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Biodegradable poly(L-lactic acid) nanofiber prepared by a carbon dioxide laser supersonic drawing

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ABSTRACT

Biodegradable poly(L-lactic acid) (PLLA) nanofiber was prepared by a carbon dioxide (CO_2) laser supersonic drawing which was carried out by irradiating the laser on an as-spun fiber in a supersonic jet. The supersonic jet was generated by blowing off air into a vacuum chamber from a fiber supplying orifice. The flow velocity from the orifice can be estimated by applying Graham's theorem from the pressure difference between the atmospheric pressure and the pressure of the vacuum chamber. The fastest flow velocity estimated was 396 m s^{-1} when the chamber pressure was 6 kPa. The PLLA nanofiber having an average diameter of 0.132 μm was obtained when the supersonic drawing was carried out by irradiating the laser at 177 W cm^{-2} on the as-spun fiber supplied at 0.1 m min^{-1} in the vacuum chamber at 6 kPa. The obtained nanofiber had a draw ratio of about 323,000 and a degree of crystallinity of 45%, and its diameter uniformity was high. The CO_2 laser supersonic drawing was a new route for preparation of various nanofibers without using any solvent.

1. Introduction

Nanofibers are applied in a variety of fields such as membrane [1–3], biomedical devices [4], and scaffold for tissue engineering [5–9]. The nanofibers are most useful in the tissue engineering because of large surface area per unit mass and very small pore size. The nanofibers are prepared by an electrospinning [10–20], a sea-island-type conjugated melt spinning, a single orifice melt blowing [21], and a jet blowing [22]. The single orifice melt blowing and the jet blowing are new methods to prepare the nanofibers. The electrospinning is the method most often used for preparing the nanofibers at the moment. In the electrospinning, in the electric field between capillary tip and metallic collector, polymer solution is sprayed onto the metallic collector, and then made into nanofibers. In the sea-island-type conjugated melt spinning, the nanofiber is prepared by removing a sea component from the sea-island-type conjugated melt spun fiber.

Poly (L-lactic acid) (PLLA) and its copolymer nanofibers are prepared by the electrospinning, their electrospun nanofibers are widely used in the study of tissue engineering because of their biocompatibility and biodegradability. The electrospun PLLA nanofibers were prepared by spraying polymer solution onto the metallic collector under a high voltage. Polymer solution was prepared by dissolving the PLLA in dichloromethane (DCM)/*n*,*n*-dimethyl-formamid or DCM/pyridine [23,24].

A carbon dioxide (CO_2) laser-thinning method developed by us could easily produce microfibers by irradiating a continuous-wave CO_2 laser on fibers, such as PET [25], nylon 6 [26], nylon 66 [27], i-polypropylene [28], poly(L-lactic acid) (PLLA) [29,30], and poly(ethylene-2,6-naphthalate) [31] fibers without highly skilled techniques. The microfibers obtained by winding on a spool in the winding speed range of 100–2500 m min^{-1} were monofilament microfibers having the minimum fiber diameter of ranging 1–3 μm. The CO_2 laser-thinning apparatus preparing the

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monofilament microfiber could be also produced the PET nonwoven fabric [32] by using an air-jet and a collecting net in place of a winder. However, no fiber of 1 μm or less in diameter was produced by the CO_2 laser-thinning method.

We found a new route to make nanofiber recently. In this approach, the nanofiber was obtained by irradiating the CO_2 laser on an as-spun fiber in the low-temperature supersonic jet (hereinafter called "the CO_2 laser supersonic drawing"). The supersonic jet was generated by blowing off air into vacuum from an orifice to put the fiber into a vacuum chamber. The adiabatic expansion of air across the orifice causes the decrease in the temperature of jet. The as-spun fiber was instantly heated by the high power laser in the low-temperature supersonic jet, tremendously deformed by a shearing force in the supersonic flow, and ultra-drawn to hundreds of thousands of times. The CO_2 laser supersonic drawing can be applied to many thermoplastic polymers, and their oriented monofilament nanofibers were obtained without using any solvent or removing the second component. The CO_2 laser supersonic drawing is a novel method preparing the nanofibers.

Here we show an approach to prepare the PLLA nanofiber by the CO_2 laser supersonic drawing and its properties.

2. Experimental

The original fiber used in this study was an as-spun PLLA fiber with a diameter of 75 μm, birefringence of 6.3×10^{-3}, and a degree of crystallinity of 36%. Its number and weight average molecular weights were 29,000 and 120,000, respectively.

The morphology of nanofiber was determined with SEM (JSM-6060LV, JEOL). SEM micrographs of the fibers were observed with an accelerating voltage of 10 kV. Before the observation, the samples were coated with gold using a sputter coater. The average diameter and the diameter distribution were obtained by using imaging analyzer.

Wide-angle X-ray diffraction (WAXD) images of the nanofiber were taken with an imaging-plate (IP) film and an IP detector *R*-AXIS DS3C (Rigaku Co.). The IP film was attached to the X-ray generator (Rigaku Co.) operated at 40 kV and 200 mA. The radiation used was Ni-filtered Cu Kα. The sample-to-film distance was 40 mm. The fiber was exposed for 5 min to the X-ray beam from a pinhole collimator with a diameter of 0.4 mm. The degree of crystal orientation (π) estimated from the half-width (H) of the meridian reflection peak. The π value was estimated from WAXD pattern measured by the imaging-plate through the software for analyzing data.

The π value is given by the equation:

$$\pi = \frac{180 - H}{180} \times 100 \tag{1}$$

Weight average molecular weight (M_w) and number average molecular weight (M_n) were measured with gel permeation chromatography (HLC-8200GPC, Tosoh Co.). The GPC analysis was performed at a column temperature of 40 °C in chloroform and differential refractive index detector. Two 30 cm gel columns (TSK gel GMH-HR-H) were used at a flow rate of 1.0 mL min^{-1}.

The DSC measurements were carried out using a THERM PLUS 2 DSC 8230 C calorimeter (Rigaku Co.). The DSC scans were performed within the temperature range of 25–200 °C using a heating rate of 10 °C min^{-1}. All DSC experiments were carried out under a nitrogen purge. About 2 mg of nanofiber mat was sealed in aluminum pan and used for the measurement. The DSC instrument was calibrated with indium. The degree of crystallinity (X_c) was determined from heat of fusion (ΔH_m) and enthalpy of cold crystallization (ΔH_{cc}) as follow:

$$X_c = \frac{\Delta H_m + \Delta H_{cc}}{-93} \times 100 \tag{2}$$

where -93 J g^{-1} is used as the heat of fusion of the crystalline phase of PLLA [33].

The apparatus used for the CO_2 laser supersonic drawing consisted of spool supplying the original fiber, a continuous wave CO_2 laser emitter (a wave number of 10.6 μm, a beam diameter of 2.4 mm), the vacuum chamber with antireflection coating Zn–Se windows, fiber supplying orifice with a diameter of 0.5 mm, power meter, and a vacuum pump as shown in Fig. 1. The laser power of more than 90% was obtained in the area of the 2.4 mm ϕ laser spot. The power intensity was estimated by dividing the measured laser power in the area of the laser spot. The maximum laser intensity in this study was 177 W cm^{-2}.

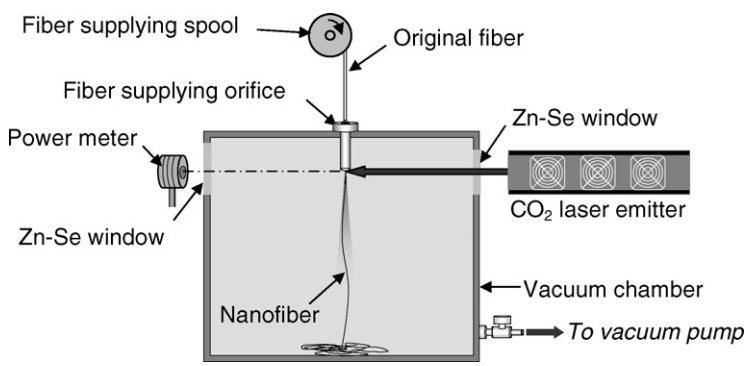

Fig. 1. Schematic diagram of apparatus used for CO_2 laser supersonic drawing in a supersonic jet.