Influence of Collecting Velocity on Fiber Orientation, Morphology and Tensile Properties of Electrospun PPESK Fabrics

Wen Qi,[1] Chun Lu,[2] Ping Chen,[1] Tianfang Cui[1]

[1]*Polymer Department School of Chemical Engineering, Dalian University of Technology, Dalian Liaoning 116012, China*
[2]*Material Engineering Department, Shenyang Aerospace University, Shenyang Liaoning 110136, China*

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ABSTRACT: Poly(phthalazinone ether sulfone ketone) (PPESK) is a novel kind of soluble thermoplastic resin with excellent thermal resistance properties. In this article, PPESK nonwoven fabrics were successfully prepared using electrospinning technique, and the influence of collecting velocity on fibers orientation, morphology and tensile properties was studied by changing the collecting velocity during electrospinning process. Results indicate that collecting velocity has a strong influence on fiber orientation and mechanical performance. When the collecting linear velocity increases from 0.36 to 3.35 m/s, fiber angular standard deviation is decreased from 63.8° to 45.5°, and tensile strength of PPESK fabrics is increased from 0.0246 to 3.677 MPa. However, when collecting velocity is higher than 3.35 m/s, fabrics tensile strength shows a declining tendency due to the breaking down of the fibers at a high of collecting speed. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2236–2243, 2010

Key words: electrospinning; poly(phthalazinone ether sulfone ketone) (PPESK); orientation; morphology; tensile properties

INTRODUCTION

Since it was introduced in the early 1930s, the electrospinning technology has become one of the most important methods to product micrometer or nanometer fibers.[1,2] In a typical electrospinning process, polymer solution or melt is polarized in a high voltage electrostatic field. When the applied electric field strength overcomes the surface tension, a jet is ejected from the surface of the charged polymer solution or melt, then travels rapidly, undergoes various instabilities, and finally splits into micrometer or nanometer fibers.[1,3–5] The electrospun fabrics have small diameter, high porosity, and high specific surface area; therefore, they can be used in a wide variety of applications such as separators used in Li-ion battery, nano-sensor, scaffolds in tissue engineering, and drug delivery.[6–11] However, electrospun fabrics are often lacking the necessary mechanical properties because of their small fiber diameter and low fiber orientation,[1,12,13] which limits their further application in various areas. Thus, it is necessary to improve the mechanical properties of the electrospun fabrics.

Recently, several techniques have been explored for improving the mechanical properties of electrospun fabrics. Sang et al.[1] used thermal treatment to introduce interfibers bonding in the electrospun poly(ε-caprolactone) (PCL) fibers, and the tensile strength of PCL fibers was successfully increased by 78%, from 5.1 to 9.1 MPa. However, this approach will lead to a decrease of porosity and specific surface area by thermal treatment. Morcy et al. and Jeong et al.[14,15] added carbon nanotubes as reinforced filler into the polymer solutions to fabricate polymer fiber-carbon nanotube composites for improving mechanical properties of electrospun fibers. Researchers prove that adding CNTs of appropriate concentration into polymer solution will result in an increase of the strength of electrospun fibers. However, the separation of CNTs bundles and their dispersion are still critical issues with regard to the mechanical properties of polymer-CNTs composite nanofibers. The tensile strength of composite fibers often shows a decrease because of poor dispersion and interfacial contact of the CNTs. In other methods, Wong et al.[16] investigated the effect of fiber diameter on tensile properties of the single electrospun PCL fiber. They found that PCL fibers with the decreasing of fiber diameter exhibited

Correspondence to: P. Chen (chenping_898@126.com).
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an abrupt shift in tensile performance, due to the increasing of crystallinity and molecular orientation. Although this finding provides a good method for changing microstructure to increase the mechanical properties of the single electrospun fiber, the tensile performance of the whole fabrics is not only determined by the single fiber properties but also by the alignment of the fibers. Several researches have shown that high orientation level of the fibers leads to an increase of the tensile strength of fabrics.[12,17–19] However, in our study, we found that when the collecting velocity surpassed a threshold value, the tensile strength of fabrics was decreased even fiber orientation kept increasing. Therefore, the purpose of this article is to study the influences of collecting velocity on fiber orientation and tensile properties of electrospun fabrics.

Poly(phthalazinone ether sulfone ketone) (PPESK) is a novel kind of soluble thermoplastic resin with high glass-transition temperature (T_g: 263–305°C).[20–22] Because of its excellent thermal resistance properties, good mechanical performance, and chemical stability, PPESK has been successfully used to prepare hollow fiber composite nanofiltration membrane, hollow fiber ultrafiltration membrane, proton exchange membrane,[23–27] and as matrix for the fiber reinforced plastic composite.[28] In this study, PPESK fabrics were prepared by using the electrospinning technique, a series of different orientation fabrics were obtained by changing the rotation rates of the collecting drum. Fiber orientation, morphology and tensile properties of electrospun PPESK fabrics were investigated, and the influence of fiber orientation and morphology on tensile properties of electrospun PPESK fabrics were further discussed.

EXPERIMENTAL

Materials

Poly(phthalazinone ether sulfone ketone)(PPESK) resin was obtained from Dalian Polymer New Material Co., Dalian, China. The chemical structure of PPESK is shown in Figure 1.[20–22]

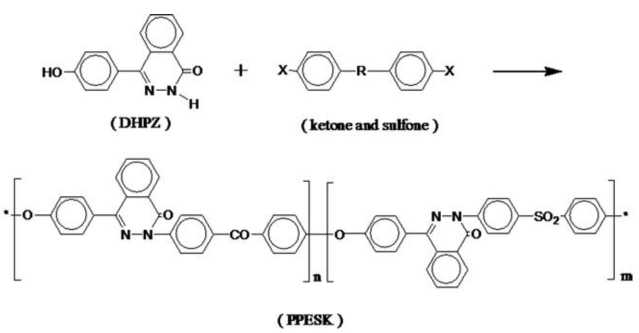

Figure 1 Chemical structure of poly (phthalazine ether sulfone ketone) (PPESK), here R is CO or SO2; X is F, Cl or Br.

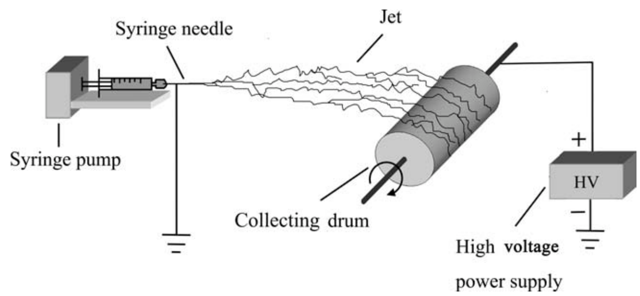

Figure 2 The schematic setup for elecrospinning.

N,N-Dimethylacetamide (DMAc) of AR. grade was purchased from Sinopharm Chemical Reagent. Co. Ltd. Shanghai, China and used as received without further purification.

Electrospinning process

The electrospining apparatus are composed of a syringe pump, a syringe needle, a metal collecting drum, and a high voltage power supply. The schematic setup for elecrospinning is shown in Figure 2. To obtain PPESK fabrics, PPESK/DMAc solution of 20 wt % was prepared by dissolving the polymer in DMAc and pumped from the syringe at a flow rate of 4.2 mL/h. The syringe needle with an inside diameter of 0.5 mm was grounded. The collecting drum located at a distance of about 10 cm from the syringe needle tip was connected to the high voltage power source. An appropriate voltage of 23 kV was supplied between the spinneret and the collecting drum. To achieve PPESK fabrics with different orientation, the collecting drum was rotated at the rates of 130 rpm, 560 rpm, 1210 rpm, and 2450 rpm (corresponding to the linear velocities of 0.36 m/s, 1.55 m/s, 3.35 m/s, and 6.79 m/s), respectively. To remove the remaining solvent, the electrospun PPESK fabrics were soaked in water bath for 0.5 h, and then dried in oven at 50°C for 2 h, 80°C for 2 h, 120°C for 2 h, 170°C for 2 h, finally dried in vacuum at 120°C for 2 h, 170°C for 2 h.

Scanning electron microscopy

Fiber morphology of the electrospun PPESK fabrics was characterized by scanning electron microscopy (SEM, Hitachi, S3400). Fiber diameter and degree of orientation (related to the direction of linear speed) were determined by analysis of SEM images manually. The degree of orientation was characterized by the angular standard deviation, σ, for a wrapped normal distribution as described in the literature[29]:

$$f(\theta) = \frac{1}{\pi}\left(1 + 2\sum_{p=1}^{\infty} \rho^{p^2} \cos(2p(\theta - \mu))\right) \qquad (1)$$

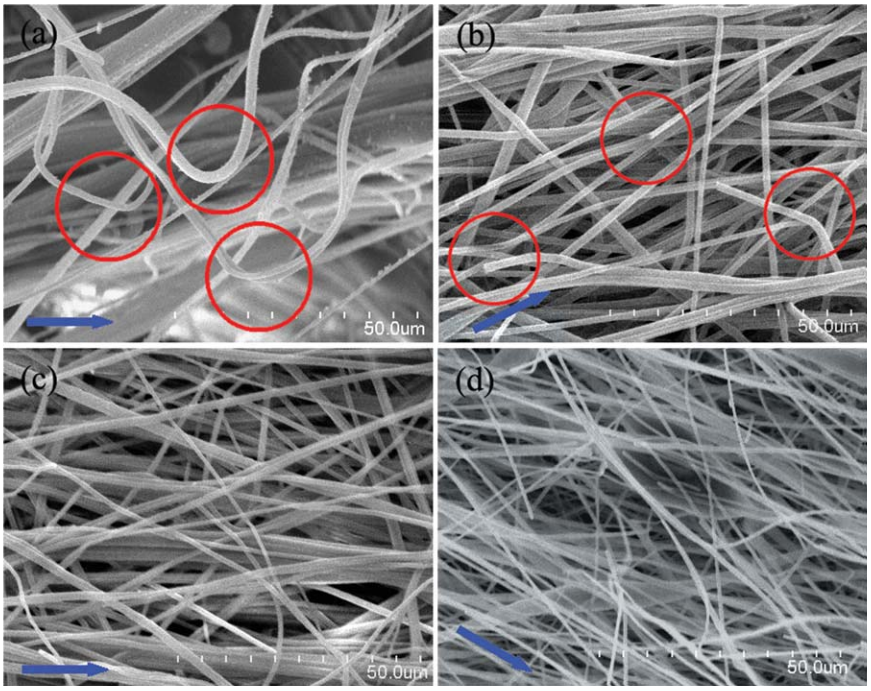

Figure 3 SEM images of electrospun PPESK fabrics collected at different linear velocities: (a) 0.36 m/s, (b) 1.55 m/s, (c) 3.35 m/s, and (d) 6.79 m/s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Where, ρ is the mean resultant length and μ is the mean angle. The both parameters were determined from a set of measured fiber orientation angles, θ_i, by the following equations:

$$\rho = \frac{1}{n}\sqrt{\left(\sum_{i=1}^{n}\cos 2\theta_i\right)^2 + \left(\sum_{i=1}^{n}\sin 2\theta_i\right)^2} \quad (2)$$

$$\mu = \tan^{-1}\left(\sum_{i=1}^{n}\sin 2\theta_i \Big/ \sum_{i=1}^{n}\cos 2\theta_i\right) \quad (3)$$

Here, fiber orientation angles, θ_i, can be defined as the angles formed between the fiber axis and the direction of the collecting linear velocity. n is the number of the measured fiber orientation angles. Finally, the angular standard deviation was calculated from the mean resultant length:

$$\sigma = \frac{1}{2}\sqrt{-2\ \ln\ \rho} \quad (4)$$

At least 40 fibers were examined for each sample to analyze fiber diameter and orientation.

Tensile testing

The tensile testing was performed on the electrospun PPESK fabrics in the collecting linear velocity direction using a testing machine of Digital force gauge (Model: HF-5, Yueqing Haibao Instrument Co., Ltd. Zhejiang, China). PPESK fabrics were cut into 15 mm × 2 mm and fixed onto a paper frame. The thicknesses of the specimens were measured by thickness meter (Chengdu Chengliang Tools Co., Chengdu, China). The both length sides of paper frame were cut off before testing. Testing machine pulled the specimens at a rate of 2 mm/min. The tensile strength of each specimen was averaged with at least 5 successful mansurements values.

RESULTS AND DISCUSSION

The effect of collecting velocities on the morphology and fiber orientation

Figure 3 shows a series of SEM images of electrospun PPESK fabrics prepared at different collecting velocities. Visual analysis of these images shows that with the increasing of collecting velocity, more and more fibers align along the direction of the collecting speed and fiber orientation is improved. At low collecting velocity [Fig. 3(a), the linear velocity of the collector is 0.36 m/s], nanofibers collect onto the drum randomly and most of them are curved. As the collecting velocity increases, more and more fibers are stretched straight. Representative SEM image [see Fig. 3(b)] shows that at the collecting velocity of 1.55 m/s, almost all the fibers are stretched straight, only a few fibers are bended with angles. Moreover, the increased take up speed results in fiber aligning along the direction of collecting speed. It is also observed

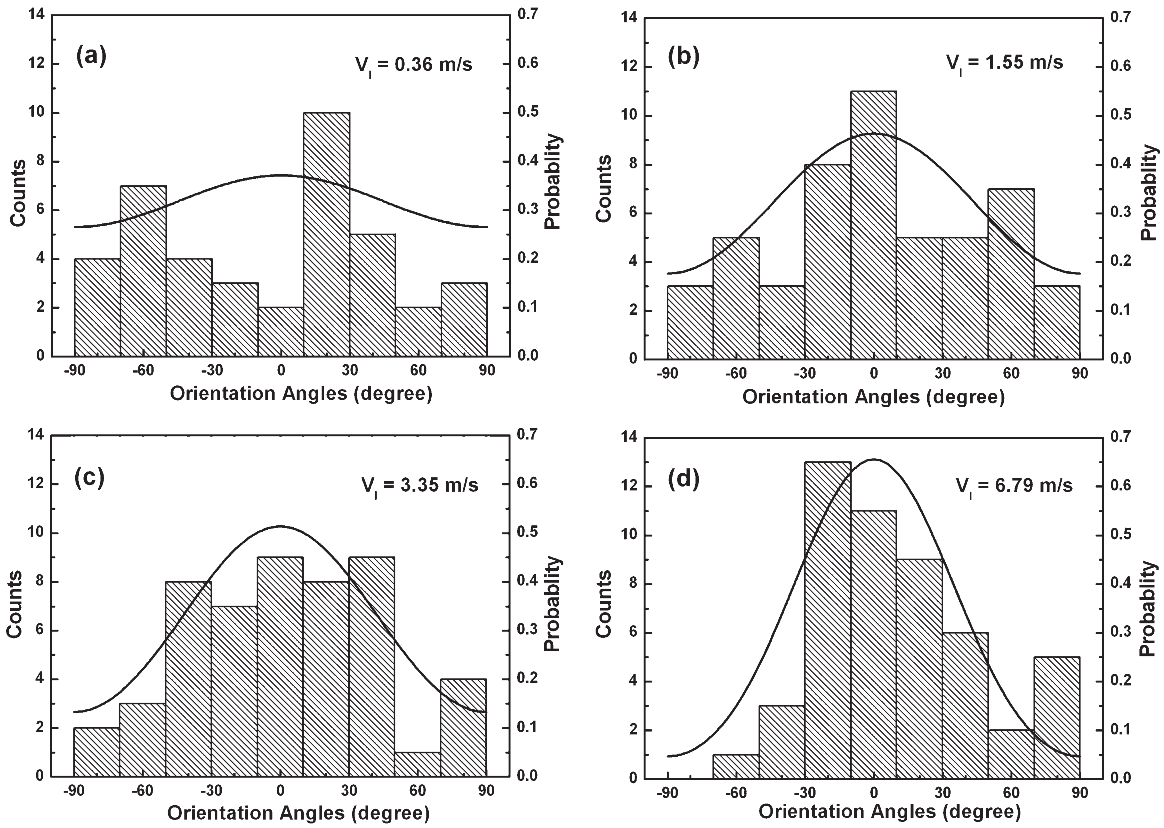

Figure 4 Normalized histograms of fiber orientation angles and wrapped normal distribution curves for different collecting velocities: (a) 0.36 m/s, (b) 1.55 m/s, (c) 3.35 m/s, and (d) 6.79 m/s.

from Figure 3(c,d) that all the fibers are straight instead of curved or bended. Fiber orientation is improved markedly at higher collecting speeds.

To study the influence of collecting velocity on fiber orientation, the normalized histograms of fiber orientation angles and wrapped normal distribution curves for different collecting velocities were characterized in Figure 4, by analysis of the SEM images (Fig. 3). The histograms show that fiber orientation angles distribution (bars) is in agreement with the wrapped normal distribution function (curve). The angular standard deviation was calculated to characterize fiber orientation degree according to eq. (4), and the results were listed in Table I. It is observed that as the linear speed increases from 0.36 to 6.79 m/s, the angular standard deviations of fibers are decreased from 63.8° to 34.8°. The increasing of collecting velocities improves fiber orientation.

These results indicate that fiber orientation of electrospun PPESK fabrics is influenced by the collecting velocities. During the electrospining process, the solution jet travels onto the collecting drum at a certain speed to form continuous fibers.[30] When the drum is rotated at a lower surface linear speed than the jet travels, the electospun fiber collects onto the drum, curved and unoriented, due to a variety of instabilities. However, if the drum is rotated at a higher surface linear speed than the jet travels, the trajectory of the continuous jet is affected by the rotation of the collecting drum. As the fiber collects onto the drum surface, it is electrostatically attached to the surface and travels at the same speed as the drum does. This can be used to stretch the following jet from its instable path to align along the rotation direction of the drum (the direction of collecting speed).[17] In another word, the increasing rotation rates of the drum results in a jet stretching effect on the solution jets. Moreover, as the rotation speed increases, the stretching effect is also improved, which leads to better alignment of the collected fibers and lower angular standard deviation due to the influenced jet trajectory by the stretching.

The effect of collecting velocities on electrospun PPESK fiber diameter

To further illustrate the jet stretching effect on the following solution jets, fiber diameter distributions of electrospun PPESK fabrics prepared in various different collecting velocities were analyzed. Figure 5 shows the PPESK fiber diameter distributions in different collecting velocities. The main distributions of fiber diameter were listed in Table I. It is observed that fiber diameter of electrospun PPESK fabrics is decreased, when the collecting drum is rotated fast enough. As the collecting linear velocities are 0.36 and 1.55 m/s, PPESK fiber

TABLE I
Fiber Diameter and Degree of Orientation in the Different Collecting Speeds

Linear speed (m/s)	Angular standard deviation (deg)	Fiber diameter (μm)
0.36	63.8	1.56 ± 0.04
1.55	49.5	1.57 ± 0.02
3.35	44.5	1.47 ± 0.04
6.79	34.8	1.14 ± 0.01

diameters are 1.56 and 1.57 μm, respectively. No remarkable change on fiber diameter is observed. However, with the further increasing of the collecting linear velocity, fiber diameter is decreased. When the collecting speed is increased to 6.79 m/s, fiber diameter is decreased to1.14 μm. The effective stretch to the following jets is improved with the increasing of the collecting velocities at higher speed, which leads to a formation of thinner fibers.

The effect of collection velocities and fiber orientation degree on tensile strength of electrospun PPESK fabrics

The tensile strength of electrospun PPESK fabrics was measured by a testing machine of force gauge, and at least five specimens were tested to obtain an average of tensile strength for each fabric with different orientation. Figure 6 shows the trend of tensile strength with the increasing of collecting velocity. It is observed that the tensile strength of PPESK fabrics is enhanced significantly as the collecting velocity increases. In particular, when the linear velocity increases from 0.36 to 3.35 m/s, the strength of PPESK fabrics is increased from 0.0246 to 3.677 MPa. In electrospinning process, as the collecting rotation rate increases, the effective stretch by the rotation can improve the fiber orientation. More fibers align along the direction of rotation, which contributes to enhancing the tensile properties of fabrics in the collecting direction. However, it is observed that when collecting velocity is higher than 3.35 m/s, the tensile strength of fabrics shows a declining tendency even fiber orientation keeps improving. As can be seen from the SEM image of electrospun PPESK fabrics (Fig. 7), a part of fibers have been broken down at the collecting velocity of 6.79 m/s. As the collecting rotation rate continues increasing, the jet stretching effect also improves. When the collecting drum is rotated at a much higher rotation rate, the following jets can not withstand the excess jet stretching effect, and broken down finally. This results in a

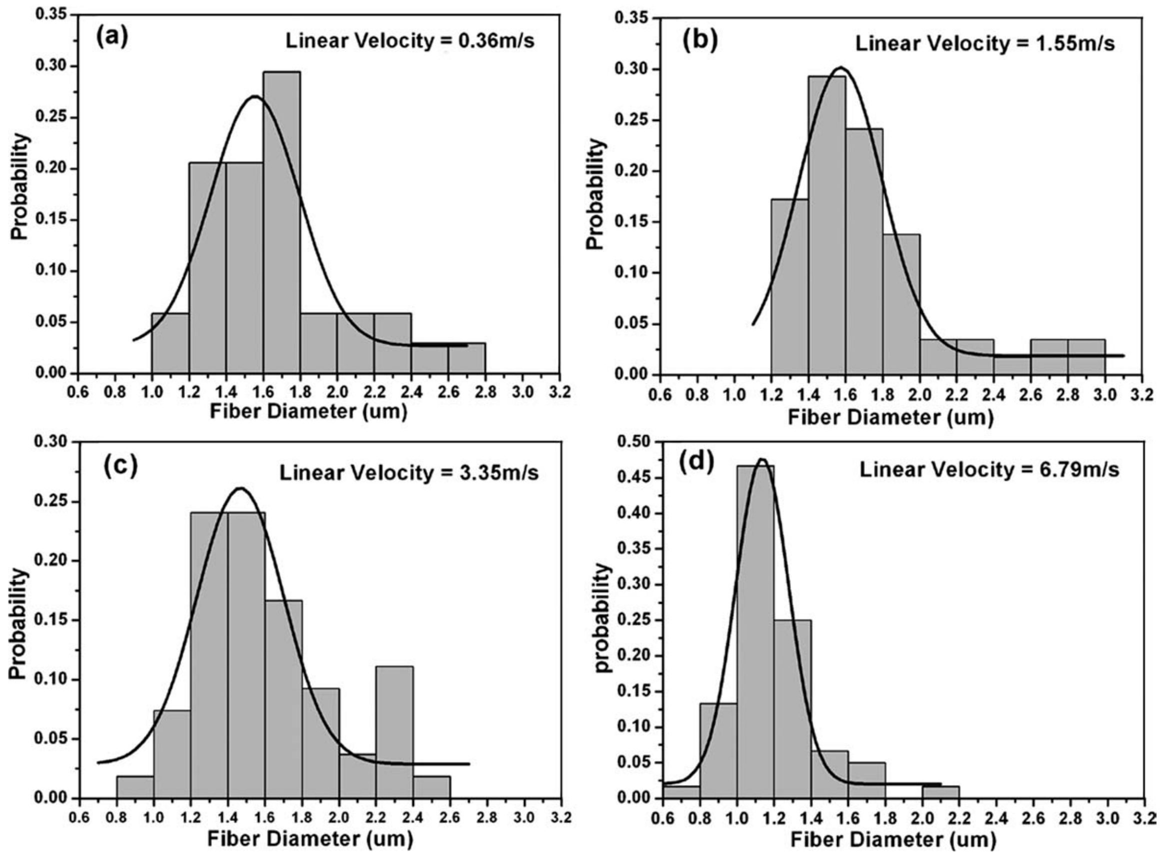

Figure 5 Fiber diameter distribution of electrospun PPESK fabrics collected at different linear velocities: (a) 0.36 m/s, (b) 1.55 m/s, (c) 3.35 m/s, and (d) 6.79 m/s.

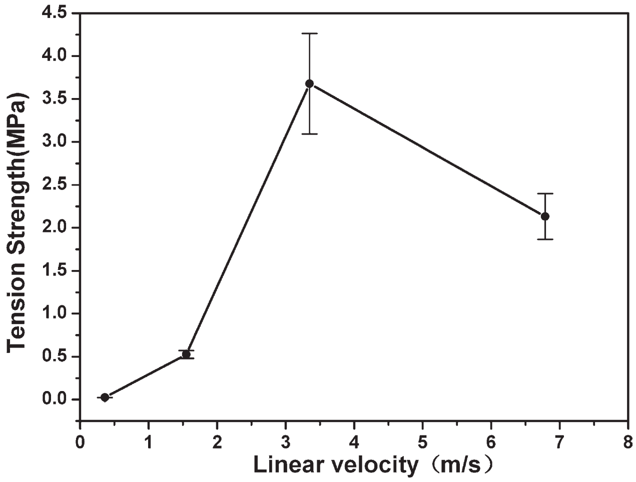

Figure 6 Tensile strength-Linear velocity curve for electrospun PPESK fabrics.

decrease of tensile properties of PPESK fabrics due to the break down of the fibers.

Mechanical behavior

Figure 8 shows the stress–strain curves of the electrospun PPESK fabrics prepared at various collecting velocities from 0.36 to 6.79 m/s. As the data show in

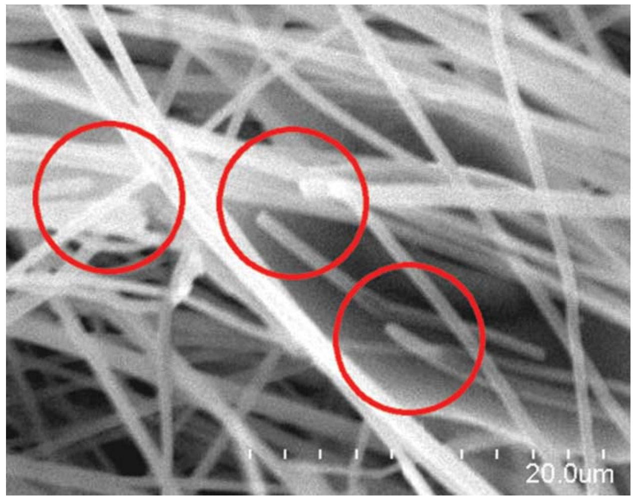

Figure 7 SEM images of electrospun PPESK fabrics collected at collecting linear velocities of 6.79 m/s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 8, the mechanical behavior of PPESK fabrics prepared at collecting velocity of 0.36 m/s is distinctly different from the others prepared at higher collecting velocities. Figure 8(a) (the linear velocity is 0.36 m/s) shows that the tensile stress increases with the increasing of the strain at the first stage,

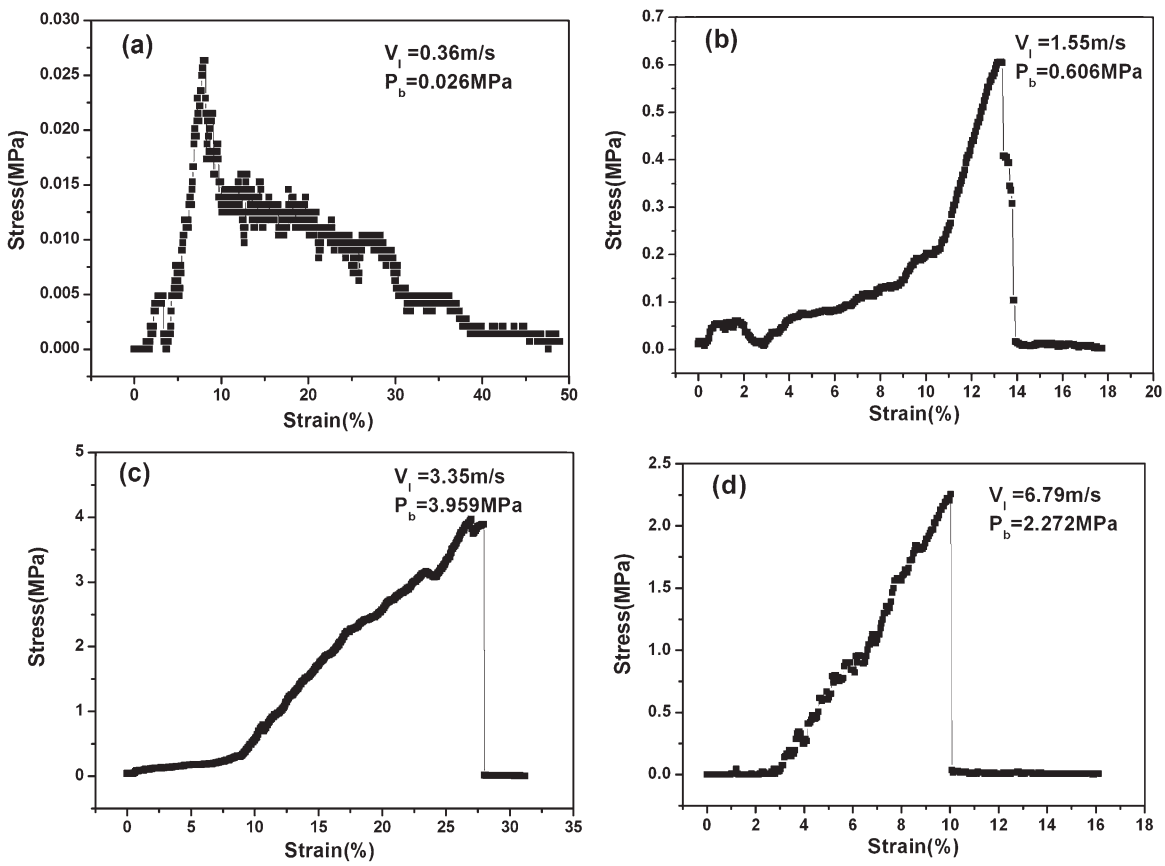

Figure 8 Stress–Strain curves of the specimens collected at different linear velocities: (a) 0.36 m/s, (b) 1.55 m/s, (c) 3.35 m/s, and (d) 6.79 m/s.

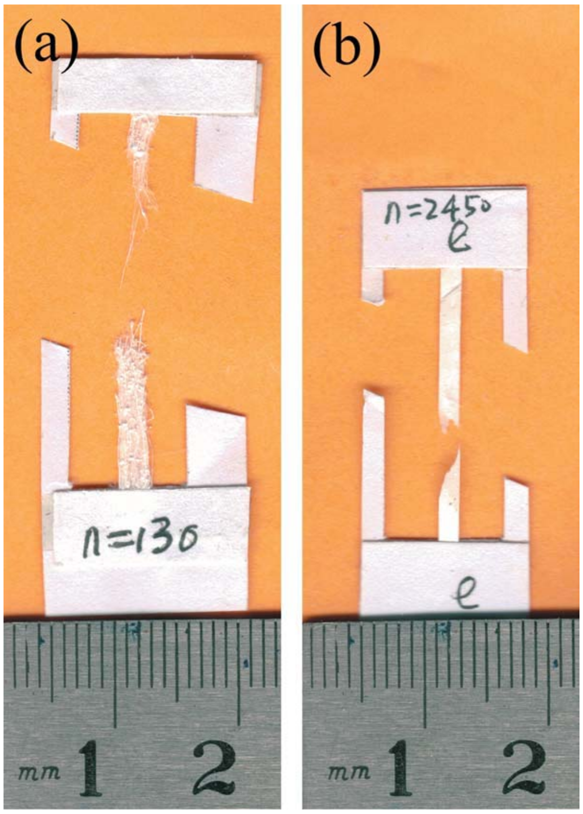

Figure 9 Fracture photographs of the specimens collected at different linear velocities: (a) 0.36 m/s, (b) 6.79 m/s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and then begins to decrease progressively after it reaches the maximum value of 0.026 MPa, finally decreases to the minimum value of 0 MPa with a large strain of 47.5%. Compared to the others, the tensile strength of the specimens is lower but with a great strain. The fabrics seem to be broken down step by step. However, the fabrics prepared at higher linear velocities display much higher tensile strength and smaller strain on their stress-strain curves [Fig. 8 (b–d)]. Even when the collecting velocity increases to 3.35 m/s, the tensile strength of PPESK fabrics increases to 3.959 MPa. Besides, it is also observed that after the stress reaches the top value, an abrupt decrease appears on the stress–strain curve, instead of progressively decreasing tendency at the collecting velocity of 0.36 m/s. Prepared at higher collecting velocities, the fibers of the fabrics seem to be broken down at the same time.

To further illustrate the mechanical behavior of PPESK fabrics in different collecting velocities, the two representative fracture photographs are shown in Figure 9. It can be seen from Figure 9(a), the specimen prepared at collecting velocity of 0.36 m/s, has a big strain after stretched, with the fibers broken irregularly. Some individual fibers are stretched very long. However, prepared at a high collecting velocity of 6.79 m/s, the specimen is broken down regularly, and the fibers are never stretched long any more [Fig. 9(b)]. These results confirm that fibers of electrospun PPESK fabrics prepared at low collecting velocity are destroyed step by step, whereas the ones prepared at a high collecting velocity are destroyed simultaneously, when they are stretched. At a low collecting velocity, most electrospun fibers are curved and distribute randomly in all direction due to the insufficient jets stretch effect. The aligned fibers only take up a small proportion. When stretched by the force gauge, the aligned fibers will be stretched first and broken down immediately. While, the most curving ones are stretched straight or oriented at first, and then ruptured. Thus, the stress–strain curve appears a low tensile strength and a slow decreasing tendency. However, when the collecting velocity is increased as fast as enough (faster than 1.55 m/s), induced by effective draw, most fibers are stretched straight and align along the direction of the collecting speed. When an external force is supplied to the specimens, almost all the fibers are broken down simultaneously, which contributes to enhancing the tensile properties of the fabrics. Therefore, the specimens prepared at higher linear velocities exhibited much higher tensile strength than those prepared at low collecting velocity did, and an abrupt decrease was observed on the stress–strain curves after the stress reached the top value.

CONCLUSIONS

In this study, it is demonstrated that the collecting speed has a strong influence on fiber orientation as well as fabrics mechanical performance. When the rotation of the collecting drum increases, electrospun fibers are stretched to align along the direction of take up speed because of the jet stretching effect, which improves fiber orientation. The tensile strength of the PPESK fabrics is enhanced by increasing the collecting velocity. When the collecting velocity is increased to 3.35 m/s, PPESK fabrics tensile strength is increased to the maximum value of 3.677 MPa. However, the tensile properties are decreased due to the breaking down of the fibers, when the collecting velocity is faster than 3.35 m/s. It is suggested that the appropriate increase of the collecting velocity contributes to improving the fabrics mechanical performance.

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