

Preparation and Characterization of Zein and Zein/Poly-L-lactide Nanofiber Yarns

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Received 18 August 2008; accepted 25 May 2009

DOI 10.1002/app.30807

Published online 30 June 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Zein and zein/poly-L-lactide (PLLA) nanofiber yarns were prepared by conjugate electrospinning using coupled spinnerets applied with two high electrical voltages of opposite polarities in this article. Structure and morphology of zein yarns were investigated by SEM and X-ray diffraction. The results showed that zein yarn consisted of large quantity of fibers with diameters ranging from several hundreds nanometers to a few microns, and zein concentration played a significant role on the diameter of nanofibers in yarns. To improve mechanical property of

nanofiber yarns, PLLA was then incorporated with zein. Zein/PLLA composite nanofiber yarns conjugate electrospun from solution with concentration of 7.5% (zein, w/v)/7.5% (PLLA, w/v) exhibited tensile strength of 0.305 ± 0.014 cN/dtex. The composite yarns showed better nanofiber alignment along the longitudinal axis. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2079–2086, 2009

Key words: zein; poly-L-lactic acid; electrospinning; nanofibers; yarn

INTRODUCTION

Electrospinning, a process that uses an electric field to control the formation and deposition of polymer nanofibers, has attracted more attention since electrospun nanofibers were identified as viable candidates for tissue engineering constructs.^{1,2} Electrospun nanofibers produced from rapidly whipping jet are often collected as randomly oriented structures in the form of nonwoven mats. Recently, Theron et al.³ suggested that well-aligned and highly ordered structures of electrospun nanofibers were much more suitable than nonwoven nanofiber mats for potential application in micro- and optoelectronics, e.g., nanowires, light emitting diodes (LEDs), and photocells etc. Recently, favorable interactions between smooth muscle cells (SMCs) and unique scaffold with aligned architecture, and directional growth of the cells along the fiber orientation were demonstrated by Xu et al.⁴ More researches revealed that aligned nanofibrous scaffolds not only served as culture environment capable of presenting nanometer-scale topographical cues with potential to modulate cell behavior^{5,6} but also produced con-

structs with anisotropic mechanical properties.^{7,8} Aligned electrospun scaffolds were also considered as promising biomaterials for engineering fibrous musculoskeletal tissues, as they reproduced mechanical anisotropy of these tissues and could direct ordered neo-tissue formation.⁹

Mechanical and electrostatic means have been explored to obtain well-aligned structure of electrospun nanofibers. Electrospun nanofibers could be aligned more parallel to each other when a drum rotating with high speed was used as a collector.¹⁰ Zussman et al.¹¹ demonstrated the use of a wheel-like bobbin as a collector to deposit and align individual polymer nanofibers into parallel arrays. Li et al.¹² prepared uniaxially aligned nanofibers over large areas by introducing a gap into conventional collector. Another method developed by Smit et al.¹³ was to deposit nanofibers into water to eliminate charges of the charged nanofibers which were collected together, and yarns were drawn out. More recently, a simple method of electrospinning to produce continuous yarns was developed using spinnerets in pairs applied with two high electrical voltages of opposite polarities respectively.^{14–16} In the previous report, the method called conjugate electrospinning and effects of process parameters on the morphology of poly-L-lactic acid (PLLA)/nanocalcium phosphate nanofiber yarns were explored.¹⁷ Besides, multiple conjugate electrospinning using several pairs of spinnerets was developed to obtain thicker yarns having higher tensile strength. The thicker and stronger aligned

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Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 50573011, 50673019.

continuous nanofiber yarns may be knitted or braided to fabricate 3-D scaffold for tissue engineering.

Zein has been widely used as raw materials for applications in adhesive, chewing gum, coatings for food products, fibers, cosmetic powder, microencapsulated pesticides, etc.¹⁸ Zein is also potential material for use in the production of biodegradable plastics.^{19,20} In recent years, many researches have provided proofs that zein may be used for promising applications in the areas of biomaterials and drug delivery.²¹ Liu et al.²² developed ivermectin-loaded zein microspheres with good biocompatibility by phase-separation method. Gong et al.²³ showed that rat mesenchymal stem cells (MSCs) could adhere, grow, proliferate and differentiate toward osteoblasts on porous zein scaffold which also exhibited osteoconductive properties in the presence of dexamethasone. In our previous study, ribbon-like zein fibers were electrospun from aqueous ethanol solutions, even in high polymer concentrations.²⁴ Zein/hyaluronic acid and zein/silk fibroin composite fibrous membranes were also produced to fabricate nanostructured scaffolds with improved mechanical properties and biocompatibility.^{25,26}

In this report, zein and zein/PLLA nanofiber yarns were prepared by conjugate electrospinning to extend the applications of zein in biomedicine and fabrics fields. Effect of zein concentration on the morphology of nanofiber yarns was investigated. PLLA was introduced to fabricate zein/PLLA composite nanofiber yarns to improve mechanical properties of nanofiber yarns.

EXPERIMENTAL

Materials

Purified zein was purchased from Acros Organics (NJ). PLLA with the average viscous molecular weight ($M\eta$) of 210,000 was synthesized from L-lactide using tin 2-ethylhexanoate as catalyst.²⁷

Preparation of zein nanofiber yarns

Zein was dissolved in aqueous ethanol with volume ratio of ethanol/water of 70/30 (v/v). Viscosity, conductivity and surface tension of the aqueous ethanol solutions with zein concentration ranging from 5 to 45% (w/v, g/mL) were measured with viscometer (NDJ-9S, ShangPing), conductivity meter (DDB-303A, Rex) and surface tension meter (BZY-1, HengPing) at 20°C, respectively. Solutions with zein concentration varied of 15, 20, 25, 30, 35% (w/v, g/mL) in aqueous ethanol with the ratio of ethanol/water 70/30 (v/v) were prepared.

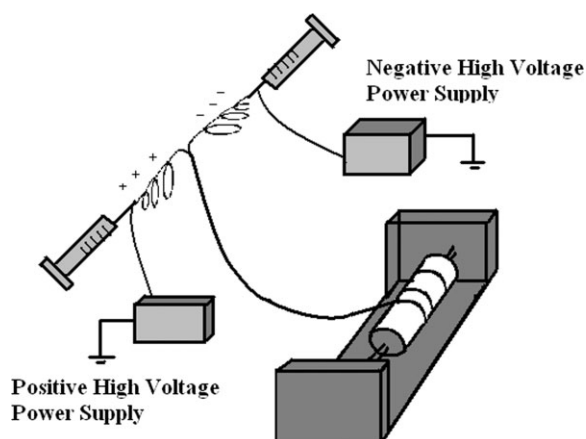


Figure 1 Schematic illustration of conjugate electrospinning and formation of nanofiber yarn.

Conjugate electrospinning of zein is carried out using setup as shown in Figure 1, which consists of two high voltage power supplies with opposite polarities, two spinnerets, syringes pumps and a receiver drum. The as-prepared spinning solutions were delivered by syringes to two spinnerets at the rate of 6 mL/h, respectively. Applied high voltage with opposite polarities was fixed in a range from ± 8 to ± 15 kV, and distance between the two spinnerets was set from 10 to 20 cm. The receiver was a rotating drum controlled by a stepping motor. Under the action of electrical field, jets on the spinnerets tips were stretched out and started whipping to form charged nanofibers. Nanofibers from the two oppositely charged electrospinning spinnerets attracted each other and strike together, forming nanofiber yarns which was then drawn out and collected by the drum receiver with a speed of 10 m/min. The obtained nanofiber yarns were dried under vacuum to constant weight.

Preparation of zein/PLLA composite nanofiber yarns

Zein and PLLA were dissolved in dimethyl formamide generating 6, 10, 15% (w/v, g/mL) stock solutions, respectively. Then zein and PLLA stock solutions with same concentration were mixed at volume ratio of 1/1 to prepare three blend solutions with zein concentration of 3, 5, and 7.5% (w/v, g/mL) and zein/PLLA weight ratio of 1/1. Zein/PLLA blend solutions were conjugate electrospun at delivery rate of 6 mL/h/spinneret and applied voltage of ± 8 kV. Distance between the two spinnerets was fixed at 20 cm. Zein/PLLA composite nanofiber yarns were drawn out and collected by the drum receiver with a speed of 20 m/min. The composite nanofiber yarns were then dried under vacuum to constant weight.

Characterization

Morphology of zein and zein/PLLA nanofiber yarns was observed by Mirero AIS2100 scanning electron microscope (Seron Technologies) after gold sputter-coating. Percents of nanofibers related to angles between long axis of the nanofiber and its expected direction in a range of 0°–90° was determined from SEM images by using GAIA Image Analysis Tool Program, with values being calculated from at least 100 measurements.

Wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) of zein powder, electrospun nanofiber mats and yarns electrospun from zein aqueous ethanol solution (70/30, v/v) with concentration of 30% (w/v) were investigated by Rigaku D/MAX 2500VL/PC diffractometer system, using Cu K α radiation at 40 kV and 200 mA. Intensities of peaks were recorded with a scan speed of 5° min⁻¹ in the 2 θ range of 3–50° (0.5° min⁻¹ in the 2 θ range of 0.4–2°) and a step size of 0.02°.

Mechanical properties of zein/PLLA composite nanofiber yarns were measured by YG001A electronic fiber strength tester (Taicang Textile Instrument Factory) at cross-head speed of 10 mm/min. Ten samples were tested for each type of the composite yarns. The tensile strength was expressed as loading (centi-Newton)/fineness. The fineness of zein/PLLA nanofiber yarns (decitex, dtex) was determined before tensile test as mass of yarn in grams per 10,000 meters length.

RESULTS AND DISCUSSION

Zein nanofiber yarns

Zein nanofiber yarns were prepared by conjugate electrospinning. Figure 2 shows typical SEM images of zein nanofiber yarns electrospun from aqueous ethanol solutions with zein concentration of 15, 20, and 30% (w/v). One single yarn consists of large quantity of zein fibers with diameters about hundreds of nanometers to several microns. Bead-on-string morphology was first obtained at zein concentration of 15% (w/v) [Fig. 2(a)]. The beaded nanofibers with small diameters held together to form tightly close yarn. Distribution density of beads decreased significantly and shape of beads became spindle-like when zein concentration was increased to 20% (w/v) [Fig. 2(c)]. A minimum zein concentration to conjugate electrospin smooth and uniform nanofibers without beads was found to be 25% (w/v). As zein concentration increased to 30% (w/v), the diameter of electrospun fibers in yarns became larger [Fig. 2(e)]. To characterize the alignment of zein nanofibers in yarns, statistical analysis on the angles between long axis of nanofiber and its expected perpendicular direction in a range of

0°–90° was determined from the SEM images. As shown in Figure 2(b,d), majority of zein nanofibers electrospun from 15 and 20% (w/v) solutions had a wide-angle distribution in the range of 0°–50°, whereas the distribution shifted to the region of 0°–30° for zein nanofibers electrospun from 30% (w/v) solution [Fig. 2(f)].

These SEM images indicated that zein nanofiber yarns produced by conjugate electrospinning exhibited concentration dependence of final nanofiber diameters, similar to conventional electrospinning. This trend is more clearly evident from statistical analysis of the average fiber diameters shown in Figure 3. With the increase of zein concentration, the viscosity of zein aqueous ethanol solution increased as shown in Figure 4(a). But, the conductivity and surface tension of zein solution changed slightly with increasing zein concentration from 15 to 35% (w/v) [Fig. 4(b)]. Polymer solution with higher viscosity usually exhibits longer stress relaxation times, which may facilitate the formation of smooth fibers with large diameters during electrospinning.²⁸ As viscosity of zein solution increased greatly from 0.104 to 0.308 Pa·s with increasing zein concentration from 25 to 35% (w/v) [Fig. 4(a)], average fiber diameter increased from 1.17 to 1.91 μ m [Fig. 3]. Therefore, it was considered that viscosity of solution was the major factor affecting diameters of zein nanofibers in yarns.

WAXD diagrams of zein powder, electrospun nanofiber mats and yarns are shown in Figure 5. Zein powder had a sharp peak at 2 θ = 8.96° (9.86 Å) and a broad peak at around 2 θ = 19.58° (4.53 Å) [Fig. 5(a)]. The shorter d-spacing around 4.5 Å is believed to be related to the average backbone distance within α -helix structure of zein, whereas the larger d-spacing around 10 Å is thought to be the spacing of the inter-helix packing or the mean distance of approach of neighboring helices as described in the literature.²⁹ Zein electrospun mats showed similar peaks at 2 θ = 8.94° (9.88 Å) and 2 θ = 20.28° (4.38 Å) as the zein powder [Fig. 5(b)]. However, zein nanofiber yarns showed a very weak peak at 2 θ = 8.94° (9.88 Å) and a very broad peak, centered at ca. 2 θ = 22.04° (4.03 Å) [Fig. 5(c)]. Since the d-spacing around 10 Å is related to the inter-helix packing or approach of neighboring helices, the decrease in its intensity implies the disruption of zein molecular aggregates. Wang et al.³⁰ indicated that basic α -helix structure in zein was stable and not easily changed by heating, dissolution, and mechanical treatment employed. So difference of two peaks among zein powder, electrospun nanofiber mats and yarns may reflect structural changes depending on the side-chain packing. Furthermore, no preferred orientation along the axis of zein nanofiber yarn was indicated.

Figure 6 shows SAXS diagrams of the same samples presented in Figure 5. Zein powder showed no

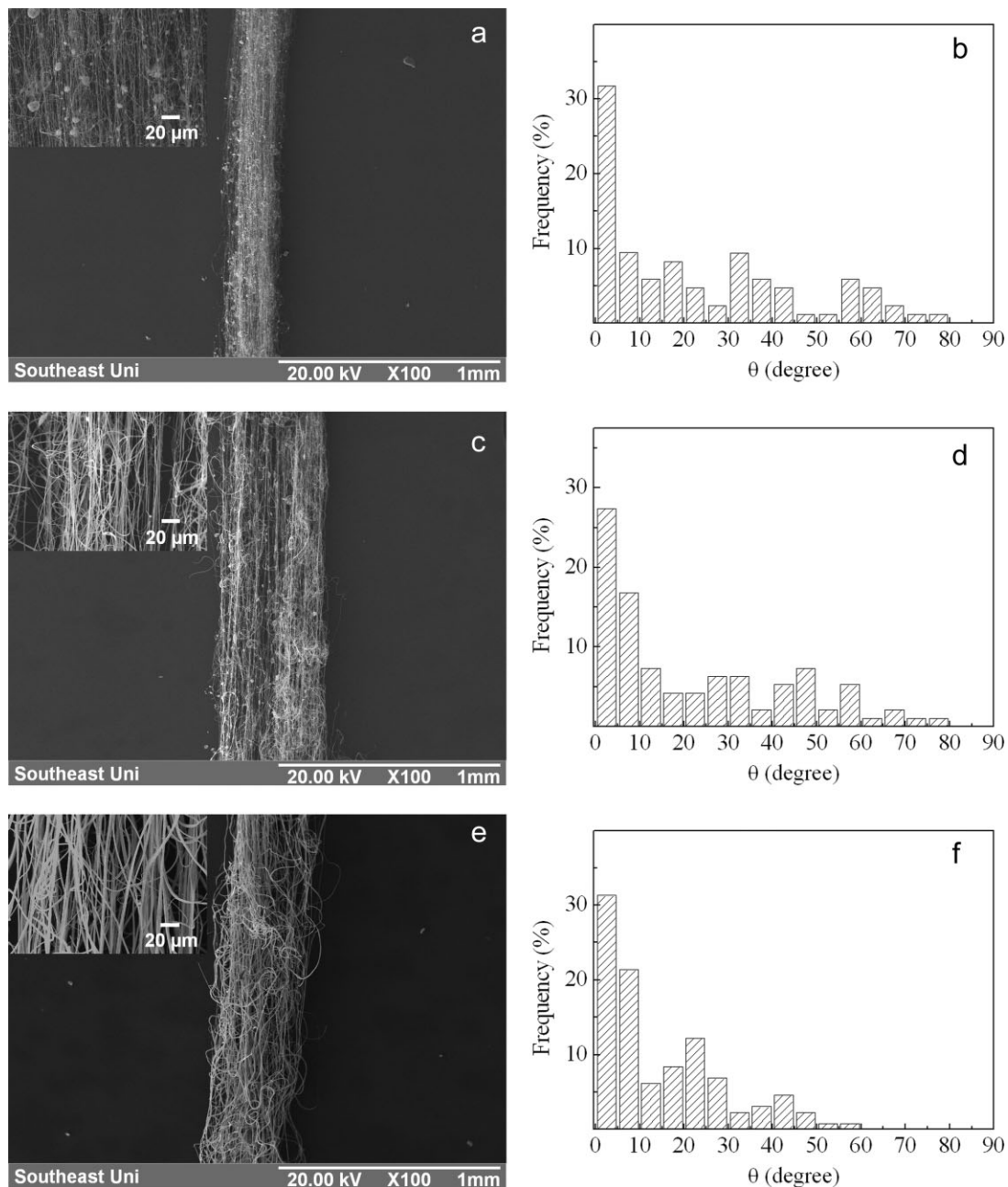


Figure 2 SEM images of zein nanofiber yarns conjugate electrospun from aqueous ethanol solutions (70%, v/v) with zein concentration of (a): 15%; (c): 20%; and (e): 30% (w/v). (b) (d) (f): Degree of aligned zein nanofibers along the axis of yarn (Percents of nanofibers related to angles between long axis of nanofiber and its expected perpendicular direction were measured from SEM images). Conjugate electrospinning condition: delivery rate: 6 mL/h/spinneret; distance between two spinnerets: 20 cm; drawing speed: 10 m/min. Scale bar: (a) (c) (e) 1 mm (inset: 20 μ m).

apparent peaks over the small-angle range, which suggested that molecular aggregates in the powder had no long-range periodicity [Fig. 6(a)]. In contrast, diffuse peaks were observed at 0.58° (152.19 Å) for zein electrospun nanofiber mats and at 0.52° (169.75 Å) for yarns [Fig. 6(b,c)]. The results indicated that electrospinning process, including dissolution, stretching and whipping, facilitated the arrangement of zein molecules into long-range periodic structures. Random coils in primary structure of zein

may unfold during the conjugate electrospinning process and enlarge molecular dimensions along the long side thus yielding larger SAXS spacing for nanofiber yarns than that for nanofiber mats.

Zein/PLLA composite nanofiber yarns

Zein nanofiber yarns were fragile and their mechanical properties could not be tested. Different zein/PLLA weight ratios were used for preparing

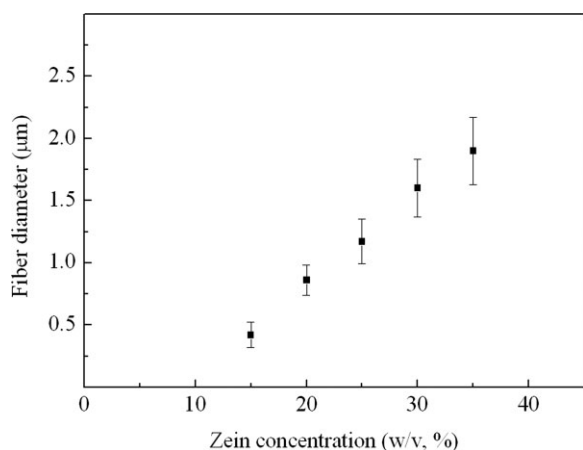


Figure 3 Average diameters of zein nanofibers in yarns electrospun from aqueous ethanol solutions (70%, v/v) with different zein concentrations.

composite nanofiber yarns in our preliminary experiments. It is found that solution jets were not stable at zein/PLLA weight ratios of 4/1, 3/1, 2/1, and the

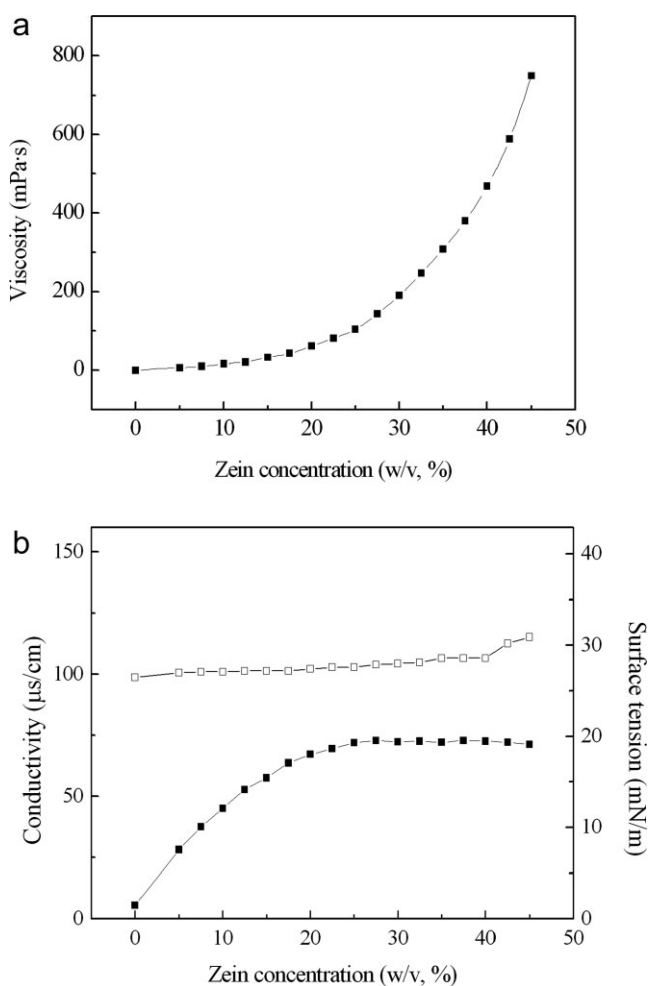


Figure 4 (a) Viscosity, (b) conductivity (■) and surface tension (□) of zein aqueous ethanol solutions (70%, v/v) with different zein concentrations.

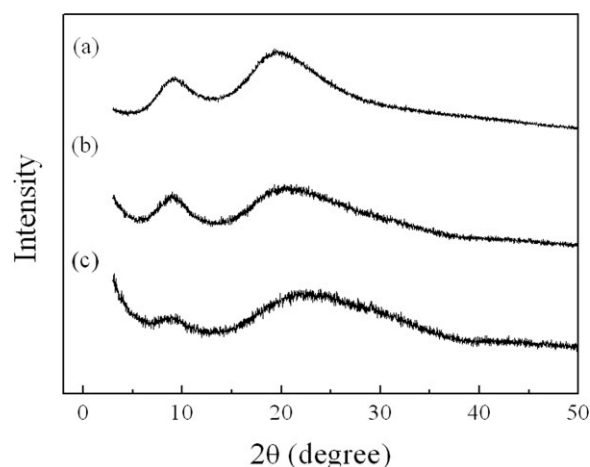


Figure 5 WAXD diagrams of (a) zein powder; (b) zein electrospun mats; (c) zein nanofiber yarns.

obtained yarns were fragile. In this work, zein was blended with PLLA at weight ratio of 1/1 to conjugate electrospin composite nanofiber yarns to improve mechanical properties and process stability. SEM images of zein/PLLA composite nanofiber yarns electrospun from mixture solution with zein concentration of 3%, 5%, 7.5% (w/v), and zein/PLLA weight ratio of 1/1 are shown in Figure 7. Tightly close nanofiber yarns with bead-on-string morphology of fibers were formed at zein concentration of 3% (w/v) and zein/PLLA weight ratio of 1/1 [Fig. 7(a)]. Average diameter of composite nanofibers in yarns was approximately 300 nm. As indicated in Figure 7(b), majority of zein/PLLA composite nanofibers had aligned angle distribution in the range of 0°–40° between long axis of nanofiber and its expected perpendicular direction. As zein/PLLA concentration increased to 5%/5%, elongated beads and fibers with larger average diameter of 460 nm were observed [Fig. 7(c)]. Nearly 80% of nanofibers

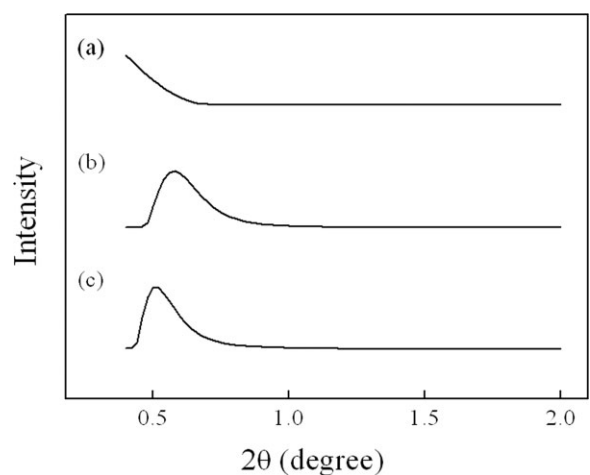


Figure 6 SAXS diagrams of (a) zein powder; (b) zein electrospun mats; (c) zein nanofiber yarns.

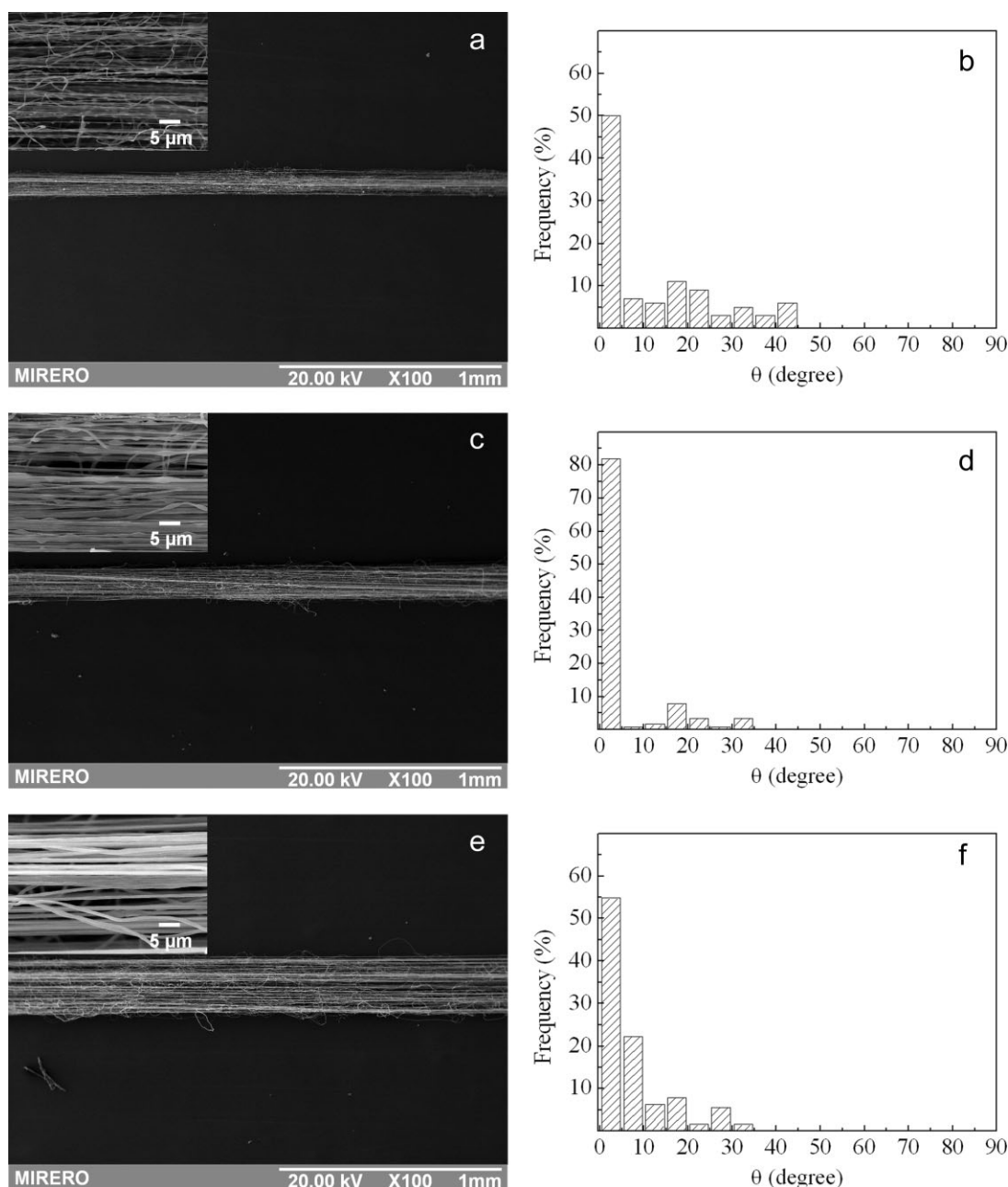


Figure 7 SEM images of zein/PLLA composite nanofiber yarns with zein/PLLA weight ratio of 1/1; zein concentration of: (a) 3%; (c) 5%; (e) 7.5% (w/v). (b) (d) (f): Degree of aligned zein/PLLA nanofibers along the axis of yarn (Percents of nanofibers related to angles between long axis of nanofiber and its expected parallel direction were measured from SEM images). Conjugate electrospinning condition: delivery rate: 6 mL/h/spinneret; distance between two spinnerets: 20 cm; drawing speed: 20 m/min. Scale bar: (a) (c) (e) 1 mm (inset: 5 μm).

in the zein/PLLA yarns were aligned well ($<5^\circ$) along longitudinal axis which formed a unique aligned topology [Fig. 7(d)]. Smooth and uniform fibers with diameter of about 800 nm were obtained at zein/PLLA concentration of 7.5%/7.5% [Fig. 7(e)], and good alignment of composite nanofibers was also achieved, having an aligned angle distribution in a range of 0° – 30° [Fig. 7(f)].

Figure 8 shows the typical tensile loading-stress curves of zein/PLLA composite nanofiber yarns.

Tensile strength and elongation at break were obtained from the curves and summarized in Table I. Zein/PLLA composite nanofiber yarns with zein concentration of 3% (w/v) and zein/PLLA weight ratio of 1/1 had the tensile loading of $1.63 \text{ cN} \pm 0.11 \text{ cN}$ and elongation of $23.03\% \pm 3.35\%$. Tensile loading of zein/PLLA composite nanofiber yarns increased dramatically from $3.62 \text{ cN} \pm 0.28 \text{ cN}$ to $10.78 \text{ cN} \pm 0.49 \text{ cN}$ as the concentration increased from 5%/5% to 7.5%/7.5%. Considering the large

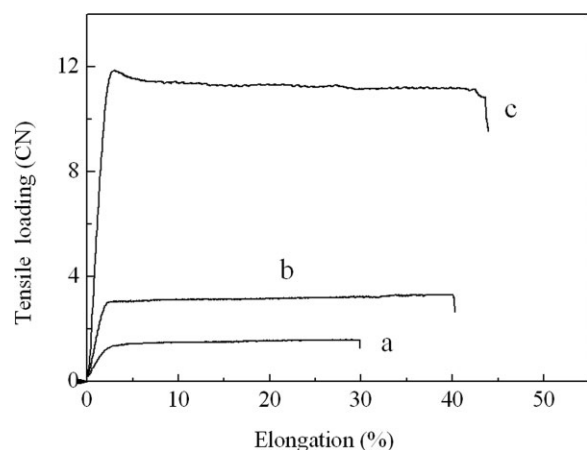


Figure 8 Tensile loading-strain curves of zein/PLLA composite nanofiber yarns electrospun from solutions with zein/PLLA concentration of (a): 3% (w/v)/3% (w/v); (b): 5%/5%; (c): 7.5%/7.5%.

fiber fineness of zein/PLLA composite nanofiber yarns electrospun from solutions with high concentrations, tensile strength of composite nanofiber yarns increased from 0.265 ± 0.021 cN/dtex to 0.305 ± 0.014 cN/dtex. Meanwhile, elongation at break of zein/PLLA composite nanofiber yarns showed no significant difference as concentration increased

TABLE I
Mechanical Properties of zein /PLLA Composite nanofiber yarns

Sample ^a	Average fiber fineness (dtex)	Maximum Tensile loading (cN)	Elongation at break (%)	Tensile strength (cN/dtex)
a	6.67	1.63 ± 0.11	23.03 ± 3.35	0.244 ± 0.016
b	13.64	3.62 ± 0.28	40.15 ± 6.56	0.265 ± 0.021
c	35.29	10.78 ± 0.49	42.14 ± 5.81	0.305 ± 0.014

^a Zein/PLLA composite nanofiber yarns samples electrospun from solutions with zein/PLLA concentration of: (a) 3% (w/v)/3% (w/v); (b) 5%/5%; (c) 7.5%/7.5%.

from 5%/5% to 7.5%/7.5%. As the concentration of zein/PLLA blend increased, diameters and uniformity of the aligned angle of nanofibers in yarn increased. Consequently, tensile strength and elongation of the composite nanofiber yarn increased. Due to the larger fiber diameter, stress-strain curve of the composite yarns with zein/PLLA concentration of 7.5%/7.5% showed typical yielding behavior similar to PLLA fibers [Fig. 8 (c)].³¹

One hundred zein/PLLA composite nanofiber yarns electrospun from mixture solution with zein concentration of 7.5% (w/v) and zein/PLLA weight ratio of 1/1 were bundled and twisted to obtain zein

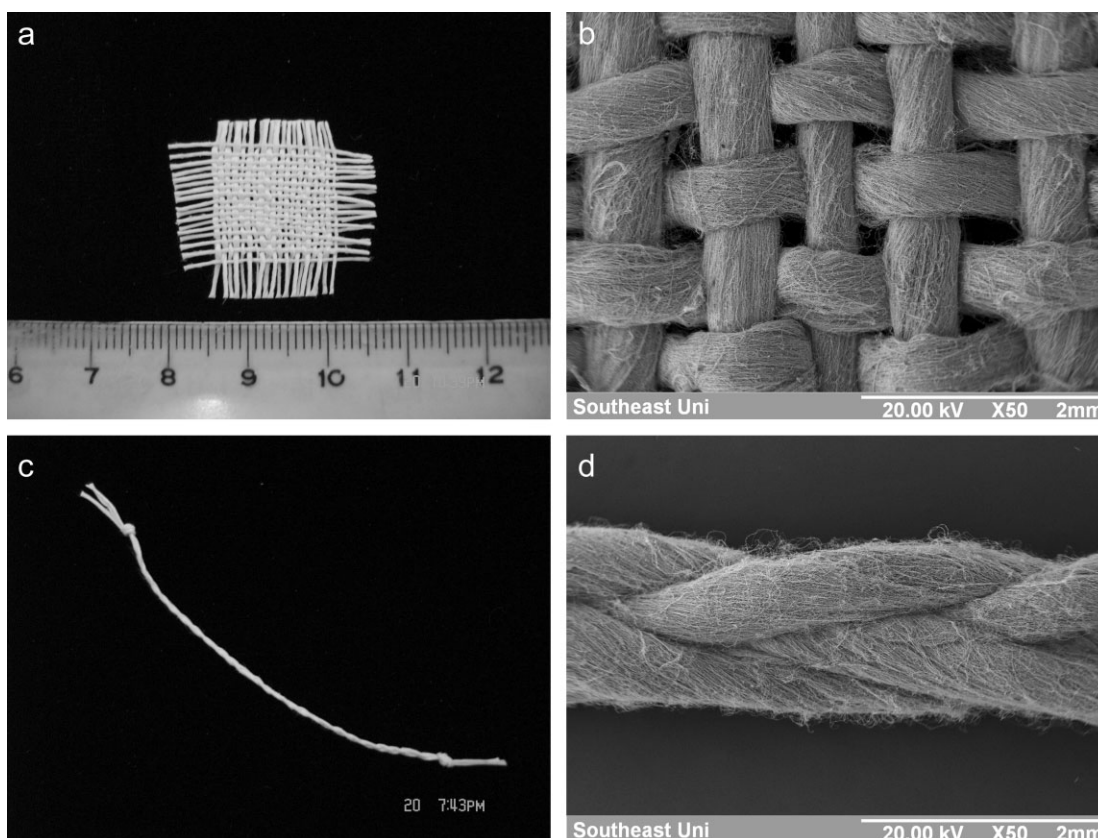


Figure 9 Photographs (a, c) and SEM images (b, d) of knitted fabric (a, b) and braided rope (c, d) of bundled zein/PLLA composite nanofiber yarns. Scale bar: (b) (d) 2 mm.

composite filaments. The as-prepared zein composite filaments were then knitted and braided manually to fabricate mesh fabric and rope as shown in Figure 9. Therefore, zein/PLLA composite nanofiber yarns with improved mechanical properties can be used to develop composite nanofiber structures, which may have potential applications in biomedicine and fabrics fields.

CONCLUSIONS

Zein nanofiber yarns were successfully prepared by conjugate electrospinning. Uniform nanofiber yarns without beads were produced with zein concentration more than 25% (w/v). Viscosity of zein solutions had a major effect on diameters of nanofibers. PLLA was incorporated into zein for conjugate electrospinning to improve mechanical properties of zein based nanofiber yarns. Majority of zein/PLLA nanofibers in the yarns were aligned along longitudinal axis. Zein/PLLA composite nanofiber yarns electrospun from solutions with higher concentration showed better tensile strength and larger elongation.

References

1. Wnek, G. E.; Carr, M. E.; Simpson, D. G.; Bowlin, G. L. *Nano Lett* 2003, 3, 213.
2. Sill, T. J.; Von Recum, H. A. *Biomaterials* 2008, 29, 1989.
3. Theron, A.; Zussman, E.; Yarin, A. L. *Nanotechnology* 2001, 12, 384.
4. Xu, C. Y.; Inai, R.; Kotaki, M.; Ramakrishna, S. *Biomaterials* 2004, 25, 877.
5. Lee, C. H.; Shin, H. J.; Cho, I. H.; Kang, Y. M.; Kim, I. A.; Park, K. D.; Shin, J. W. *Biomaterials* 2005, 26, 1261.
6. Dang, J. M.; Leong, K. W. *Adv Mater* 2007, 19, 2775.
7. Ayres, C.; Bowlin, G. L.; Henderson, S. C.; Taylor, L.; Shultz, J.; Alexander, J.; Telemeco, T. A.; Simpson, D. G. *Biomaterials* 2006, 27, 5524.
8. Courtney, T.; Sacks, M. S.; Stankus, J.; Guan, J. J.; Wagner, W. R. *Biomaterials* 2006, 27, 3631.
9. Baker, B. M.; Mauck, R. L. *Biomaterials* 2007, 28, 1967.
10. Fennessey, S. F.; Farris, R. J. *Polymer* 2004, 45, 4217.
11. Zussman, E.; Theron, A.; Yarin, A. L. *Appl Phys Lett* 2003, 82, 973.
12. Li, D.; Wang, Y. L.; Xia, Y. N. *Nano Lett* 2003, 3, 1167.
13. Smit, E.; Buttner, U.; Sanderson, R. D. *Polymer* 2005, 46, 2419.
14. Li, X. S.; Yao, C.; Song, T. Y. CN Patent ZL 200510038571.5 (2005).
15. Pan, H.; Li, L. M.; Hu, L.; Cui, X. J. *Polymer* 2006, 47, 4901.
16. Li, X. S.; Yao, C.; Sun, F. Q.; Song, T. Y. Preprints of Polymeric Materials Science and Engineering, 231st American Chemical Society National Meeting; Atlanta, GA, 2006; 94, 26.
17. Li, X. S.; Yao, C.; Sun, F. Q.; Song, T. Y.; Li, Y. H.; Pu, Y. P. *J Appl Polym Sci* 2008, 107, 3756.
18. Shukla, R.; Cheryan, M. *Ind Crop Prod* 2001, 13, 171.
19. Lai, H. M.; Padua, G. W. *Cereal Chem* 1997, 74, 771.
20. Wu, Q. X.; Yoshino, T.; Sakabe, H.; Zhang, H. K.; Isobe, S. *Polymer* 2003, 44, 3909.
21. Dong, J.; Sun, Q. S.; Wang, J. Y. *Biomaterials* 2004, 25, 4691.
22. Liu, X. M.; Sun, Q. S.; Wang, H. J.; Zhang, L.; Wang, J. Y. *Biomaterials* 2005, 26, 109.
23. Gong, S. J.; Wang, H. J.; Sun, Q. S.; Xue, S. T.; Wang, J. Y. *Biomaterials* 2006, 27, 3793.
24. Yao, C.; Li, X. S.; Song, T. Y. *J Appl Polym Sci* 2007, 103, 380.
25. Yao, C.; Li, X. S.; Song, T. Y. *J Biomat Sci Polym E* 2007, 18, 731.
26. Yao, C.; Li, X. S.; Song, T. Y.; Li, Y. H.; Pu, Y. P. *Polym Int* 2009, 58, 396.
27. Gilding, D. K.; Reed, A. M. *Polymer* 1979, 20, 1459.
28. Fong, H.; Chun, I.; Reneker, D. H. *Polymer* 1999, 40, 4585.
29. Lai, H. M.; Geil, P. H.; Padua, G. W. *J Appl Polym Sci* 1999, 71, 1267.
30. Wang, Y.; Filho, F. L.; Geil, P.; Padua, G. W. *Macromol Biosci* 2005, 5, 1200.
31. Mezghani, K.; Spruiell, J. E. *J Polym Sci Pol Phys* 1998, 36, 1005.