Melt-Electrospinning of Poly(ethylene terephthalate) and Polyalirate

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ABSTRACT: Rodlike polymer samples were made from three kinds of poly(ethylene terephthalate) (PET) pellets with different intrinsic viscosities (*IV*), and from polyalirate (Vectra) pellets. PET and Vectra fibers were produced using a melt-electrospinning system equipped with a CO_2-laser melting device from these rodlike samples. The effects of *IV* value and laser output power on the fiber diameter of PET were investigated. Furthermore, the effect of the laser output power on the fiber diameter of Vectra was investigated. The crystal orientation of these produced fibers was also investigated by X-ray photographs. The following conclusions were reached: (i) the diameter of PET fiber decreases with increasing laser output power; (ii) the minimum average diameter of PET fibers is scarcely influenced by the value of *IV*; (iii) the electrospun PET fibers show isotropic crystal orientation; (iv) fibers having an average fiber diameter smaller than 1 μm cannot be obtained from PET and Vectra using the system developed; and (v) preferred liquid crystal orientation can be seen in electrospun Vectra fibers. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 1127–1132, 2007

Key words: melt-electrospinning; poly(ethylene terephthalate); polyalirate; 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 is a simple technique for the production of nanofibers, and is classified into solution and melt types.[4] Since the melt type has many advantages, we developed a new melt-electrospinning system with a CO_2 laser heating device in a previous work.[5]

Poly(lactide)(PLA) and poly(ethylene-*co*-vinyl alcohol)(EVAL) are biomaterials. Scaffolds for cell growth are produced from nanofibrous mats made of these materials using the solution-electrospinning method.[6,7] However, residual solvent in fibers is not favorable for medical applications. Therefore, we devised a melt-electrospinning system, which has no issues related to solvent, and used it to make fibers from poly(lactide) and poly(ethylene-*co*-vinyl alcohol).[8] Our system has other two features: (i) the fibers can be produced from polymers having high melting points; and (ii) fibers can be produced from polymers containing impurities because the nozzle is not used for making fibers but fibers can be produced directly from rodlike samples; PLA nanofibers have been recently produced with the melt-electrospinning system equipped with the nozzle.[9]

In this study, we try to produce fibers with relatively high melting points using our developed melt-electrospinning system.

Poly(ethylene terephthalate) (PET) has melting point of ca. 260°C and is a thermoplastic polymer resin of the polyester family that is used in synthetic fibers; beverage, food, and other liquid containers; thermoforming applications; and engineering resins often in combination with glass fiber. One of the most important characteristics of PET is its intrinsic viscosity or *IV*, which increases with increasing molecular length. The value of *IV* is supposed to affect the properties of the fibers produced with the melt-electrospinning system.

Polyalirate (Vectra) is a wholly aromatic polyester, and a thermotropic liquid crystal polymer; its melting point is about 330°C. Its molecules are stiff, rodlike structures organized in ordered domains in the solid and melt states. Therefore, fibers made from Vectra, Vectran, are noted for thermal stability at high temperatures, high strength, and modulus, low creep, and good chemical stability. During the heat treatment of polyalirate, solid-state polymerization takes place accompanied by the formation of by-product gas. The fugacity of the gas from fine polyalirate fibers is expected to be relatively high because the surface area of fine fibers is large. Heat-treatment of the fine polyalirate fibers would increase its molecular weight easily; consequently, fibers having

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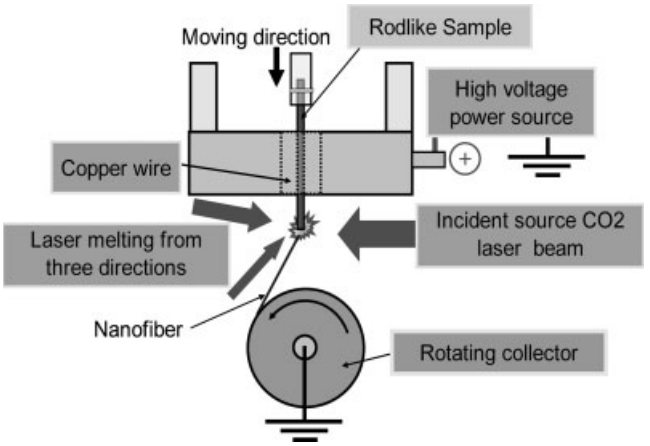

Figure 1 Schematic diagram of the melt-electrospinning system used.

high strength and good chemical stability should be produced within a relatively short time.

Fine fibers made from PET and Vectra can be used for many applications such as high-temperature gas filters and separators for secondary batteries. It is clear that these fibers cannot be industrially produced using the solution-electrospinning method owing to solvent-related issues. However, there is no study concerning melt-electrospinning of these polymers. In this work, three kinds of rodlike PET samples with different *IV* values and rodlike Vectra sample were prepared, and fibers were produced from these rods using our melt-electrospinning system equipped with a laser melting device. The effects of the value of *IV* and laser output power on the diameter of the PET fibers were studied, and their physical properties were investigated. Vectra fibers were also produced and their structure was investigated.

EXPERIMENTAL

Materials

Three kinds of fiber-grade PET samples with different *IV* values were supplied by KURARAY CO., LTD (Osaka, JAPAN); specifically, samples having $IV = 0.512$ dL/g, $IV = 0.637$ dL/g, and $IV = 0.706$ dL/g were used. The samples will be referred to by their *IV* values. Vectra pellets (apparent viscosity was 3.358 Pa's measured at 340°C and apparent shear rate = 1.918 E + 04 s^{-1}) were also supplied by KURARAY CO., LTD (Osaka, Japan). Many types of Vectra with different melt properties were tried to produce fibers. However, it was found that fibers were produced only from the above Vectra; its melt viscosity had the lowest value.

Rodlike samples, 0.2–0.5 mm in diameter, were made from the pellets with a Shimadzu Flow Tester CFT-500 (Kyoto, JAPAN); the temperature at the melting zone and pressure were adjusted for each polymer. These rodlike samples were provided for the melt-electrospinning tests.

Melt-electrospinning

Figure 1 shows the melt-electrospinning system used in this study. The details of the system can be found in the previous work.[5,8] A rodlike sample was fed to the laser irradiating part; the feed rate was 1–3 mm/min. The end of the rod was melted by the irradiation of laser beams; the output power of a source laser beam will be denoted as L_p. Voltage at the level just preceding an electric discharge was applied between the melted part of the rod and the grounded collector; this voltage, H_v, was 18–20 kV. The molten end-to-collector distance, C_d, was 25 mm. The flat cupper plate and a rotating aluminum disk were used for the collection of fibers.

Characterization of fibers

The morphology of the electrospun fibers was examined with a Hitachi *S*-2300 scanning electron microscope (SEM, Tokyo, JAPAN) equipped with a camera. Using a digitizer on the enlarged photographs, we estimated the fiber diameter and its standard deviations from thirty measurements of fibers obtained at each spinning condition. The average diameter and its standard deviation will be referred to as D and σ, respectively.

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

For the evaluation of the crystal orientation of the fibers, unidirectionally aligned fiber bundles were produced from PET and Vectra using a rotating disk as a collector; the circumferential speed was about 1 m/min. X-ray diffraction photographs of the aligned fibers were obtained with a Toshiba D-3 apparatus (Tokyo, Japan).

RESULTS

Melt-electrospinning of PET

Although we expected that many fibers would be simultaneously formed from a rod, it was found that only a single fiber was actually formed from a rod during the melt-electrospinning process. Figure 2 shows typical examples of the fibers produced from PET rods. At a low laser output power, only fibers can be seen irrespective of *IV*. However, at a high laser output power, fibers with beads can be seen.

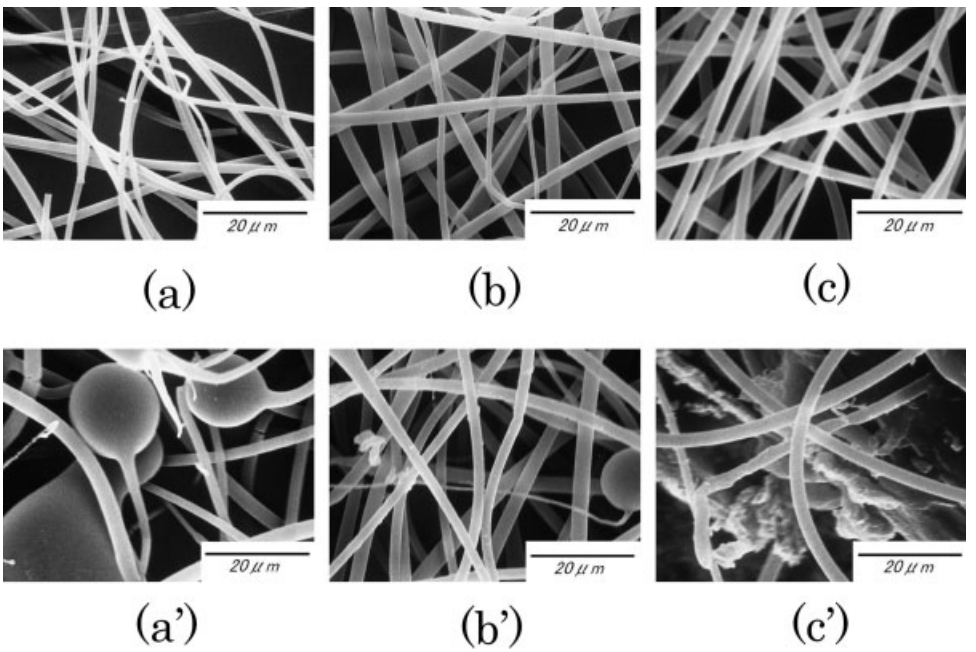

Figure 2 Photographs of electrospun PET. (a) $IV = 0.512$, $L_p = 8$ W, (a′) $IV = 0.512$, $L_p = 9$ W, (b) $IV = 0.637$, $L_p = 10$ W, (b′) $IV = 0.637$, $L_p = 11$ W, (c) $IV = 0.706$, $L_p = 10$ W, (c′) $IV = 0.706$, $L_p = 11$ W.

Figure 3 shows the effects of the laser output power and the value of *IV* on the fiber diameter of electrospun PET fibers. The diameter seems to decrease and then increase with increasing laser output power, irrespective of *IV*. At a high laser output power, not only fibers but also beads can be seen. The minimum value of the average fiber diameter is independent of the value of *IV*, although PET with a low *IV* attains a minimum at a lower laser output power. It should be noted that the minimum value of average fiber diameter obtainable from our system is about 1.7 μm irrespective of the *IV* value. This result suggests that the obtainable fiber diameter is not influenced by the molecular weight of the PET. To obtain fibers with a diameter smaller than 1 μm, we must improve our electrospinning system that stretches markedly the melt jet,[9] since the material's *IV* parameter, which dominates the melt viscosity, does not affect the minimum average fiber diameter.

Figure 4 shows an X-ray photograph of an electrospun $IV = 0.512$ sample. Weak diffraction rings can be seen. This means that small crystals were formed with isotropic crystal orientation in the fibers. Figure 5 shows the DSC curves of electrospun fibers and rods. An exothermal peak can be seen in the electrospun fibers at about 130°C. This means that the fibers

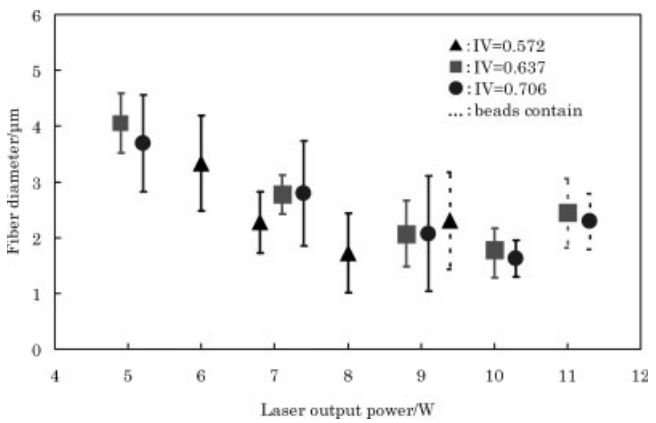

Figure 3 Effects of laser output power and *IV* on the fiber diameter of PET.

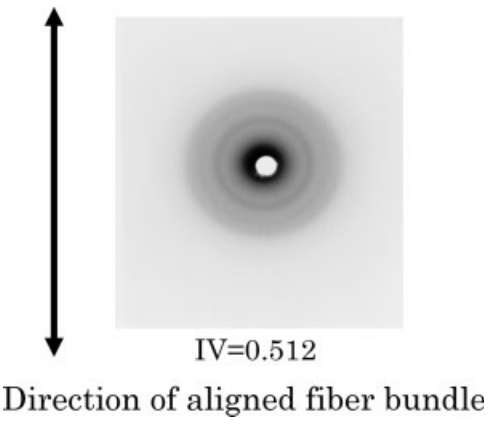

Figure 4 X-ray photograph of aligned fiber bundles of PET which were produced using laser output power 7 W.

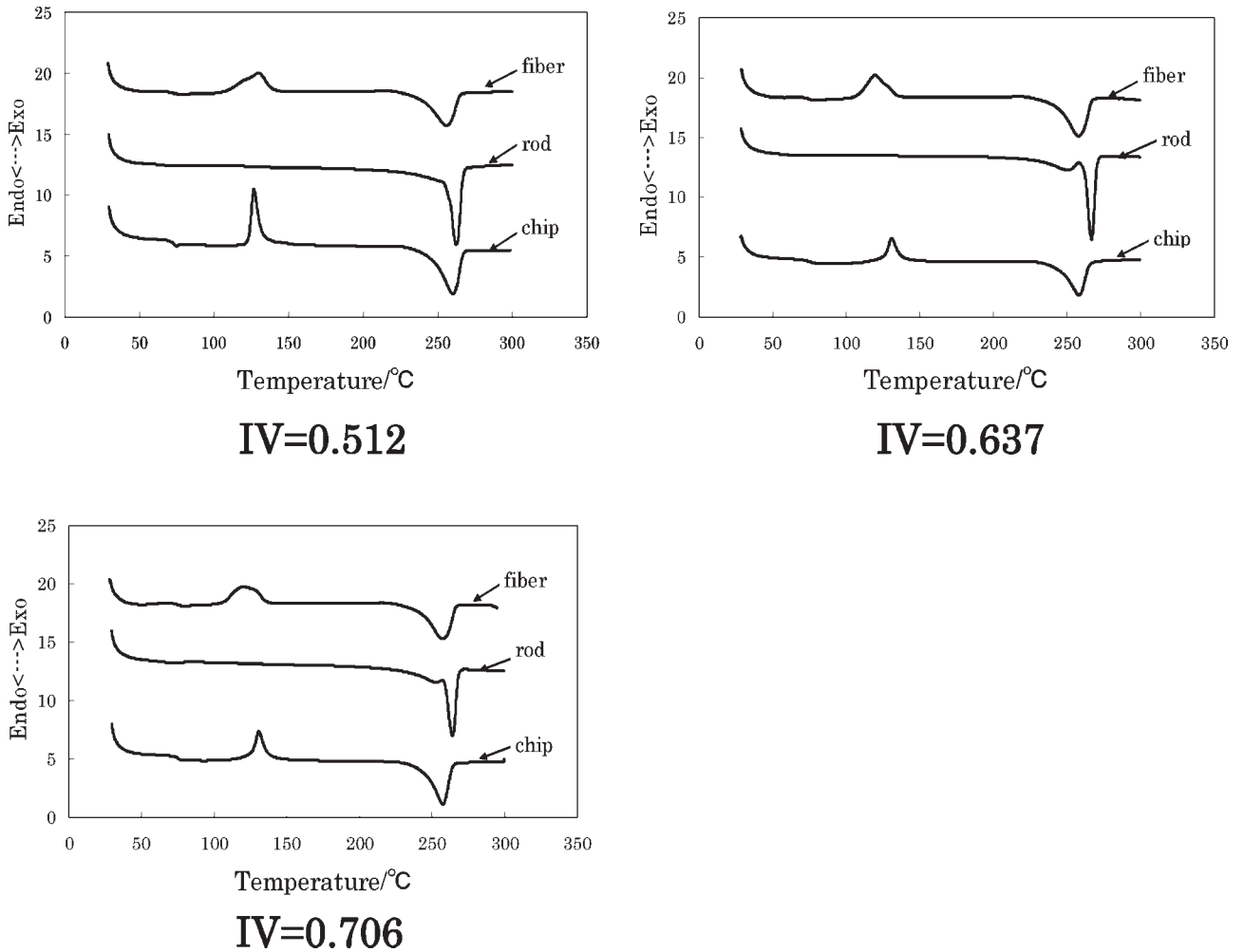

Figure 5 DSC curves of electrospun fibers. L_p values of $IV = 0.512$, $IV = 0.637$, and $IV = 0.706$ were 7 W, 9 W, and 9 W, respectively.

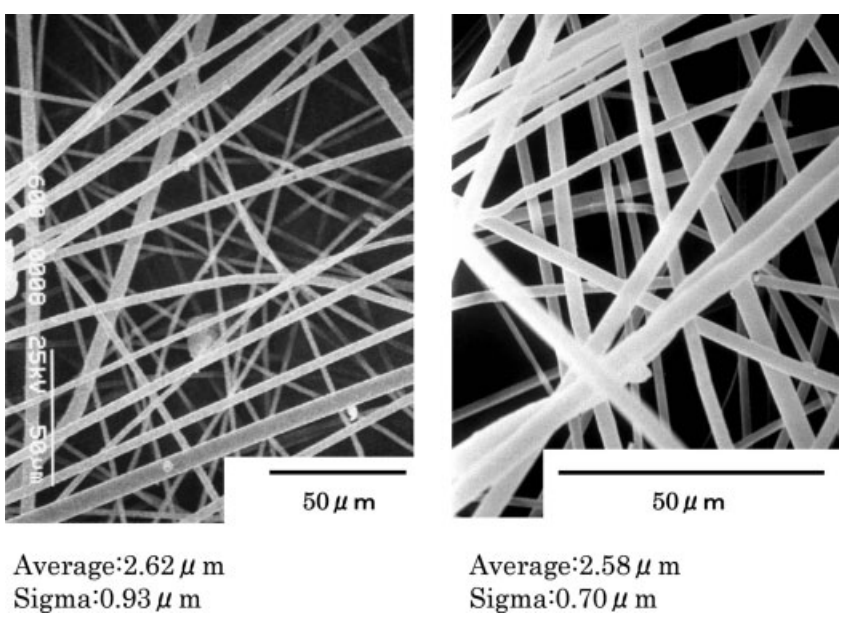

Figure 6 Photographs of Vectra fibers produced.

contain polymers in an amorphous state, and well-developed large crystals are not formed in the fibers.

Melt-electrospinning of polyalirate

In the spinning process, a single fiber was formed. Figure 6 shows the typical Vectra fibers produced. It was found that fibers could be formed when the laser output power was smaller than 10 W. However, the laser output power increases over this value, not only fibers but also beads could not be seen, instead, powder-like substances could be seen; the substances may be thermolysis products. Figure 7 shows the effect of laser output power on the fiber diameter. It can be seen that the diameter decreases with increasing laser output power. This means that the reduction of the melt viscosity is necessary for the production of the fine fibers to some extent. However, there is a limit on obtaining fine fibers by increasing laser output power. It should be noted; however, that Vectra fibers with an average fiber diameter of 2.5 μm were produced by our system. Vectra fibers with such a small diameter were not commercially produced with a melt-blowing method. Figure 8 shows an X-ray diffraction photograph of a bundle of fibers. The intensity maximums can be seen on the equator. This means that preferred liquid crystal orientation takes place along fiber direction. This result should be noted because PET fibers show isotropic crystal orientation. Since Vectra has rodlike molecules, preferred liquid crystallization is believed to take place easily during the melt-electrospinning process.

In the melt-electrospinning process of both PET and Vectra, only a single fiber was formed. To obtain nanofibers from these polymers, we should amplify the whipping motion which stretches a main melt-jet, because the jet instability that takes place in solution electrospinning process cannot be seen in our melt-electrospinning process.[7,9]

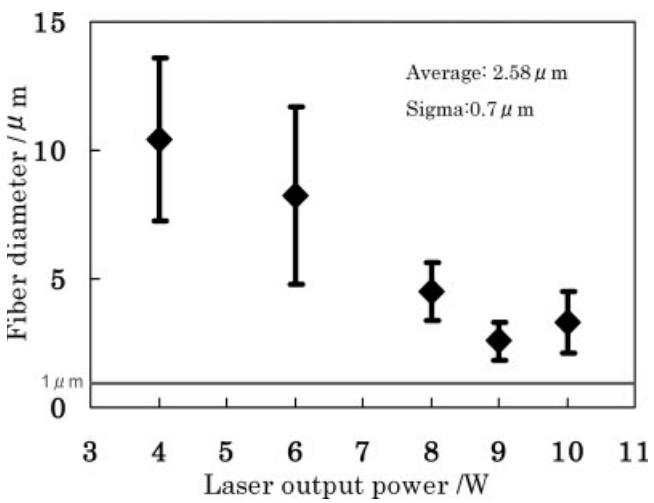

Figure 7 Effect of laser output power on the fiber diameter of Vectra.

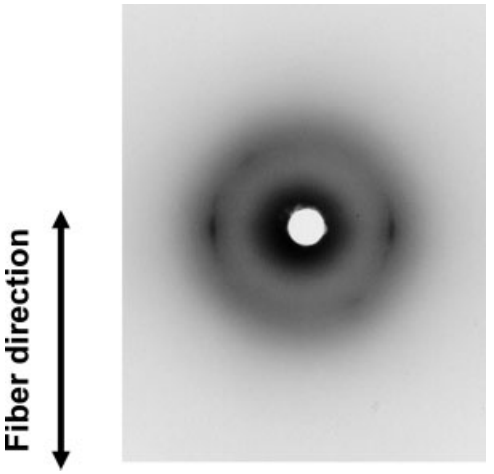

Figure 8 X-ray photograph of aligned fiber bundles of Vectra.

DISCUSSION

The fiber producing process in the solution electrospinning process is generally considered as follows: (1) a solution jet ejects from the Taylor cone; (2) the jet is stretched with the vaporization of solvent (3) the electrical charge density in the jet increases with the vaporization; (4) the jet is extensively stretched with whipping motion; and (5) nanofibers were, consequently, formed and collected on the collecting plate.[10] Zhou et al. reported that the fiber diameter is markedly decreased with decreasing nozzle diameter, with increasing nozzle temperature, spinning temperature, and electric field strength.[9] This result suggests that we should increase the electrical charge density and stretch the jet markedly to obtain nanofibers from the melt-electrospinning process. Current our system can only response to increase the melt temperature. Therefore, taking account of these parameters aforementioned, we should improve our system to obtain fibers with diameter smaller than 1 μm.

CONCLUSIONS

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

i. Only a single fiber was formed from PET and Vectra rods during the melt-electrospinning process. This means that the jet instability which takes place in solution electrospinning is not

fierce in the melt-electrospinning process. In other words, this implies that we should amplify the whipping motion of melt-jet to obtain nanofibers from PET and Vectra.

ii. The diameter of PET fiber decreases with increasing laser output power.

iii. The minimum average fiber diameter of PET was scarcely influenced by its intrinsic viscosity.

iv. The electrospun PET fibers show isotropic crystal orientation.

v. Fibers having an average fiber diameter smaller than 1 μm cannot be obtained from PET or Vectra using the system developed.

vi. Preferred liquid crystal orientation can be seen in electrospun Vectra fibers.

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