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Poly(L-lactic acid) nanofiber multifilament prepared by carbon dioxide laser supersonic multi-drawing

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ABSTRACT

Poly(L-lactic acid) (PLLA) nanofiber multifilament (NFMF) was continuously prepared by CO_2-laser supersonic multi-drawing (CLSMD), which was conducted by laser irradiation of the PLLA fibers in a supersonic jet. The CLSMD apparatus used for the continuous preparation of NFMF consists of a fiber supply spool, a continuous-wave CO_2 laser, a vacuum chamber with Zn–Se windows, a fiber injection orifice plate, a net conveyor, an interlacer, and a take-up roll. NFs collected onto the net conveyor were intermingled by the interlacer and then wound by the take-up roll. PLLA-NFMF obtained at a laser power of 40 W and a chamber pressure of 30 kPa was composed of approximately 85,000 NFs with an average diameter of 0.311 μm. The obtained NFMF was annealed at 85 °C under an applied tension of 5.14 MPa to improve the mechanical properties; the annealed NFMF had a Young's modulus of 2.1 GPa and a tensile strength of 68 MPa. NFMF braid could be prepared with a braiding machine because the mechanical properties were improved by annealing. CLSMD is a new route for the preparation of NFMF composed of various polymers without the use of a solvent.

1. Introduction

Nanofibers (NFs) are used in a variety of applications, such as membranes [1–3], biomedical devices [4], and scaffolds for tissue engineering [5–9]. NFs have been produced by electrospinning [10–18], melt electrospinning [19–21], sea-island-type conjugated melt spinning, single-orifice melt blowing [22], and jet blowing [23]. We have previously proposed a technique for the production of NFs referred to as CO_2-laser supersonic drawing (CLSD). CLSD is a novel technique that uses laser irradiation of fibers in a supersonic jet, and can easily prepare various NFs. CLSD employs only CO_2 laser irradiation and does not require additional processes or solvents, unlike electrospinning, which requires a solvent, or sea-island-type conjugated melt spinning that requires the removal of a second component. CLSD has already been applied to prepare NFs of poly(L-lactic acid) (PLLA) [24], poly(ethylene terephthalate) (PET) [25], poly(ethylene-2,6-naphthalate) [26], poly(glycolic acid) (PGA) [27], ethylene tetrafluoroethylene copolymer [28], nylon 66 [29], and poly(phenylene sulfide) [30].

Modification of the CLSD technique has led to the development of CO_2-laser supersonic multi-drawing (CLSMD) for the formation of large NF sheets with highly uniform thickness. CLSMD employs a vacuum chamber with several fiber injection orifices and a winding spool to collect NFs. CLSMD has already been applied to produce rectangular NF sheets of PET [31] and isotactic polypropylene [32] that were 17 cm wide and 18 cm long.

Furthermore, we have proposed a CLSMD technique that can address the requirements for the mass production of NF sheets, and an apparatus for the production of long and broad NF sheets by CO_2-laser supersonic continuous multi-drawing (CLSCMD) was designed [33]. Long and broad PET NF sheets were continuously produced using the CLSCMD apparatus equipped with a 80 zigzag orifice plate and a single laser. The obtained PET-NF sheets were composed of uniform-diameter NFs and were wound on a take-up roll together with a PET film used as the isolating layer.

However, NF nonwoven fabrics have been restricted in their applications due to their poor mechanical properties. Attempts to produce NF yarns from electrospun NFs were reported by many researchers. In the early stages, the production of aligned NFs was attempted using a high speed rotating drum collector and a tapered wheel, and short NF yarns were obtained with such setups [34–36]; however, continuous NF yarns were not successfully produced. Recently, electrospinning setups have been improved by a variety of new techniques and devices, and have been developed

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to produce continuous NF yarns. As a result, twisted NF yarns with improved mechanical properties have been prepared by twisting NF web with a rotating disk collector and a rotating funnel [37,38].

PLLA and its copolymer NFs are prepared by electrospinning, and the electrospun NFs are widely used in tissue engineering research due to their biocompatibility and biodegradability. The electrospun PLLA-NFs were prepared by spraying polymer solution onto a metallic collector under a high voltage. The polymer solution was prepared by dissolving PLLA in dichloromethane (DCM)/*N*,*N*-dimethylformamide or DCM/pyridine [39,40].

The PLLA-NFs were collected not only as nonwoven fabric, but also as continuous NF yarns. Continuous twisted PLLA microfiber yarn with an average diameter of 6.0 ± 1.9 μm was prepared using the electrospinning setup with a rotating funnel target, and its mechanical properties were better than those of electrospun NF yarn collected parallel to the fiber direction [37].

PLLA-NFs were also produced by the CLSD technique and were collected as nonwoven fabric using the CLSD setup with a collecting spool [24]. NFs obtained by CLSD can be made indefinitely long because the fiber is supplied at a constant speed and is continuously irradiated with a laser beam. Continuous NF yarns may be produced from long supersonic-drawn NFs using a CLSD setup improved for the preparation of continuous NF yarns.

In this study, a CLSMD setup was newly designed and manufactured to prepare a continuous PLLA-NF multifilament (NFMF), and their superstructure and mechanical properties were characterized.

2. Experimental

The original fiber used in this study was a commercial-grade drawn PLLA fiber with a diameter of 51 μm and a 44.4% degree of crystallinity. The original PLLA fiber has a high degree of crystal orientation, as shown in the wide-angle X-ray diffraction (WAXD) pattern in Fig. 1, and the degree of crystal orientation estimated using Eq. (1) was 0.960.

The morphology of NFMF was determined using scanning electron microscopy (SEM; JCM-5700, Jeol). SEM micrographs of the fibers were observed at an accelerating voltage of 10 kV. Prior to observations, the samples were coated with platinum using a sputter coater. The average diameter and the diameter distribution were obtained using an imaging analyzer.

WAXD patterns of the NFMF were obtained using an imaging-plate (IP) film and an IP detector (*R*-AXIS DS3C, Rigaku Co.). The IP film was attached to an X-ray generator (Rigaku Co.) operated at 40 kV and 200 mA. The radiation used was Ni-filtered CuKα radiation. The sample-to-film distance was 40 mm. The fiber was exposed for 60 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 in the WAXD pattern measured with the imaging-plate using data analysis software.

The π value is given by:

$$\pi = \frac{180 - H}{180} \times 100. \quad (1)$$

The *d*-spacing between the planes in the atomic lattice is estimated from Bragg's law:

$$n\lambda = 2d \sin\theta, \quad (2)$$

where n is an integer, λ is the wavelength of the incident X-ray beam, and θ is the angle between the incident ray and the scattering planes.

Differential scanning calorimetry (DSC; Thermo Plus 2 DSC 8230C, Rigaku Co.) measurements were performed within the temperature range of 25–200 °C using a heating rate of 10 °C min^{-1}. All DSC experiments were performed under a nitrogen purge. Approximately 2 mg sample of NFMF was sealed in an aluminum pan for measurement. The DSC instrument was calibrated using indium as a standard. The degree of crystallinity (X_c) was determined from the heat of fusion (ΔH_m) and the enthalpy of cold crystallization (ΔH_{cc}) as follows:

$$X_c = \frac{\Delta H_m + \Delta H_{cc}}{-93} \times 100, \quad (3)$$

where −93 J g^{-1} was used as the heat of fusion for the crystalline phase of PLLA [41].

The mechanical properties of NFMF were determined using a tensile testing machine (Autograph, Shimadzu Co.,) with a gage length of 5 cm and an elongation rate of 10 mm min^{-1}. The average of 10 measurements was taken as an experimental result.

Fig. 2 shows a schematic diagram of the CLSMD apparatus newly designed and manufactured for the continuous preparation of NFMF, including a photograph of the winding NFMF. The apparatus consists of a fiber supply spool, nip rolls to supply the original fiber to the injection orifice at a constant speed, a continuous-wave CO_2 laser with an output wavelength of 10.6 μm and a maximum power of 40 W, a power meter, a vacuum pump, a vacuum chamber with Zn–Se windows, an orifice plate with 25 fiber injection orifices, a

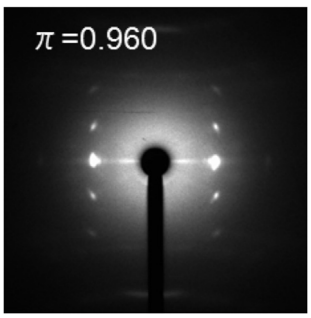

Fig. 1. WAXD pattern for PLLA original fiber including the degree of crystal orientation (π).

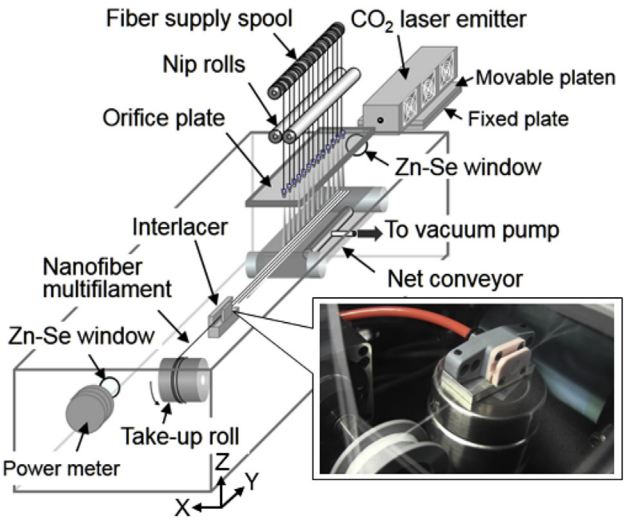

Fig. 2. Schematic diagram of the CLSMD apparatus used for the continuous preparation of NFMF.