Formation of Polypropylene Nanofibers from Poly(ethylene-co-vinyl alcohol)/Polypropylene/Poly(ethylene-co-vinyl alcohol) Three-Layer Sheets by Using Laser-Assisted Melt Electrospinning

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Abstract: We used our new nozzle-free melt-electrospinning (M-ESP) system to produce polypropylene (PP) nanofibers. The M-ESP system includes a line-like CO2 laser beam melting device. We fabricated core (PP)-clad [poly(ethylene-co-vinyl alcohol): EVOH] nanofibers from EVOH (melt flow rate [MFR]: 14 g/10 min)/PP (MFR: 12 g/10 min)/EVOH three-layer sheets using the M-ESP system. The core-clad structure was formed by a wrapping phenomenon that is the result of the difference in the MFR values of the EVOH and PP melts. By removing the EVOH, we obtained PP nanofibers with the avg. dia. of 0.21 μm from the core-clad nanofibers. The nanofiber dia. was decreased by decreasing the MFR of the PP melt and the thickness of the PP layer in the EVOH/PP/EVOH sheet.

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1. INTRODUCTION

Polypropylene (PP) fibers are generally applied for the production of industrial materials (e.g., rope, canvas, tent cloth, carpeting, and fishing nets). Polypropylene is the lightest chemical fiber, and it provides both high strength and high chemical resistance. PP fibers are produced industrially by melt spinning, and PP fibers have been prepared by using melt electrospinning (M-ESP) [1]. Lyons and colleagues reported the dependence of the diameter of PP fibers on the viscosity of the PP, and they developed a melt extruder by grounding the nozzle and by applying high voltage to the collector [2]; they were unable to produce PP nanofibers with an average diameter <1 μm, however. The first report of the production of PP nanofibers using M-ESP was by Warner et al. [3], but the nanofibers that they obtained were mixed to some extent with PP microfibers. A viscosity-reducing additive used with PP was introduced by Dalton et al., and their method resulted in a reduction of the melt electrospun fiber dia. from 35±8 μm to 840±190 nm [4].

Nayak et al. attempted to prepare PP nanofibers by using M-ESP from their PP melts by the addition of conductive compounds, i.e., sodium oleate (SO) or sodium chloride (NaCl) [5], and the fiber dia. obtained from the pure PP melt was 3.01 μm. However, their PP nanofibers (average dia. 606 and 780 nm) were prepared by adding SO at 7% and NaCl at 7%, respectively.

An experimental study and theoretical prediction of the diameter of melt-electrospin PP fibers was reported by Shen et al., but the fiber dias. were >2 μm [6]. Daenicke et al. prepared PP nanofibers by the addition of sodium stearate (6 wt%) and Irgastat® P 16 (2 wt%) during the M-ESP process [7]. The fiber diameter was minimized to 210 nm by the optimized process. We note that the electrospinning systems used in the above-cited reports were designed as an extension of solution electrospinning, because they changed only the spinning liquids from the polymer solutions to polymer melts in reservoirs (e.g., syringes).

We have designed a new nozzle-free M-ESP system for the mass production of nanofibers that includes a line-like CO2 laser beam melting device [8, 9]. This method enables us to directly form polymeric nanofibers from sheets. In our previous study, we

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used our device to successfully form nanofibers from PP/poly(ethylene-co-vinyl alcohol) (EVOH)/PP three-layer sheets [9]. The diameter of the nanofiber obtained (approx. 0.9 µm) was significantly smaller than that of the as-spun PP fibers obtained from the monolayer PP sheet. This result would be attributable to the towing effect of PP with EVOH (which has a stronger electrostatic attractive force) during the melted polymer jet process. The structure of the fibers depended on the combination of the melt flow rates (MFRs) between PP and EVOH. If the MFR value of the PP melt is higher than that of the EVOH melt, the fibers that are obtained from the PP/EVOH/PP three-layer sheet will have a core (EVOH)-clad (PP) structure because of the ‘wrapping phenomenon’ [10, 11].

We also formed hollow PP nanofibers from the core-clad nanofibers by removing EVOH from the as-spun nanofibers [9]. In the present study, we used our new M-ESP system to form thinner PP nanofibers from EVOH/PP/EVOH three-layer sheets with a stronger towing effect of PP with EVOH.

2. EXPERIMENTAL METHODS

2.1 Materials

We purchased two types of pellet-like PP with differing MFR values (MFR: 12 g/10 min and 35 g/10 min) from Sigma-Aldrich (Tokyo, Japan). A third type of pellet-like PP (MFR: 75 g/10 min) was supplied by the Japan Polypropylene Corporation (Tokyo, Japan). We used EVOH as the co-spinning material. The pellet-like EVOH (grade G110) was from Kuraray (Tokyo, Japan). The EVOH pellets’ characteristics were as follows: ethylene content: 48 mol%, Tc: 183°C, MFR: 14 g/10 min.

2.2 Preparation of EVOH/PP/EVOH three-layer sheets

We formed sheet-like samples (40 mm × 100 mm) by melt-pressing the above-described pellets. The melt pressing (pressure, 5.0 MPa) of both the PP and EVOH was performed at 190°C for 10 min. The obtained PP and EVOH sheets were heat-sealed for 2 min at 150°C (pressure, 0.1 MPa) to fabricate EVOH/PP/EVOH three-layer sheets. Each resultant sheet was used in the M-ESP tests.

2.3 The melt electrospinning (M-ESP) system

A schematic illustration of the main part of the melt electrospinning system is provided in our report [9]. The line-like laser beam was generated by a spot-like CO2 laser beam generator (model #ULR-50, dia. 4 mm, nominal output power: 50 W, wavelength: 10.6 µm; Universal Laser Systems, Scottsdale AZ, U.S.) with the use of our custom-built optical system. We designed the line-like laser beam to provide a uniform and top-hat-shaped output intensity distribution that was >150 mm long and <2 mm wide. The optical system is comprised of three mirrors, a collimator lens, a cylindrical convex lens, a cylindrical concave lens, and a laser beam homogenizer.

For the M-ESP tests, each sheet sample was fed into the line laser’s melting zone (feed rate: 4.0 mm/min). The laser beam melted one end of each sheet (width, 40 mm) both locally and linearly. We applied high voltage (5 kV/cm) to the linearly melted zone through a copper slit in the electrode. The minimum distance between the copper slit’s edge and the line laser beam was 5 mm. The fibers that were produced were collected onto a 150 mm × 150 mm × 5 mm copper anode collector plate. The distance between the collector and the electrode was 100 mm.

We treated electrospun fibers obtained from the EVOH/PP/EVOH three-layer sheets with a 2-propanol/water mixture solution (20 g, weight ratio, 7:3) for 40 min at 90°C to remove the EVOH from the fibers.

2.4 The characterization of the electrospun fibers

We used scanning electron microscopy (SEM, Keyence VE-9800, Osaka, Japan) to investigate the electrospun fibers’ morphology. We gold-sputter-coated the fiber samples with an ion coater (SC-701; Sanyu Electron, Tokyo, Japan). We determined the average fiber diameter (D) and the standard deviation (σ), Japan from 100 measurements of the fibers obtained in each spinning condition. The Adobe Photoshop CS3 extended program was used for this purpose. We created cross-sectional samples for the SEM observations as follows: the fibers were placed on a Teflon sheet and then hardened with epoxy resin; the sheet was immersed in liquid nitrogen for 20 min, and the fibers were sliced with a knife.

We measured the thermal behavior of the fibers in a nitrogen atmosphere by differential scanning calorimetry (model #DSC-60; Shimadzu, Kyoto, Japan) with 4°C/min as the cooling scan rate.

3. RESULTS AND DISCUSSION

Fig. 1 (a)-(c) provides SEM images and histograms of the pure PP (MFR: 12 and 35 g/10 min) and pure
EVOH fibers that we obtained from each monolayer sheet (40 mm × 100 mm, 300 µm thick) with the M-EPS system. The D values of the pure PP fibers (MFR: 12 and 35 g/10 min) obtained were 2.84 µm and 2.27 µm, respectively. In the case of the PP (MFR: 75 g /10 min) sheet, the resultant PP was in the form of a bead, and PP fibers were not obtained due to its low melt viscosity. In contrast, EVOH nanofibers of uniform sizes were obtained; the D was 0.63 µm (σ was 0.13 µm); these values are smaller than those of the PP fibers. Charging EVOH is relatively easy because it is a polar polymer and thus has lower volume resistivity compared to PP, a nonpolar polymer. The strong electrostatic attractive force between the Taylor cone and the grounded collector thus strongly attracts the EVOH fibers.

In our earlier study, PP fibers were formed from a PP (MFR: 35 g/10 min)/EVOH (MFR: 14 g/10 min) two-layer sheet by M-EPS [9]. The D and σ values were 1.06 µm and 0.12 µm, respectively, and these are much smaller than those of the pure PP fibers in Fig. 1 (b). The cross-section of the electrospun fibers revealed a two-layer structure; a fiber with a circular cross-section was overlapped by another fiber with a crescent-like cross-section, and the structure depended on the disparity in their MFRs (i.e., melt viscosity) due to the wrapping phenomenon during the melted polymer jet.

Fig. 2 provides SEM images and histograms of the fibers obtained from the EVOH/PP (MFR: 35 g/ 10 min)/EVOH three-layer sheet by M-EPS before and after EVOH extraction. Each of the films was 100-µm thick (total 300 µm). The D values of the fibers in panels (a) and (b) of Fig. 2 were 0.70 µm and 0.46 µm, respectively (the σ values were almost the same), which are much smaller than those of the pure PP fibers in Fig. 1 (b) and of the PP fibers formed from the PP/EVOH two-layer sheet [9]. We were thus able to significantly reduce the diameter of the PP fibers by removing EVOH from the as-spun fibers.
Fig. 2 SEM image and histogram of EVOH/PP/EVOH fibers obtained (a) before and (b) after EVOH extraction. The distance between the collector and the electrode was 100 mm.

Fig. 3 presents the differential scanning calorimetry (DSC) curves (first cooling) of each fiber. The as-spun fiber obtained from the EVOH/PP/EVOH three-layer sheet had a crystallization peak for PP (crystallization temperature \( T_c \) = 118.1°C) and another for EVOH \( T_c = 138.6°C \). The \( T_c \) values of the as-spun pure PP and the pure EVOH fibers were 120.9°C and 139.7°C, respectively. However, only one crystallization peak \( T_c = 120.8°C \) could be seen in the DSC curve for the EVOH/PP/EVOH fiber after immersion in the 2-propanol/water mixture. This result indicated that EVOH was completely removed from the EVOH/PP/EVOH fiber by immersion in the 2-propanol/water mixture. The \( T_c \) values of PP and EVOH in the as-spun EVOH/PP/EVOH fibers were lower than those of the as-spun pure PP and as-spun pure EVOH fibers. It is likely that each crystallization would be inhibited by the interface with another polymer.

We formed PP nanofibers from EVOH/PP (MFR: 35 g/10 min)/EVOH laminated sheets with different PP layer thicknesses (EVOH/PP/EVOH = 100/100/100, 100/50/100, 100/30/100 µm) and after the removal of EVOH. Fig. 4 illustrates the effect of the distance between the nozzle tip and the collector on the obtained fiber diameter. The fiber diameters decreased as the distance increased by 100 mm due to
the whipping of the polymer jet. In addition, the fiber diameters decreased as the PP layer thickness decreased. This would be attributable to the decrease in the amount of PP melt and to the increase in the drawing effect of co-spun EVOH during M-ESP. In this experiment, the finest PP nanofiber \( (D = 0.25 \mu m, \sigma = 0.06 \mu m) \) was obtained under the following conditions: thickness, EVOH/PP/EVOH = 100/30/100 \((\mu m)\), collector distance = 100 mm. The diameter is close to one-tenth of the diameter of PP fibers (i.e., 2.27 \( \mu m \), see Fig. 1 (b) obtained from a pure PP sheet.

The effects of the PP layer thickness and the MFR of PP (MFR=12, 35 and 75 g/10 min) in the EVOH/PP/EVOH sheets (EVOH/PP/EVOH = 100/100/100, 100/50/100, and 100/30/100 \((\mu m)\)) on the fiber diameter of the PP nanofibers after the removal of EVOH are shown in Fig. 5. The collector distance was 100 mm. As observed in the figure, the fiber diameters decreased as the sheet thickness decreased for all grades of PP, for the same reason as the data in Fig. 4. This result was similar to those obtained on pure EVOH films. Taylor cones can well-develop with thick films and it means that a sufficient amount of molten polymers can be fed at the melting area and thick fibers have been produced [8]. In addition, the fiber diameters decreased as the MFR of the PP decreased. The electrostatic spinning with laser melting mainly depends on the repulsion of electric charge, creates the force for fiber drawing. Thus, under the same spinning conditions, polymer having a lower viscosity is easily stretched and reduce the fiber diameter, and the towing effect of PP increases in the presence of polar polymer, EVOH, during the polymer jet. EVOH consists of polar hydroxyl groups that easily accumulate the charges during high voltage electrospinning, and conceive a huge electric charge repulsion.

Fig. 6 is SEM images and the histograms of the fibers obtained from the three-layer [EVOH/PP (MFR: 12 g/10 min)/EVOH] sheet before and after EVOH removal. The \( D \) values of the fibers before and after the EVOH removal were 0.47 \( \mu m \) and 0.21 \( \mu m \).

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**Fig. 5** Effect of MFR (PP) and PP layer thickness on the fiber diameter after EVOH removal.

**Fig. 6** SEM images and histograms of EVOH/PP (MFR = 12 g/10 min)/EVOH fibers obtained (a) before and (b) after EVOH extraction.
respectively. Fig. 6 (b) presents the finest PP nanofiber obtained in this study; the nanofibers showed the same diameter as that in ref. [7] without the addition of conductive compounds.

Fig. 7 provides cross-sectional SEM images of the as-spun fibers that we obtained from EVOH/PP/ EVOH (100/30/100 μm) three-layer sheets. The MFRs of the PP were 12, 35 and 75 g/10 min. The core-shell structure can be seen in Fig. 7 (a) (the core and the shell were PP and EVOH, respectively), but it is not observed in the dashed squares in panels (b) and (c) of Fig. 7 because the MFRs of the PP were higher than that of EVOH (14 g/10 min). Thus, the diameters of the PP nanofibers shown in Fig. 6 (b) were greatly reduced by the wrapping phenomenon and following EVOH removal.

4. Conclusion

Core (PP)-clad (EVOH) nanofibers were created from three-layer EVOH/PP/EVOH sheets with the application of our novel melt-electrospinning system with a line-like CO₂ laser beam. The fiber structure depends on the MFR values, and if the MFR value of the EVOH melt is greater than that of the PP melt, the fibers obtained will have a core-clad structure that is in stable condition because of the wrapping phenomenon. PP nanofibers were created due to the PP’s towing effect with EVOH and the subsequent EVOH removal. The diameter of the as-spun fibers was decreased by decreasing both the MFR of the PP melt and the thickness of the PP layer in the EVOH/PP/EVOH sheet. Our present findings can be used to design new and functional nanofibers from many types of polyolefin, engineering plastics and other materials by using the M-ESP system described herein.

References

1. Z.-M. Huang, Y.-Z. Zhang, M. Kotaki, and S. Ramakrishna, Comp. Sci. Tech., 63, 2223 (2003).