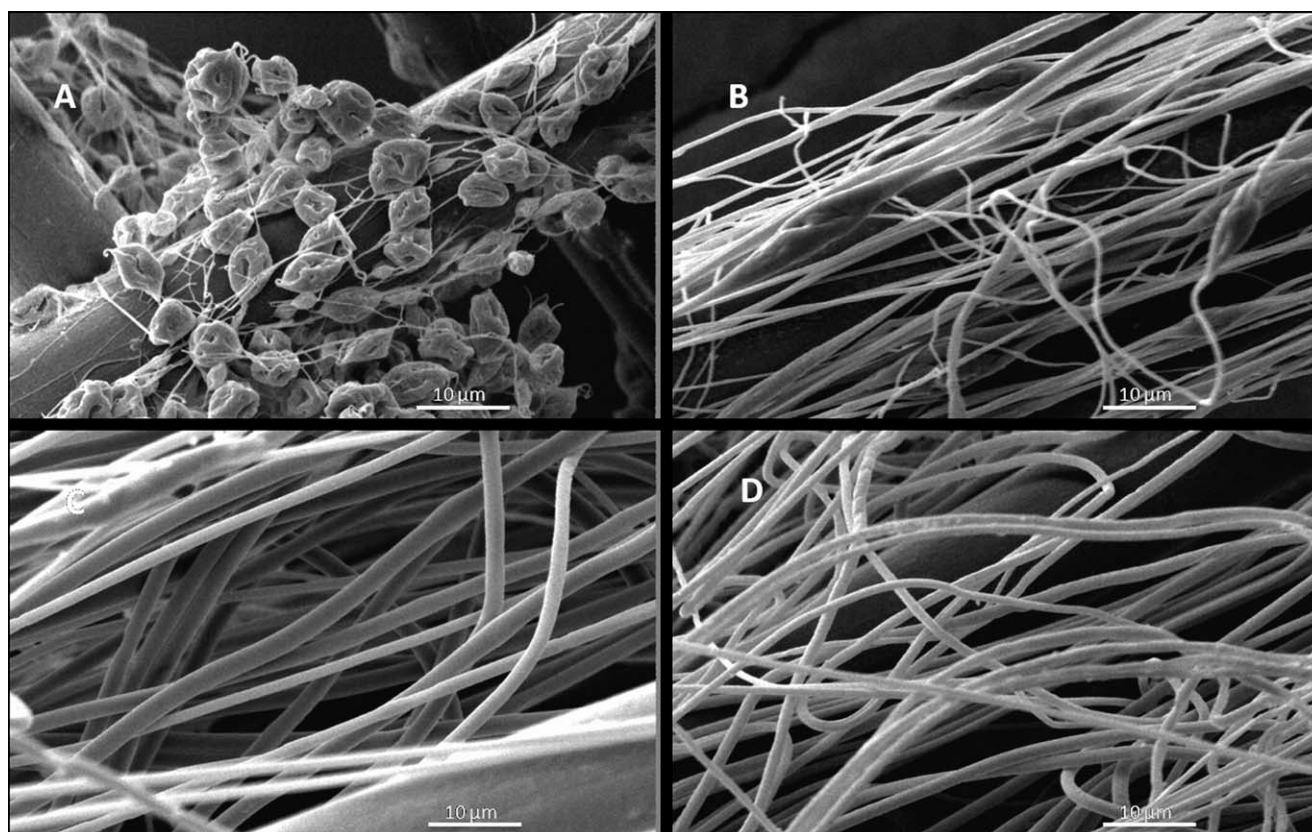
Figure 3 SEM images of PLLA nanofibers electrospun onto PLA microfibers from polymer solutions of (A) 5 wt %, (B) 7.5 wt %, (C) 10 wt %, and (D) 15 wt % PLLA. Solvent used was 7 : 3 (vol) ratio of chloroform/ethanol. The scale bar is 10 μm in all images.

microfibers (Fig. 4). A 10 wt % polymer concentration was chosen to show representative images of made observations. The same trends were seen with all polymer concentrations (5–15 wt %). As can be seen in the SEM images in Figure 4, collecting nanofibers at a microfiber moving at a high speed yields a high degree of nanofiber alignment along the microfiber [Fig. 4(A)], whereas a slower movement

of the microfiber yields a random distribution of fiber orientations [Fig. 4(B)]. It has been seen in previous studies that a high degree of alignment of nanofibers can be achieved with a fast rotating mandrel.[7,12,13] However, in this case it is most likely another mechanism that causes the observed alignment since the "high speed" of the microfiber is as low as 21×10^{-3} m/s, a speed which is not
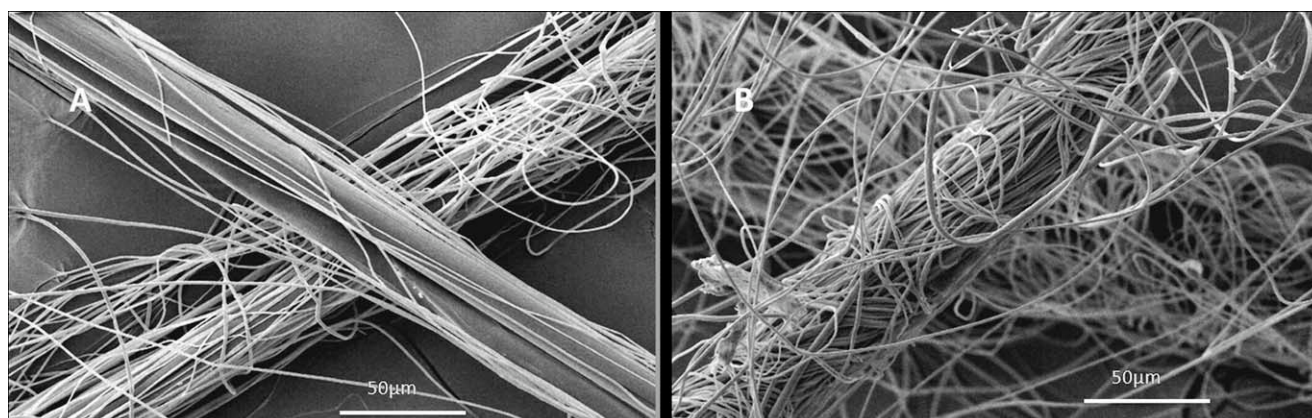

Figure 4 PLA microfibers coated with electrospun PLLA fibers achieved with a 10 wt % PLLA solution in 7 : 3 (vol) ratio of chloroform/ethanol and with fiber collection rates of (A) 21×10^{-3} m/s and (B) 5×10^{-3} m/s.
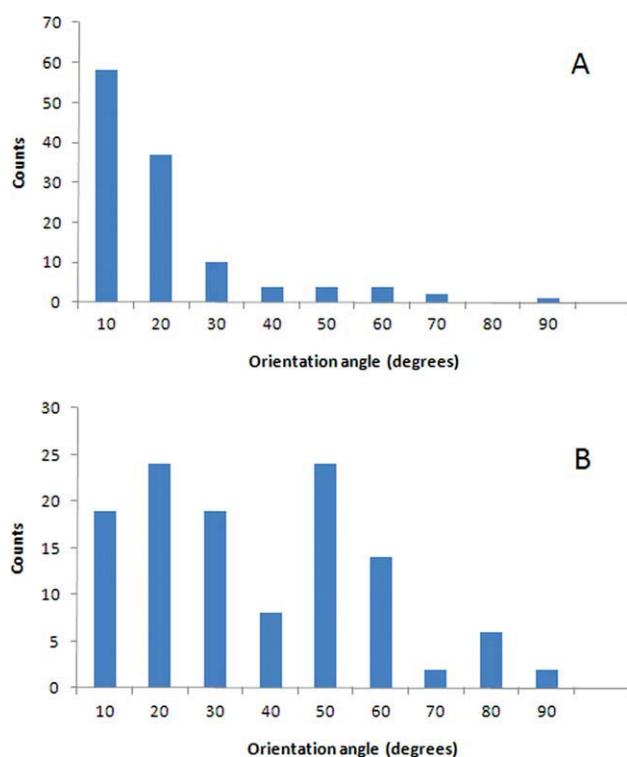
Figure 5 Distribution of nanofiber orientation angles when using (A) a high (21×10^{-3} m/s) and (B) a low (5×10^{-3} m/s) fiber collection speed, as seen as the angle difference between each fiber and a reference line set along the direction of the microfiber. Data from a total of 120 nanofibers for each speed was collected. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

comparable to the much faster speed required for alignment on a rotating mandrel.[7,12,13] Further studies are necessary to understand this mechanism.

Beside the visual difference in fiber orientation between the two fiber collection speeds, as seen in Figure 4, measuring the angles between a reference line along the axis of the microfiber and each nano-

fiber resulted in a distribution of orientation angles such as seen in Figure 5. Again, a high fiber collection speed resulted in a more aligned structure with a narrower span of angles [Fig. 5(A)]; whereas, a low fiber collection speed resulted in a wider distribution of nanofiber orientations [Fig. 5(B)].

The results of the study show that it is possible to control the alignment of nanofibers along the direction of the microfiber. This is very promising, not least in tissue engineering where cell guidance is of great interest, for example in nerve regeneration.[12,19,22] In assembling the nanofiber-coated microfibers with aligned nanofibers, it could be possible to create very intricate, carefully tailored, structures of aligned fibers.

Nanofiber loading

The loading of nanofibers on the microfiber (g/m) can be controlled by the polymer feeding rate. A higher feeding rate results in more nanofibers on the microfiber, as seen in Figure 6. At a polymer feeding rate of 0.6 mL/h, the nanofiber loading was limited, the nanofibers were few, and the distances between them were relatively large [Fig. 6(A)]. When increasing the feeding rate to 4 mL/h a much higher nanofiber loading, i.e., a more dense nanofiber layer, was observed [Fig. 6(B)]. When increasing the feeding rate above 4 mL/h, the electrospinning process became instable, observable as large variations in the amount of deposited nanofibers, and fibers not attaching to the microfiber but rather to the Teflon tube that helps to direct the nanofibers toward the microfiber. A 10 wt % polymer concentration was chosen to show representative images of made observations. The same trends were seen with all polymer concentrations (5–15 wt%).

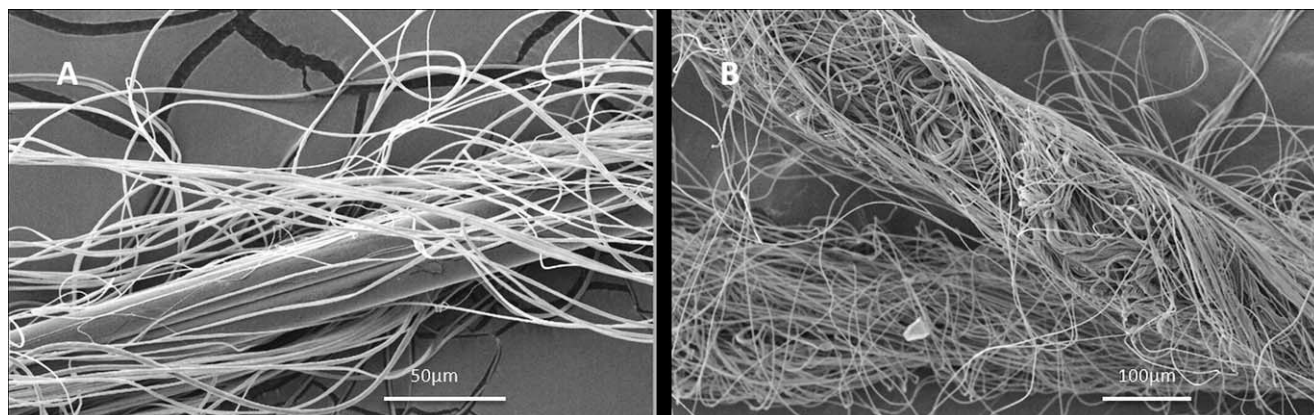The observed increase in nanofiber loading was confirmed by preliminary data from UV absorbance

Figure 6 PLA microfibers coated with electrospun PLLA fibers achieved with a 10 wt % PLLA solution in 7 : 3 (vol) ratio of chloroform/ethanol and with polymer feeding rates of (A) 0.6 mL/h and (B) 4.0 mL/h.

measurements of a methyl red derivative incorporated in the nanofibers. An almost five-fold increase (119 μg/m vs 25 μg/m) in mass of nanofibers per meter of microfiber was indicated when comparing a nanofiber-coated microfiber produced at a high polymer feeding rate (2mL/h) compared to a low (0.6 mL/h). More measurements must be made to confirm these results, but it can be concluded that the presented method is valid for evaluating the nanofiber loading and could be used in further studies.

In further investigations, increasing the conductivity of the microfiber would be very interesting to even more carefully directing the nanofibers toward the microfiber and thereby possible allowing for even higher nanofiber loading and a higher production rate. Surface modifications, incorporations of particles (CNTs, etc.), or use of different materials could be viable approaches to increase the conductivity of the microfiber.

Another parameter that affects the nanofiber loading is the fiber collection speed, i.e., the speed of the collection of nanofiber-coated microfiber controlled by the size of the collection wheel. At a lower speed, the microfiber gets a higher load of nanofibers as it stays in the electric field for a longer time, whereas, at a higher speed it is the opposite (Fig. 4).

For further investigations, the diameter of the microfiber is another parameter that most likely would affect the nanofiber loading, as a larger microfiber would make it possible for more nanofibers to be deposited.

CONCLUSIONS

It can be concluded that electrospinning is a highly versatile method, and by modifying it to produce nanofiber-coated microfibers, it can be used to create carefully designed hierarchically structured materials for a wide variety of applications. It was seen in this study that fiber diameters, nanofiber alignment, and nanofiber loading could be modified by parameters such as polymer concentration, speed of collection of the nanofiber-coated microfiber, and polymer feeding rate. Thus, the material design using the method of nanofiber-coated microfibers stretches over nano scale as well as micro scale, opening up for almost endless possibilities of variations and modifications beneficial for different applications.

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