Spot Laser Melt Electrospinning of a Fiber Bundle Composed of Poly(lactide)/Poly(ethylene-*co*-vinyl alcohol) Pie Wedge Fibers

Naoki Shimada, Nobuo Ogata, Koji Nakane, Takashi Ogihara

Department of Materials Science and Engineering, University of Fukui, Fukui 910-8507, Japan

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ABSTRACT: The melt-electrospinning system with a spot-like carbon dioxide laser melting device was used to form fibers directly from solid-like polymer rods. Fiber bundles were made from pie wedge fibers comprised of poly(lactide) (PLA) and poly(ethylene-*co*-vinyl alcohol) (EVOH) by gathering the fibers and twisting them together, and then melt electrospinning was performed for the bundles using the spinning system. Nanofibers with an average fiber diameter of *ca*. 400 nm were successfully obtained from the bundle by the optimization of manufacturing parameters such as laser output power, voltage, and collector distance. To investigate the morphological structure of the electrospun fibers, each structural component was extracted from the fibers with its solvent. It was found that three types of fibers with different morphology were produced during the melt-electrospinning process: fibers consisting of only a PLA component, fibers consisting of only an EVOH component, and fibers consisting of a PLA/EVOH mixture. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: melt electrospinning; bicomponent fiber; laser melting

INTRODUCTION

Electrospinning is a simple technique for the production of nanofibers that can be classified into two kinds of methods: solvent electrospinning methods and melt-electrospinning methods.[1,2] Although solvent electrospinning methods have solvent recycling issues, studies using these methods abound because the setup is inexpensive and simple. The melt-electrospinning methods eliminate the issues related to solvents, and thus melt electrospinning is considered to be a more ecofriendly, versatile, and low-cost production method. However, there are few studies on melt electrospinning.[3–7] In these situations, we developed a melt-electrospinning system with a spot-like carbon dioxide laser beam melting device and obtained nanofibers from several rod-like polymer materials with this system.[8–11]

Poly(lactide) (PLA) is an ecofriendly and biodegradable polymer. That is, this polymer is synthesized from natural resources and can be hydrolyzed, degraded by microbes, and finally changed to carbon dioxide and water under natural circumstances. Furthermore, PLA is innocuous and biocompatible with human tissues. Therefore, PLA has been used not only in the packaging field but also in the field of orthopedic surgery.[12,13]

Poly(ethylene-*co*-vinyl alcohol) (EVOH) is a random copolymer of ethylene and vinyl alcohol. This polymer has the following features: (i) due to the ethylene repeat units, it is both highly hydrophilic and water insoluble; and (ii) it is nonbiodegradable yet biocompatible. Focusing on these properties, several researchers have studied the application of EVOH as a biomaterial.[14] If a new fibrous biomaterial could be produced from PLA/EVOH composite material, it would have many positive properties.

In the previous work, we developed a melt-electrospinning system with a line-like carbon dioxide laser beam melting device for mass production of nanofibers.[15] As a result, we can produce uniform nanofiber mats with 150 mm in width from both EVOH and Nylon 6/12. However, produced nanofibers have large diameter (*ca*. 800–900 nm) compared with solution electrospun nanofibers (*ca*. ~ 800 nm). In this work, we focus entirely on thinning process of melt electrospinning using a spot-like carbon dioxide laser melting device. Fibers about 1 μm in diameter were obtained from both PLA and EVOH rods using spot laser melt electrospinning.[8,9] The functional groups in these polymers appeared to contribute to the formation of the fine fibers. We assume that the mutual interaction between melts of

Correspondence to: N. Shimada (shimada@sozai.matse.u-fukui.ac.jp).

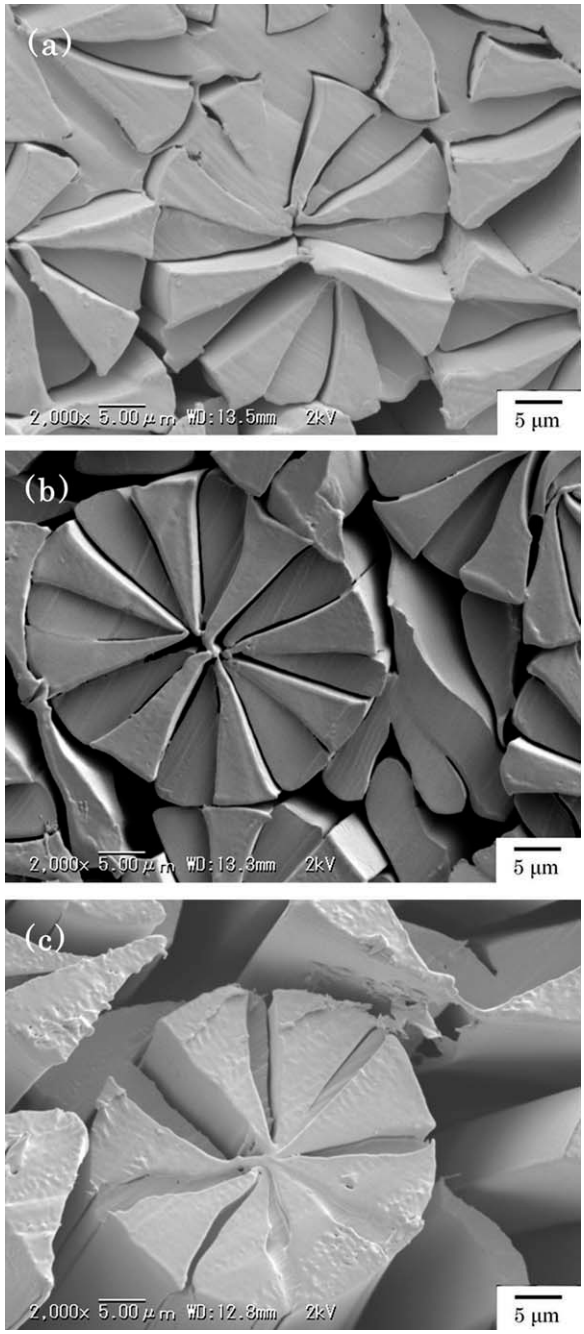

Figure 1 (a–c) Pie wedge fibers used in this work: (a) PLA/EVOH = 3/7, (b) PLA/EVOH = 5/5, and (c) PLA/EVOH = 7/3.

these polymers during the melt-electrospinning process enabled the remarkable decrease in the fiber diameter. This assumption leads us to expect that finer fibers could be obtained from rods consisting of both EVOH and PLA.

Bicomponent fibers are coextruded with two different polymers in the cross-section. In these fibers, the pie wedge fibers have a round cross-section made of many adjacent wedges. Each wedge of polymer has a wedge of another polymer on either side. In this work, melt electrospinning was performed for a fiber bundle consisting of the PLA/EVOH pie wedge fibers using the spot laser melt-electrospinning system; the system enables direct formation of the fibers from solid-like polymer rods. Here, we report the effects of processing conditions and the PLA/EVOH composition ratio on the fiber diameter and describe the structure of the spun fibers.

EXPERIMENTAL PROCEDURES

Materials

Pie wedge fibers 40 μm in diameter were produced from PLA (MFI at 230°C and 21.2 N loading = 45 g/10 min) and EVOH (MFI at 230°C and 21.2 N loading = 45 g/10 min) by an undisclosed Japanese company. Figure 1 shows the pie wedge fibers used in this work. Each pie wedge fiber had 16 adjacent wedges, and each polymer had eight wedges. Pie wedge fibers having three different EVOH/PLA volume ratios, that is, 3/7, 5/5, and 7/3, were supplied. The fiber bundles were made by gathering 300 fibers with the same composition, twisting them together, and soaking the bundle in water maintained at 80°C for 3 min. From the fiber bundle, the fibers were produced using the spot laser melt-electrospinning method. The fiber bundle and the electrospun fibers were characterized by the PLA/EVOH ratio of the pie wedge fibers, and these ratios are referred to as their values. For example, the PLA/EVOH = 3/7 bundle and the PLA/EVOH = 3/7 fiber mean the fiber bundle and electrospun fibers produced from the PLA/EVOH = 3/7 pie wedge fibers, respectively.

Melt electrospinning

Figure 2 shows a schematic diagram of the spot laser melt-electrospinning system used in this work.[8–10] A fiber bundle was fed to the laser melting zone at a feed rate (F_r) of 7 mm/min unless otherwise noted. One end of the rod was locally melted with an Onizca PIN-20R carbon dioxide laser apparatus (Tokyo, Japan); the wave length was 10.6 μm, the diameter of the laser spot was 6 mm, and the maximum power of the laser was 35 W. The output laser power (L_p) was 10 W unless otherwise noted. A grounded copper plate (100 × 100 × 2 mm) was used to collect the fibers. High voltage (H_v) was applied between the molten polymer, which was melted by the laser beam, and the grounded collector; the voltage was 30 kV unless otherwise noted. The molten end-to-collector distance, or the "collector distance" (C_d), was 100 mm unless otherwise noted. We

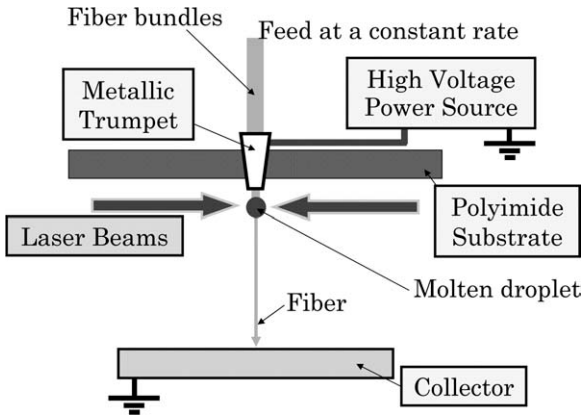

Figure 2 Schematic diagram of the spot laser melt-electrospinning system used in this work.

produced fibers from the fiber bundles under several sets of these processing parameters.

Characterization of fibers

The morphology of the electrospun fibers was examined with a Keyence scanning electron microscope (SEM, VE-9800, Kyoto, Japan). The fiber samples were gold-sputter coated with a Sanyuudensi ion coater (SC-701, Tokyo, Japan) as a previous treatment. The average fiber diameter (D) and standard deviation (σ) were determined from 200 to 250 measurements of fibers obtained for each spinning condition using an Adobe Photoshop CS3 extended program.

To investigate the morphological structure of the electrospun fibers, the fibers were treated with solvents; chloroform and 2-propanol/H_2O mixture solution (volume ratio, 7/3) were used for the removal of PLA and EVOH components, respectively. The electrospun fibers in samples of about 1 g were soaked in each solvent. After being stirred for 8 h, the mixture was suction filtrated; the temperature of the chloroform was about 26°C and that of the 2-propanol/H_2O mixture solution was about 80°C. Finally, the resultant fibers were washed with water and then dried. It was confirmed that the one component of electrospun fibers was almost removed by effective weight loss caused by selective leaching. The morphology of the resultant fibers was observed with SEM.

RESULTS AND DISCUSSION

Effect of processing conditions on fiber diameter

Figure 3 shows an example of electrospun fibers; the fibers were obtained under $C_d = 60$ mm condition. The electrospun fibers, in which two different polymers were melted and spun together, appear to have a uniform fiber diameter distribution. High-power laser heating enabled the melts to be formed instantaneously even when the solid-like material consisted of different polymers. The melts formed from different polymers appeared to interact with each other. Since the difference between the melting temperatures of PLA and EVOH is not so large, both polymers were simultaneously melted by the laser beam and spun under the mutual interaction between the polymer melts.

Figure 4 shows the effect of the applied high voltage, H_v, on the fiber diameter. As Figure 4 shows, the fiber diameter decreased as H_v increased irrespective of the EVOH/PLA ratio. The electric force seems to be increased as H_v increased and consequently, the fiber diameter may be decreased. Fibers <1 μm in diameter were obtained. Furthermore, the decrease in fiber diameter with increasing H_v was marked in the sample having a high EVOH volume ratio. This means that the EVOH component decreased the fiber diameter markedly. EVOH has a high-specific permittivity derived from the hydroxyl functional group (—OH). This appeared to reduce the fiber diameter effectively. In previous work on

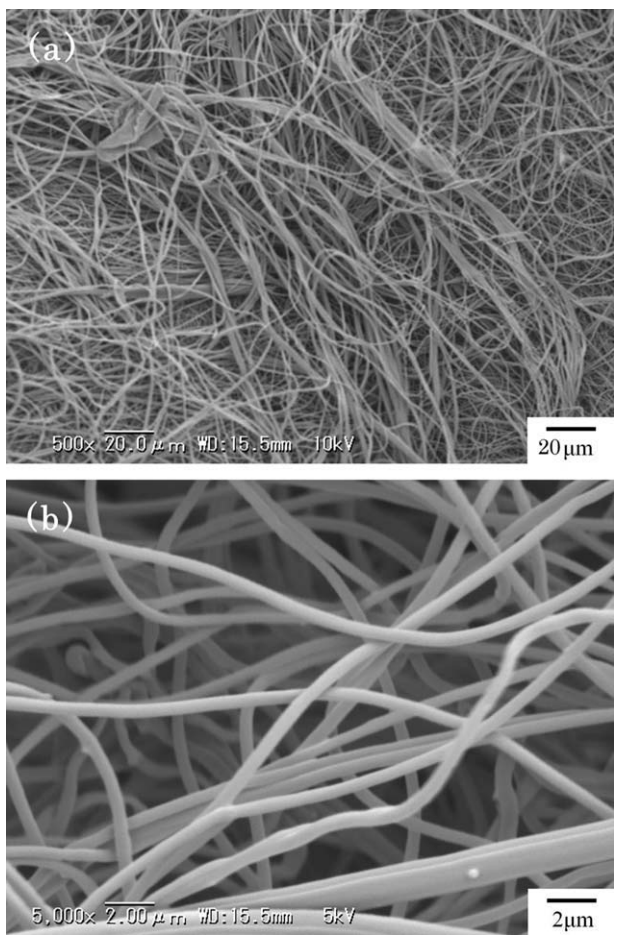

Figure 3 (a,b) Examples of fibers produced from the spot laser electrospinning: (a) low magnification and (b) high magnification.

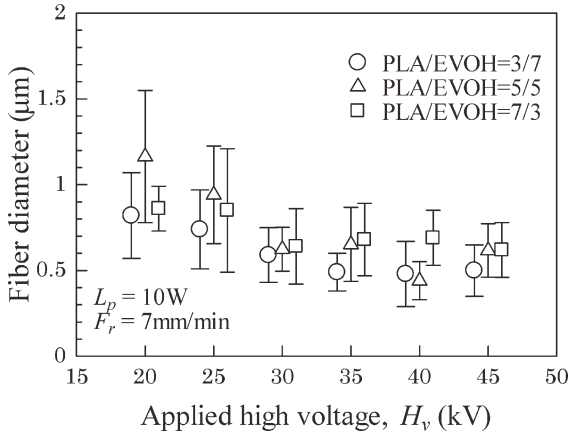

Figure 4 Effects of applied high voltage, H_v, and composition of the fiber bundle on fiber diameter.

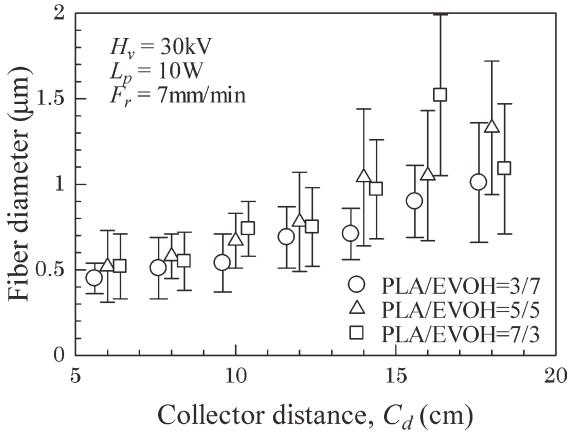

Figure 6 Effects of collector distance, C_d, and composition of the fiber bundle on fiber diameter.

melt electrospinning of a bundle consisting of poly (propylene)/EVOH core-shell fibers, PP nanofibers having D = 660 nm and σ = 160 nm were obtained by the removal of the EVOH component from electrospun fibers.[11]

Figure 5 shows the effect of the laser power, L_p, on the fiber diameter. As Figure 5 shows, the fiber diameter decreased as L_p increased, irrespective of the PLA/EVOH ratio. The melt viscosity decreased as L_p increased, and consequently the fiber diameter was decreased. We were able to obtain fibers about 400 nm in diameter, and the EVOH component decreased the fiber diameter effectively.

Figure 6 shows the effect of the collector distance, C_d, on the fiber diameter. Figure 6 shows that the fiber diameter decreased as C_d decreased. This result means that electric force increased as C_d decreased, and consequently the fiber diameter was decreased. We note that fibers 400 nm in diameter could be successfully electrospun from the fiber bundle consisting of the PLA/EVOH pie wedge fibers.

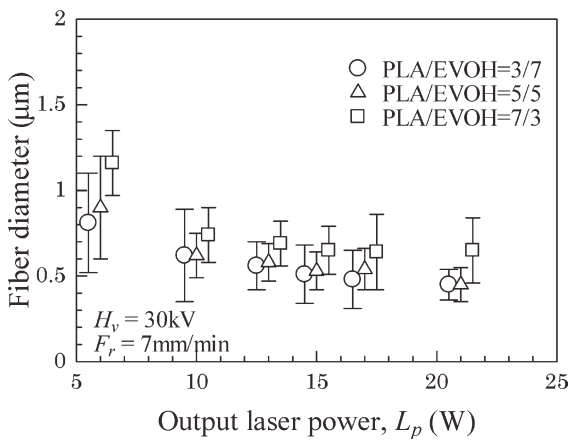

Figure 5 Effects of output laser power, L_p, and composition of the fiber bundle on fiber diameter.

Morphological structure of the fibers

Figure 7 shows the effect of the extraction of one component from the PLA/EVOH = 5/5 fibers on the fiber diameter; the fibers were produced under L_p = 13 W. The fiber diameter appears to have become smaller because of the extraction of the EVOH component. Very fine fibers can be seen after the extraction. Although the fiber diameter histogram of electrospun fibers shows a normal distribution, after the removal of the EVOH component, the histogram shows a smaller mean value. The reason for the changes will be discussed later. As with the extraction of EVOH, very fine fibers can be seen.

Figure 8 shows the cross-sections of the PLA/EVOH = 3/7 fibers after removal of the EVOH component. It can be seen that there are small holes, which cannot be seen on the cross-section of as-spun fibers. The number of fibers with holes increases with increasing EVOH component. The holes were also observed on the cross-section of the fibers after removal of the PLA component. Considering that these holes can be seen and that the histograms of fiber diameter show a bimodal distribution after removal of each component from electrospun fibers, we conclude that three types of fibers with different morphology were produced from the bundle consisting of the PLA/EVOH pie wedge fibers during the spot laser melt-electrospinning process: fibers consisting of only the PLA component, fibers consisting of only the EVOH component, and fibers consisting of only a PLA/EVOH mixture. The structure of electrospun fibers does not appear to be strongly influenced by that of the fiber bundles, because the pie wedge nanofibers cannot be formed. This implies that homologous deformation from rod to fiber does not take place during the fiber formation process. In other words, a new fiber, whose structural composition is not strongly influenced by that of the bundle, appears to be formed from the molten state of

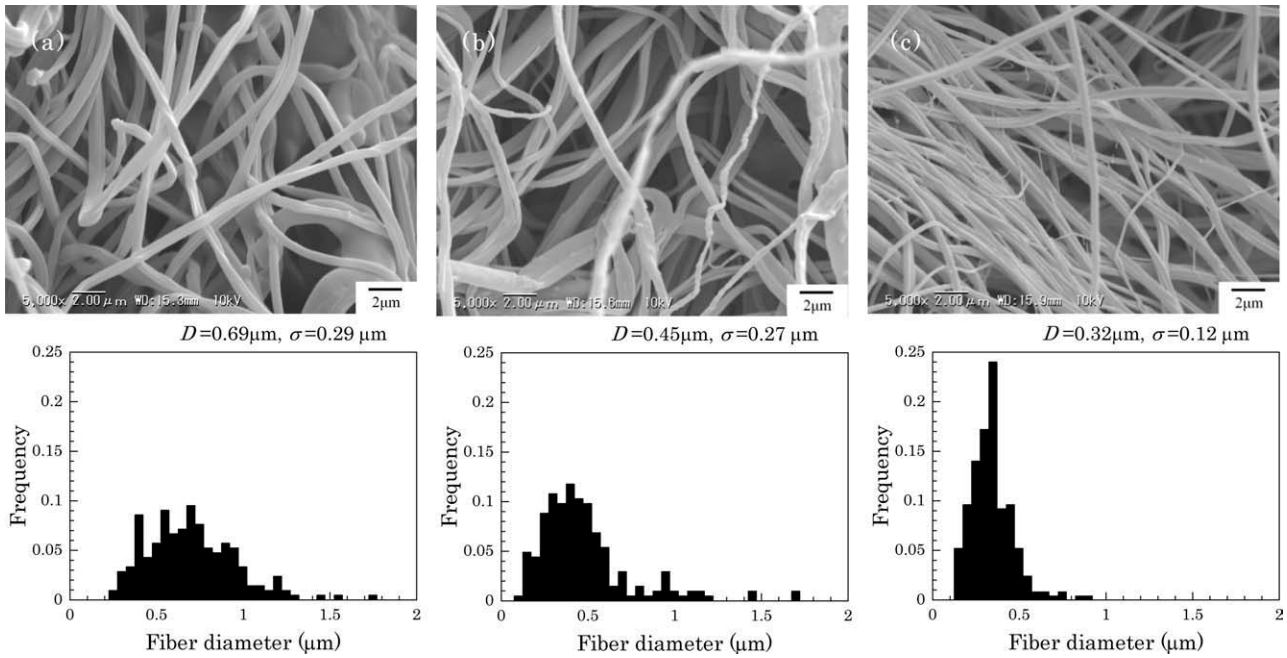

Figure 7 (a–c) Effect of the removal of one component from PLA/EVOH = 5/5 fibers: (a) as spun fibers, (b) after extraction of EVOH, and (c) after extraction of PLA.

polymers during the spot laser melt-electrospinning process. The laser heating causes drastic structural changes in the molten state of polymers because the heating affects the melt viscosities of polymers, the composition of the melt, and the surface tensions of polymers, and other changes.

Figure 9 shows the thermal behavior of the electrospun fibers and raw material (PLA/EVOH = 3/7). An exothermal peak can be seen in each of the electrospun fibers and the EVOH extracted fibers at about 85°C. This means that the fibers are an amorphous polymer state, and the well-developed crystals are not formed in fibers. Additionally, melting temperature of electrospun fibers is lower than that of raw material. This means that the laser beam irradiation induces thermal degradation of polymers.

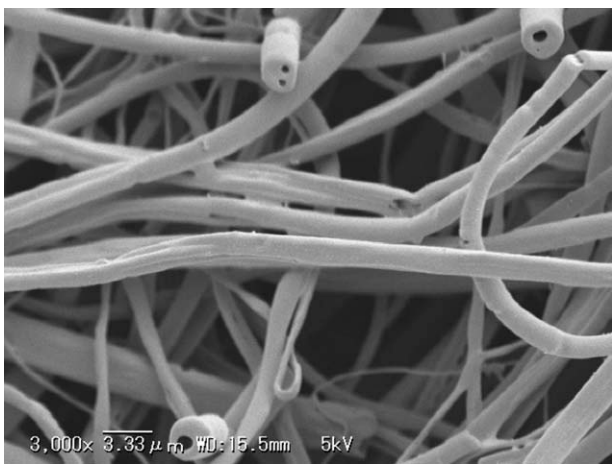

Figure 8 Effect of the removal of EVOH component from PLA/EVOH = 3/7 fibers on the morphological structure of cross-section of fibers.

CONCLUSION

Using a spot laser melt-electrospinning system, we produced fibers from a fiber bundle consisting of PLA/EVOH pie wedge fibers. We investigated the morphology of electrospun fibers and reached the following conclusions:

1. Nanofibers with an average fiber diameter of *ca*. 400 nm were successfully obtained from the bundle by the optimization of manufacturing parameters such as laser output power, high voltage, and collector distance. The EVOH

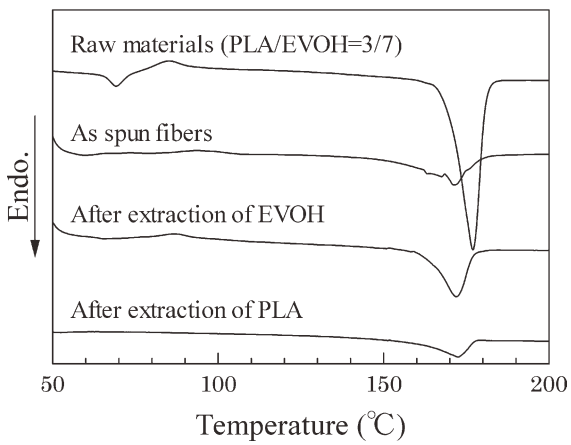

Figure 9 DSC curves of the electrospun fibers and raw material.

component reduced the diameter of the electrospun fibers effectively.
2. The fiber diameter decreased as the laser output power and the applied voltage increased. The fiber diameter decreased as the collector distance decreased.
3. Three types of fibers were produced: fibers composed of only PLA, fibers composed of only EVOH, and fibers composed of PLA and EVOH.
4. Fibers contain polymers in an amorphous state and well-developed crystals are not formed in fibers.
5. Thermal degradation of polymers was caused by laser beam irradiation.

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