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The Effect of Molecular Weight and the Linear Velocity of Drum Surface on the Properties of Electrospun Poly(ethylene terephthalate) Nonwovens

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Abstract: In this study, we evaluated the effect of the molecular weight of the polymer on electrospun poly(ethylene terephthalate) (PET) nonwovens, and their mechanical properties as a function of the linear velocity of drum surface. Polymer solutions and electrospun PET nonwovens were characterized by means of viscometer, tensiometer, scanning electron microscope (SEM), wide angle X-ray diffraction measurement (WAXD) and universal testing machine (UTM). By keeping the uniform solution viscosity, regardless of molecular weight differences, electrospun PET nonwovens with similar average diameter could be obtained. In addition, the mechanical properties of the electrospun PET nonwovens were strongly dependent on the linear velocity of drum surface. From the results of the WAXD scan, it was found that the polymer took on a particular molecular orientation when the linear velocity of drum surface was increased. The peaks became more definite and apparent, evolving from an amorphous pattern at 0 m/min to peaks and signifying the presence of crystallinity at 45 m/min.

Keywords: Poly(ethylene terephthalate) (PET), Nanofibers, Electrospinning, Morphology, Mechanical properties

Introduction

Electrospinning has developed into a very useful technique over last two decades. The most attractive aspect of this technique, compared to the typical methods such as melt, dry and wet spinning, is that it provides a simple and easy method of producing nanofibers with diameters ranging from a few nanometers to a few microns [1,2].

The electrospinning principle is that a high voltage is used to create an electrically charged jet of polymer solution or melt. This jet is emitted from the apex of the cone formed on the surface of a droplet of polymer solution or melt [3-5]. As the jet travels through the air, with the electric field generated between the positive and the negative electrode, it solidifies to leave behind polymer fiber that can be collected on an electrically grounded collector. Because of the small fiber diameter and large surface area per the volume ratio of resulting fibers, they have the potential to be used in a wide range of applications. For example, the electrospun nonwovens composed of nanoscale fibers can be used as the separation membranes, scaffolds for tissue engineering or other biomedical devices, reinforced composites, as wll as in nanoelectronics and many other applications [6-10]. Recently, there have been many studies on electrospinning process, which focused on the processing parameter, system parameter and ambient parameter. The system parameters are related to solution properties, such as the polymer solution viscosity, conductivity and surface tension. The processing parameters consist of the spinning conditions, which include the hydrostatic pressure in the capillary, the applied voltage and the tip-to-collector distance. These parameters can be controlled during the electrospinning process. Finally, the ambient or environmental conditions in the chamber are the temperature, humidity, and air velocity [11].

The objective of this study is to investigate the effect of molecular weight of the polymer on the morphology and the mechanical properties of electrospun PET nonwovens as a function of the linear velocity of drum surface.

Experimental

Materials

Two kinds of poly(ethylene terephthalate) with IV(Intrinsic viscosity) 0.64 and 0.80 were obtained from Huvis (Jeonju, Republic of Korea) in the form of chips. A trifluoroacetic acid (TFA) and a methylene chloride (MC) purchased from Showa (Japan) were used as a solvent without further purification.

Electrospinning Apparatus

A variable high voltage power supply (CPS-60 k02v1, Chungpa EMT Co., Republic of Korea) was used in the experiment. A schematic diagram of the electrospinning apparatus is shown in Figure 1. Polymer solution is drawn up a 5 m*l* syringe with a capillary tip having a diameter of 1 mm, which is fixed at approximately 5 ^{o} to the horizontal, in order for a small drop to be maintained at the end of capillary tip due to the surface tension of the solution. One end of a copper wire is attached to the positive electrode while the other end is inserted into the syringe to supply the electrical force, and the rotational collector covered with Al-foil is charged by the negative electrode.

Surface Tension and Viscosity

The surface tension and viscosity of the polymer solutions

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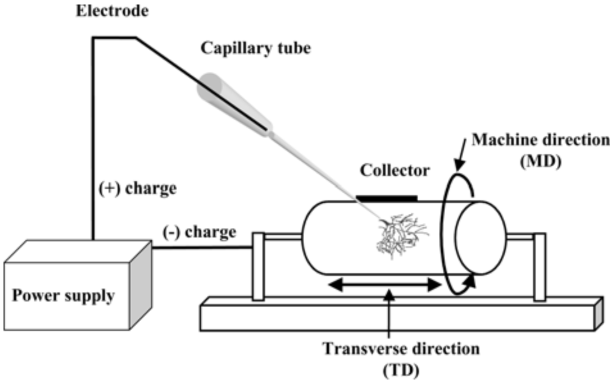


Figure 1. Schematic diagram of electrospinning devices used in this study.

were measured at 20 °C by means of a tensiometer of the Wilhelmy plate type (K 10ST, Krüss Co., Germany) and a Rheometer (DV III of Brookfield Co., USA), respectively.

Morphology

The morphology of the electrospun PET nonwovens was determined using a scanning electron microscope (GSM-5900, JEOL. Co., Japan). A small fraction of electrospun PET nonwovens was placed on the SEM sample holder and sputter-coated with gold (Denton Desk-1 Sputter Coater). An Amray 3000 SEM with an accelerating voltage of 25 kV was used to take the SEM photographs. To measure the diameters of the electrospun PET nonwovens and fiber orientation angle, an image analyzer (Image-proplus, Media Cybernetics Co., USA) was used.

WAXD

Wide angle X-ray diffraction (WAXD) measurements were carried out at room temperature by means of a Philips Diffractometer with a Geiger counter, connected to a computer. The diffraction scans were collected at the 2θ value of between 1.5° and 50°.

Mechanical Properties

The electrospun PET nonwovens were prepared considering the transverse direction (TD) and machine direction (MD) with a width of 220 mm width, a length of 400 mm, and a thickness of 0.7~0.8 mm. The mechanical properties of the electrospun PET nonwovens were determined by means of a universal test machine (UTM AG-5000G, Shimadzu, Japan) with a crosshead speed of 10 mm/min at room temperature. All of the samples were prepared on the basis of ASTM D638, for the experiments in both the machine direction (MD) and transverse direction (TD).

Determination of Point Bonding

The number of point bonding were determined by quantifying the average number of bonding point per millimeter from 10 different SEM images corresponding to the linear velocity of drum surface.

Results and Discussion

Molecular Weight Effect

The solution concentration and surface tension are known to affect the diameters of electrospun fibers and their distribution [1-5,7-9,12]. It was reported in these studies that the viscosity of polymer solution is an important factor during electrospinning. However, these studies focused on the effect of the viscosity of a solution containing a single polymer. Therefore, in this study, we compared the viscosities of PET solutions using polymers with different molecular weights. Figure 2 shows the surface tension and viscosity as a function of the polymer content dissolved in the mixture of TFA/MC (v/v, 50/50).

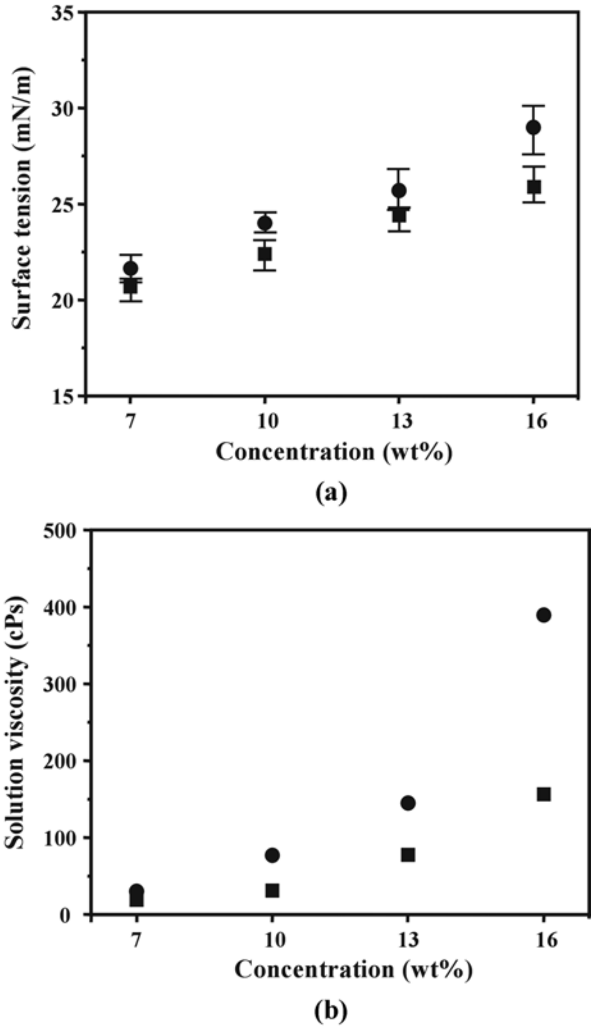
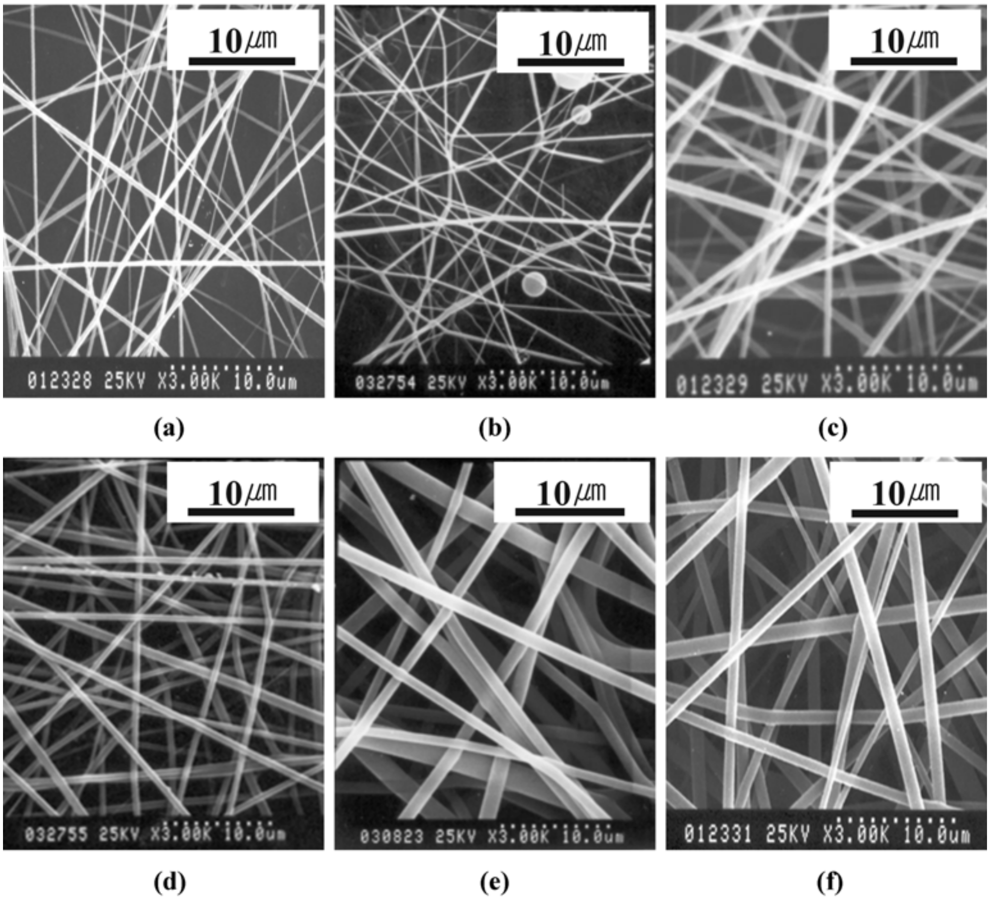


Figure 2. Solution properties: (a) solution viscosity and (b) surface tension as a function of solution concentration: ■ IV 0.64 and ● IV 0.80.



(a) **(b)** **(c)**

(d) **(e)** **(f)**

Figure 3. SEM images of the electrospun PET nonwovens with different molecular weights: (a) 10 wt% of IV 0.64, (b) 7 wt% of IV 0.80, (c) 13 wt% of IV 0.64, (d) 10 wt% of IV 0.80, (e) 16 wt% of IV 0.64, and (f) 13 wt % of IV 0.80.

With increasing the concentration of polymer solutions prepared using polymers with different molecular weight, the viscosity of polymer solutions was found to increase due to the densely entangled polymer chains. Furthermore, the surface tension also increased as the polymer concentration increased. These properties are thought to play an important role in the morphology and mechanical behaviors of the electrospun PET nonwovens. The morphologies of the fibers electrospun from these solutions are given in Figure 3.

In the case of the low viscosity (19 cPs) solutions of IV 0.64, beads were produced instead of fibers due to the combined effect of electrically driven jet and instability [3,5]. The 10 wt% solutions of IV 0.64 PET and 7 wt% solutions of IV 0.80 PET dissolved in a mixture of TFA/MC (50/50, v/v) had similar viscosities and produced fibers exhibiting similar diameter distributions. As the concentration of the solution increased, the viscosity and surface tension increased, regardless of the molecular weights of the polymer. The fiber diameters and their distribution varied in a similar manner to the solution viscosity and surface tension, as shown in Figure 4.

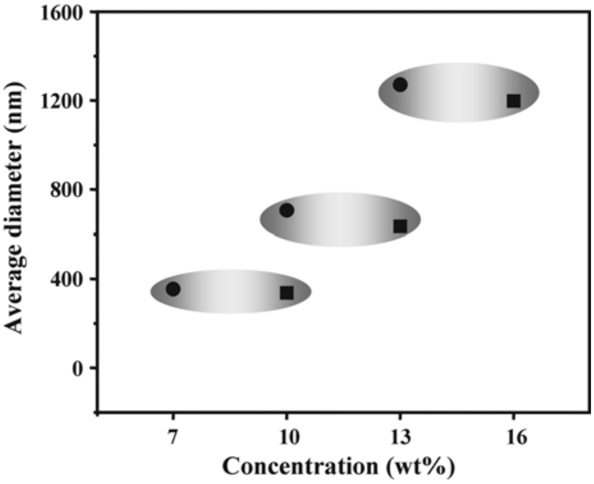


Figure 4. Average diameter of the electrospun fibers as a function of solution viscosity prepared from two different polymers ■ IV 0.64 and ● IV 0.80.

Even though polymers with different molecular weights are used, fibers having a similar average diameter can still be obtained, as long as the viscosity of polymer solution is maintained at a similar level.

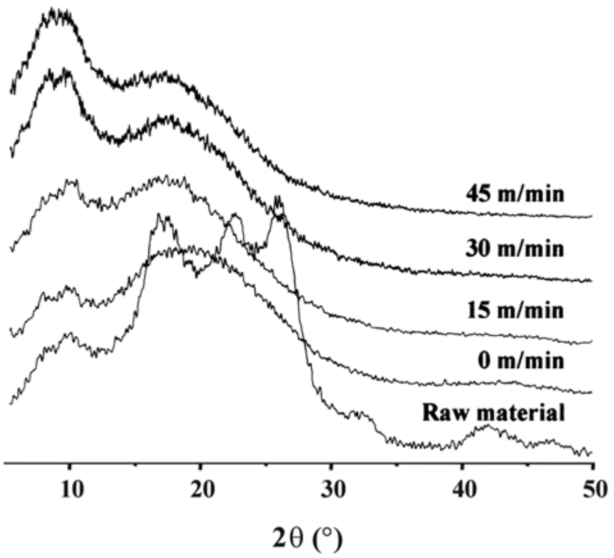


Figure 5. WAXD patterns of the electrospun PET nonwovens as a function of the linear velocity of drum surface.

Wide-angle X-ray Diffraction

Many researchers [8,13,14] reported that fibers prepared by electrospinning technique suffered from retarded crystallization. This phenomenon is universal in the field of electrospinning and implies that the formation of crystals in the electrospun fibers is hindered during the electrospinning process due to the rapid solidification of the stretched chains at high elongational rates. Namely, the electrospun fibers have insufficient time to arrange themselves into a suitable crystal formation before the polymer chains are solidified by rapid solvent evaporation. Therefore, in this study, we evaluated the crystalline state of electrospun PET nonwovens with submicron diameters as a function of the linear velocity of drum surface. The WAXD patterns obtained are shown in Figure 5. In comparison with the WAXD patterns of the electrospun PET nonwovens made using various linear velocities of drum surface, the WAXD patterns of the raw materials show a number of crystalline peaks, which reflect the semi-crystalline structure of PET. The electrospun PET nonwovens show a typical amorphous pattern. The WAXD patterns show an evolution from the crystalline to amorphous peaks, (010), with this change becoming more pronounced as the linear velocity of drum surface is increased. The presence of the (010) peak indicates that the crystals have a significant orientation, which is induced by the linear velocity of drum surface. These WAXD results are similar to those presented by Llana and Boyce [15], and Salem [16]. Finally, although the electrospun PET nonwovens presented partial ordering due to the linear velocity of drum surface, the crystallinity of electrospun PET nonwovens shows very lower according to the results of WAXD patterns than that of raw material.

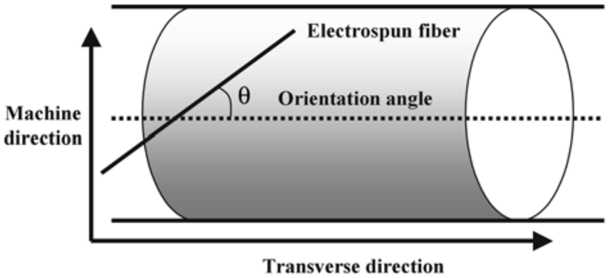


Figure 6. Definition of fiber orientation angle: MD: 60-120 °, TD: 0-30 ° and 150-180 °.

Effects of Linear Velocity of Drum Surface on the Mechanical Properties

In a typical fiber web structure which uses mechanical forces to produce fibers from the extrusion of polymer fluids, the mechanical properties of nonwoven fabric highly dependent on the arrangement of the fibers in the nonwovens, binding elements (single fiber, strand, thread), and a number of binding/bonding elements (bonding intensity). Important factors of fiber structure in the nonwovens are fiber orientation, the frequency distribution of the fiber arrangement, and fiber curl. The bond structural arrangements in the nonwovens involve the segmented bonding structures, agglomerated bonding structures, and point-bonded structure. The bonding structure and bonding elements are significantly related to the mechanical properties of the nonwovens. Also, the fiber angle distributions and bonding elements can have a significant effect on the properties of nonwoven fabric [17].

The effects of the fiber orientation and the density of point bonding per unit area are required to evaluate the relation between these and the mechanical properties in the case of the electrospun nonwovens. In this study, two effects were investigated. One was the frequency distribution of fiber orientation angle, the other was the density of point bonding within the nonwovens. We defined the fiber orientation angles of the electrospun PET nonwovens, which were considered in the machine direction (MD) and the transverse direction (TD) in Figure 6.

The stress-strain behaviors of the electrospun PET nonwovens were tested as a function of the linear velocity of drum surface. As shown in Figure 7, the young's modulus, yield stress and tensile strength of MD were higher than those of TD. These results suggest that the fiber arrangement toward the MD is higher than that toward the TD, because the rotation force generated by the drum rotation is increased toward the MD, as shown in Figure 8. At the same time, however, the collecting area is narrow. The fibers in the electrospun PET nonwovens are therefore arranged toward the MD rather than TD, regardless of the linear velocity of drum surface. As a result, the young's modulus, yield stress and tensile strength of electrospun PET nonwovens are dependent on the linear velocity of drum surface, because

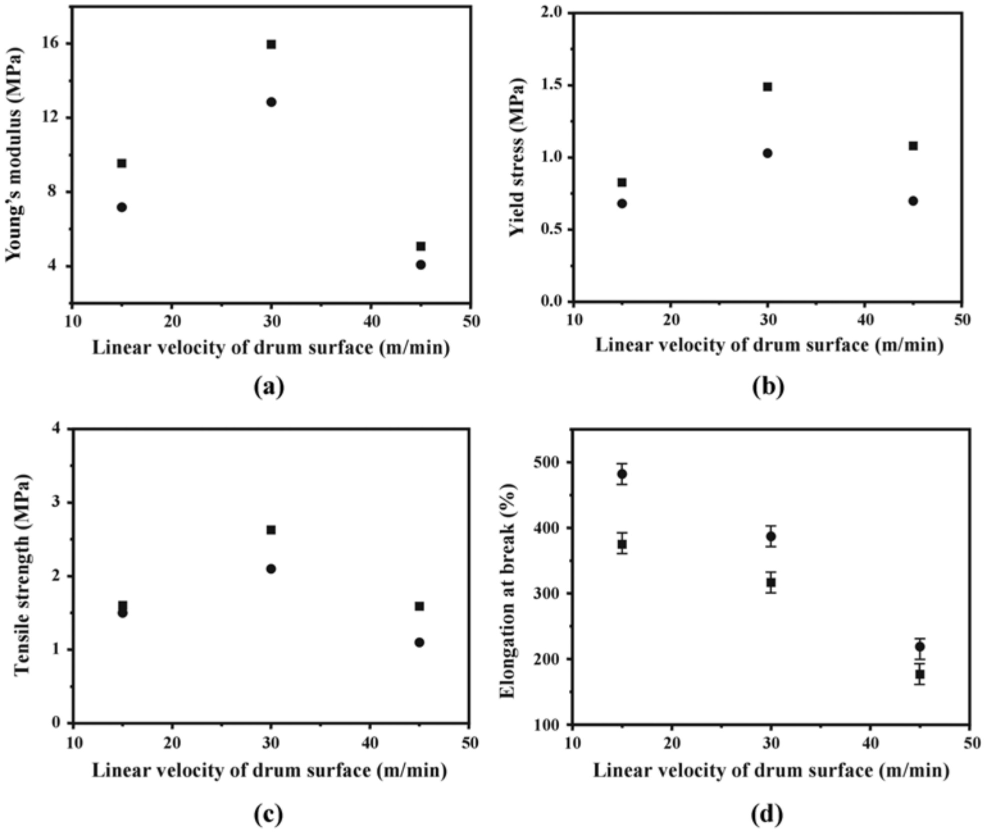


Figure 7. Stress-strain curves of the electrospun PET nonwovens as a function of the linear velocity of drum surface: ■ MD and ● TD.

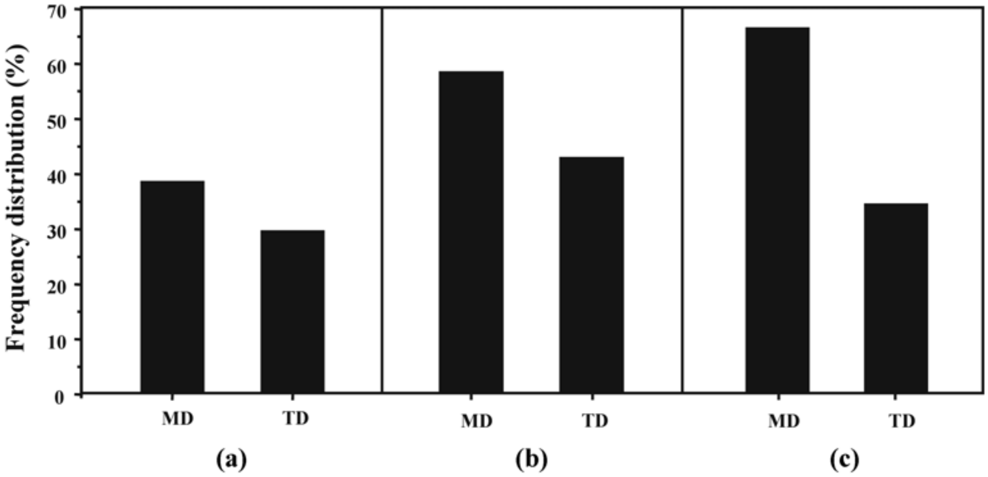


Figure 8. Frequency distributions of fiber orientation angle of the electrospun PET nonwovens as a function of the linear velocity of drum surface: (a) 15 m/min, (b) 30 m/min, and (c) 45 m/min.

the electrospun fibers are deposited by the force of collector rotation in the direction corresponding to the linear velocity of drum surface. Also, the young's modulus, yield stress and tensile strength initially increased with increasing the linear velocity of drum surface. However, the same properties tend to decrease above 30 m/min, instead of continuous increasing as might have been expected. Meanwhile, at linear velocity of drum surface of 45 m/min during electrospinning, many of the fibers were observed to fly into the air instead of being deposited on the collector. This is thought to occur because the number of bonding points in the electrospun PET nonwovens decreases as the linear velocity of drum surface increases. Therefore, the number of bonding points are investigated and quantified in Figure 9. These results show a

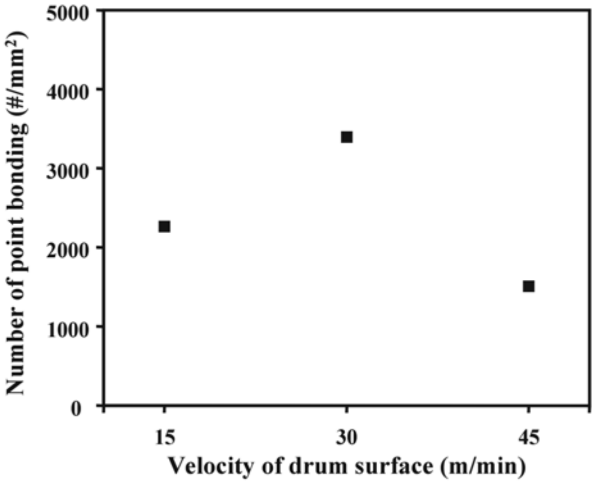


Figure 9. Number of bonding points on the electrospun PET nonwovens as a function of the linear velocity of drum surface.

similar trend to those of the mechanical test. As the linear velocity of drum surface increases, the density of point bonding increases up to 30 m/min. However, above 45 m/min, it decreases. Consequently, the mechanical properties of the electrospun PET nonwovens composed of nanoscale fibers rely on the arrangement of fibers and the number of point bonding within the nonwovens, which are affected by the linear velocity of drum surface.

Conclusions

In this study, it was found that the sub-micron diameter PET nonwovens can be obtained by controlling the solution viscosity and linear velocity of drum surface. The average fiber diameters of electrospun nonwovens obtained from solutions with similar viscosities were comparable, regardless of the polymer molecular weight. The young's modulus, yield stress and tensile strength of the electrospun PET nonwovens increased with increasing the linear velocity of drum surface up to 30 m/min, but decreased above 45 m/min. Also, as the linear velocity of drum surface increased, the fibers arranged themselves more and more towards MD rather than the TD.

Acknowledgements

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