

## Effects of Laser Beam Width on the Diameter and Molecular Weight of Laser-Electrospun Polylactide Fiber

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**Abstract:** Effects of spinning conditions (laser beam width, applied voltage, and laser power) on reduction of molecular weight by thermal degradation, fiber diameter, and its evenness were investigated for the laser-heated electrospinning process of polylactide fiber webs. Thinner fibers were obtained under the conditions of the narrower laser beam width, the lower applied voltage, and the higher laser power. Moreover, the thinner, the more uniform, and less degraded fiber can be obtained for the narrower beam width, while thermal degradation was inevitable for producing thinner fiber by varying applied voltage and laser power.

(Received 22 August, 2014 ; Accepted 19 May, 2015)

### 1. Introduction

In recent years, the electrospinning method, which produces nano and submicron fibers, has been actively studied [1-4]. Nano and submicron fibers are expected to find application in filtration, biomedical uses, and sensor materials because of their high specific surface area.

Polylactide (PLA) is a biodegradable and bioabsorbable polymer which is derived from renewable resources such as corn starch. Therefore, nano and submicron PLA fibers are an excellent candidate for application in biomedical materials including drug delivery systems and scaffolds for cell cultures. Preparation of nano or submicron PLA fibers by laser-heated electrospinning (LES) using a CO<sub>2</sub> laser to heat the polymer has been reported [5-9]. Ogata et al. revealed that the diameter of electrospun poly(L-lactide) fiber of less than 1 μm was achieved, while the fiber molecular weight decreased exponentially with an increase in the laser power [5]. We have also carried out LES using various polymers, and investigated the dependence of LES conditions (applied voltage, laser power, and laser beam width) on the fiber diameter [10-13]. In particular, when the laser beam width is thinner, suppression of thermal degradation and stabilization of elongational deformation is expected because the heating duration becomes shorter. In fact, we have found that more fine and uniform thermoplastic polyurethane (TPU) fiber was

obtained because the fiber temperature rose sharply and the fiber thinned rapidly when using a thinner laser beam width [12].

In this study, in addition to the effect of the applied voltage and laser power, which have been reported previously, we investigate the effect of laser beam width on decreases in molecular weight, average diameter, and uniformity of electrospun PLA fibers.

### 2. Experimental

#### 2.1 Materials

PLA fiber (average diameter, 150 μm) was used for LES process. It was prepared by melt spinning of PLA pellets (Toyota ecoplastic U'z S-32, Toyota Tsusho Corp.) with a melt flow rate of 22.3 g/(10 min) at 190 °C and optical purity (L-lactide content) of 99.2%. Prior to the melt spinning, the PLA pellet was dried at 100 °C in the vacuum oven for 6 h then at 120 °C in a vacuum oven for 12 h. The fiber was extruded from a spinneret with a single hole 1 mm diameter nozzle at 210°C, and was taken-up at 610 m/min. The throughput rate was 4 g/min.

#### 2.2 Laser-heated electrospinning

The LES apparatus used in this study consisted of a CO<sub>2</sub> laser system (PIN-30R, Onizuka Glass Co., Ltd.) and an electrospinning system (NEU-010, Katotech Co., Ltd.) [12]. The PLA fiber was fed by a feed roller at a rate of 40 mm/min. The fiber was heated rapidly by laser irradiation (wavelength, 10.6 μm), and was drawn by applying a high voltage to the nozzle. PLA fiber webs

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**Table 1** Fiber diameter and molecular weight of PLA fibers prepared under various LES conditions.

No.	$2r_{//}$ (mm)	Applied voltage (kV)	Laser power <sup>a</sup> (W)	Fiber diameter		$M_v$	Reduction of $M_v$ (%)	
				Average ( $\mu\text{m}$ )	C.V. (%)			
1	Initial	---	---	150	---	32400	0.0	
2	0.9	15.0	9	1.7	10	---	---	
3		17.5		4.4	16	28300	12.7	
4		20.0		5.6	11	32400	0.0	
5		17.5		12	2.5	11	---	---
6		15		2.4	11	17000	47.5	
7		9		21.2	12	---	---	
8	2.3	17.5	12	11.7	28	---	---	
9				15	8.7	18	30000	7.4

<sup>a</sup>Laser power measured upstream of the slit

were prepared by collecting the drawn fibers onto a copper collector plate. The collector plate was positioned 50 mm from the nozzle of 20 gauges, which had an outer diameter of 0.91 mm and inner diameter of 0.60 mm. The laser beam axis was positioned 0.7 mm from the tip of the nozzle. The relative humidity was maintained below 30% by a dry air flow.

The laser power, the applied voltage, and laser beam width were varied as listed in Table 1. The laser beam width was also varied by applying an alumina slit. The laser beam width parallel to the fiber-running direction ( $2r_{//}$ ), measured by the previously reported method [12], was 0.9 mm with the slit and 2.3 mm without the slit. Because the laser beam perpendicular to the fiber-running direction ( $2r_{\perp}$ ), 7.3 mm with the slit and 24 mm without the slit, were far larger than the fiber diameter, laser irradiation density can be considered constant. Thus, the laser beam width shown hereafter is the  $2r_{//}$ .

Fiber thinning phenomena in the LES process was observed by Victor TK-C1461 video camera, equipped with a Optart tele-centric lens magnification of 2. Sony Handycam DCR-HC90 was used for recording video-images.

### 2.3 Scanning electron microscopy observation

The electrospun fibers were observed using scanning electron microscopy (SEM; S-2380N, Hitachi High Technologies Co., Ltd.). The average fiber diameter and coefficient of variation of the diameter (C.V.) were obtained for every 80 fibers.

### 2.4 Measurement of molecular weight

The viscosity-average molecular weight  $M_v$  of the PLA fibers was obtained for chloroform solution using the Mark-Houwink-Sakurada equation [14]:

$$[\eta] = KM_v^a \quad (1)$$

where  $K$  and  $a$  are constants,  $K = 5.45 \times 10^{-4}$  (dL/g) and  $a = 0.73$  [15], and  $[\eta]$  is the intrinsic viscosity. The

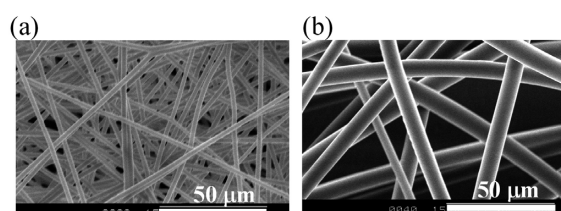
reduction of  $M_v$  for an electrospun fiber to a raw fiber was calculated by the values. The intrinsic viscosity was obtained by the extrapolation of reduced viscosity measured by Cannon-Fenske type capillary viscometer at 25 °C [16]. The concentration were 0.19 - 1.30 g/L.

## 3. Results and Discussion

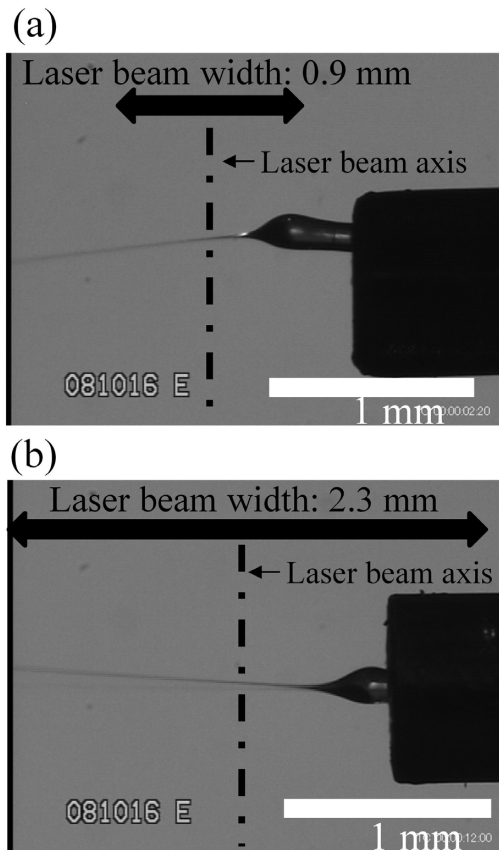
### 3.1 Effect of laser beam width

Figure 1 shows SEM images of the PLA fibers prepared with different laser beam widths. The averaged fiber diameter and the C.V. are listed in Table 1. Both the average and C.V. of diameter decreased for the narrower laser beam width (Nos. 2-6 of Table 1). This trend agrees with the results of previously reported TPU fibers [12]. On the other hands, by comparing for the same applied voltage and laser power (Nos. 6 and 9), the higher molecular weight reduction ( $M_{vDR}$ ) was observed for the narrower beam width. However, by comparing the condition No. 4 with No. 9, the thinner, the more uniform, and less degraded fiber was obtained for the narrower beam width.

The fiber thinning behavior is shown in Fig 2. The diameter profiles shown in Figure 3 were obtained by the image analysis of Fig 2. In comparison with the case of No. 9 and No. 6, the steeper fiber thinning was observed for the narrower beam width. This may be attributed to



**Fig. 1** SEM images of laser-electrospun PLA fibers for laser beam widths of (a) 0.9 mm (No. 6) and (b) 2.3 mm (No. 9) at a laser power of 15 W and applied voltage of 17.5 kV.



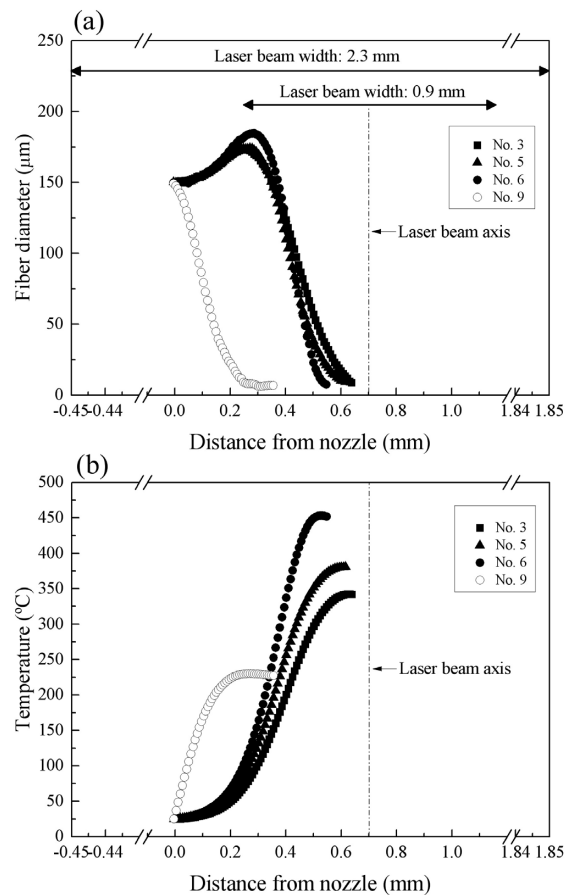
**Fig. 2** Thinning behavior of PLA fibers for conditions of laser beam width of (a) 0.9 mm (No. 6) and (b) 2.3 mm (No. 9) at a laser power of 15 W and applied voltage of 17.5 kV.

the rapid heating of fiber by the narrower beam [12].

The fiber temperature profiles were estimated using the energy balance equation [12, 17, 18]. The density of  $1.24 \text{ g/cm}^3$  [19] and the specific heat of  $1.5 \times 10^3 \text{ J K}^{-1}\text{kg}^{-1}$  [20] were used in the calculations. The absorbance of the fiber ( $A = 0.696$ ) was calculated by the absorption coefficient of  $9.7 \times 10^3 \text{ m}^{-1}$ , which was obtained by the absorbance at the wavelength of  $\text{CO}_2$  laser measured for PLA films of different thicknesses (101, 477, and  $994 \mu\text{m}$ ) by the FT-IR spectrometer.

In comparison with the case of No. 9 and No. 6, fiber temperature also shows the steeper increase and higher peak temperature for the narrower beam width. It is suggested that the fiber temperature became higher due to the increase of the amount of the laser irradiation energy per unit volume of the fiber. The laser irradiation energy was decided not only by the laser irradiation power but also by fiber running speed. And although the fiber running speed was increased by the decrease of fiber viscosity, it was still slower than the case of ordinary beam width.

The fiber was also elongated steeply after the steep increase of fiber temperature for the beam width of



**Fig. 3** (a) Diameter profiles and (b) temperature profiles of PLA fibers in the LES process.

0.9 mm because of the steep decrease of fiber viscosity. The elongation process of the low viscosity melts tends to be unstable by capillary breakage. Thus, it can be stabilized by the rapid cooling. This is the reason why the uniformity of fiber diameter was improved by the narrower beam width. On the other hand, higher peak temperature caused the harder thermal degradation and the lower molecular weight of resultant fiber if the laser power and applied voltage were the same. The thinner and more uniform fibers with lower molecular weight reduction could be obtained because the stabilizing effect exceeds the effect of thermal degradation enhancement.

Comparing the diameter profile of PLA with that of TPU fibers [12], the PLA fiber showed clear diameter increase before the thinning of the fiber. The fiber temperature at which the diameter increase began, estimated  $60\text{--}70^\circ\text{C}$  as shown Fig. 3(b), corresponds to the glass transition temperature of PLA. Therefore the increase of fiber diameter can be attributed to fiber shrinkage caused by the relaxation of the molecular orientation. On the other hand, TPU is an elastomer consisting a little part of crystalline hard segment and soft segment having the glass transition temperature far lower than the room temperature. Thus, the TPU fiber did not

shrink during the LES process because the molecular orientation in the TPU fiber was fully relaxed when the TPU raw fiber was cut before the LES was performed.

### 3.2 Effect of applied voltage and laser power

For the same laser beam width of 0.9 mm, the average fiber diameter increased with the applied voltage, and decreased with the laser power. This results are the same as those of poly(ethylene terephthalate) and TPU fibers [10,12]. On the other hands, no obvious dependence was shown for its C.V.. Together with the finer fiber diameter, the molecular weight reduction became evident for lower applied voltage and higher laser power. For the lowest applied voltage condition of No. 2, even the finest fiber was obtained for this condition, the polymer should be severely degraded because the degradation gas was observed in the LES process. The thinner diameter and the harder thermal degradation are both caused by the higher temperature with the higher laser irradiation energy. Of course the higher laser power causes the higher irradiation energy, the lower applied voltage also causes the higher irradiation energy because the lower electrostatic force leads to the slower fiber running speed. Therefore, thermal degradation was inevitable if you want the thinner fiber by varying applied voltage and laser power.

### Acknowledgments

This work was supported by Special Coordination Funds for Promoting Science and Technology of the project for “Innovation Creative Center for Advanced Interdisciplinary Research Areas” from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

### References

1. Z. M. Huang Zhang, M. Kotaki, and S. Ramakrishna, *Comp. Sci. Techn.*, **63**, 2223 (2003).
2. I. S. Chronakis. *J. Mater. Process. Techn.*, **167**, 283 (2005).
3. N. Bhardwaj and S. C. Kundu, *Biotechnol. Adv.*, **28**, 325 (2010).
4. S. Agarwal, A. Greiner, and J. H. Wendorff, *Progr. Polym. Sci.*, **38**, 963 (2013).
5. N. Ogata, S. Yamaguchi, N. Shimada, G. Lu, T. Iwata, K. Nakane, and T. Ogihara, *J. Appl. Polym. Sci.*, **104**, 1640 (2007).
6. G. Nishikawa, M. Yamamoto, A. M. Afifi, Y. Kawahara, and H. Yamane, *Sen'i Gakkaishi*, **66**, 124 (2010).
7. N. Ogata, N. Shimada, S. Yamaguchi, K. Nakane, and T. Ogihara, *J. Appl. Polym. Sci.*, **105**, 127 (2007).
8. N. Shimada, N. Ogata, K. Nakane, and T. Ogihara, *J. Appl. Polym. Sci.*, **125**, E384 (2012).
9. X. Li, H. Liu, J. Wang, and C. Li, *Polymer*; **53**, 248 (2012).
10. M. Takasaki, H. Fu, K. Nakata, Y. Ohkoshi, and T. Hirai, *Sen'i Gakkaishi*, **64**, 29.(2008).
11. K. Nakata, S. Kinugawa, M. Takasaki, Y. Ohkoshi, Y. Gotoh, and M. Nagura, *Sen'i Gakkaishi*, **65**, 257 (2009).
12. M. Takasaki, K. Sugihara, Y. Ohkoshi, T. Fujii, H. Shimizu, and M. Saito, *Sen'i Gakkaishi*, **66**, 168 (2010).
13. M. Takasaki, K. Hara, Y. Ohkoshi, T. Fujii, H. Shimizu, and M. Saito, *Polym. Eng. Sci.*, **In Press**.
14. H. C. Beachell and J. C. Peterson, *J. Appl. Polym. Sci. Part A-1*, **7**, 2021 (1969).
15. L. Lu, S. J. Peter, M. D. Lyman, H. L. Lai, S. M. Leite, J. A. Tamada, J. P. Vacanti, R. Langer, and A. G. Mikos, *Biomaterials*, **21**,1595 (2000).
16. M. L. Huggins, *J. Am. Chem. Soc.*, **64**, 2716 (1942).
17. W. Okumura, T. Yamaguchi, Y. Ohkoshi, Y. Goth, and M. Nagura, *Int. Polym. Proc.*, **17**, 125 (2002).
18. T. Yamaguchi, Y. Ohkoshi, Y. Goth, and M. Nagura, *Seikei-Kakou*, **17**, 649 (2005).
19. L.-T. Lima, R. Aurasb, and M. Rubinob, *Progr. Polym. Sci.*, **33**, 820 (2008).
20. M. Hamoudeha, H. Fessi, H. Mehier, A. A. Faraj, E. Canet-Soulas, *Intern. J. Pharm.*, **348**, 125 (2008).
21. S. Kase and T. Matsuo, *J. Polym. Sci. A*, **3**, 2541 (1965).