Melt Electrospinning from Poly(L-lactide) Rods Coated with Poly(ethylene-*co*-vinyl alcohol)

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ABSTRACT: Rodlike poly(L-lactide) (PLLA) samples coated with poly(ethylene-*co*-vinyl alcohol) (EVOH) were made. Fibers were produced from these rodlike samples by using a melt electrospinning system equipped with a laser irradiating device, and the effects of EVOH content and the processing parameters of the melt electrospinning on fiber diameters were investigated. We also studied the fiber formation mechanism from the rods during the laser melt electrospinning process. The following conclusions were reached: (i) coating of EVOH on PLLA rods has a remarkable effect on decreasing fiber diameter from 3 μm to around 1 μm; (ii) increases in the electric field strength and temperature of spinning space decrease the average diameter of fibers produced from pure PLLA rods, and longer collector distance leads to lager PLLA fiber diameter; and (iii) the migration of PLLA component from the core to the surface of electrospun fibers takes place during the fiber formation process. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1282–1288, 2009

Key words: PLLA; EVOH; laser melt electrospinning; SEM; DSC

INTRODUCTION

The polymer fiber materials with nano-scale fiber diameter have several amazing characteristics, such as a large surface area to volume ratio (up to 10^3 times greater than that of microfiber), flexibility in surface functionalities, and superior mechanical properties (e.g., high bending capacity). Electrospinning has been recognized as a nano- and microfiber manufacturing technique through the action of electrostatic forces, more than 50 polymers were successfully spun into fibers through this technique.[1–3] The collected fibers as nonwoven mats have great potential in filtration, biomedical applications for the tissue engineering of cell constructs, and sensing applications.[4–6] It is well known that both polymer solutions and polymer melts can be electrospun, but most previous work on electrospinning has focused on polymer solutions because its apparatus and processing conditions are simple. There is little study on melt electrospinning, because there are some underlying difficulties in melt electrospinning, including a high-temperature setup, high melt viscosity, and low conductivity of polymer melts. Studies on melt electrospinning reported in the earlier literature[7–9] have showed the formation of micron-scale fibers up to 10–50 μm in diameter, which are much larger than those obtained in solution electrospinning. However, recent melt electrospinning publications demonstrate that continuous fibers of approximately 1 μm in diameter are possible.[10–18]

Melt electrospinning can offer several advantages over solution electrospinning. First of all, in melt electrospinning the dissolution of polymers in organic solvents and their removal/recycling are no longer required. Second, a higher throughput can be achieved due to there being no loss in mass by solvent evaporation. Zhou et al.[13] concluded that the temperatures at the nozzle and in the spinning region strongly influence the average fiber diameter of polylactic acid fibers. Dalton et al.[15] demonstrated that using a viscosity-reducing additive or a gap method of alignment for collection can reduce fiber diameter from micron-scale diameters to hundreds of nanometers.

Our research group previously developed a melt electrospinning system with a CO_2 laser melting device.[16–18] The features of the system are as follows: (i) the system is simpler than that developed by other researchers because no nozzle is used, (ii) the laser beam heating prevents the electric discharge problems of the conventional melt electrospinning because heating is performed from a distance, (iii) the molten polymer can be locally and instantaneously melted

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TABLE I
Characterization of Rodlike Samples

Sample code	Sample 1	Sample 2	Sample 3
Volume ratio (PLLA : EVOH)	1 : 0	≈ 2 : 1	≈ 1 : 2
Diameter of rod (μm)	420–460	530–560	750–800

The core is PLLA and the sheath is EVOH.

and spun, avoiding long-term thermal degradation; the nozzle extruding method used in the traditional melt electrospinning systems exposes molten polymer to an elevated temperature in long term, and (iv) the system has a high fiber production rate.

Both poly(L-lactide) (PLLA) and poly(ethylene-*co*-vinyl alcohol) (EVOH) are biomaterials, and PLLA and EVOH fibers with a submicron average diameter have been successfully electrospun by using the laser melt electrospinning system.[16,17] Nanofiber mats made from these materials can be used as a scaffold for cell growth. In particular, PLLA is a biodegradable and biocompatible polymer that is being used in many applications, including packaging and biomedical fields. PLLA has an ecological significance, because it is synthesized from renewable resources.

In our previous studies, we found that fibers with smaller diameter can be produced from polymers that have polar groups, such as C=O and —OH by using the our developed system.[16,17] We also studied the melt electrospinning from rod/bundle consisting of PP/EVOH conjugated fibers; PP has no polar group and EVOH has polar —OH group.[19] It was found that PP/EVOH nanofibers can be produced from the rods, and PP nanofibers can be produced by the removal of EVOH component from the electrospun fibers; PP nanofibers cannot be produced from rods consisting of pure PP fibers. As an extension of the study, we are interested in the fiber formation process from PLLA/EVOH bicomponent system. In this work, rodlike PLLA/EVOH samples with core-shell structures were prepared to obtain PLLA/EVOH nanofibers using the laser melt electrospinning system, and we studied the relationship between fiber diameter and various process parameters, such as laser output power, high voltage, the collector distance, and the temperature of the spinning space. We also investigated the effects of EVOH content on fiber diameter and morphology. To study the structure of electrospun fibers, EVOH component was removed from the fibers with a proper solvent and we examined the morphological features of fibers formed during the laser electrospinning process.

EXPERIMENTAL PROCEDURES

Materials

Pellet-like PLLA samples were supplied by Cargill Dow (6251D, US). The characterization of PLLA pellets is as follows: MFI (210°C, applied load 21.6) = 76.9, D (%) = 1.4, L (%) = 98.6, T_m = 170.7°C, M_n = 96080. EVOH pellet-like samples were supplied by Kuraray Co. (Osaka, Japan). The characterization of EVOH pellets is as follows: MFI (190°C, applied load 21.6) = 1.6, the Ethylene content (mol %) = 32, Density (g/cc) = 1.19, T_m = 183°C.

Rodlike PLLA samples, 0.4–0.5 mm in diameter, about 30 cm in length, were made from the melt of these pellets with a Shimadzu Flow Tester CFT-500 (Kyoto, Japan); the temperature at the melting zone was 169°C, and the applied stress was 1 MPa. EVOH pellets were dissolved in 2-propanol/water (70 : 30, weight ratio) solution at 100°C with a magnetic stirrer to a concentration of 10 wt %. Some rodlike PLLA samples were hung in the air and dipped into EVOH solution every 10 min for different times and then held for 2 days. The thickness of EVOH layer was controlled by dipping times, and the layer thickness was measured with a dial thickness gauge after drying. The surface of these rods was unsmooth in this work. Table I shows the property of the rodlike samples. These rodlike samples were provided for melt electrospinning experiments.

Melt electrospinning system

The diagram of the laser melt electrospinning system[17–19] developed is schematically shown in Figure 1. A rodlike sample was fed to the laser melting zone at a rate of 10 mm/min. One end of the rod

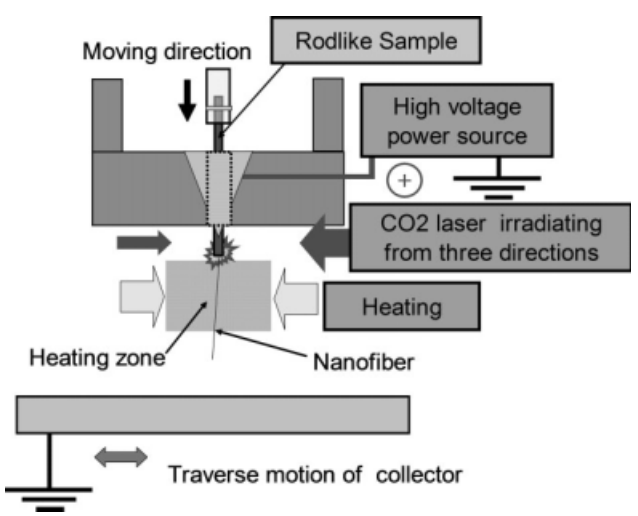

Figure 1 Schematic diagram of the laser melt electrospinning system.

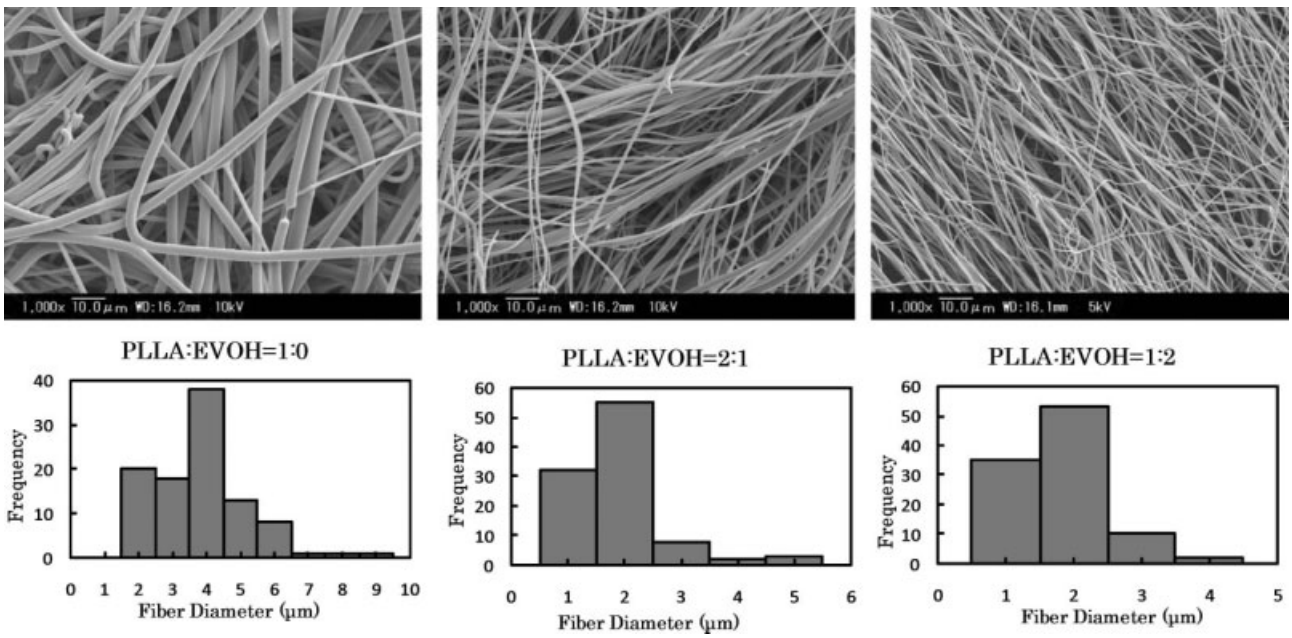

Figure 2 SEM images and the diameter distribution of fibers produced under the same electrospinning condition (H_v = 25 kV, L_p = 12 W, C_d = 5 cm, T_s = room temperature). Sample 1 (PLLA : EVOH) = 1 : 0): D = 3.38 μm, σ = 0.94 μm; Sample 2 (PLLA : EVOH = 2 : 1): D = 1.44 μm, σ = 0.79 μm; Sample 3 (PLLA : EVOH = 1 : 2): D = 1.32 μm, σ = 0.63 μm.

was locally melted with an Oniza PIN-20R laser apparatus (Tokyo, Japan); the laser wave length was 10.6 μm, the diameter of the laser spot was 5 mm, and the maximum power of the laser was 39 W. The end of the rod was irradiated by laser beams from three directions to form a homogeneous molten state. The laser output power, which is denoted as L_p, was at a height of level of power just before firing of rod appeared. A high voltage was applied to the end of the melted rod through bulky copper wires from a black-strained aluminum electrode. A grounded plate was used to collect the fibers. The voltage between the electrode and the grounded collector was denoted as H_v. The collector distance from the laser melting position to the grounded collector was denoted as C_d. The temperature of the spinning space was denoted as T_s. Our apparatus had no nozzle, which distinguishes our system from the traditional melt electrospinning systems.

Extraction of EVOH from fibers

To study the structure of electrospun PLLA/EVOH fibers, we removed the EVOH component from PLLA/EVOH fibers by 2-propanol/water (70 : 30, weight ratio) solution at 50°C for 1 h with a magnetic stirrer; the mixing speed was 100 × rpm.

Characterization

The morphology of the electrospun fibers was examined with a Keyence VE-9800 scanning electron microscope (SEM) (Osaka, Japan). The average fiber diameter and its standard deviation were determined from 100 measurements of fibers obtained at each spinning condition using an Abode Photoshop CS3 extended program. The average fiber diameter and its standard deviation will be referred to as D and σ, respectively.

To study the effect of annealing on fiber property, we held the PLLA/EVOH fibers at 95°C in an oven for 0.5 h under nitrogen atmosphere. The thermal properties of fibers were analyzed by a Shimadzu DSC60 differential scanning calorimeter (DSC; Kyoto, Japan) at a heating rate of 10°C/min in a nitrogen atmosphere until the temperature reached 280°C.

RESULTS AND DISCUSSION

Effect of the EVOH coating on fiber morphology and diameter

We observed that only a single fiber was formed from the Taylor cone at the tip of a rod during all melt electrospinning tests in this work. Figure 2 shows the effect of EVOH coating on fiber morphologies and the diameter distribution. As the figure shows, the average fiber diameter decreases sharply from 3 μm to around 1 μm and the fiber diameter distribution seems to be narrower as a result of the coating. However, the fiber diameter produced from coating with EVOH is almost independent of the volume ratio of EVOH. The decrease in fiber diameter and narrowing of diameter distribution by

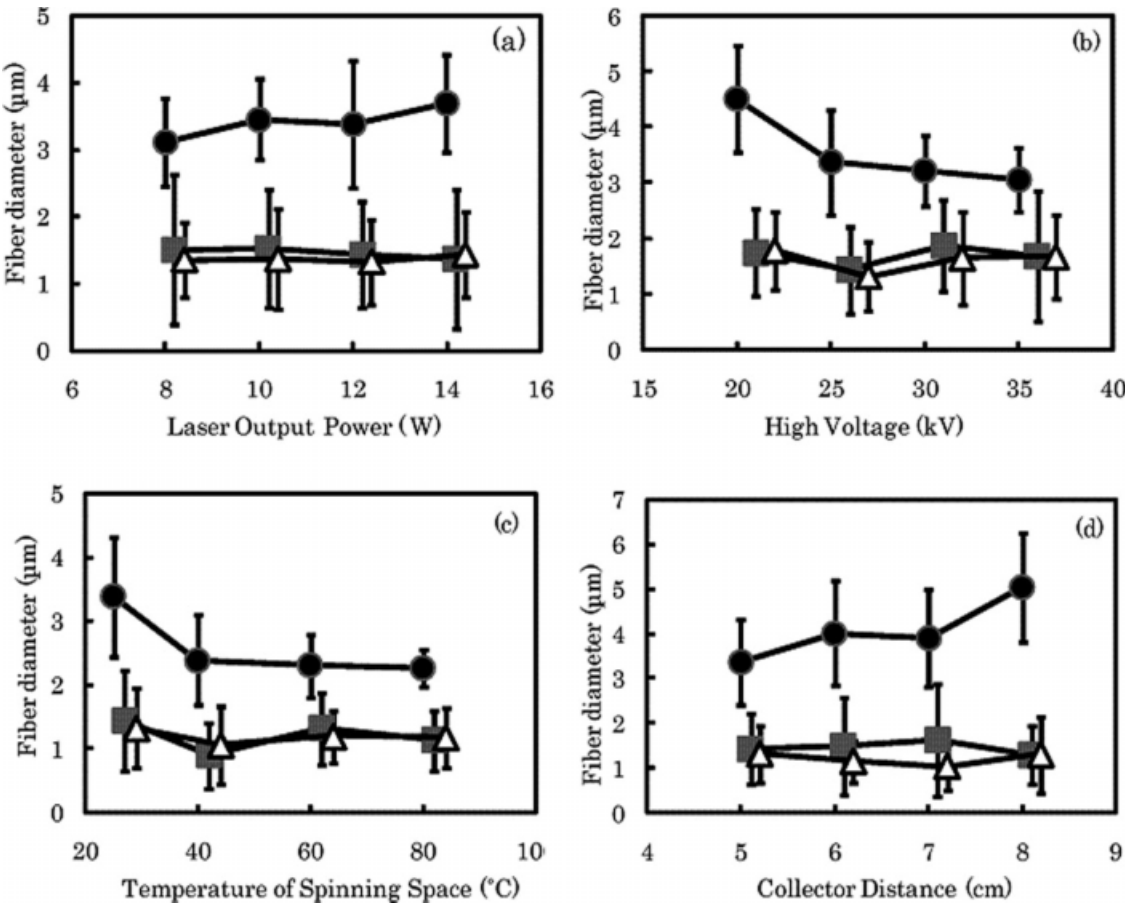

Figure 3 Effects of processing parameters on fiber diameter. ●, PLLA : EVOH = 1 : 0; ■, PLLA : EVOH = 2 : 1; △, PLLA : EVOH = 1 : 2. (a) H_v = 25 kV, C_d = 5 cm, T_s = room temperature; (b) L_p = 12 W, C_d = 5 cm, T_s = room tempeature; (c) H_v = 25 kV, L_p = 12 W, C_d = 5 cm; (d) H_v = 25 kV, L_p = 12 W, T_s = room temperature.

EVOH coating was observed in all experiments, when various electrospinning parameters were changed. As seen in Samples 2 and 3, PLLA/EVOH fibers smaller than 1 μm diameter have been obtained after coating of EVOH on rods. Therefore, a coating of EVOH on PLLA rods has a significant effect on decreasing the fiber diameter. In the laser melt electrospinning of the rods consisting of PP/EVOH conjugate fibers, the average diameter of melt-spun fibers decreased with increasing EVOH content.[19] However, in this work, the EVOH coating content on the PLLA rods may be so small that the fiber diameter seems to be not influenced by the EVOH content; the presence of EVOH layer decreases the fiber diameter.

Since PP nanofibers cannot be obtained from the melt electrospinning of the rods consisting of pure PP fibers, —OH groups in EVOH may contribute the reduction of the fiber diameter of electrospun fibers. There could be yet another possibility that the interfacial boundary of EVOH and PLLA components may hold larger electrical charges. As a result, fine diameter is achieved. Although we cannot explain the mechanism that coating of EVOH on PLLA rods reduces the fiber diameter, our experimental result should be noted. Further experimental and theoretical approaches are necessary to discuss the blending of polymers on the diameter of electrospun fibers.

Effect of processing conditions on fiber diameter

Figure 3 shows the effect of processing parameters on fiber diameter. As the figure shows, fiber diameters are almost independent of the laser output power despite the composition of rods. For pure PLLA rods (Sample 1), consistent with the past studies on melt electrospinning,[16–18] an increase in electric field strength and spinning temperature decreases the average fiber diameter. The increase in electric field strength increases the electrical pull-out force, and the increase in spinning temperature prevents the melt jet from solidifying before reaching the collector and then enables the melt jet to go through thinning for a longer period of time; as a result the average fiber diameter continues to decrease. We also found that the collector distance is an important parameter during the electrospinning process, where the molten rods undergo

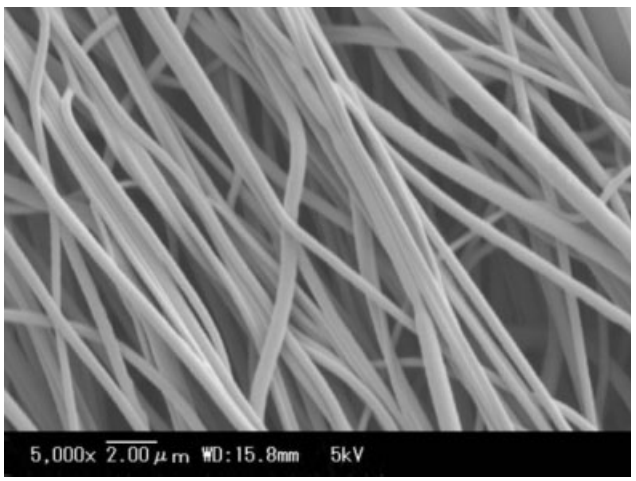

Figure 4 SEM images of PLLA/EVOH fibers with 845 ± 500 nm in diameter.

deformation and become sub-microfibers. A longer collector distance promotes a lager fiber diameter because of the lower electric field strength.

Although the electrospinning process parameters, such as applied electric field strength, spinning temperature, and collector distance are changed for PLLA rods coated with EVOH, the average diameter of the PLLA/EVOH fibers obtained is almost independent of these parameters. The influence of coating is so large that the influences of electrospinning parameters may be neglected, although these parameters also seem to affect the fiber diameter.

By combining all of the optimum processing factors, we have successfully obtained PLLA/EVOH melt electrospun fibers with an average diameter of 845 ± 500 nm as seen in Figure 4 under the following conditions: $H_v = 25$ kV, $L_p = 12$ W, $C_d = 5$ cm, $T_s = 40°C$.

PLLA sub-micron fibers after removal of EVOH

Figure 5 shows the morphology and fiber diameter distribution of PLLA fibers after the removal of EVOH. Comparing Figure 5 with Figure 2 shows that the fibers have slightly smaller diameter and narrower diameter distribution after the removal of EVOH. Furthermore, fibers having a trough structure can be seen.

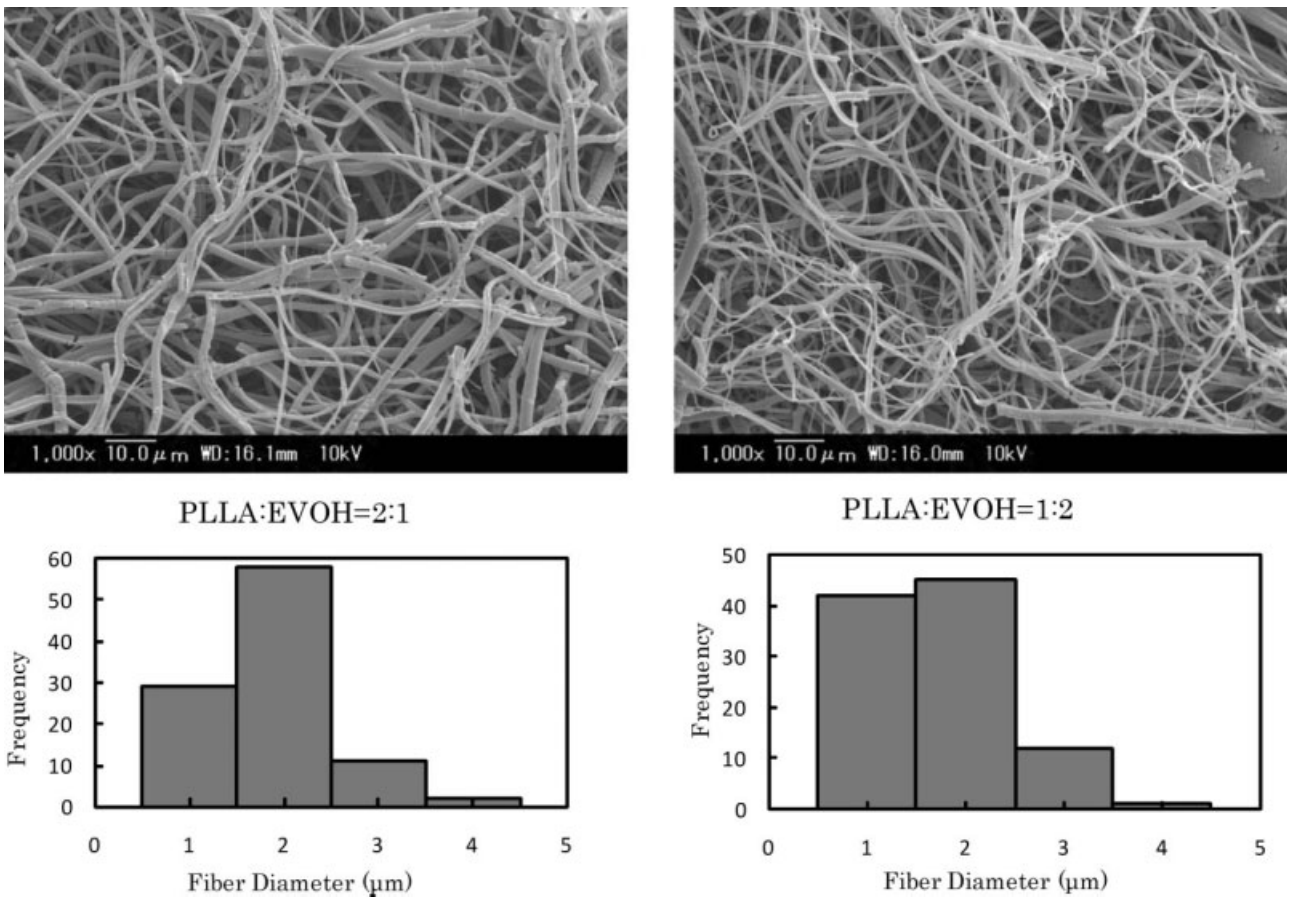

Figure 5 SEM images and the fiber diameter distribution after the removal of EVOH. The spinning condition is as follows: $H_v = 25$ kV, $L_p = 5$ cm, $T_s =$ room temperature. Sample 2 (PLLA : EVOH = 2 : 1): $D = 1.38$ μm, $\sigma = 0.53$ μm; Sample 3 (PLLA : EVOH = 1 : 2): $D = 1.21$ μm, $\sigma = 0.60$ μm.

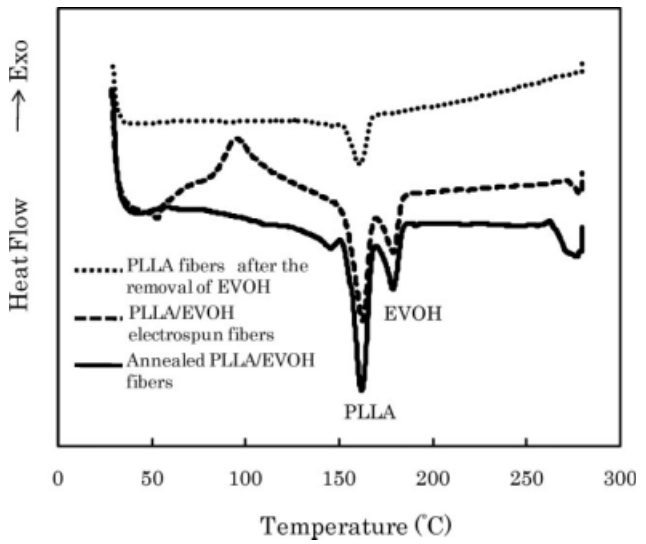

Figure 6 DSC thermograms of Sample 2 (PLLA : EVOH = 2 : 1) melt electrospun PLLA/EVOH fibers, annealed PLLA/EVOH fibers, and PLLA fibers after the removal of EVOH. The spinning condition is as follows: $H_v = 25$ kV, $L_p = 12$ W, $C_d = 5$ cm, $T_s =$ room temperature.

The melts underwent a lager deformation from 530 to 800 μm to 1 to 2 μm in diameter during the melt electrospinning process; therefore, many types of structures might be produced. Before this experiment, we expected that homologous deformation would take place during the fiber formation process. However, fibers having a trough structure were actually obtained after the removal of EVOH, independent of its volume ratio. Furthermore, there was no remarkable decrease in the fiber diameter after EVOH was removed. These results mean that homologous deformation does not take place during the fiber formation process. There is a possibility that PLLA component might be migrated to the surface of electrospun fibers.

Finally, the solution used for the removal of EVOH component was more benign to the human body than chloroform, which is used as a solvent for solution electrospinning of PLLA. Therefore, our method has an advantage for the industrial production of PLLA nanofibers.

Thermal properties

Figure 6 shows the DSC curves for melt electrospun PLLA/EVOH fibers, annealed PLLA/EVOH fibers, and PLLA fibers obtained after the removal of EVOH by 2-propanol/water solution. In DSC curves of electrospun fibers, it can be seen that there are two humped peaks originating from PLLA and EVOH components; the lower peak and higher peak are derived from PLLA and EVOH, respectively. The melting point of PLLA in electrospun fibers is lower than that of PLLA pellets ($T_m = 170.7$°C). This means that the thermal degradation takes place during the laser melt electrospinning process. As seen in Figure 6, the curve of fibers after removal of EVOH component has a single peak derived from PLLA only. This result means EVOH was completely removed. For the electrospun fibers, a cold crystallization peak at around 95°C can be seen. The electrospun fibers were cooled quickly before reaching the collector, and the crystallization of the PLLA component did not take place, although the PLLA rod was coated with EVOH. Since the exothermal peak was observed for PLLA fibers produced from solution electrospinning,[20,21] it seems that the molecular structure of electrospun PLLA fibers exhibits an amorphous state irrespective of melt electrospinning or coating of EVOH on PLLA.

Fiber formation

Under the irradiation of the laser beams, the EVOH outer sheath of rods was melted first so that EVOH could extend more easily than the PLLA inner core. On the other hand, the viscosity of EVOH melts is different with that of PLLA melts, and the situation of surface tension is much more complicated. For these reasons, the solidification and whipping motion of the molten jet during the melt electrospinning process may be more irregular, and it thus may produce fibers with various phase-separated inner structures.

CONCLUSIONS

Fibers with submicron diameter were produced from rodlike PLLA/EVOH samples by using a melt electrospinning system equipped with a laser melting device. We investigated the characteristics of those fibers produced from PLLA rods coated with EVOH layer and examined the relationship between processing conditions and fiber morphologies. We reached the following conclusions:

1. Coating of EVOH on PLLA rods decreases the diameter of electrospun fibers.
2. An increase in electric field strength and the temperature of the spinning space decreases the fiber diameter produced from pure PLLA rods, and a longer collector distance leads to a lager fiber diameter.
3. Combining all optimum processing factors, we can produce PLLA/EVOH fibers with an average diameter of 845 ± 500 nm under the following conditions: $H_v = 25$ kV, $L_p = 12$ W, $C_d = 5$ cm, $T_s = 40$°C.
4. PLLA might be migrated to the surface of electrospun fibers during laser beam

electrospinning process. After the removal of EVOH, PLLA fibers with trough structure can be obtained.

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