Ethylene tetrafluoroethylene nanofibers prepared by CO₂ laser supersonic drawing

A. Suzuki*, H. Hayashi

Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, Takeda-4, 400-8511 Kofu, Japan

Received 19 December 2012; accepted in revised form 19 February 2013

Abstract. Ethylene tetrafluoroethylene (ETFE) nanofibers were prepared by carbon dioxide (CO₂) laser irradiation of as-spun ETFE fibers with four different melt flow rates (MFRs) in a supersonic jet that was generated by blowing air into a vacuum chamber through the fiber injection orifice. The drawability and superstructure of fibers produced by CO₂ laser supersonic drawing depend on the laser power, the chamber pressure, the fiber injection speed, and the MFR. Nanofibers obtained using a laser power of 20 W, a chamber pressure of 20 kPa, and an MFR of 308 g·10 min⁻¹ had an average diameter of 0.303 μm and a degree of crystallinity of 54%.

Keywords: nanomaterials, ETFE, CO₂ laser supersonic drawing, melt flow rate, flow-induced crystallization

1. Introduction

Nanofibers are used in various applications including membranes [1–3], biomedical devices [4], and tissue engineering scaffolding [5–9]. Nanofibers can be prepared by electrospinning [10–13], sea-island conjugated melt spinning, single-orifice melt blowing [14], and jet blowing [15]. While electrospinning is widely used to fabricate various nanofibers, it cannot be applied to polymers that show really high resistance to solvents, such as polyolefins and fluoropolymers.

We have developed a new approach for producing nanofibers, which we term carbon dioxide (CO₂) laser supersonic drawing (CLSD). CLSD can be used to easily prepare various nanofibers because it involves only CO₂ laser irradiation; it does not require any other processes or solvents. It involves irradiating a fiber with radiation from CO₂ laser while air drawing it at a supersonic velocity. A supersonic jet is generated by blowing air into a vacuum

chamber through the orifice used to inject the fiber into the vacuum chamber. Adiabatic expansion of the injected air across the orifice cools the jet. Irradiating the cold supersonic jet by a high-power laser beam instantly melts the fiber. It is then tremendously deformed by the shear and compressive forces generated by the supersonic flow and is ultra-drawn to a draw ratio of the order of 10⁵. Nanofibers obtained by CLSD can be made indefinitely long because the fiber is supplied at a constant speed and is continuously irradiated by the laser beam. Both its amorphous and crystalline phases are oriented parallel to the fiber axis. Because CLSD is performed in vacuum, the nanofibers are not scattered in air. This closed-system technique also offers superior environmental safety than electrospinning and melt blowing, which are performed in open systems. CLSD has been used to produce poly(L-lactic acid) [16], polyethylene terephthalate [17], poly(ethylene-2,6-naphthalate) [18], poly(glycolic acid) [19], and isotactic polypropylene [20] nanofibers.

*Corresponding author, e-mail: a-suzuki@yamanashi.ac.jp
© BME-PT

Ethylene tetrafluoroethylene (ETFE) is a thermoplastic fluororesin that is formed from the copolymers tetrafluoroethylene (C_2F_4) and ethylene (C_2H_4). It is chemically resistant and has electrical properties equivalent to those of poly(tetrafluoroethylene) (PTFE), poly(tetrafluoroethylene-co-perfluoropropyl vinyl ether) (PFA), and poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), which are typical fluororesins. ETFE exhibits an excellent chemical resistance in almost all reagents including strong acids and alkalis, has a high weather resistance, and has stable mechanical and electrical properties over a wide temperature range. However, ETFE nanofibers cannot be produced by electrospinning due to the excellent chemical resistance of ETFE.

In this study, ETFE fibers having various melt flow rates (MFRs) were drawn at various air drawing conditions. We investigated the relationship between the drawability and the MFR and the properties of ETFE nanofibers produced by CLSD.

2. Experimental

As-spun ETFE fibers with four different MFRs supplied by Asahi Glass Co., Ltd., Japan (see Table 1) were used as the initial ETFE fibers used in this study. The morphologies of the produced nanofibers were investigated by scanning electron microscopy (SEM; JSM-5700, JEOL Ltd., Japan) using an accelerating voltage of 10 kV. Prior to SEM observations, the samples were sputter coated with platinum. The average diameter and the diameter distribution of the nanofibers were measured using an image analyzer. The average fiber diameter was obtained by averaging the diameters measured at 100 different locations on the collected nanofibers.

To observe the supersonic drawing process, necking of the fiber formed by heating laser was observed using a high-speed camera (Motion Analysis Microscope VW-6000, Keyence, Japan) equipped a long-range zoom lens (VH-Z50L/W, Keyence, Japan). This high-speed camera can record up to 24 000 frames·s⁻¹

and the zoom lens has a focal distance of 85 mm at a maximum magnification of $\times 500$.

Wide-angle X-ray diffraction (WAXD) patterns of the nanofibers were obtained using an imaging-plate (IP) film and an IP detector (R-AXIS DS3C, Rigaku Co. Japan). The IP film was attached to an X-ray generator (Rigaku Co. Japan) operated at 40 kV and 200 mA. The radiation used was Ni-filtered Cu K_{α} . The sample-to-film distance was 40 mm. The fiber was exposed for 5 min to the X-ray beam from a 0.4 mm-diameter pinhole collimator. The d-spacing and crystal size were determined from the WAXD patterns with using the software for data analysis (RIGAKU R-AXIS, Rigaku Co. Japan).

Differential scanning calorimetry (DSC) measurements were conducted using a calorimeter (Therm Plus 2 DSC 8230C, Rigaku Co., Japan). DSC scans were performed in the temperature range 25–290°C at a heating rate of 10°C·min⁻¹. All DSC measurements were performed under a nitrogen purge. The DSC instrument was calibrated using indium. The degree of crystallinity (X_c) was determined from the heat of fusion (ΔH_m) using Equation (1):

$$X_c = \frac{\Delta H_m}{-113.4} \cdot 100 \quad (1)$$

where the heat of fusion of ETFE was taken to be $-113.4 \text{ J} \cdot \text{g}^{-1}$ [21].

Figure 1 shows the apparatus used for CLSD. It consists of a spool that supplies the fiber, a continuous-wave CO₂ laser (output wavelength: 10.6 μm ; maximum power: 40 W), a vacuum chamber with Zn–Se windows and a 0.5 mm-diameter fiber injection

Figure 1. Schematic diagram of apparatus used for CO₂ laser supersonic drawing

Table 1. Fiber diameters (d_{av}) of initial fibers with four different melt flow rates (MFRs)

Fiber	MFR [g·10 min ⁻¹]	d_{av} [μm]
MFR ₃₀₈	308	125.1
MFR ₆₅₃	653	116.6
MFR ₈₉₉	899	120.2
MFR ₁₄₇₃	1473	123.1

Figure 2. Photograph of nonwoven fabric collected on the net

tion orifice for supplying the fibers to the laser irradiation point, a power meter, a movable platen, and a vacuum pump. The vacuum chamber was placed on the movable platen, which consists of a micro-alignment stage, a laboratory jack, and a turntable. The turntable can be moved parallel to the Y and Z axes and can be rotated about the laser irradiation point on the fiber, allowing fine adjustments to be made. Over 90% of the laser power was contained in a 3.6 mm-diameter spot. The nanofiber was collected as a nonwoven fabric on the net placed about 10 cm away below the orifice, as shown in Figure 2.

3. Results and discussion

The fiber drawability in CLSD strongly depends on the melt viscosity of the necking formed by laser irradiation of the initial fiber. To elucidate the super-drawing mechanism in CLSD, fibers produced using four different MFRs were drawn under various air drawing conditions and the relationship between the air drawing conditions, the MFR, and their characteristics was investigated.

3.1. MFR dependence of drawability

The drag force that draws the fiber in CLSD is generated in the supersonic jet when the chamber pressure is low. In a previous study [17], we investigated the relationship between the chamber pressure, the flow rate of the air jet, and the drag force by using a three-dimensional finite element method to esti-

Figure 3. Chamber pressure dependence of the average diameters of the fibers obtained by air drawing the initial fibers with MFRs of $\bullet$ 308, $\circ$ 653, $\blacksquare$ 899, and $\square$ 1473 $\text{g} \cdot 10 \text{ min}^{-1}$

mate the drag force acting on a fiber in the supersonic jet. The drag force is the result of the parallel and perpendicular forces acting on the fiber surface (shear and compressive forces, respectively). It increases with decreasing chamber pressure.

Figure 3 shows the chamber pressure dependences of the average diameter of fibers obtained by air drawing initial fibers with four different MFRs. In this series of experiments, the fiber supply speed was $0.1 \text{ m} \cdot \text{min}^{-1}$ and the laser power was 20 W. As the chamber pressure (p_{ch}) decreases, the average fiber diameter decreases significantly for each MFR; it is less than $1 \text{ } \mu\text{m}$ at $p_{\text{ch}} = 70 \text{ kPa}$ for all four MFRs. The MFR dependence of the average diameter is large at high chamber pressures, but is small at low chamber pressures. A reduction in the chamber pressure implies an increase in the drag force and a larger drag force induces a higher plastic flow rate, resulting in a thinner nanofiber being produced.

Figures 4 and 5 show histograms of the diameter together with SEM micrographs and the MFR dependence of the standard deviation of the fiber diameter for fibers obtained by air drawing the initial fibers with four different MFRs at $p_{\text{ch}} = 20$ and 90 kPa. For $p_{\text{ch}} = 20 \text{ kPa}$, the nanofiber diameter depends very little on the MFR; it is in the range $0.30\text{--}0.35 \text{ } \mu\text{m}$ and the diameter distributions are narrow. The standard deviation at $p_{\text{ch}} = 20 \text{ kPa}$ is $0.1 \text{ } \mu\text{m}$ or smaller and is almost independent of the MFR. For $p_{\text{ch}} = 90 \text{ kPa}$, the fiber diameter hardly depends on the MFR, and the fiber distributions are considerably wider than those of fibers obtained at

Figure 4. Histograms of fiber diameters along with SEM micrographs of fibers obtained by air drawing initial fibers with four different MFRs at $p_{\text{ch}} = 20$ and 90 kPa

Figure 5. MFR dependence of standard deviations of diameter of fibers obtained at chamber pressures of $\circ$ 20 and $\bullet$ 90 kPa

$p_{\text{ch}} = 20$ kPa. The average diameters of the fibers obtained at $p_{\text{ch}} = 90$ kPa are over 1.0 μm , and the standard deviation increases linearly with decreas-

ing MFR. The fiber with the lowest MFR (i.e., highest melt viscosity) is not stably drawn because the drag force is low at the higher chamber pressure. Unstable air drawing widens the fiber diameter distribution and increases the average fiber diameter. For air drawing at $p_{\text{ch}} = 20$ kPa, even the fiber with the lowest MFR is stably drawn and it has a uniform diameter due to the large drag force.

Figure 6 shows photographs (magnification: $\times 500$) showing necking produced by laser heating of the initial fibers with four different MFRs at $p_{\text{ch}} = 20$ and 90 kPa. These photographs were taken perpendicular to the laser beam using the high-speed camera equipped with the long-range zoom lens. The initial fibers were irradiated by light from a laser located on the left side of the photographs.

In melt spinning, a melted polymer ejected from the spinneret expands; this phenomenon is known as the Barus effect [22]. In the case of CLSD performed at $p_{\text{ch}} = 20$ kPa, all the initial fibers were drawn without exhibiting the Barus effect, whereas in CLSD performed at $p_{\text{ch}} = 90$ kPa, except for the MFR1473

Figure 6. Photographs (magnification: $\times 500$) of necking during laser heating of initial fibers with four different MFRs at $p_{\text{ch}} = 20$ and 90 kPa

Figure 7. Fiber supply speed dependence of average fiber diameter for fibers drawn with MFRs of ● 308, ○ 653, ■ 899, and □ 1473 g·10 min⁻¹

fiber, the initial fibers were drawn with the Barus effect. In CLSD performed at $p_{\text{ch}} = 20$ kPa, the larger drag force generated in the supersonic jet inhibits expansion of the melt fiber due to its viscoelasticity, but the melted fiber expands because the drag force generated at $p_{\text{ch}} = 90$ kPa is small. The MFR1473 initial fiber has the lowest melt viscosity; consequently, it did not exhibit the Barus effect even at $p_{\text{ch}} = 90$ kPa.

Figure 7 shows the fiber supply speed dependence of the average fiber diameter for the drawn fibers with four different MFRs. In this series of experiments, the chamber pressure was 20 kPa and the laser power was 20 W. The average fiber diameter of the MFR₃₀₈ fiber is largely influenced by the fiber supply speed; those with higher MFRs are little affected by the fiber supply speed. In CLSD of the MFR₃₀₈ initial fiber, the melt viscosity does not decrease enough because the heating time is too short when the fiber supply speed is fast. Thus, the fiber diameter does not decrease. In contrast, nanofibers are produced when the supply speed is sufficiently low that the fiber is melted by laser heating, even at the lowest MFR. For very low MFRs, the fiber supply speed is strongly dependent on the MFR.

3.2. MFR dependence of superstructure

To investigate the effect of the MFR on the superstructure and thermal properties of the fibers obtained for various air drawing conditions, the

fibers were characterized by WAXD and DSC measurements.

Figure 8 shows WAXD patterns obtained from the initial fibers with four different MFRs and the fibers obtained by air drawing the initial fibers at $p_{\text{ch}} = 20$ and 90 kPa. The WAXD patterns of the initial and drawn fibers were obtained from bundles and nonwoven fabrics as shown in Figure 2, respectively. Only the WAXD pattern of the initial MFR₃₀₈ fiber exhibits equatorial arc reflection due to oriented crystallites. The WAXD patterns of the other initial fibers exhibit Debye–Scherrer rings due to the crystallites being randomly oriented. These reflections are attributable to hexagonal (100) reflections [23] from crystallites that formed by strain-induced crystallization during melt spinning. The initial fibers, which were produced by conventional melt spinning, generally exhibit Debye–Scherrer rings, whereas only the initial MFR₃₀₈ fiber has oriented crystallites formed by strain-induced crystallization during melt spinning. Because MFR₃₀₈ was melt spun at a high pressure due to its high melt viscosity, the melted MFR₃₀₈ was subjected to a large shear force at the spinneret so that crystallites oriented parallel to the fiber axis formed without orientation relaxation.

The nonwovens of the air-drawn fibers exhibit Debye–Scherrer rings in their WAXD patterns. In addition, the drawn fibers contain crystallites that formed by flow-induced crystallization during CLSD. These WAXD patterns, which were obtained from nonwoven fibers, do not indicate whether the crystallites are oriented parallel to the fiber axis.

To confirm the existence of oriented crystallites formed by flow-induced crystallization during CLSD, WAXD measurements were performed on nanofiber bundles. Figures 9a and 9b respectively show an SEM micrograph and a WAXD pattern of the MFR₁₄₇₃ nanofiber drawn at $p_{\text{ch}} = 20$ kPa. The WAXD pattern shows a wide equatorial arc reflection due to oriented crystallites because the filaments are not perfectly aligned in the bundle, as the SEM micrograph shows. However, the equatorial arc reflection indicates that even the MFR₁₄₇₃ initial fiber with the highest MFR, CLSD forms crystallites aligned with the fiber axis. The equatorial reflection observed in the MFR₃₀₈ initial fiber is also observed in the WAXD pattern of the MFR₁₄₇₃ fiber drawn by CLSD, although the equatorial reflection

Figure 8. WAXD patterns of initial fibers with four different MFRs and fibers obtained by drawing them at $p_{ch} = 20$ and 90 kPa

Figure 9. (a) SEM micrograph and (b) WAXD pattern of MFR₁₄₇₃ nanofiber drawn at $p_{ch} = 20$ kPa

is not visible in the WAXD pattern of the MFR₁₄₇₃ initial fiber. These WAXD patterns experimentally demonstrate that the crystallites formed by flow-induced crystallization during CLSD are oriented parallel to the fiber axis and they did not undergo orientation relaxation. Even for the initial fiber with the highest MFR (i.e., the lowest intermolecular

force) oriented crystallites were formed by supersonic-drawing and quenching in the low-temperature supersonic jet, which was cooled by adiabatic expansion at the fiber injection orifice.

Figure 10 shows DSC curves obtained from the initial fibers with the four different MFRs and from the fibers produced from them at $p_{ch} = 20$ and

Figure 10. DSC curves of initial fibers with four different MFRs and of their fibers obtained at $p_{ch} = 20$ and 90 kPa

90 kPa. The initial and drawn fibers exhibit a broad endothermic peak (melting) in the temperature range 245–250°C. This melting peak can be attributed to crystals formed by strain-induced crystallization during melt spinning and that grew during DSC scanning. Except for the MFR₁₄₇₃ initial fiber, which has a melting point (T_m) of 249°C, the initial fibers have $T_m > 253^\circ\text{C}$ (see Table 2). For all four MFRs, the T_m of the drawn fibers is 1–4°C lower than that of the initial fibers. This reduction in T_m indicates that the degree of perfection of the crystal decreases and that the crystal formed by flow-induced crystallization during CLSD has a lower degree of perfection than the crystal formed by strain-induced crystallization during melt spinning. The MFR₃₀₈ fiber has the smallest difference in T_m

between the initial and drawn fibers of the four MFR fibers. CLSD of the MFR₃₀₈ initial fiber is likely to form crystallites with the highest degree of perfection because effectiveness of the air drag force to elongate the molecular chains in the MFR₃₀₈ fiber is the strongest.

Table 2 lists the melting temperature (T_m), the degree of crystallinity (X_c) estimated from the heat of fusion, the d-spacing, and the crystal size of the initial fibers with the four different MFRs and the fibers drawn from them at $p_{ch} = 20$ and 90 kPa. The MFR₁₄₇₃ initial fiber has $X_c = 42\%$ and the highest X_c of the initial fibers. The MFR₁₄₇₃ ETFE fiber that has a high fluidity is easy to crystallize during melt spinning, whereas ETFE fibers with low MFRs are difficult to crystallize during melt spinning due to

Table 2. Melting temperature (T_m), degree of crystallinity (X_c), d-space (d), and crystal size (X_s) for initial fibers with four different melt flow rates (MFRs) and fibers drawn them at chamber pressures (p_{ch} s) of 20 and 90 kPa

Sample	MFR ₃₀₈				MFR ₆₃₀				MFR ₈₉₉				MFR ₁₄₇₃			
	T_m [°C]	X_c [%]	d [Å]	X_s [Å]	T_m [°C]	X_c [%]	d [Å]	X_s [Å]	T_m [°C]	X_c [%]	d [Å]	X_s [Å]	T_m [°C]	X_c [%]	d [Å]	X_s [Å]
Initial fiber	253	36	5.01	57	253	39	4.97	60	256	35	5.03	57	249	42	5.00	67
$p_{ch} = 20$ kPa	252	54	4.98	46	252	45	5.01	41	254	54	5.00	53	245	49	5.04	48
$p_{ch} = 90$ kPa	252	47	5.01	44	251	43	5.04	42	253	49	5.03	45	246	48	5.04	45

its lower fluidity. The X_c values of the initial fibers depend on MFR: as MFR decreases, X_c tends to decrease.

X_c increases on CLSD and nanofibers obtained at $p_{ch} = 20$ kPa have higher X_c values than the initial fibers and the fibers obtained at $p_{ch} = 90$ kPa. The MFR₃₀₈ and MFR₈₈₉ nanofibers obtained at $p_{ch} = 20$ kPa have the highest X_c of the drawn fibers. CLSD promotes crystallization of fibers with a low MFR more effectively than melt spinning. CLSD performed at the lower chamber pressure generates a larger drag force, which rapidly deforms the molten polymer at a higher plastic flow rate and the larger MFR produces a stronger intermolecular force. The larger drag force and the stronger intermolecular force are effective in promoting flow-induced crystallization.

The d-spacing values are independent of the MFR and whether the fiber has been drawn; they have a constant value of about 5 Å. The crystal sizes of the drawn fibers are obviously smaller than those of the initial fibers although the drawn fibers have larger X_c values than the initial fibers. This suggests that CLSD produces a superstructure in which many small crystals are dispersed. The crystal size tends to increase at lower chamber pressures, whereas no clear relation was observed between the crystal size and the MFR.

4. Conclusions

ETFE initial fibers with MFRs in the wide range of 308–1473 g·10 min⁻¹ were ultradrawn by CO₂ laser irradiation of a supersonic jet, which was cooled by adiabatic expansion at the fiber injection orifice. The nanofibers obtained at $p_{ch} = 20$ kPa have average fiber diameters in the range of 0.30–0.40 μm. The MFR significantly affects the drawability of fibers in CLSD and is extremely important in forming the superstructure. CLSD performed at a lower chamber pressure generates a larger drag force, which rapidly deforms the molten polymer at a higher plastic flow rate and the larger MFR produces a stronger intermolecular force. A large drag force and a strong intermolecular force are effective for generating flow-induced crystallization. CLSD can be used for all thermoplastic polymers containing polyolefins and fluoropolymers, which are almost insoluble in solvents. CLSD can produce

indefinitely long nanofibers because the fiber is supplied at a constant speed and is continuously irradiated by a laser beam. CLSD can easily be used to prepare various nanofibers using only CO₂ laser irradiation; it does not require any additional processes. It is a novel technique for simple production of nanofibers using only a CO₂ laser.

Acknowledgements

This work was made possible by a Grant-in-Aid for Scientific Research (B) from the Japan Society for the Promotion of Science. We are also grateful to Asahi Glass Co., LTD for providing the ETFE fibers.

References

- [1] Yeo Y-J., Jeon D-W., Kim C-S., Choi S-H., Cho K-S., Lee Y-K., Kim C-K.: Effects of chitosan nonwoven membrane on periodontal healing of surgically created one-wall intrabony defects in beagle dogs. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, **72**, 86–93 (2005). DOI: [10.1002/jbm.b.30121](https://doi.org/10.1002/jbm.b.30121)
- [2] Lee K-H., Givens S., Chase D. B., Rabolt J. F.: Electrostatic polymer processing of isotactic poly(4-methyl-1-pentene) fibrous membrane. *Polymer*, **47**, 8013–8018 (2006). DOI: [10.1016/j.polymer.2006.08.070](https://doi.org/10.1016/j.polymer.2006.08.070)
- [3] Zong X., Kim K., Fang D., Ran S., Hsiao B. S., Chu B.: Structure and process relationship of electrospun bio-absorbable nanofiber membranes. *Polymer*, **43**, 4403–4412 (2002). DOI: [10.1016/S0032-3861\(02\)00275-6](https://doi.org/10.1016/S0032-3861(02)00275-6)
- [4] Meng J., Song L., Meng J., Kong H., Zhu G., Wang C., Xu L., Xie S., Xu H.: Using single-walled carbon nanotubes nonwoven films as scaffolds to enhance long-term cell proliferation *in vitro*. *Journal of Biomedical Materials Research Part A*, **79**, 298–306 (2006). DOI: [10.1002/jbm.a.30787](https://doi.org/10.1002/jbm.a.30787)
- [5] You Y., Min B-M., Lee S. J., Lee T. S., Park W. H.: *In vitro* degradation behavior of electrospun polyglycolide, polylactide, and poly(lactide-co-glycolide). *Journal of Applied Polymer Science*, **95**, 193–200 (2005). DOI: [10.1002/app.21116](https://doi.org/10.1002/app.21116)
- [6] Kim B-S., Mooney D. J.: Engineering smooth muscle tissue with a predefined structure. *Journal of Biomedical Materials Research*, **41**, 322–332 (1998). DOI: [10.1002/\(SICI\)1097-4636\(199808\)41:2<322::AID-JBM18>3.0.CO;2-M](https://doi.org/10.1002/(SICI)1097-4636(199808)41:2<322::AID-JBM18>3.0.CO;2-M)
- [7] Higgins S. P., Solan A. K., Niklason L. E.: Effects of polyglycolic acid on porcine smooth muscle cell growth and differentiation. *Journal of Biomedical Materials Research Part A*, **67**, 295–302 (2003). DOI: [10.1002/jbm.a.10599](https://doi.org/10.1002/jbm.a.10599)

- [8] Gao J., Niklason L., Langer R.: Surface hydrolysis of poly(glycolic acid) meshes increases the seeding density of vascular smooth muscle cells. *Journal of Biomedical Materials Research*, **42**, 417–424 (1998). DOI: [10.1002/\(SICI\)1097-4636\(19981205\)42:3<417::AID-JBM11>3.0.CO;2-D](https://doi.org/10.1002/(SICI)1097-4636(19981205)42:3<417::AID-JBM11>3.0.CO;2-D)
- [9] Boland E. D., Telemeco T. A., Simpson D. G., Wnek G. E., Bowlin L.: Utilizing acid pretreatment and electrospinning to improve biocompatibility of poly(glycolic acid) for tissue engineering. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, **71**, 144–152 (2004). DOI: [10.1002/jbm.b.30105](https://doi.org/10.1002/jbm.b.30105)
- [10] Ding B., Kimura E., Sato T., Fujita S., Shiratori S.: Fabrication of blend biodegradable nanofibrous non-woven mats via multi-jet electrospinning. *Polymer*, **45**, 1895–1902 (2004). DOI: [10.1016/j.polymer.2004.01.026](https://doi.org/10.1016/j.polymer.2004.01.026)
- [11] Gupta P., Wilkes G. L.: Some investigations on the fiber formation by utilizing a side-by-side bicomponent electrospinning approach. *Polymer*, **44**, 6353–6359 (2003). DOI: [10.1016/S0032-3861\(03\)00616-5](https://doi.org/10.1016/S0032-3861(03)00616-5)
- [12] Ayutsede J., Gandhi M., Sukigara S., Micklus M., Chen H-E., Ko F.: Regeneration of *Bombyx mori* silk by electrospinning. Part 3: Characterization of electrospun nonwoven mat. *Polymer*, **46**, 1625–1634 (2005). DOI: [10.1016/j.polymer.2004.11.029](https://doi.org/10.1016/j.polymer.2004.11.029)
- [13] Fong H.: Electrospun nylon 6 nanofiber reinforced BIS-GMA/TEGDMA dental restorative composite resins. *Polymer*, **45**, 2427–2432 (2004). DOI: [10.1016/j.polymer.2004.01.067](https://doi.org/10.1016/j.polymer.2004.01.067)
- [14] Ellison C. J., Phatak A., Giles D. W., Macosko C. W., Bates F. S.: Melt blown nanofibers: Fiber diameter distributions and onset of fiber breakup. *Polymer*, **48**, 3306–3316 (2007). DOI: [10.1016/j.polymer.2007.04.005](https://doi.org/10.1016/j.polymer.2007.04.005)
- [15] Borkar S., Gu B., Dirmeyer M., Delicado R., Sen A., Jackson B. R., Badding J. V.: Polytetrafluoroethylene nano/microfibers by jet blowing. *Polymer*, **47**, 8337–8343 (2006). DOI: [10.1016/j.polymer.2006.09.069](https://doi.org/10.1016/j.polymer.2006.09.069)
- [16] Suzuki A., Aoki K.: Biodegradable poly(L-lactic acid) nanofiber prepared by a carbon dioxide laser supersonic drawing. *European Polymer Journal*, **44**, 2499–2505 (2008). DOI: [10.1016/j.eurpolymj.2008.05.021](https://doi.org/10.1016/j.eurpolymj.2008.05.021)
- [17] Suzuki A., Tanizawa K.: Poly(ethylene terephthalate) nanofibers prepared by CO₂ laser supersonic drawing. *Polymer*, **50**, 913–921 (2009). DOI: [10.1016/j.polymer.2008.12.037](https://doi.org/10.1016/j.polymer.2008.12.037)
- [18] Suzuki A., Yamada Y.: Poly(ethylene-2,6-naphthalate) nanofiber prepared by carbon dioxide laser supersonic drawing. *Journal of Applied Polymer Science*, **116**, 1913–1919 (2010). DOI: [10.1002/app.29805](https://doi.org/10.1002/app.29805)
- [19] Suzuki A., Shimizu R.: Biodegradable poly(glycolic acid) nanofiber prepared by CO₂ laser supersonic drawing. *Journal of Applied Polymer Science*, **121**, 3078–3084 (2011). DOI: [10.1002/app.33982](https://doi.org/10.1002/app.33982)
- [20] Suzuki A., Arino K.: Polypropylene nanofiber sheets prepared by CO₂ laser supersonic multi-drawing. *European Polymer Journal*, **48**, 1169–1176 (2012). DOI: [10.1016/j.eurpolymj.2012.04.003](https://doi.org/10.1016/j.eurpolymj.2012.04.003)
- [21] Gürsel S. A., Schneider J., Youcef H. B., Wokaun A., Scherer G. G.: Thermal properties of proton-conducting radiation-grafted membranes. *Journal of Applied Polymer Science*, **108**, 3577–3585 (2008). DOI: [10.1002/app.27947](https://doi.org/10.1002/app.27947)
- [22] Ishibashi T.: Barus effect in nylon 6 polymer melts. *Journal of Applied Polymer Science*, **18**, 2427–2433 (1974). DOI: [10.1002/app.1974.070180820](https://doi.org/10.1002/app.1974.070180820)
- [23] Ono Y., Kakiage M., Yamanobe T., Yukawa Y., Higuchi Y., Kamiya H., Arai K., Uehara H.: Structural and property changes during uniaxial drawing of ethylene-tetrafluoroethylene copolymer films as analyzed by *in-situ* X-ray measurements. *Polymer*, **52**, 1172–1179 (2011). DOI: [10.1016/j.polymer.2010.12.040](https://doi.org/10.1016/j.polymer.2010.12.040)