Preparation and Anisotropic Mechanical Behavior of Highly-Oriented Electrospun Poly(butylene terephthalate) Fibers

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ABSTRACT: This work describes the effect of the speed of drum-type rotating collector in an electrospinning process on the orientation of electrospun poly(butylene terephthalate) fiber mats, and its effect on the tensile properties. The degree of orientation increased with the increase in the drum speed (surface velocity) up to a critical level, and thereafter, wavy fibers were observed. The average diameter reduced and its distribution became narrower with increase in the velocity. The mechanical properties in a parallel direction improved about three times with increase in the surface velocity. The anisotropic mechanical behavior could be predicted with a simple classical equation. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2017–2021, 2006

Key words: anisotropic mechanical behavior; electrospun fibers; orientation effect; poly(butylene terephthalate)

INTRODUCTION

The electrospinning process has been suggested as a useful method to produce the nonwoven fabrics made of submicron or nanoscale fibers.[1–3] Compared with conventional fiber spinning methods, the electrospinning technique offers many advantages because of the very large surface area to volume ratio. They have high flexibility in surface functionalities and superior mechanical performance such as stiffness and tensile strength. However, the application is somewhat limited so far, because most of the electrospun fibers are in isotropic nonwoven mats form. A cylindrical collector has been tried to align the electrospun fibers by controlling the drum speed during processing of poly(glycolic acid)[4,5] and poly(acrylonitrile).[6] By considering the importance of orientation of electrospun fibers in industrial applications point of view, a further study on the orientation effect is clearly necessary for many other polymeric materials.

In this study, the influence of drum speed on the fiber morphology, the fiber alignment, and the anisotropic tensile properties of the mats was investigated using one of the typical engineering plastics, a poly(butylene terephthalate) (PBT). A theoretical prediction of the anisotropic behavior was also made with a simple classical model.

EXPERIMENTAL

PBT (TRIBIT 1700s) was obtained from Samyang Company (Korea). 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP; bp 58 °C) was obtained from TCI (Japan) and used as a solvent for PBT.

Pure PBT pellets were dissolved in HFIP, by stirring for 24 h at room temperature, to get the final solution for electrospinning. The solution concentration was set to be 8 wt %. The schematic representation of the electrospinning apparatus along with its side view is shown in Figure 1, based on Doshi and Reneker.[1] The tip to collector distance was 18 cm, and a constant high DC voltage of 20 kV was applied using a high voltage supplier (model RR30–1.25P, Gamma High Voltage Research, USA). The rotation speed of drum was varied by 400, 800, 1200, and 1600 rpm, where the corresponding surface velocity was 4.3, 8.6, 12.9, and 17.2 m/s, respectively, by considering the drum diameter of 206 mm.

The characterization of the electrospun fiber was carried out by observing the morphology of the fiber using a field emission-scanning electron microscope (FE-SEM, Hitachi *S*-4700, Japan). To figure out the average fiber diameter, the number of fibers within every 500-nm intervals of diameter ranges was carefully counted over the magnified FE-SEM photographs, using an image tool for windows (UTHSCSA Image Tool version 3.0). To avoid repeated counting, the FE-SEM images were opened with exactly same size in the computer screen using both image tool and photoshop software, and each measured fiber in the

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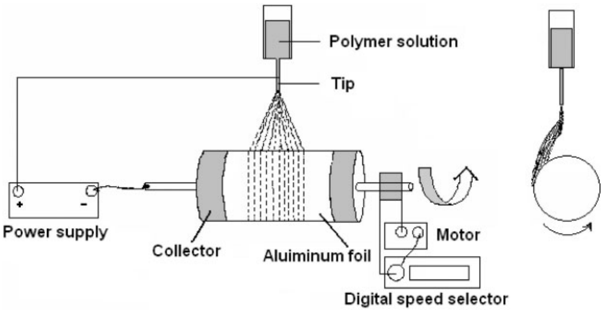


Figure 1 Schematic diagram of experimental set-up (left) and side view (right) of electrospinning process.

image tool software was marked in the photoshop image just after measurement.

To study the mechanical properties, dumbbell-shaped specimens were cut from the electrospun mats at various angles from parallel to transverse direction to drum rotation to figure out any effect of fiber orientation, as shown in Figure 2. Modulus, tensile strength, and elongation at break were obtained from stress–strain curves by using a tensile tester (Lloyds, UK) at room temperature and at a cross-head speed of 500 mm/min, according to the procedure described in ASTM D 412. The tensile stresses were calculated by dividing the measured forces with apparent cross section (i.e., width times thickness of mats), even though there were lots of free voids made from characteristic structure of mats formed by each fibers. Thus, all the reported values for tensile stresses and moduli in this study are apparent.

RESULTS AND DISCUSSION

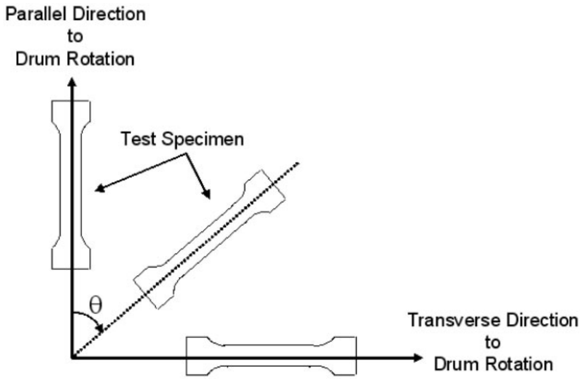


Figure 2 Schematic representation of sample preparation for tensile testing at different orientation angles of fiber mats.

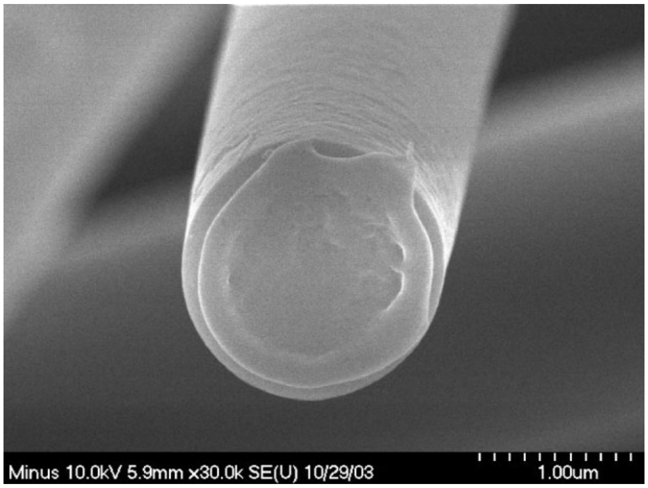


Figure 3 Cross-sectional view of a typical fiber.

Figure 3 shows a typical cross-sectional view of a single fiber, showing a circular shape. Thus, the determination of fiber diameter based on SEM micrograph seems to be reasonable. Figure 4 shows the FE-SEM micrographs of electrospun fiber mats at different surface velocities. It can be seen that the alignment of fibers was achieved with increase in the surface velocity. The best alignment was observed at 12.9 m/s, not at the highest velocity. It has been previously observed that the best alignment of the electrospun fiber in the mat occurs when the linear velocity of the rotating cylinder surface matches that of evaporating jet depositions.[4–7] They have explained that the ejected electrospun fibers are taken up on the rotating cylinder surface tightly in a circumferential manner, which results in good alignment. Thus, the optimum alignment surface velocity seems to be around 12.9 m/s (corresponding rotation speed of 1200 rpm) in our case. Moreover, Fennessey and Farris[6] reported that the maximum orientation was observed at the surface velocity of 9.84 m/s, which was a comparable level to our value even though many processing parameters such as polymer type and solution concentration were different. It should be noted that somewhat wavy fibers were observed, instead of straight fibers at extremely high surface velocity of 17.2 m/s (1600 rpm). This might come from the occurrence of a turbulent air flow around the perimeter of the rotating drum. Thus, it can be concluded that there is an optimum point for rotation speed of drum-type collector to get the best alignment of the electrospun fibers of the mats.

Another point we can expect to be affected by the drum rotation speed is fiber diameter and its distribution. Figure 5 shows the distribution based on the counting the number of fibers within every 500 nm range, using an image tool. A unimodal distribution was observed regardless of rotation speed, although some cases based on other polymer systems showed bi-modal and even trimodal distribution.[8,9] Moreover, the distribution of fiber diameter became much narrower with increased surface velocity, because the

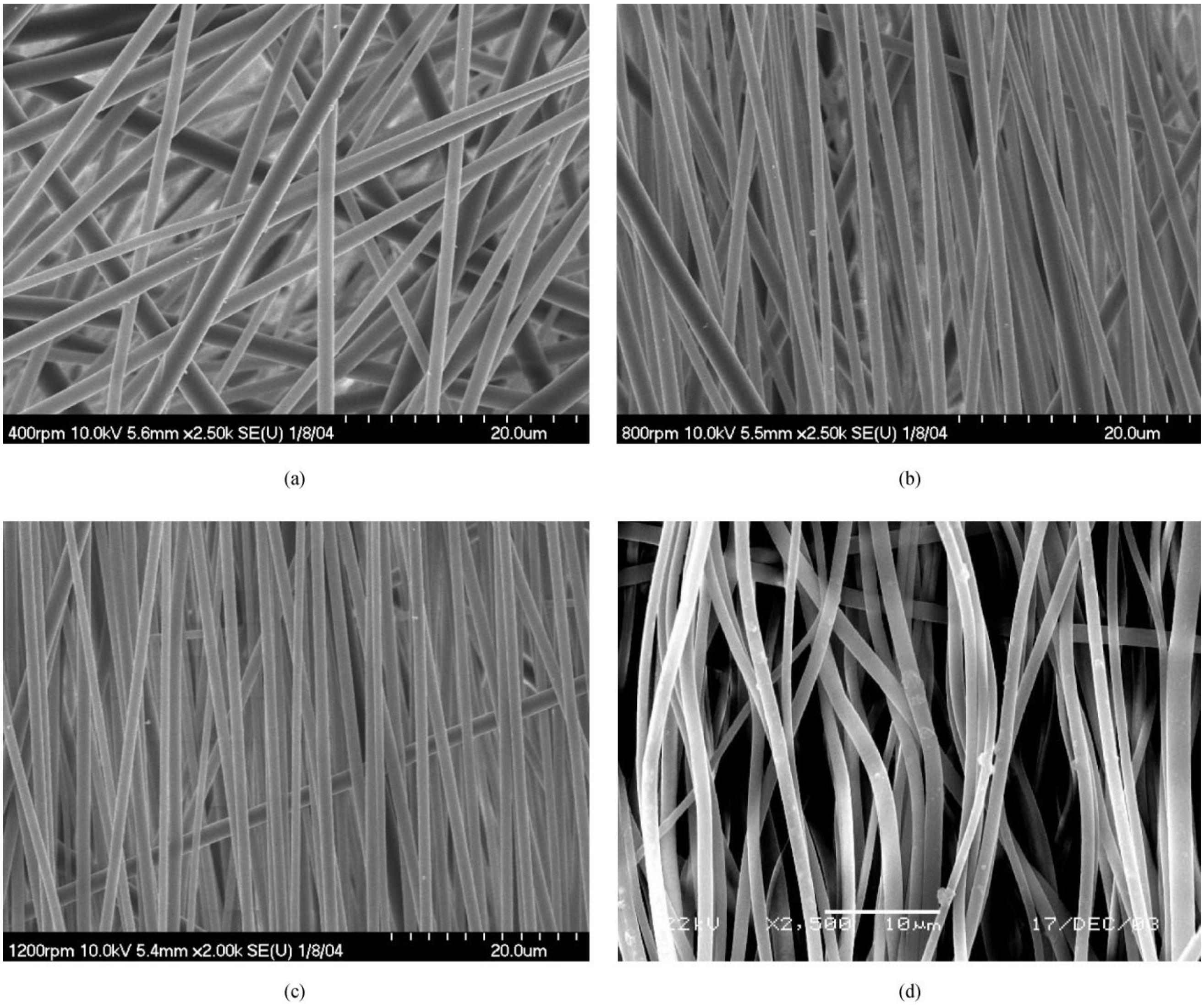


Figure 4 FE-SEM micrographs of electrospun fiber mats at various surface velocities: (a) 4.3 m/s, (b) 8.6 m/s, (c) 12.9 m/s, and (d) 17.2 m/s. The direction of rotating drum is downward.

portions of higher diameter range over 1.5 μm considerably disappeared. To figure out more information on fiber diameter, the number-averaged diameter, D_n, was calculated as follows:

$$D_n = \frac{\Sigma N_i D_i}{\Sigma N_i} \tag{1}$$

where N_i and D_i are number and diameter of ith diameter range. Figure 6 shows the D_n as a function of linear surface velocity. The average diameter decreased somewhat rapidly at low and high surface velocities. The initial rapid drop can be explained by reduced proportions of fibers having higher diameters as can be conjectured from Figure 5. The final rapid drop can be explained by more mechanical stretching leading thinner fibers. For instance, the electrospun

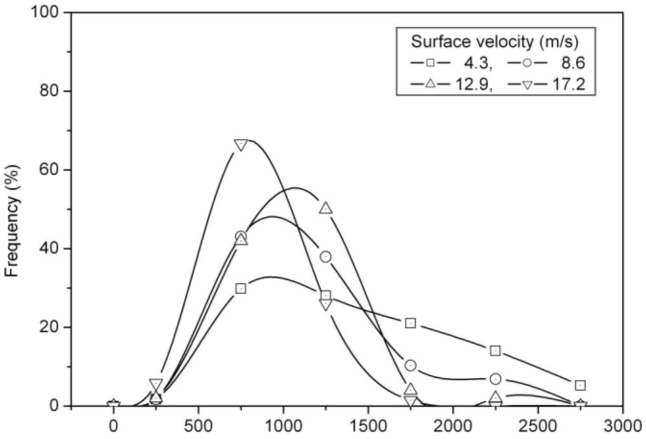


Figure 5 Change in the distribution of fiber diameters depending on the surface velocity.

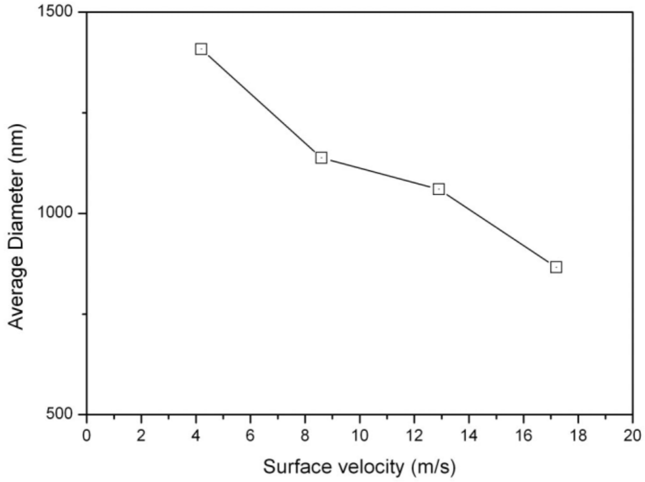
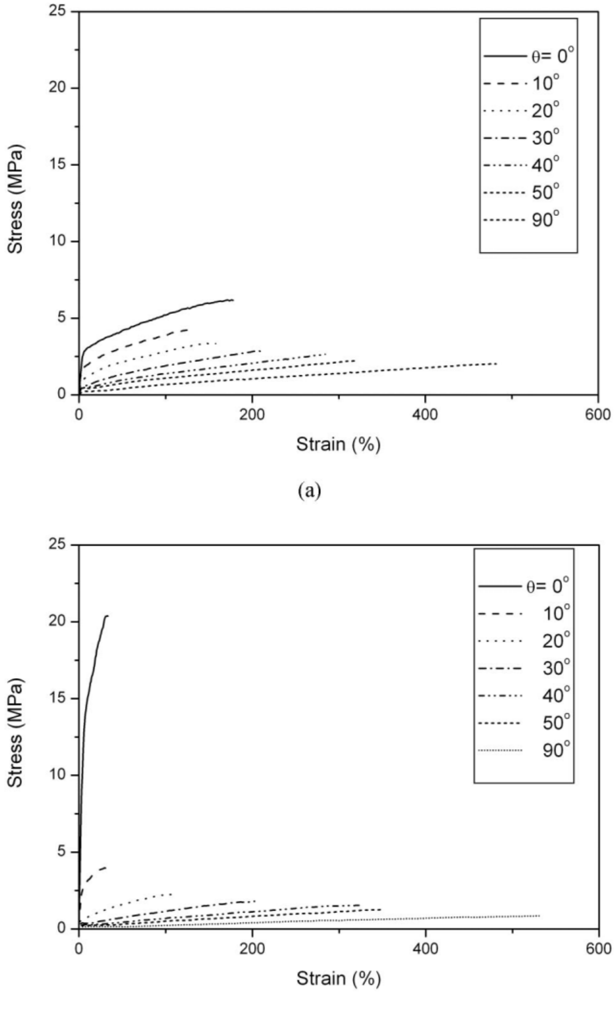


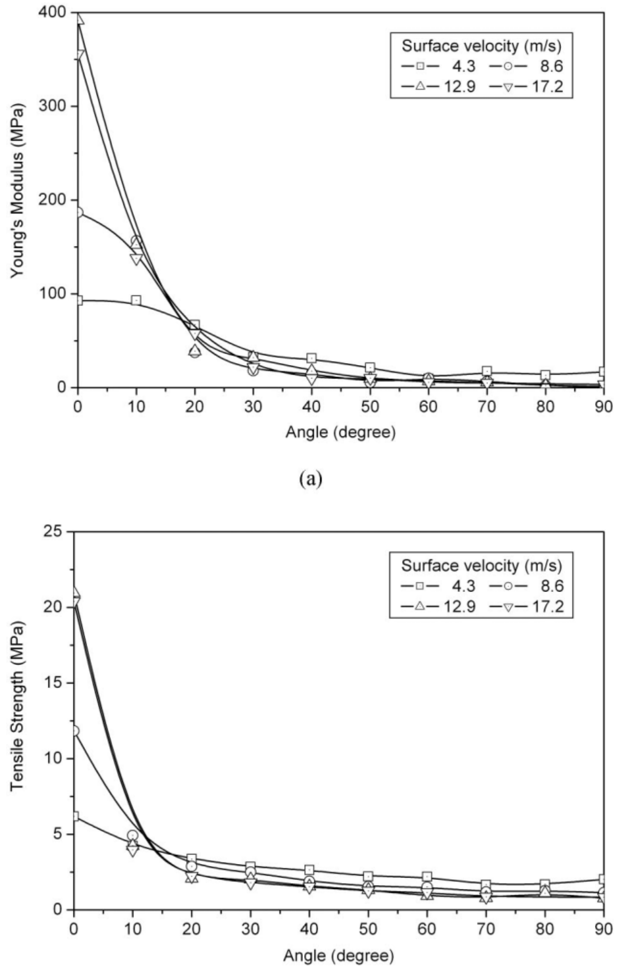
Figure 6 Effect of surface velocity on number-averaged diameter.



(a)

(b)

Figure 7 Anisotropic effect on tensile property at two extremely different surface velocities: (a) 4.3 m/s and (b) 17.2 m/s.



(a)

(b)

Figure 8 Dependence of angle and velocity on (a) Young's modulus and (b) tensile strength.

fibers are extended as they touch the rotating collection drum with higher velocity than that of fibers.

As the degree of alignment of fibers depends on the drum speed, it is interesting to see its influence on mechanical properties of the electrospun mats. For this purpose, various dumbbell-shaped specimens were cut at various angles from 0° for parallel direction and 90° for perpendicular direction of fiber orientation, as described earlier (Fig. 2).

Figure 7 shows the stress–strain curves at various angles for two extreme cases of surface velocity of 4.3 and 17.2 m/s. As can be expected, the modulus and tensile strength decreased, while the strain at break increased as the angle was increased. This behavior was observed at all rotation speeds. Moreover, the dependence of angle was much more significant at 17.2 m/s than at 4.3 m/s, because of higher orientation level. In the case of higher speed, the stress–strain curve shifted closer to the *y*-axis, showing a similar curve for a pure fiber. This again indicates the higher extent of fiber alignment at higher drum rotation speeds.

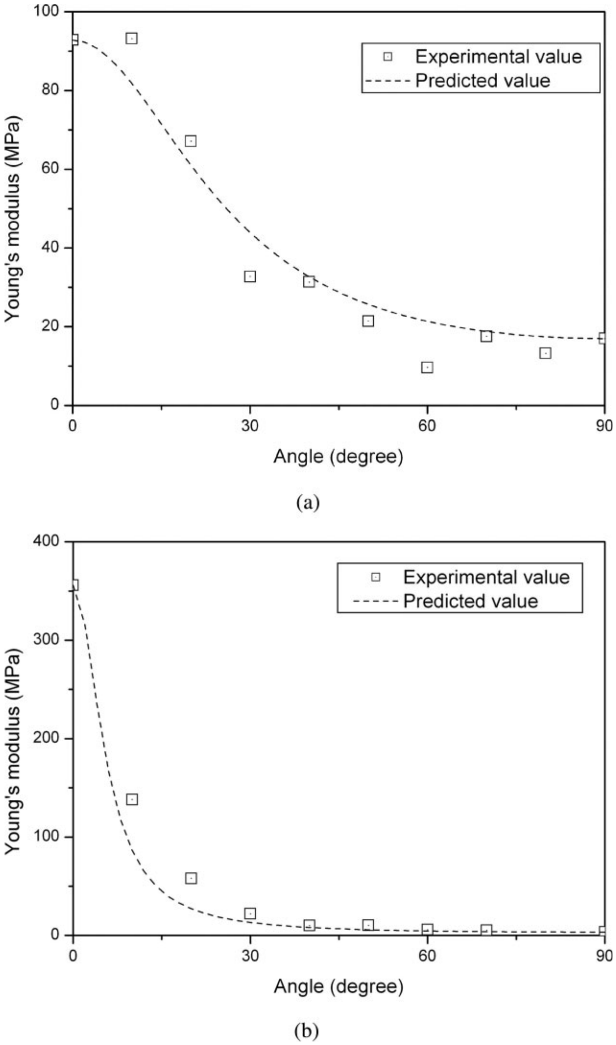


Figure 9 Comparison between experimental and predicted values of Young's modulus at surface velocity of (a) 4.3 m/s and (b) 17.2 m/s.

To figure out the dependence of both the speed and angle, Young's modulus calculated from the initial linear slope of the stress–strain curves and tensile strength are plotted as a function of angle for all speed conditions in Figure 8. The effect of angle and speed was remarkable at relatively lower ranges of angles. At 0° angle, the properties improved approximately four times, as the surface velocity was increased from 4.3 to 17.2 m/s. This strong effect almost diminished at above 20° for Young's modulus and at 10° for tensile strength. Thus, in view of mechanical properties, no marginal improvement can be obtained above these angles by adjusting the speed.

In an attempt to predict theoretically the angular dependence of Young's modulus, a classical equation, originally used for the prediction of angular dependence of tensile modulus in the case of short fiber-reinforced rubber composites,[10] was used. This equation based on the competition between sine and cosine functions is given by

$$\frac{1}{E_\theta} = \frac{(\cos^2\theta)}{E_L} + \frac{(\sin^2\theta)}{E_T} \qquad (2)$$

where E_θ is the modulus of composite wherein fibers deviate from the direction of test by an angle θ, E_L is the longitudinal composite modulus at $\theta = 0°$ and E_T is the transverse composite modulus at $\theta = 90°$. Figure 9 shows some typical prediction results along with the experimental data. A reasonable agreement was found between theoretical and experimental values for all surface velocities. Thus the prediction of the angular dependence of mechanical properties of oriented fiber mats can also be predicted using a simple classical equation.

CONCLUSIONS

The drum speed in the electrospinning process strongly affected the morphology and orientation of fibers, resulting in a considerable change in the mechanical properties of the mats. The best fiber orientation was achieved at the surface velocity of around 12.9 m/s (corresponding drum speed of 1200 rpm). The distribution of fiber diameter became much narrower with increased drum speed, due to reduced portion of fibers having higher diameter. The effect of surface velocity on the tensile properties was more apparent for higher surface velocities. At 0° angle, the properties improved nearly four times with the increased drum speed. The anisotropic mechanical properties for oriented electrospun fiber mats could be predicted with a reasonable accuracy with a simple classical equation.[10]

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