Poly(ethylene-co-vinyl alcohol) and Nylon 6/12 Nanofibers Produced by Melt Electrospinning System Equipped with a Line-like Laser Beam Melting Device

Naoki SHIMADA[1)], Shinji Yamaguchi[2)], Koji NAKANE[3)] and Nobuo OGATA[3)]
1) Headquarters for Innovative Society-Academia Cooperation, University of Fukui, Bunkyo 3-9-1, Fukui 910-8507, Japan
2) Future Textile Materials Tech., Sakazu 1660-6, Kurashiki 710-0801, Japan
3) Graduate School of Engineering, University of Fukui, Bunkyo 3-9-1, Fukui 910-8507, Japan

Introduction

Recently, nanofibers have been desired and developed in the fiber industry. The fibers are potentially useful in a variety of engineering applications in which a large surface area and fibrous structure are demanded [1-3]. Electrospinning is a simple technique for the production of nanofibers, and is classified into two kinds of methods: solvent electrospinning methods and melt electrospinning methods. The melt electrospinning methods eliminate the issues related to solvents. Therefore, melt electrospinning is thought to be a more eco-friendly, versatile, and low-cost production method [4-6]. However, there are few studies on the melt electrospinning because it is suspected that nanofibers are produced without the thinning process due to solvent evaporation.

We developed a melt electrospinning system with a spot-like laser beam melting device. We obtained nanofibers from some polymers using the system [7-9]. A large problem of this system is that the amount of production is small since only a single nanofiber is produced from the rod-like polymer. To solve the problem, we have developed a new melt electrospinning system which can produce nanofibers from a polymer sheet, aiming at the mass production of nanofibers.

In this work, a new electrospinning system equipped with a line-like laser beam melting device has been developed. We try to produce fibers from poly(ethylene-co-vinyl alcohol) (EVOH) and Poly(hexamethylene dodecanediamide) (Nylon6/12) sheets with the system.

Experimental

Materials

Pellet-like EVOH (#F104B) was supplied by Kuraray Co., Ltd. (Osaka, Japan). The characterization of the pellets is as follows: the ethylene content = 32mol%, T_m = 183°C, *MFI* = 4.4 (190°C, 21.2N). Pellet-like Nylon6/12 is purchased from Sigma-Aldrich Inc.. The characterization of the pellets is as follows: T_m = 218°C, T_g = 46°C, density = 1.3g/mL at 25°C. The sheets (150×100mm) with 0.5mm, 0.75mm and 1.0mm in thicknesses were produced by the melt press of these pellets. The temperatures used for the melt press of EVOH and Nylon6/12 were 200°C and 230°C, respectively. These sheets were provided for the melt electrospinning tests.

Melt-electrospinning system

A line-like laser beam was generated from a spot-like CO_2 laser beam generator (Universal Laser System, ULR-50, φ4mm, nominal output power = 50W, USA) using a custom-built optical system; the line-like laser beam was designed to show a top-hat-shaped uniform laser output intensity distribution over 150mm in length and less than 2mm in width.

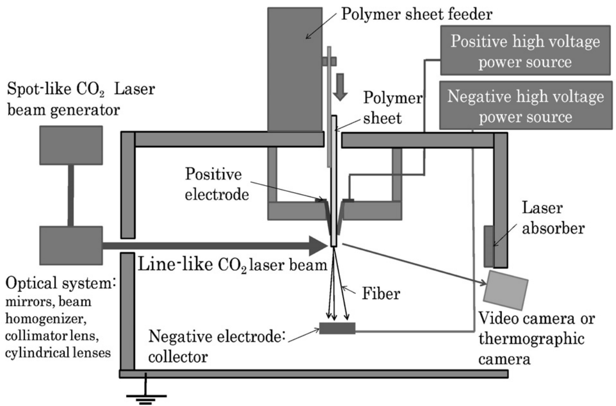

Figure 1 Schematic diagram of the line laser melt electrospinning system used in this work.

Figure 1 shows a schematic diagram of the main part of the melt electrospinning system invented in this work. A sheet sample was fed to the line laser melting zone at a rate of 0.05~1mm/s. One end of the sheet was locally and linearly melted by the laser beam. A high voltage (+40kV) was applied to the linearly melted zone through a copper cathode slit. The fibers produced can be collected onto the copper anode collector.

Observation of fiber formation process

The fiber formation process was observed with a High-Definition video camera (Canon, iVIS HV20, Japan). The temperature of the linearly melting zone was measured using a thermographic camera (Apiste, FSV-7000E, Japan) with a notch filter which prevented scattering laser (wavelength 10.6μm) from incoming to the camera.

Result and discussion

Formation of the Taylor cones

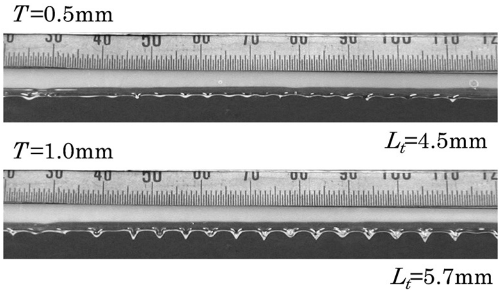

Figure 2 Effect of EVOH sheet thickness, *T*, on the formation of the Taylor cone.

Figure 2 shows the effect of the sheet thickness (*T*) of EVOH on the formation of the Taylor cone. Upper area of the photograph is the positive electrode being attached to a scale. Central white area is un-melted sheet and following dark colored area is melted area. When the polymer sheet was melted by the laser beam in the presence of a high voltage, wave-like perturbations, meniscus instability, took place on the surface of molten polymer and then these developed to the Taylor cones. From the tip of the Taylor cone, only a single fiber was spun toward the collector. The fibers were formed with accompanying the generation of fine bubbles in the Taylor cone and gas formation. It should be noted that the length between Taylor cones is almost constant (ca. 5mm), although the laser has a intensity distribution. This result suggests that there is a static electric repulsion between the cones. Since the length between Taylor cones was considered to be a determining factor of the uniformity of the fiber mats produced, we measured the length. When the Taylor cones were undeveloped, the distances between the apexes of wave-like perturbation were measured; the length will be referred as L_t. The meniscus instability can be seen on the T = 0.5mm sheet. Well developed Taylor cones can be seen on the T = 1.0mm sheet. This result means that an enough amount of molten polymers is necessary to develop the cone. The value of L_t of the T = 1.0mm sheet seems to be larger than that of the T = 0.5mm sheet. This result suggests that the value of L_t would be determined by the electrostatic repulsion of the Taylor cones.

Thermographic analysis of melting zone

The temperature of the linearly melting zone was measured with a thermographic camera. It was found that the temperature at a point in the linearly melting zone changes in time. We set the center line perpendicular to the linearly melting zone and parallel to sheet feeding direction. Along this center line, four pixels, P_1, P_2, P_3 and P_4 were defined from the tip of the Taylor cone in an upward direction; the interval between pixels was about 1mm. That is, P_1 is the point in the vicinity of the Taylor cone, P_4 is the point in the vicinity of un-melted area.

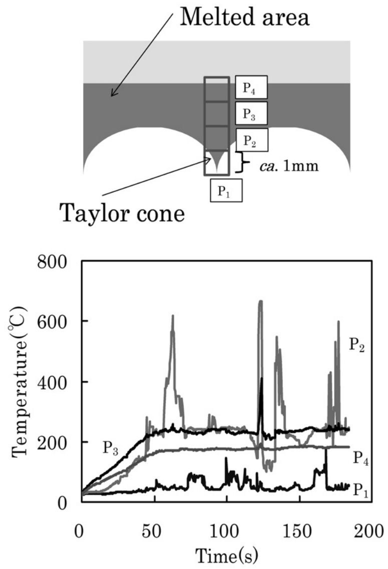

Figure 3 Temperature variation of each point of EVOH sheet with time.

Figure 3 shows the temperature variation of each point of EVOH sheet with time. The temperatures measured at P_3 and P_4 become constant with time. However, it can be seen that the temperature at P_2 has a mean value but changes markedly in the range from 220°C to 600°C around the mean value with time. Considering this temperature changes and the fact that gas is generated and bubble is formed during the fiber formation process, we can say at least that fibers are formed with accompanying with a marked temperature changes in the vicinity of the Taylor cone.
Finally, by using this system, we obtained the fibers with the diameter smaller than 1μm.

References

1. Huang, Z-M.; Zhang, Y-Z.; Kotaki, M; Ramakrishna, S. Comp Sci Tech 2003, 63, 2223.
2. Chronakis, I. S. J Mater Process Tech 2005,167,283.
3. Nasir, M.; Matsumoto, H.; Danno, T.; Minagawa, M.; Irisawa, T.; Shioya, M.; Tanioka, A. J.Polym Sci: Part B Polym Phys 2006, 44, 779.
4. Lyons, J.; Li, C.; Ko, F. Polymer 2004, 45, 7597.
5. Zhou, H.; Green, T. B. ; Joo, Y.L. Polymer 2006 , 47,7497.
6. Dalton, P.D.; Grafahrend, D.; Klinkhammer, K.; Klee, D.; Möller, M.; Polymer 2007 ,48, 6823.
7. Ogata, N.; Lu, G.; Iwata, T.; Yamaguchi, S.; Nakane, K.; Ogihara, T. J Appl Polym Sci 2007, 104, 1368.
8. Ogata, N.; Yamaguchi, S.; Shimada, N., Lu, G.; Iwata, T.; Nakane, K.; Ogihara, T. J Appl Polym Sci 2007, 104, 1640.
9. Ogata, N.; Shimada, N. ; Yamaguchi, S.; Nakane, K.; Ogihara, T. J Appl Polym Sci 2007, 105, 1127.