Effects of Ethylene Content of Poly(Ethylene-*co*-vinyl alcohol) on Diameter of Fibers Produced by Melt-Electrospinning

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ABSTRACT: Rodlike samples were made from four kinds of poly(ethylene-*co*-vinyl alcohol) (EVAL) pellets with different ethylene contents. From these rodlike samples, fibers were produced using a melt-electrospinning system equipped with a CO_2-laser melting device. The effects on the fiber diameter of the ethylene content and the moisture regain of the rodlike samples were investigated. Furthermore, the physical properties of the fibers were investigated. The following conclusions were reached: (i) EVAL fibers having an average fiber diameter smaller than 1 μm can be obtained using the system developed; (ii) the diameter of EVAL fiber is influenced by the ethylene content and the moisture regain of the starting rods; (iii) the laser heating does not greatly decrease the melting point and the molecular weight of EVAL; and (iv) preferred crystal orientation can be seen in electrospun EVAL fibers. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1368–1375, 2007

Key words: poly(ethylene-*co*-vinly alcohol); melt-electrospinning; laser melting

INTRODUCTION

Nanofibers have several amazing characteristics such as very large surface-area-to-volume ratio, flexibility in surface functionalities, and superior mechanical performance.[1–3] Electrospinning method(ELSP) is a simple technique to produce nanofibers and is classified into two kinds of methods: solvent-based method (S-ELSP) and melt-based method (M-ELSP). Although S-ELSP has issues related to solvent recycling and low productivity, studies about the use of these methods abound because their setup is inexpensive and simple. M-ELSP solves the issues related to solvents so that M-ELSP is thought to be a more eco-friendly, versatile, and low-cost production method. Despite these many potential benefits, the work on M-ELSP is still relatively scarce.[4–6] The reasons why M-ELSP is not widely used are as follows: (i) it is thought that the fibers with smaller fiber diameters are produced by S-ELSP because the solvent in the spinning liquid is vaporized during the fiber formation process; (ii) the viscosity of molten polymer is high when compared with that of polymer solution, so that, given the mechanism for fiber formation, nano-diameter fibers seem less likely to form; (iii) the system for applying high voltage to the molten polymer is difficult to manufacture because of electric discharge problems; and (iv) there are scarcely any successful examples of using M-ELSP for obtaining nano-diameter fibers.

In a previous work, we developed a new melt-electrospinning system with a CO_2 laser heating device, and using the system, we obtained poly(lactide) fibers with nanosized diameters. We also studied the properties of the fibers to discuss the feasibility of our system as a production method of nanofibers.[7]

Poly (ethylene-*co*-vinyl alcohol) (EVAL) is a random copolymer of ethylene and vinyl alcohol; its molecular formula is represented by $—(CH_2—CH_2)_m—(CH_2—CH(OH))_n—$. This polymer has the following features: (i) because of the ethylene repeated 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 EVAL as a biomaterial. For example, EVAL nanofibrous mats have been produced as scaffolds for cell growth; the cells grow well on such electrospun scaffolds.[8] EVAL is a solvent-soluble polymer, so that its nanofibers can be produced using S-ELSP; an isopropanol/water mixture is generally used as a solvent.[9,10] Since EVAL is also a thermoplastic polymer, EVAL nanofibers can also be produced using M-ELSP. It is apparent that M-ELSP is a more favorable method for producing EVAL nanofibers, which are intended to use especially for tissue engineering because solvent is not used in this method.

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TABLE I
Characterization of EVAL Samples Used in This Work

Sample code	Ethylene content (mol %)	Average viscometric degree of polymerization	Melt flow index (g/10 min)[a]
EVAL1	32	515	15.1
EVAL2	44	820	6.0
EVAL3	48	595	14.9
EVAL4	51	510	4.7

[a]Measured at 190°C under 21.6 N.

Now, let us consider the effect of the hydrophilic units in EVAL on the melt-electrospinning process. The EVAL molecule has hydrophilic units, which allow water to be absorbed into it; the absorbing capacity decreases with increasing ethylene content. The absorbed water can decrease the melt viscosity of the molten sample because water acts as a plasticizer even at a high temperature above its melting point. The surface tension of the melt at a given temperature may decrease as the hydroxyl groups increase because the groups attract atmospheric moisture. Since the fibers are electrospun when the electric force overcomes the surface tension and the viscoelastic force of the polymer solution or polymer melt, reductions in the melt viscosity and surface tension seems to be important for the formation of nanofibers. From these reasons, we think that the diameter of EVAL fibers produced by ELSP is strongly influenced by the hydroxyl content, in other words, by the ethylene content of the EVAL molecules and the moisture regain. Recently, Lu et al. have reported that the diameter of EVAL fibers made from S-ELSP is determined by the relaxation times of molecules.[9]Taking into account this report, we will consider the formation mechanism of EVAL fibers during the melt-electrospinning process.

In this work, four kinds of rodlike EVAL with different ethylene contents were prepared, and fibers were produced from the rods using our developed melt-electrospinning system equipped with a laser melting device. The effects of the ethylene content and moisture regain of EVAL on the diameter of the fibers were studied. Furthermore, their physical properties were investigated to discuss the feasibility of our system as a production method of nanofibers.

EXPERIMENTAL

Materials

Four kinds of pellet-like EVAL samples with different ethylene contents were supplied by KURARAY (Osaka, Japan). The samples with the ethylene contents of 32, 44, 48, and 51 mol % will be referred to as EVAL1, EVAL2, EVAL3, and EVAL4, respectively.

To evaluate the melt properties of EVALs, the pellets were dried at 80°C for at least 24 h in vacuum, and the melt flow indexes (MFI) of these dried EVALs were measured with a Takara Kogyo Melt indexer (Tokyo, Japan) according to ASTM D3985; 190°C, 21.6*N*. The average viscometric degree of polymerization, P_v, of EVAL was also estimated from the measurements of these viscosities; the method will be described later. Table I shows the characterization of EVAL samples evaluated using these methods.

Rodlike samples, 0.2–0.5 mm in diameter, were made from the melt of these pellets with a Shimadzu Flow Tester CFT-500 (Kyoto, Japan); the temperature at the melting zone was about 150–200°C, and the applied stress was 1 MPa. These rodlike samples were provided for the melt-electrospinning tests. Furthermore, other rodlike samples were soaked in distilled water and held there for more than 24 h. After being wiped with paper, these samples were also provided for the melt-electrospinning tests.

Melt-electrospinning system

Figure 1 shows a schematic diagram of the melt-electrospinning system developed in our previous work.[7] A rodlike EVAL sample was fed to the laser melting zone at a rate of 2–4 mm/s by a feeder with a stepping motor. One end of the rod was locally melted with an Onizca 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 35 W.

Figure 2 shows a schematic plan view of the laser irradiating beams. To melt the rodlike sample homogeneously, the end of the rod was irradiated by the laser beams from three directions. Details of the irradiation method are as follows: a source incident beam (1) (5 mmφ) was partially absorbed by the sample (ca.

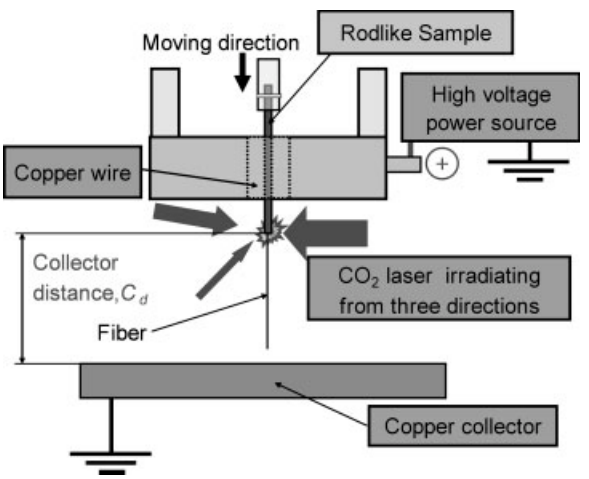

Figure 1 Schematic diagram of the melt-electrospinning system developed.

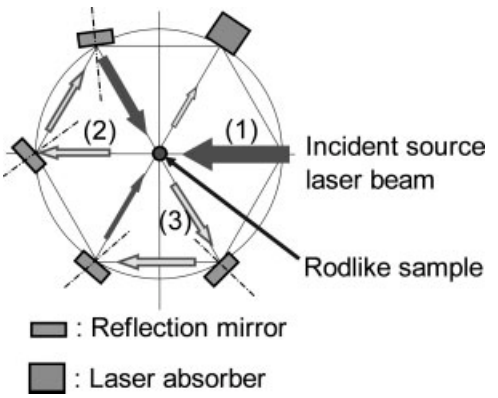

Figure 2 Schematic plan view of laser irradiation beams.

0.5 mmφ), the nonabsorbed and remaining beams (2) were reflected by two mirrors, again irradiated the sample, and the nonabsorbed beam and remaining beam from that process (3) were reflected by two mirrors and irradiated the sample; the smallest angle between irradiating laser beams was 120°. Finally, the remaining beam was absorbed by laser absorber.

A high voltage was applied to the end of the melted rod through bulky copper wires from a black-stained aluminum electrode. A grounded plate was used to collect the fibers. A rotating disk was also used as a collector to obtain unidirectionally aligned fibers.

Melt-electrospinning conditions

Voltage at the level just preceding an electric discharge was applied between the electrode and the grounded collector; this voltage will be denoted as H_v. The end of the rod was also irradiated by laser beams. The laser output power used in this work is the power of source beam (see Fig. 2). The laser output power at a height just before firing of rod appeared was applied; the power will be denoted as L_p. The molten end-to-collector distance, C_d, was 20 mm.

Since high-output laser beams are dangerous to the human body, the melt-electrospinning was performed in a black-stained box with transparent poly(methyl methacrylate) windows; and we employed adequate safety measures during the laser irradiation.

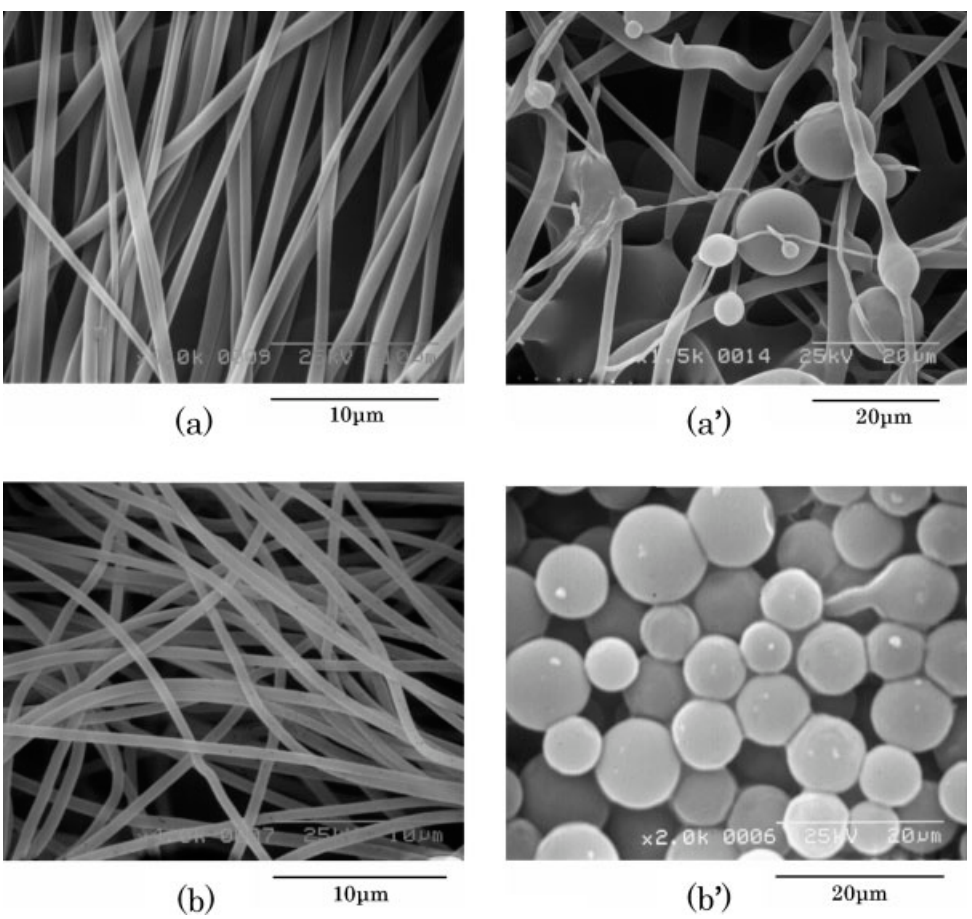

Figure 3 SEM images of EVAL fibers produced from dry rods. (a) EVAL1, D = 740 nm, σ = 265 nm, H_v = 15 kV, L_p = 12 W; (a′) EVAL1, H_v = 15 kV, L_p = 14 W; (b) EVAL2, D = 792 nm, σ = 227 nm, H_v = 15 kV, L_p = 8 W; (b′) EVAL2, H_v = 15 kV, L_p = 10 W.

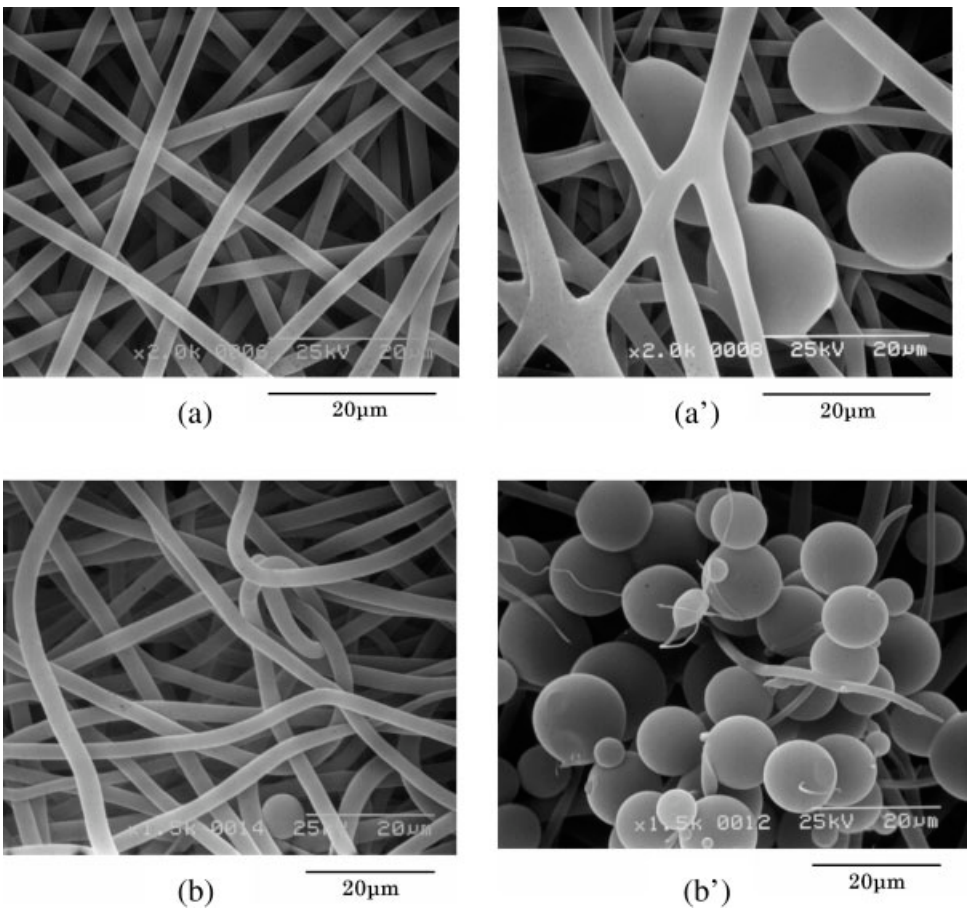

Figure 4 SEM images of EVAL fibers produced from dry rods. (a) EVAL3, $D = 2.294$ μm, $\sigma = 134$ nm, $H_v = 15$ kV, $L_p = 12$ W; (a′) EVAL3, $H_v = 15$ kV, $L_p = 14$ W; (b) EVAL4, $D = 2.842$ μm, $\sigma = 405$ nm, $H_v = 15$ kV, $L_p = 9$ W, (b′) EVAL4, $H_v = 15$ kV, $L_p = 10$ W.

Characterization of fibers

The morphology of the electrospun EVAL fibers was examined with a Hitachi *S*-2300 scanning electron microscope (SEM, Tokyo, Japan). The average and standard deviation of the fiber diameter were determined from 10 measurements of fibers obtained at each spinning condition; the average diameter and its standard deviation will be referred to as D and σ, respectively.

Many fibers are formed simultaneously from the polymer solution during the solution electrospinning process. This leads to a broad distribution of fiber diameter. However, only a single fiber was formed from a Taylor cone during our laser melting electrospinning process. This formation mechanism could possibly lead to a narrow distribution of fiber diameter (see Figs. 3–6). From this reason, we determined that 10 measurements of fibers were enough to evaluate the values of D and σ.

To investigate the effect of laser heating on the decrease in molecular weight of EVAL, we evaluated the average viscometric degree of polymerization, P_v, of EVAL using the following procedure. Well-dried EVOH 0.1 g was dissolved into a 20 mL aqueous phenol solution (water:phenol = 15 : 85 wt %). The solution was held at 60°C for 4 h, and then the viscosity of the solution was measured at 30°C with a conventional Ostwald viscometer; the measuring time was about 500 s. From the values of the viscosity and EVAL concentration in solution, the intrinsic viscosity [η]was evaluated. The value of P_v was calculated from the values of [η]and the ethylene content, E, using the following equation:[11]

$$P_v = ([\eta]/0.0013 \times \exp(-0.13 \times E/100))^{(1/0.65-0.059\times(E/100-0.2))} \quad (1)$$

The thermal behavior of the fibers was measured with a Shimadzu DSC60 differential scanning calorimeter (DSC, Tokyo, Japan) at a heating scan rate of 10°C/min.

To evaluate the crystal orientation of the fibers, unidirectionally aligned fibers were produced from the dry EVAL2 rods using a rotating disk as a collector. An X-ray diffraction photograph of the fibers was obtained with a Toshiba D-3 apparatus (Tokyo, Japan).

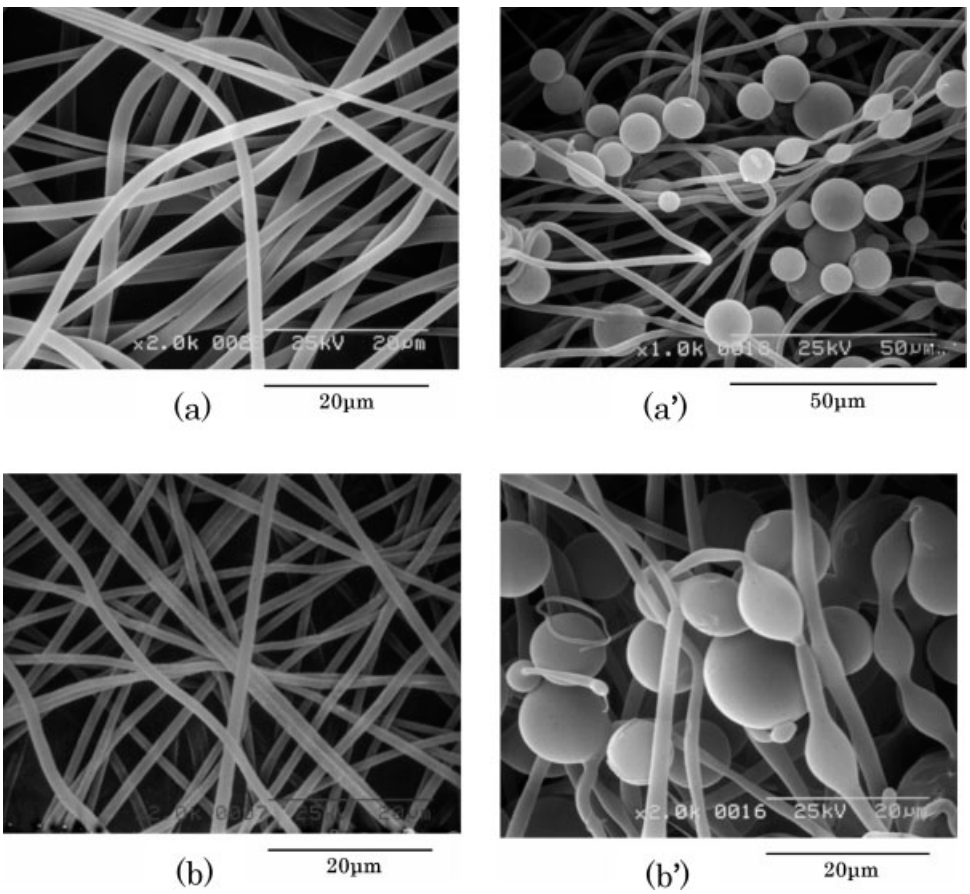

Figure 5 SEM images of EVAL fibers produced from wet rods. (a) EVAL1, $D = 1.705$ μm, $\sigma = 425$ nm, $H_v = 15$ kV, $L_p = 14$ W; (a′) EVAL1, $H_v = 15$ kV, $L_p = 16$ W; (b): EVAL2, $D = 1.242$ μm, $\sigma = 263$ nm, $H_v = 15$ kV, $L_p = 14$ W; (b′) EVAL2, $H_v = 15$ kV, $L_p = 22$ W.

RESULTS AND DISCUSSION

Effect of processing conditions on fiber diameter

Although we expected that many fibers would be simultaneously formed from melt jet, it was found that only a single fiber was actually formed during the melt-electrospinning process. In the solvent-based electrospinning process, solution jet ejects from the apex of a conical droplet, undergoes jet instability, and splits into small filaments. It is clear that the melt-electrospinning has no such instability. Since the melt viscosity is higher, the perturbation of the surface charge and the repulsive of the jet current do not seem to take place extensively. This implies that the nanofibers cannot be obtained by splitting of the melt jet but only by the elongation of the melt jet.

Figures 3 and 4 show typical examples of the fibers produced from the dry EVAL rods. The fiber diameter distribution seems to be narrow, and the mean fiber diameter produced at a low laser output power appears to be smaller than 1 μm. This result should be noted because the current study of M-ELSP shows that nanofibers have been recently produced with a mixture of micron-sized fibers.[6] Moreover, fibers with beads, particles, and very fine fibers probably created from the molten jet can be seen at a high laser output power. These shapes were usually seen in the samples produced by a conventional S-ELSP in which a polymer solution with low viscosity was used. Thus, the actual melt viscosity during our melt-elctrospinning process seems to have been markedly low. Since an interconnected structure can be also seen between the fibers, their temperature of fibers reached at the collector would be higher than their melting point. It is apparent that sufficient thermal energy is provided to the fibers by the laser heating. The effect of the laser output power on the fiber diameter was investigated, and we found that the adequate range of the laser output power for making the fine fibers was very narrow. In any case, it should be noted that fibers with an average diameter smaller than 1 μm can be obtained by the use of our system.

Figures 5 and 6 show typical examples of the fibers produced from the wet rodlike EVAL samples. The mean diameter of the fibers produced from wet rods is larger than for fibers produced from dry

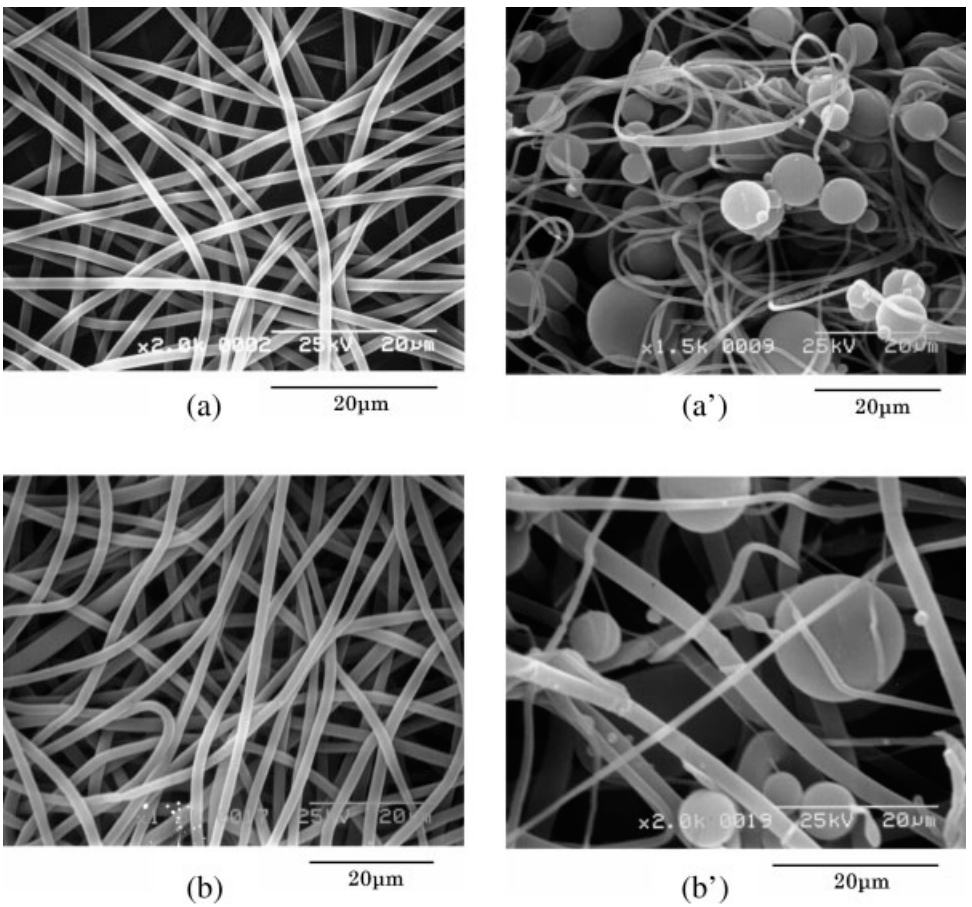

Figure 6 SEM images of EVAL fibers produced from wet rods. (a) EVAL3, $D = 1.271$ μm, $\sigma = 277$ nm, $H_v = 15$ kV, $L_p = 10$ W; (a′) EVAL3, $H_v = 15$ kV, $L_p = 16$ W; (b) EVAL4, $D = 1.791$ μm, $\sigma = 187$ nm, $H_v = 15$ kV, $L_p = 13$ W; (d′) EVAL4, $H_v = 15$ kV, $L_p = 15$ W.

rods. It should be noted that the fibers with diameter size smaller than 1 μm were not produced from the wet samples.

From these photographs of fibers made from wet and dry rods, we evaluated the average value and the standard deviation of the fiber diameter.

Figure 7 shows the effects of the ethylene content on the fiber diameters. The mean diameter of the fibers made from the dry rods appears to increase systematically with increasing ethylene content, suggesting that the fiber diameter is strongly influenced by the molecular structure. As stated previously, there are no systematic dependence of the ethylene content on the values of *MFI* and P_v (see Table I). This result means that *MFI* and P_v are not crucial factors in determining the fiber diameter.

The actual melt viscosity of EVAL would decrease with increasing ethylene content because the melting point of EVAL decreases with increasing ethylene content (see Table I). If the melt viscosity was a crucial factor in determining the fiber diameter, the diameter would decrease with increasing ethylene content. However, the experimental result does not support this idea. From this consideration, we conclude that the melt viscosity is not a crucial factor in determining the fiber diameter.

The mean diameter of fibers made from wet rod is almost independent of the ethylene content. We assumed that the fiber with smaller diameters would be produced from the wet rods because of the action of water on the melt-spinning process described ear-

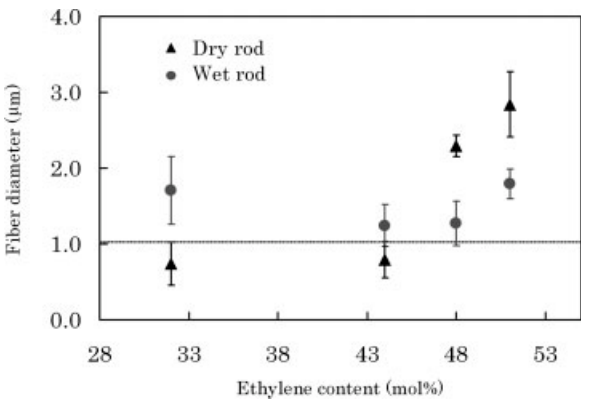

Figure 7 Effects of ethylene content on the diameter of EVAL fibers.

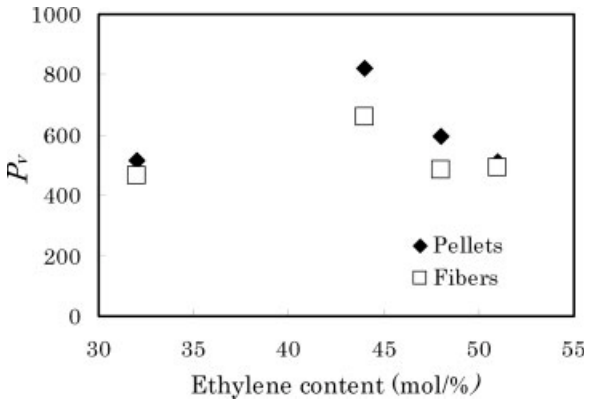

Figure 8 Effect of laser melting on the average viscometric degree of polymerization of EVAL, P_v.

lier. However, the experimental result does not support this assumption. The vaporization of water deprives the rod of heat so that the melt viscosity may increase, and therefore fibers with large diameters may be produced from the wet EVAL rods.

Since the mean diameter of EVAL fibers produced from the dry rod using M-ELSP increases with increasing ethylene content, we can say that the fiber diameter is influenced by its molecular structure. However, the formation mechanism of fibers is not clear in this work.

Finally, it should be noted that fibers having an average diameter smaller than 1 μm can be produced from EVAL with a low ethylene content using our melt-electrospinning system.

Physical properties of the fibers

Figure 8 shows the effect of laser melting on the average viscometric degree of polymerization, P_v, of EVAL. At a given ethylene content, the value of P_v

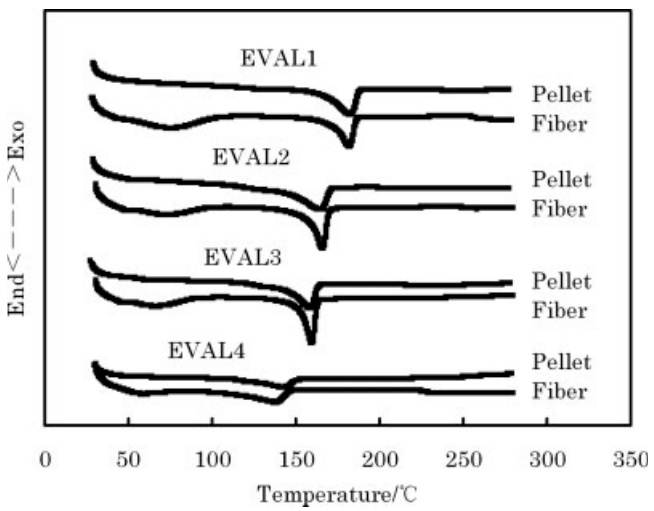

Figure 9 DSC curves of EVAL fibers made from the melt-electrospinning system developed.

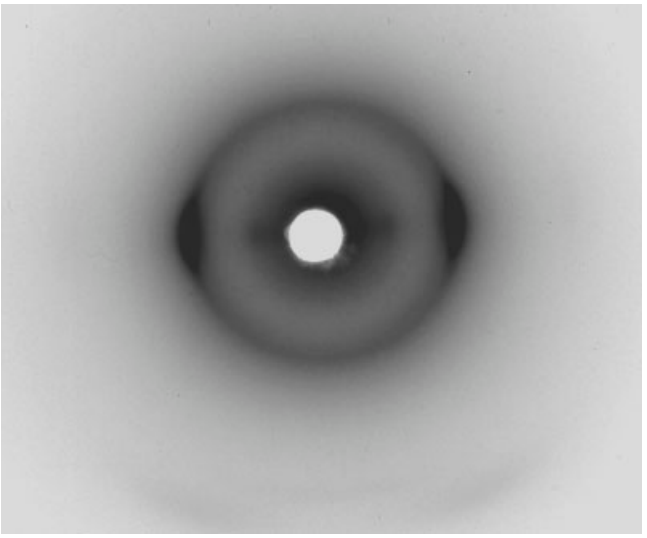

Figure 10 Wide angle X-ray photograph of fibers produced from dry EVAL2 rod.

of the fibers is smaller than that of the pellets; the laser heating causes P_v to decrease up to 20%. This small decrease should be noted because the laser heating causes the number average molecular weight of poly(lactide) to decrease from 89,000 to 13,000;[7] the thermal degradation of the ester bonds takes place markedly during the melt-electrospinning of poly(lactide). Since EVAL has no ester bonds, the molecular scission does not occur seriously during the melt-electrospinning of EVAL.

Figure 9 shows the thermal behavior of the EVAL fibers produced from dry rods. It can be seen that the melting point decreases with increasing ethylene content. The melting points of the fibers appear to be slightly lower than those of the original pellet samples, and the endothermal peaks of the fibers seem to be sharper than those of pellet samples. This result may mean that a decrease in the molecular weight of EVAL occurs during laser melting and that small crystals are formed from the molecules during the fiber formation process.

Figure 10 shows an X-ray photograph of the nanofibers which were made from the dry EVAL2 rod using a rotating collector; the rotating speed was 1 m/s. The fibers were aligned in a meridian direction. The photograph shows that the *c*-axis (fiber axis) of the crystals is parallel to the fiber direction.[12] This result suggests that the preferred crystallization takes place easily; the melt jet is elongated and then preferred crystallization takes place. It should be noted that such oriented crystallization could not be seen in other melt-electrospun thermoplastic such as poly(ethylene) and poly(ethylene terephthalate) fibers, although the same rotating speed was used for the melt-electrospinning.[13] It so happened that the crystallization rate was higher than the relaxation rate of

molecules during the melt-electrospinning of the dry EVAL2 rod.

The feasibility of a melt-electrospinning system equipped with a laser melting device as a production method for nanofibers is hard to discuss at this stage. We will discuss this issue after trying to produce various other fibers with our melt-electrospinning system and gathering more data on the physical properties of melt-electrospun fibers.

CONCLUSIONS

Fibers were produced from rodlike EVAL samples using a melt- electrospinning system equipped with a laser melting device, and then the morphology and thermal properties of the fibers were investigated. The following conclusions were reached:

1. Only a single fiber was formed from EVAL rods irrespective of ethylene content and moisture regain during the melt-electrospinning process. This means that jet instability in which solution jet split into smaller filaments is not fierce in the melt-electrospinning process. In other words, this implies that the elongation process of the melt jet is important to obtain fibers with fine diameter.
2. The fibers having an average fiber diameter smaller than 1 μm can be produce from dry EVAL rods with low ethylene content.
3. The average diameter of fibers produced from dry EVAL rods increases by increasing ethylene content.
4. The average diameter of fibers produced from wet EVAL rods is larger than that of fibers produced from dry EVAL rods, and is almost independent of the ethylene content.
5. The laser heating does not decrease markedly the melting point and the average viscometric degree of polymerization of EVAL.
6. Preferred crystal orientation can be seen in the electrospun EVAL 2 fibers which were made from dry rod using a rotating rotor.

References

1. Huang, Z.-M.; Zhang, Y.-Z.; Kotaki, M.; Ramakrishna, S. Compos Sci Technol 2003, 63, 2223.
2. Chronakis, I. S. J Mater Process Technol 2005, 167, 283.
3. Nasir, M.; Matsumoto, H.; Danno, T.; Minagawa, M.; Irisawa, T.; Shioya, M.; Tanioka, A. J Polym Sci Part B: Polym Phys 2006, 44, 779.
4. Reneker, D. H.; Chun, I. Nanotechnology 1996, 7, 216.
5. Lyons, J.; Li, C.; Ko, F. Polymer 2004, 45, 7597.
6. Warner, L. S.; Ugbolue, S.; Jaffe, M.; Patra, P. FY2005 New Project Proposal, National Textile Center, USA, 2005. No. F05-MD01.
7. Ogata, N.; Yamagichi, S.; Shimada, N.; Lu, G.; Iwata, T.; Nakane, K.; Ogihara, T. J Appl Polym Sci, to appear.
8. Zhang, Y.; Hung, Y.; Wang, L.; Li, F.; Gong, G. Mater Chem Phys 2005, 91, 217.
9. Lu, C.; Chen, P.; Li, J.; Zhang, Y. Polymer 2006, 47, 915.
10. Kenawy, E. R.; Layman, J. M.; Watkin, J. R.; Bowlin, G. L.; Matthews, J. A.; Simpson, D. G.; Wnek, G. E. Biomaterials 2003, 24, 907.
11. Uchiumi, N.; Wakui, T. (Kuraray Company Ltd., Japan) Patent WO 2004 2004092234.
12. Takahashi, M.; Tashiro, K.; Amiya, S. Macromolecules 1999, 32, 5860.
13. Ogata, N.; Yamagichi, S.; Shimada, N.; Iwata, T.; Nakane, K.; Ogihara, T., unpublished result.