Studies on the Electrospun Submicron Fibers of SiS and Its Mechanical Properties

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ABSTRACT: The submicron fibers were prepared via electrospinning the styrene–isoprene–styrene (SIS) triblock copolymer from a pure solvent of tetrahydrofuran (THF) and a mixed solvent of THF and *N, N*-dimethylformamide (DMF). The addition of DMF to THF resulted in a beneficial effect on the fiber formation and the electrospinnability. The obtained results revealed that the fibers were only formed in a narrow solution concentration range of 8–15 wt %; the morphology, diameter, structure, and mechanical performance of as-spun fibers from PS and SIS solutions were affected by the composition weight ratio and the solution properties; and those from the solution at the intermediate concentration of 10 wt % exhibited a maximum tensile strength and strain at break. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1580–1586, 2009

Key words: elastomer; electrospun; submicron fibers; SIS; mechanical property

INTRODUCTION

Electrospinning is an efficient method for producing nanometer or submicron fibers from various polymers. The electrospinning research was first introduced by Formhals[1] in 1934, and has been extensively studied in recent years. Compared with conventional spinning techniques, electrospinning process can produce fibers with the diameters ranged from nanometer to submicrometer. The nonwoven mats of the as-spun fibers exhibit several interesting characteristics, for example, a very high ratio of surface area to mass and lots of small pores among fibers. Because of their high specific surface area and high porosity,[2] polymer nanofibres are attractive materials for a wide range of conventional and high technology applications, such as filtration media,[3] reinforcing fibers in composite materials,[4] tissue scaffolds,[5] wound dressing in medical materials,[6] electronic and optical devices, sensors, ion exchangers,[7] and so on. A large amount of materials have been electrospun into nanofibers. Research on electrospinning of elastomers has been found only in a few reports,[8–10] it was found that it was more difficult to prepare ultra fine fibers via electrospinning from elastic polymers than other polymers. Furthermore, there is no report about the electrospinning process of SIS elastomer in the open literature.

Triblock copolymer SIS is a kind of microphase-separated thermo-elastomer, which has received great attention in the recent years not only due to its rich morphological textures, but also due to its potential applications as compatibilizer in polymer blends, photosensitive material, packing belt, pressure adhesives, reinforcing fibers, and filtrating media in nanotechnology.[11,12] The crystallization of semi-crystalline block within a microphase-separated structure will form the nanocomposite materials with various morphologies, which might contribute to the improvement of mechanical, optical and other properties of these materials.[13] So, it is reasonable to expect that the ultra thin fibers of SIS by electrospinning will play a more important role in a variety of applications, especially in nanotechnology.

It is evident that different materials with varying mechanical properties result in different applications. Many polymeric nanometer or submicron fibers were applied in particular fields.[14] For example, elastomers such as polyurethanes,[15] collagen,[16] and poly(vinyl-alcohol) cryogel(PVA-c)[17] proposed for the soft layer were considered for application in hip, knee, and joint replacements. Recent studies have shown that polyurethane provides a lower coefficient of friction compared with standard

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polyethylene. Moreover, when polyurethane is replaced with water-swollen porous hydro-gels, the friction and impact effect is even more reduced. This indicates a high potential for this soft material in the articular surface. This can promote fluid film lubrication and lower the wear, thus lower implant failure. Moreover, elastic materials, having lower stresses at the implant-bone, thus result in lowering the risk of implant loosening. Thus, it is necessary to prepare fibers with different mechanical performances according to different needs.

In this article, nonwoven mats containing submicron fibers of SIS were electrospun by applying pure THF and mixtures of THF and DMF as solvent. The electrospinning solution with SIS mass concentration in a range of 8–15 wt % had been successfully electrospun into ultra fine fibers at room temperature. However, a lower or a higher concentration was difficult to produce fibers. Upon the scanning electron microscope (SEM), the influences of concentration and solvent system on the electrospinnability, the fiber morphology and the fiber diameters were analyzed. The mechanical properties were also investigated by using the tensile testing machine (Instron). The mechanical properties of the submicron fibers varied from the fibrous structures and the diameters.

EXPERIMENTAL

Materials

The triblock copolymer SIS used in this article was from Shell Chemical Co. (Kraton D1107), supplied in the form of rubbery pellets, containing 14% polystyrene in weight, with molecular weight (M_n) of 22×10^4; THF as a good solvent for SIS was purchased from Peking Chemical Co, China; DMF was provided by Tong Gong Chemical Co, China. The polymer and solvents were used without further purification.

Solution preparation and electrospinning

The experimental set-up is shown in Figure 1. A rotating motor was covered by a piece of aluminum foil, a syringe with a capillary tip was pushed by a propeller, and a DW-D303-2AC high power device was applied (Tianjin High Voltage Research, China). The range of the adjustable supply voltage was $0 \sim 100$ KV.

SIS was dissolved in the mixture of THF and DMF (100–20/0–80, v/v), and stirred at room temperature for 6 h until transparent solutions attained. Different solutions of 8, 10, 12 and 15 wt % were prepared in order to investigate the electrospinnability, the morphologies, and the mechanical properties of the resulting submicron fibers. Each solution was kept in a 10 mL syringe with a capillary tip whose inner diameter was 0.7 mm. The applied electrostatic field power and the tip-to-collector distance (TCD) were adjusted according to the solution concentration. During the electrospinning, all the non-woven mats from different solutions were collected by the aluminum foils, and dried at 100°C in a vacuum oven for two days.

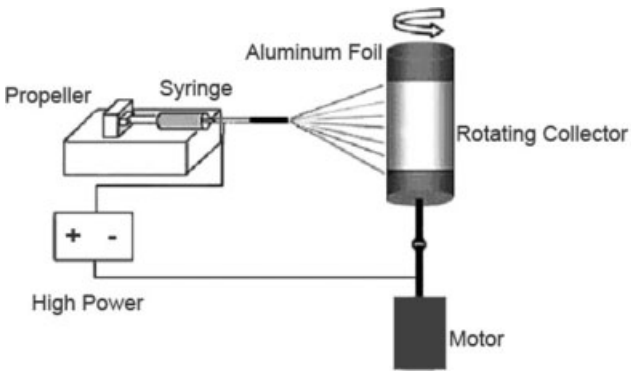

Figure 1 Schematic electrospun set-up.

Characterization

The viscosities of solutions were measured by a viscometer (NDJ-79, Instrument Co. Shanghai) at 25°C. The dielectric properties were measured with an electric conductivity meter (DDS-11A, Instrument Co. Shanghai) at 25°C. The surface tensions were tested by an optical contact angle meter (OCA-20, German) at 25°C. The morphologies and the thicknesses of the as-spun SIS fibers were observed under a JSM-6360LV (Japan) scanning electron microscope (SEM) at a voltage of 15 kV. Before SEM observation, the samples were sputter coated with gold under a KYKY.SBC-12 for 4 min. Based on these SEM images, the fiber diameters and the fiber thicknesses were analyzed through a kind of image visualization software. The mechanical properties were tested with a tensile tester (Instron, 1122, England) using a load cell of 10N at 25°C. A cross-head speed of 100 mm/min was used for the specimen testing. Prior to the testing, the specimens were cut into a planar dimension of width $\times$ length $=$ 5 mm $\times$ 10 mm (according to the report[18]). Five replicate specimens were tested for each sample.

RESULTS AND DISCUSSION

The effect of solvent on the diameter and the morphology of as-spun fibers

Figure 2 presents SEM images of SIS submicron fibers with different solvent systems (THF/DMF, v/v, 100–20/0–80) under the same processing

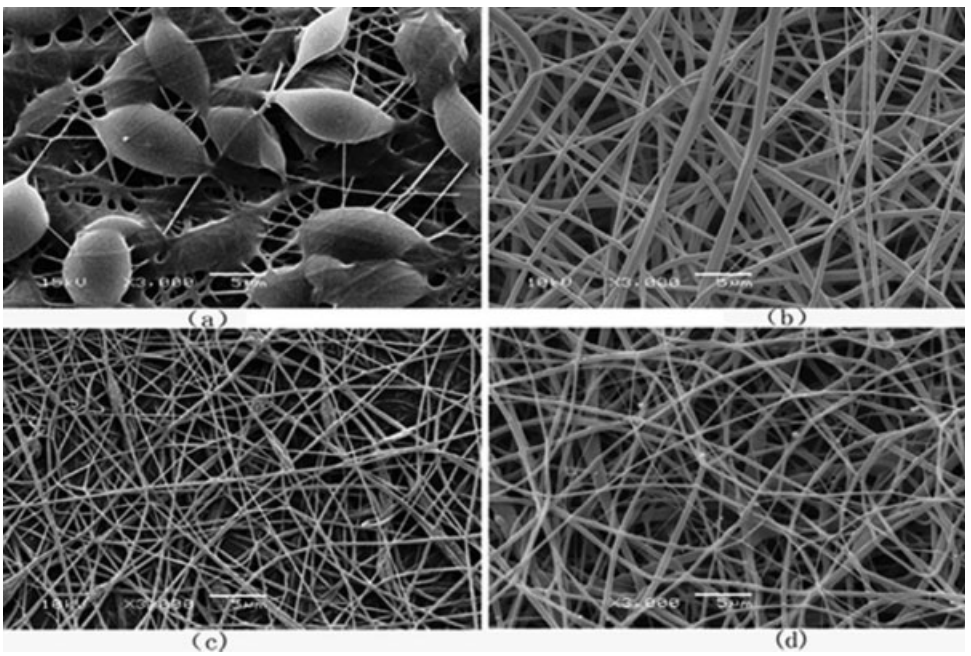

Figure 2 SEM micrographs of electrospun SIS fibers with 12 wt % concentration using different solvents. Solvents were (a) THF, (b) THF/DMF (80/20), (b) THF/DMF (50/50), and (d) THF/DMF (20/80).

conditions (concentration, 12 wt %; voltage, 18 KV; and TCD, 15 cm). It is observed that when using pure THF as a solvent, the nozzle was easily blocked and few as-spun fibers with many bead-thread structures could be attained as shown in Figure 2(a). The bead-thread structures of the as-spun fibers sharply decreased with increasing DMF amount as shown in Figure 2(b,c,d). Furthermore, when DMF and THF ratio reached 80/20, the bead-thread structures almost disappeared and more homogenous fibers formed as shown in Figure 2(b). As DMF and THF ratio arrived to 50/50, the spun fibrous diameters were finer than other fibers. Probably, this is due to the interactions of DMF and THF during the solvents evaporation change, which results in different morphological structures and diameters. From Figure 2, we found that the addition of DMF contributed to the bead-free fibers and more homogonous fibers. The findings were explained by some scholars[19–21] that bead-thread structures were because THF easily absorbed oxygen at the ambient condition, with low boiling point and low dielectric constant (36.71), and DMF could slow the evaporation speed of solvent in the solution. Therefore, it can be concluded that the fiber morphologies and diameters are related to the solvent systems.

During the experimental processing, we found that the solution viscosity, surface tension, and conductivity were influenced by the addition of DMF as shown in Table I. With increasing DMF content, the solution viscosity increased while the conductivity and the surface tension decreased, which resulted in the formation of more homogenous structures. Our findings were similar to previous reports[22,23] that in the electrospinning process of polymer solution, the choice of solvent used was one of the main contributors influencing the solution properties, e.g., viscosity, surface tension, and conductivity, which in turn, influenced the electrospinnability of solution and the distribution of diameter. Although much work has been undertaken to determine the relationship between morphologies and these factors, there was no conclusive evidence found for the effects of various parameters in electrospinning on fibrous morphologies.

In this article, when the volume ratios of DMF/THF were more than 80/20, they did not facilitate electrospinning fibers, because it was difficult to dissolve SIS in DMF at the room temperature. In summary, in this experiment, we found that solution properties, fiber diameters and fiber morphologies were affected by the addition of DMF.

TABLE I
The Properties of 12 wt % SIS Solution from Different Solvent Systems

Solvent system THF/DMF (%)	Viscosity (mPa/s)	Surface tension (dynes/cm)	Conductivity (μs/cm)
100	76	24.58	5.824
80/20	168	24.16	3.573
50/50	210	20.24	2.782
20/80	340	21.96	2.471

TABLE II
The Solution Properties from the Mixture Solvent of THF and DMF (80/20) by Varying Concentration

SIS mass concentration (wt%)	Viscosity (mPa/s)	Surface tension (dynes/cm)	Conductivity (μs/cm)
8	28	25.71	7.491
10	168	24.16	3.573
12	230	22.62	2.961
15	750	26.78	2.858

The effects of solution concentration

Many parameters affected the electrospinnability, morphology of as-spun fiber and diameters. The solution concentration or viscosity was considered one of the most influential variables to decide the fiber's morphology and average diameter among all processing parameters such as applied electric field strength and TCD. At the same time, some researchers[21,24] found the conductivity or the viscosity was as functions of concentration, that is, the conductivity slightly increased, and the viscosity obviously increased with increasing concentration. The similar tendency was observed in our work as shown in Table II. It was also found that the surface tension first dropped and then increased slightly with the solution concentration. Thus, it was thought that the surface tension was independent of the solution concentration. Fong et al.[19] reported that the formation of beads was not only related to the solution viscosity and the net charge density carried by the electrospinning jet but also to the surface tension. With decreasing surface tension, fibers without beads were made, so reduced surface tension could promote the formation of more homogenous fibers.

In the experimental process, we found that at the concentration below 8 wt %, the electrospinning process generated droplets due to the jet breaking up into droplets known as electrospray at a lower concentration. Electrospinning from the solutions with concentrations higher than 15 wt % was prohibited by the higher viscosity (750 mPa/s), which prevented the polymer solution from continuously flowing to the capillary tip. Obviously, a proper solution concentration is critical in the processing of cylindrical polymer nanofibers or submicron fibers by electrospinning. In this study, the suitable solution concentration is in the range of 8–15 wt %, corresponding to the viscosities range of 28–750 mPa/s and surface tensions range of 22.62–26.78 dynes/cm (Table II).

The images of morphology and diameter distribution of electrospun non-woven fibers at the THF/DMF volume ratio of 80/20 with SIS solution concentrations ranging from 8 to 15 wt % are shown in Figures 3 and 4, respectively. It was found that the

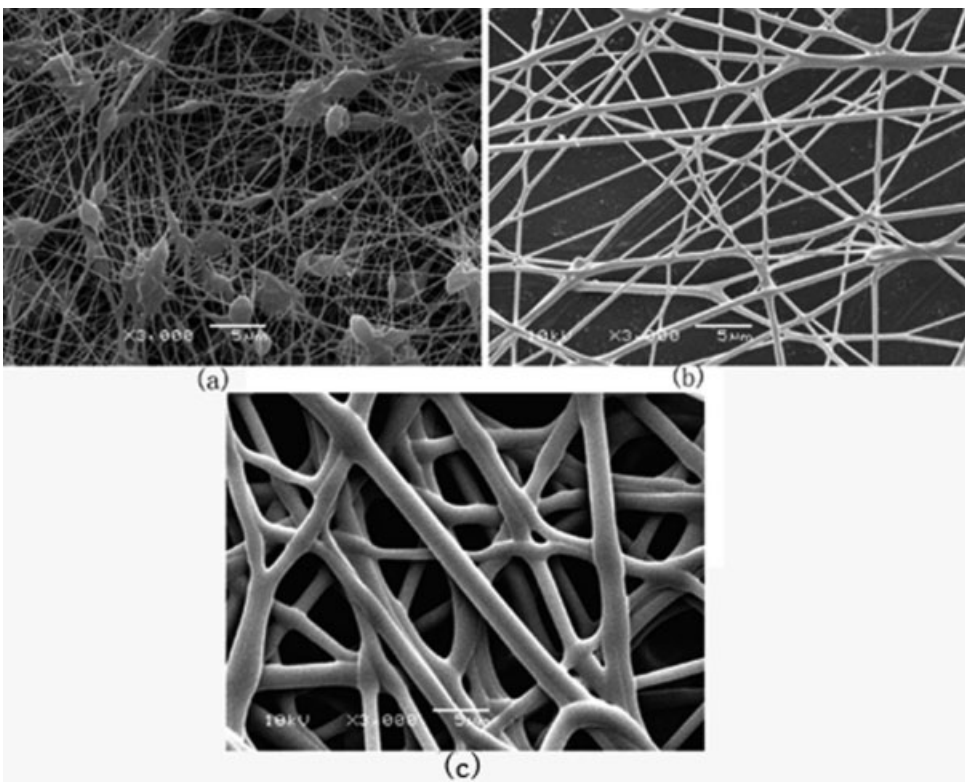

Figure 3 SEM micrographs of electrospun SIS fibers from different concentrations. Concentrations were (a) 8 wt %, (b) 10 wt %, and (c) 15 wt %.

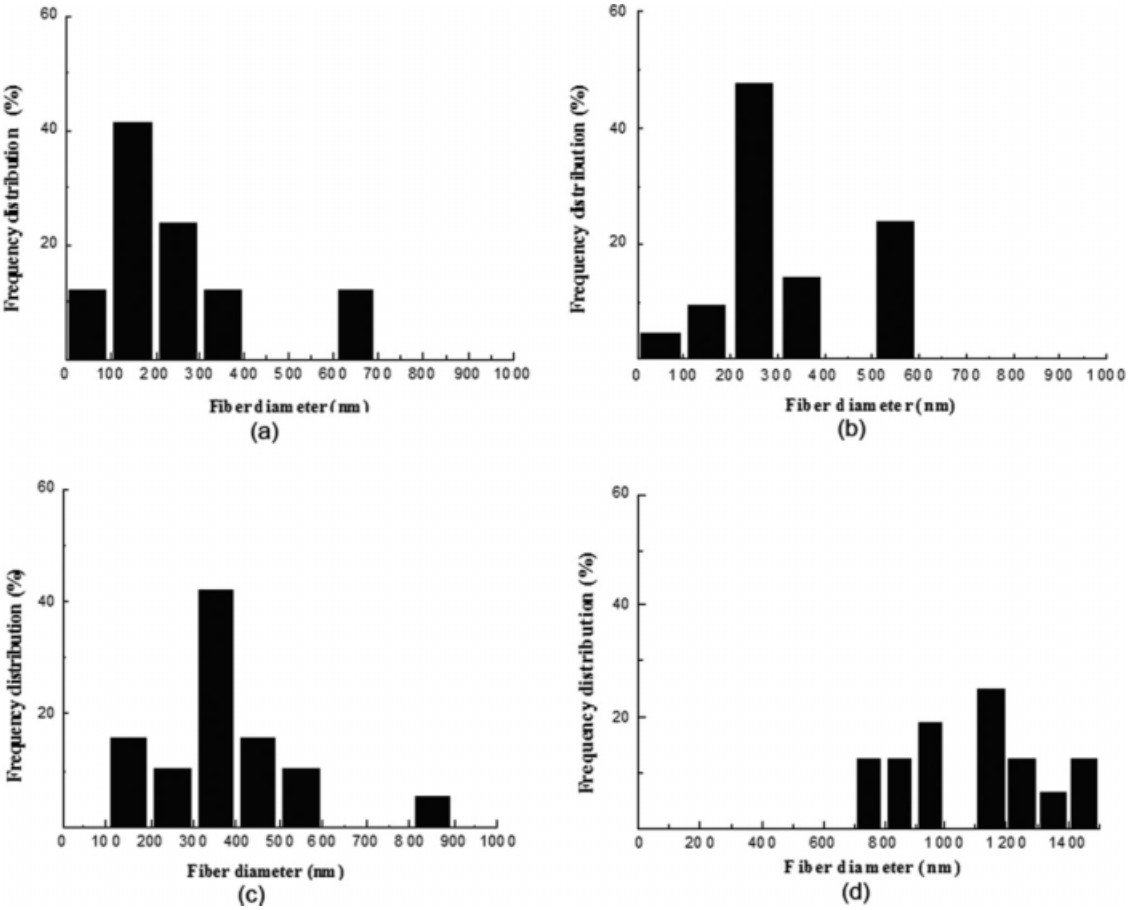

Figure 4 Diameter distribution images of electrospun SIS fibers from different solution concentrations. Solution concentrations were (a) 8 wt %, (b) 10 wt %, (c) 12 wt %, and (d) 15 wt %.

fibrous diameters and morphologies varied in terms of solution concentrations. At 8 wt %, the average diameter of fibers with many bead-thread structures was on the order of 100 nm as shown in Figure 3(a) and Figure 4(a). Mckee et al.[25] and other researchers[26,27] reported that the formation of nanofibers with beads corresponded to the minimum concentration required for electrospinning, and the uniform fibers were produced at 2–2.5 times Ce. Ce is the boundary between the semidilute unentangled and semidilute entangled regimes in the solution. With the concentration up to 10 wt %, the fibrous diameter was around 300 nm, and the bead-thread structures decreased [as shown in Figs. 3(b) and 4(b)]. At 12 wt %, the diameters were larger than that of the above fibers and the average diameter was around 350 nm [Figs. 2(b) and 4(c)]. The diameters of as-spun fibers from 15 wt % solution were the largest [Figs. 3(c) and 4(d)]. Moreover, in comparison with the diameter distribution of electrospun SIS fibers obtained from various solutions, some significant phenomena were shown: The diameter distribution was gradually broader with increasing solution concentration, and the average diameters of the fibers from 8 to 15 wt % solutions increased from 100 to 1200 nm. Therefore, it was concluded that with increasing solution concentration, the morphology changed from bead-thread fibers to uniform bead-

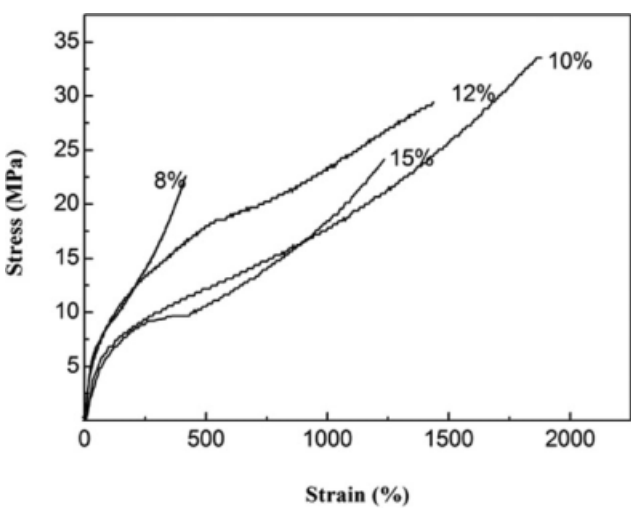

Figure 5 Strain-stress curves of the electrospun SIS submicron fiber mats from various solution concentrations.

TABLE III
Tensile Performances of the Submicron Fibers Electrospun from SIS Solutions with Different Concentrations

Mass concentration (wt %)	8	10	12	15
Averaged diameter of fibers (nm)	245	331	344	1197
Sample mass (g)	0.0118	0.0134	0.0148	0.0147
Thickness of mats (mm)	0.288	0.324	0.356	0.359
Stain at break (%)	412 ± 20	1711 ± 40	1446 ± 40	1240 ± 20
ultimate tensile strength (MPa)	22.4 ± 5	33.5 ± 3	29.5 ± 3	24.0 ± 5
Tensile modulus (MPa)	0.215 ± 0.01	0.010 ± 0.001	0.041 ± 0.01	0.043 ± 0.01

free fibers, the fiber diameters also increased from 100 to 1200 nm gradually, and the fiber distribution became gradually broader.

Mechanical performance of as-spun fibers

The tensile stress-strain curves of the electrospun SIS submicron fiber with SIS solutions from 8 to 15 wt % were shown in Figure 5, and the tensile modulus, the fibrous diameter, the thickness, the mass, the strain at break, and the ultimate tensile strength of as-spun fibrous mats with the respective concentration were summarized in Table III. From Table III and Figure 5, an interesting phenomenon could be seen that the optimal mechanical performance of the fiber mats did not correspond to that from the lowest or the highest concentration. However, the fiber mats obtained from the 10 wt % solution exhibited the greatest strain at break and the maximum ultimate tensile strength (strain at break with 1711%, ultimate tensile strength with 33.5 MPa). Further, the fibers from 12 wt % and 15 wt % solutions presented comparably lower and smaller mechanical performances and the fibers from 8 wt % had lowest mechanical properties (strain at break with 412%, ultimate tensile strength with 22.4 MPa). The similar findings were available in the literature by Huang et al.[12] They explained that this could be attributed to the fact that their 10 wt % solution provided the finest fibers compared with other solutions, and resulted in the tightest cohesion thereby. Although the 8 wt % solution resulted in an even smaller fiber diameters, at the same time it gave rise to too many beads on fibers than the 10 wt % solution did (as shown in Fig. 3). The beads on the fibers might considerably decrease the cohesive force between the fibers of the nonwoven mats, and hence a poorer mechanical performance of the fibers from 8 wt % solution was attained than that from 10 wt % solution. To further analysis this tissue, a considerable work has been done. It can be confirmed that fibers of 10 wt % solution with the maximum tensile strength and the greatest elongation ratio were not related to the mass and thickness of the fiber mats. The tensile testing performed indicates that the fibers have different mechanical properties which need further exploration to specifically meet design requirement; furthermore the information in this article could be used as a reference for nano-technological development.

CONCLUSIONS

Electrospinning of the triblock copolymer, SIS, was first investigated in this article. Although SIS could be well dissolved in THF, the as-spun fibers from pure THF had many bread-thread structures. The mixed solvent, THF/DMF (80–20/20–80, v/v), had been found to be suitable for producing fibers via electrospinning. The range of suitable solution concentration for electrospining was 8–15 wt %, and the fiber average diameters ranged from 100 to 1200 nm. Different solvent systems and solution properties resulted in different morphological structures and diameters. Mechanical characterization indicated that both the fiber diameters and the beads on the fiber surface influenced the mechanical performance of the electrospun submicron fibers. The nonwoven fibrous mats containing the finest and bead-free fibers from the 10 wt % solution exhibited the maximum ultimate tensile strength and strain at break.

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