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Mechanical Behaviors and Characterization of Electrospun Polysulfone/Polyurethane Blend Nonwovens

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Abstract: In the present study we investigated the relationship between the morphology and mechanical properties of electrospun polysulfone (PSF)/polyurethane (PU) blend nonwovens, by using the electrospinning process to prepare three types of electrospun nonwovens: PSF, PU and PSF/PU blends. The viscosity, conductivity and surface tension of the polymer solutions, were measured by rheometer, electrical conductivity meter and tensiometer, respectively. The electrospun PSF/PU blend nonwovens were characterized by scanning electron microscopy (SEM) and with a universal testing machine. The SEM results revealed that the electrospun PSF nonwoven had a structure consisting of cross-bonding between fibers, whereas the electrospun PU nonwoven showed a typical, point-bonding structure. In the electrospun PSF/PU blend nonwovens, the exact nature of the point-bonding structure depended on the PU contents. The mechanical properties of the electrospun PSF/PU blend nonwoven were affected by the structure or the morphology. With increasing PU content, the mechanical behaviors, such as Young's modulus, yield stress, tensile strength and strain, of the electrospun PSF/PU blend nonwovens were improved by up to 80%.

Keywords: polymer blends, electrospun nonwovens, mechanical behaviors.

Introduction

Polysulfone (PSF) fits well into the category of super engineering plastics, which are characterized by their excellent thermal properties, good resistance to inorganic acids and bases, and outstanding hydrolytic stability against hot water and steam sterilization. Therefore, PSF has been employed in a wide variety of applications, such as membranes (hemodialysis, gas separation, etc.), medical accessories (surgical trays, nebulizers, humidifiers, etc.), and plumbing (hot water fittings, manifolds, mixer tap cartridges, etc.).[1,2] In this study, polyurethane (PU) was blended with PSF to form a composite material. PU can be prepared with different properties, by controlling the relative content of the hard and soft segments in the main chains during the polymerization process. The hard segments of the PU, which have a relatively high transition temperature, have improved mechanical properties, whereas the soft segments of the PU have better elasticity. Also, PU has good blood compatibility, which causes it to be of considerable value in medical devices. As a result, the applications in which it is most used are closely related to its blood compatibility, such as artificial blood vessels.[3,4]

Recently, interest in electrospinning has been increasing rapidly, because the polymer fibers prepared by this technique have a sub-micron diameter.[5] In this technique, an electric field is induced by a high voltage power supply, which is then applied to a polymer solution or melt placed in a container that has a millimeter size nozzle, causing it to be ejected from the capillary tip of the nozzle in the form of a liquid jet. Electrospinning has the advantage of allowing for the simple processing and easy preparation of nanofi-

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bers, compared with previous spinning techniques.[6] Also, electrospun fibers have a high surface area and porosity, which causes them to be of considerable value in a variety of applications, such as membranes, filters, artificial blood vessels, reinforced composite materials, and drug delivery systems.[7,8] Especially, electrospun PSF nonwovens are suitable for use in hemodialysis membranes.[8,9]

On the other hand, electrospun nonwovens have low mechanical properties, due to the orientation within the fibers, because there is no drawing involved in their processing.[10,11] The research conducted so far on the electrospinning process can be classified into various categories, including studies of the processing parameters, the spinning conditions, the morphology of the electrospun fibers, and the instability zone between the capillary tip and the collector.[5-12] However, there have been few studies of the mechanical behaviors of the electrospun fibers themselves.[11,13,14]

The objective of this study is to investigate how the mechanical behavior is affected by changes in the morphology and structure of the electrospun PSF/PU blend nonwovens at various blending ratios.

Experimental

Materials. PSF (Mw: 65,000, BASF. Germany) and thermal plastic polyurethane (pellethane 2363-80AE, Dow Chemical Co., USA) were used to prepare the electrospun nonwovens composed of nanofibers. These materials were dissolved in *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF) purchased from Showa, Ltd. (Japan). Various polymer blend solutions were prepared with PSF/PU by the weight ratios of 100/0, 90/10, 85/15, 80/20, 20/80 and 0/100. All chemicals used in this study without further purification.[15]

Electrospinning Process. A variable high voltage power supply (CPS-60 K02v1, Chungpa EMT, Co., Korea) was used to provide the electric field. A rotating metal drum, which was capable of winding and transverse motion, and whose velocity could be controlled, was used to collect the fibers.

The polymer solution was drawn up into a 5 mL syringe with a capillary tip having an inner diameter of 0.6 mm. The syringe was inclined approximately 10° to the vertical so as to hang onto the end of the capillary tip from the ground. Copper wire connected to the positive electrode was inserted into the polymer solution. A metal drum wrapped in Al foil was connected to the negative electrode and the winding velocity was fixed at 64 rpm/min.

Preparation of Electrospun Nonwoven. From the preliminary experiment, it was found that the electrospun PSF fiber could be prepared using a solution concentration ranging from 10 to 24 wt%, and the electrospun PU fiber could be prepared using a solution concentration ranging from 6 to 16 wt%. Solution concentration of 18 wt% for PSF and 8 wt% for PU were found to be the optimal conditions for the production of the electrospun fibers, and these concentrations were selected to investigate the mechanical properties of the electrospun nonwovens. The electrospun PSF/PU blend nonwovens were prepared with PSF/PU by the weight ratios of 100/0, 90/10, 85/15, 80/20, 20/80 and 0/100. Then, each sample was dried at 25 °C for 1 week under a vacuum to remove the residual solvent.

Solution Properties. The solution viscosity, electrical conductivity and surface tension were measured at room temperature using a rheometer (DV III, Brookfield Co.) with spindle NO. 63 at 100 rpm, an electrical conductivity meter (G series, CM-40G, TOA Electronics Ltd., japan), and a tensiometer (K10ST, Kruss Co., Germany), respectively.

Morphology. The morphology of the electrospun PSF/PU blend nonwovens was investigated with a scanning electron microscopy (SEM, GSM-5900, JEOL, Japan). We used an image analyzer (Image-proplus, Media Cybernetics Co., USA) to measure the fiber diameter and distributions.

Mechanical Behavior. The mechanical behavior of each prepared nonwoven was investigated at room temperature with a universal testing machine (UTM, AG-5000G, Shimadzu Corp., Japan) under a crosshead speed of 10 mm/min. In accordance with ASTM D-638, samples were prepared in the form of a dumbbell-shape and, then, five specimens were tested as a function of PSF/PU blend composition by weight ratio. All the tests were conducted for five samples, and the average values were reported.

Results and Discussion

Solution Properties. Amongst the various processing parameters involved in electrospinning, the solution properties are known to be of paramount importance. The viscosity of the PSF solution increased with increasing solution concentration, because this increased concentration promoted the topological entanglement interactions of the chains. The surface tension was slightly affected by the solution concentration. The viscosity and surface tension of the PSF dissolved in the mixed solvent consisting of DMF and THF (80/20, v/v) are shown in Figure 1.

Also, the relationship between the viscosity and the electrical conductivity of the PSF dissolved in the mixed solvent are indicated in Figure 2. The values of these properties decreased with increasing THF content. The viscosity of the polymer solution was influenced by molecular interactions, either attractive or repulsive, and was therefore affected by changing to a different or mixed solvent.[10] The viscosity increased with increasing DMF content, due to the action of DMF in the polymer solution, being more attractive than THF. Also, DMF has a high dipole moment and dielectric constant compared with THF. In detail, the DMF's dipole moment and dielectric constant is well known at 3.8 and 37, respectively. For THF, they are at 1.6 and 7.58. Thus, the

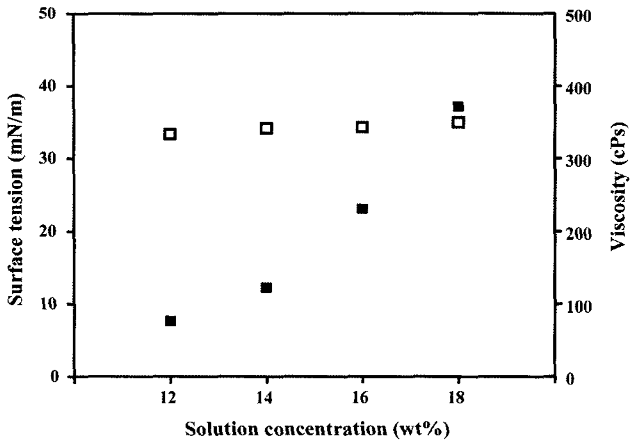

Figure 1. Surface tension and viscosity of polysulfone as a function of the solution concentration in a mixture of DMF/THF by 80/20 of volume ratio; □: surface tension, ■: viscosity.

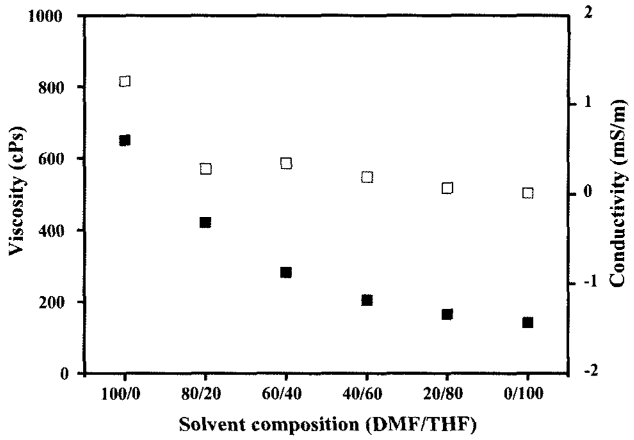

Figure 2. Viscosity and conductivity of polysulfone as a function of the solvent composition; ■: viscosity, □: conductivity.

electrical conductivity increased with increasing DMF content, because it becomes dissociated in solution to form negatively and positively charged particles.[10]

Morphology. The morphology of the electrospun nonwoven is related to many parameters.[5-12] Amongst these parameters, the solution concentration is the factor which has the most effect on the process of fiber formation and the resulting fiber diameter. Generally, electrospun fibers cannot be formed at low concentration, but the fiber formative ability and fiber diameter increase with increasing solution concentration.[16] At low concentration, micron size droplets formed which coalesced so as to constitute an electrospray, but as the solution concentration increased fibers began to be formed, as shown in Figure 3.

Also, the formation of beads was suppressed as the solution concentration increased. The fiber formative ability and its morphology were closely related to the solvent composition within the solution. Figure 4(a) represents the case where PSF was dissolved in DMF and shows many beads and poor fiber formation ability. This result was interpreted as being due to the fact the unvaporable solvent resulted in beads forming between the tip and the collector, because of its high boiling point at 153 °C, however, the amount of beads decreased when using a mixture of solvents (DMF and THF) (Figure 4(b)), and the electrospun PSF was prepared

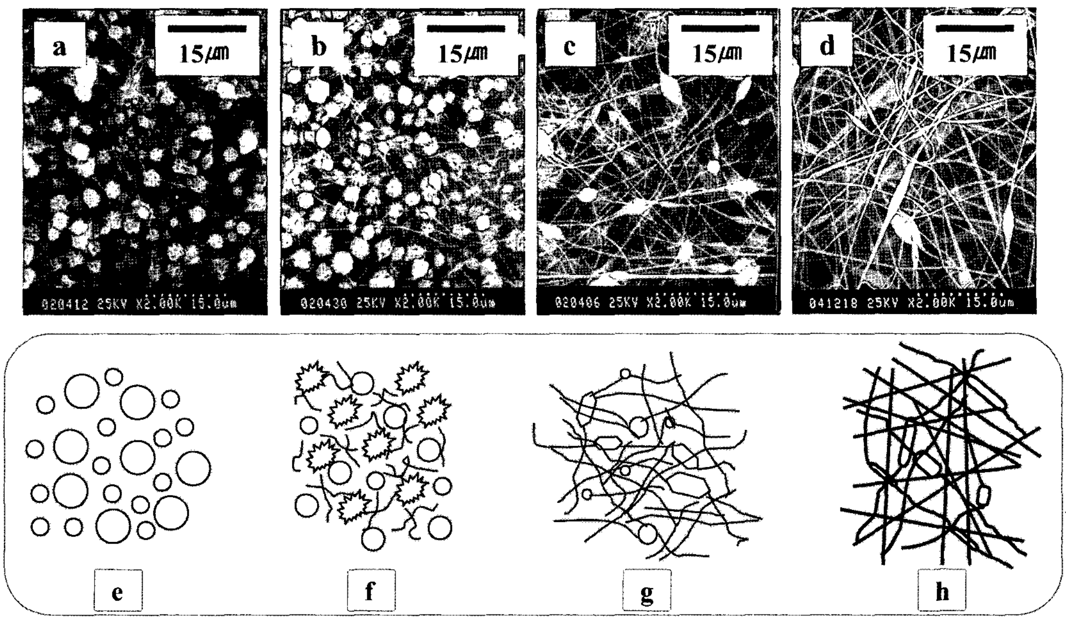

Figure 3. SEM images of polysulfone as a function of the solution concentration, along with a model of the morphology changes; (a) and (e) 12 wt%, (b) and (f) 14 wt%, (c) and (g) 16 wt%, (d) and (h) 18 wt%.

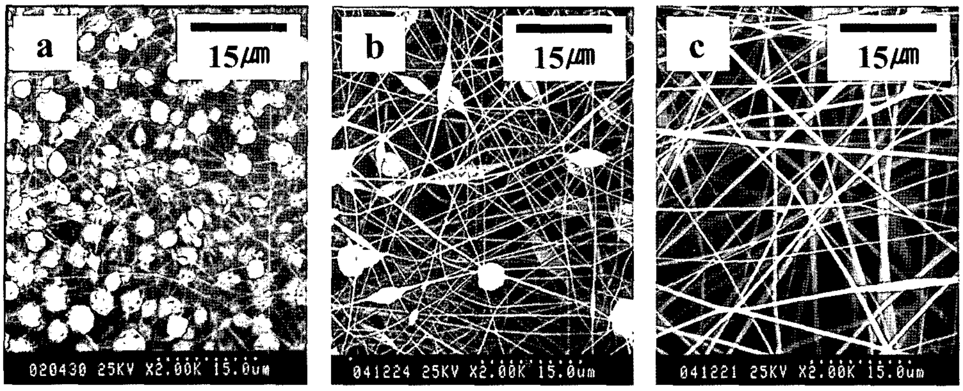

Figure 4. SEM images of polysulfone as a function of the solvent composition (DMF/THF, v/v); (a) 100/0, (b) 80/20, and (c) 50/50.

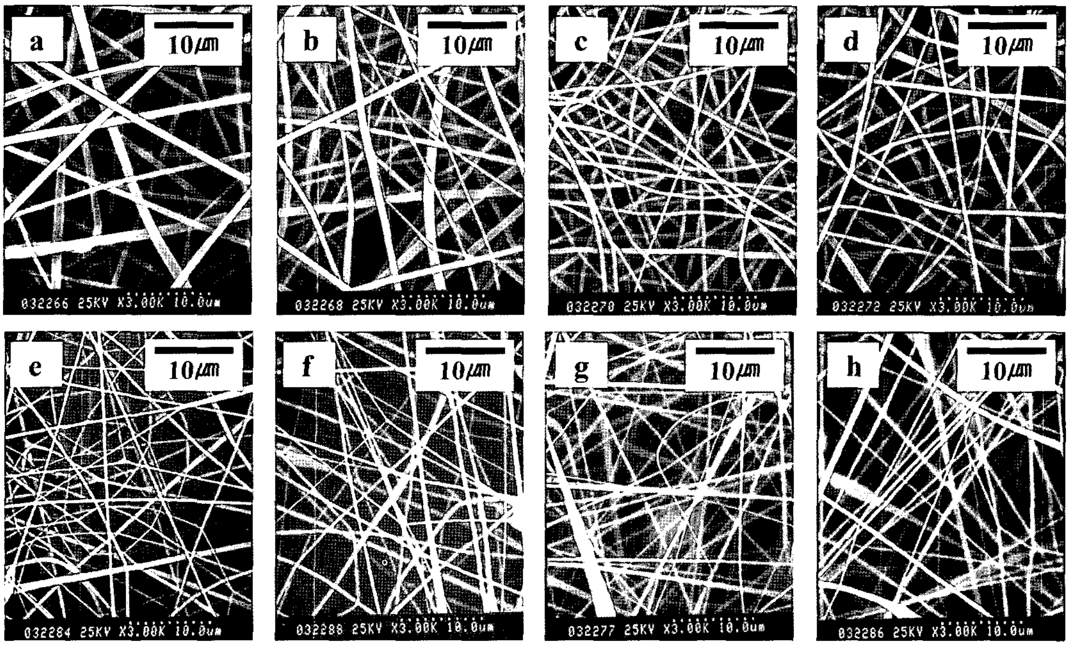

Figure 5. SEM images of polysulfone electrospun nonwovens as functions of the applied voltage and tip-to-collector distance; (a) 7 cm, (b) 10 cm, (c) 13 cm, (d) 16 cm under 18 wt% and 15 kV, (e) 7 kV, (f) 10 kV, (g) 15 kV, and (h) 18 kV under 14 wt% and 13 cm.

with sub-micron diameters, as shown in Figure 4(c) (DMF/THF: 50/50, v/v). In contrast, it was not easy to make the PSF electrospun with a THF content above 50%.

Figure 5 contains SEM images showing the change in fiber diameter as the voltage and tip-to-collector distance are varied. The average fiber diameter decreased as the tip-to-collector distance was increased from 7 cm (about 800 nm) to 16 cm (about 600 nm), however, the voltage also influenced the average fiber diameter (data not shown).

Figure 6 shows how the collecting area varied as a function of the voltage and the tip-to-collector distance, as viewed by a digital camera. The digital images show that the width of collecting area became larger at both an increasing voltage and longer tip-to collector distance. The reason for this is that electrical repulsion was brought actively under other constant parameters like a certain tip-to-collector distance, solution concentration. In other word, the jet stretches when the polymer solution was applied a voltages, forms the single jet, split. And stretching jet moves rapidly toward the collector. Small loops form near region of single jet. When they experienced the spiral motion, grew an advanced loop near the collector surface. The electric repulsion of fibers was strongly induced. Thus, electrically charged fibers were deposited widely on the surface of collector. These trends clearly appeared at higher applied voltages. The resulting of fibers obtained on the collector was observed that the width of deposited fibers increased with increasing the applied voltages. Thus, improved electrical repulsion leads to be

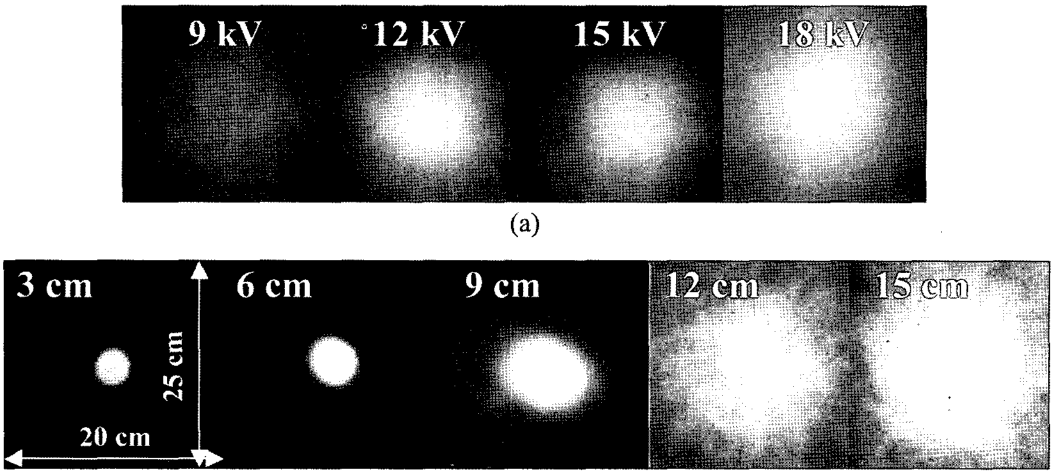

Figure 6. Photographs of deposition areas of polyurethane electrospun as functions of the applied voltage and tip-to-collector distance; (a) as a function of the applied voltage for 10 wt% and 12 cm and (b) as a function of the tip-to-collector distance for 10 wt% and 9 kV.

broadly areas of collecting fibers. In the effects of tip-to-collector distances, the increasing deposition areas of electrospun fibers grow bigger, because the pathway of fibers enlarged when the spinning distances increased. The smallness loop formed an enlarging loops consisting of fibers charged. The width of fibers collected reveals broad areas.

Mechanical Behavior. Generally, the physical and mechanical properties of the nonwovens were closely related to the geometric arrangement and fiber diameter, which are the most important component parts of the point-bonding structure.[17,18] However, the electrospun nonwovens have no a property of distinct bearing to take random and shape. Moreover, the fibers of an electrospun nonwoven form either a point-bonding structure (chemical bonding) or a cross structure (physical bonding). The morphology of each arrangement is reflected in the polymer's properties. From the results of our preliminary experiments, it was found that the electrospun PU nonwovens had a typical point-bonding structure, however, the electrospun PSF nonwovens had a cross bonding structure, as shown in Figure 7. Therefore, the structure of the electrospun nonwoven is related to its mechanical properties.

The electrospun PSF nonwoven was not suited to mechanical behaviors like cotton causing it to rise from the surface. Hence, the mechanical behaviors were measured as a function of the PU content with PSF being considered as the main matrix. It was found that the PSF/PU blend nonwovens had a point-bonding structure whose point-bonding area was increased in size compared to the pure PSF nonwovens (Figure 8). Also, beads formed in the electrospun nonwoven and the mechanical behaviors were closely related to the presence of these beads, which represented a significant defect at a low PU content.

Figure 9 shows the typical stress-strain curves as a function of the polymer blend ratio of PSF and PU. From the results, it can be seen that the yield point shows a maximum peak at

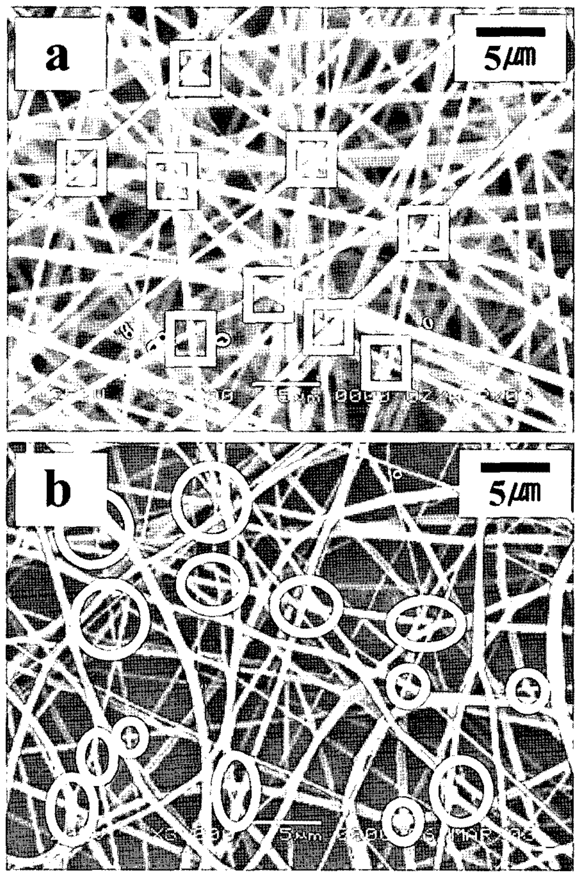

Figure 7. SEM images of cross and point-bonding structures; (a) polysulfone and (b) polyurethane. □: cross structure, ○: point-bonding structure.

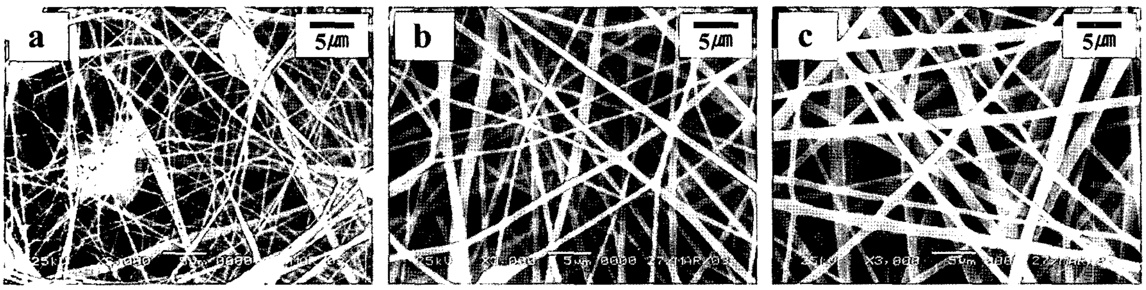

Figure 8. SEM images of polyblend electrospun nonwovens as a function of the blending composition (PSF/PU, w/w); (a) 90/10, (b) 85/15, and (c) 80/20.

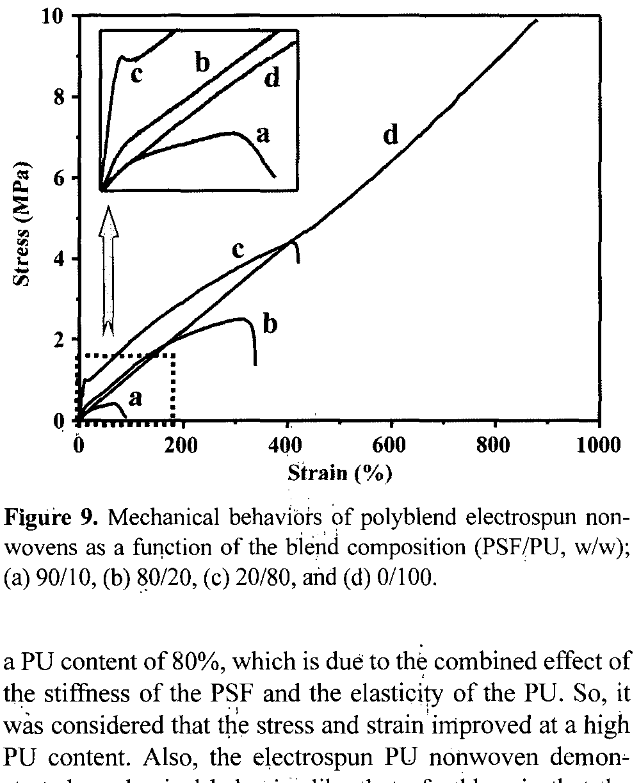

Figure 9. Mechanical behaviors of polyblend electrospun nonwovens as a function of the blend composition (PSF/PU, w/w); (a) 90/10, (b) 80/20, (c) 20/80, and (d) 0/100.

a PU content of 80%, which is due to the combined effect of the stiffness of the PSF and the elasticity of the PU. So, it was considered that the stress and strain improved at a high PU content. Also, the electrospun PU nonwoven demonstrated mechanical behavior like that of rubber, in that the stress-strain curves showed linear elasticity as their intrinsic material property, as shown in Table I. Finally, the addition of PU leaded to be the point -bonding structures in PSF/PU blend nonwovens, which acted as a load-bearing effect applied some forces.

Conclusions

We prepared electrospun PSF/PU blend nonwovens with various PSF/PU ratios and for which the fibers had submicron diameters. The amount of beads decreased, but the fiber diameters increased with increasing PU content. When using a mixed solvents (DMF and THF), the morphology of the electrospun PSF/PU blend nonwovens changed, resulting in the formation of fibers rather than beads at a high THF content, and these fibers had an increasingly smooth surface. The mechanical properties of the electrospun PSF/PU blend nonwovens included improved stress-strain values, due to the point-bonding structure that increased with increasing PU content. Consequently, in this study, we clearly established that the mechanical behaviors of the electrospun blend nonwovens were closely related to the PU characteristics. With increasing the PU fraction in PSF/PU blend nonwovens, the point-bonding structure revealed, which led to the load-bearing effect under applying load. Thus, mechanical properties depended on the morphological structure of PSF/PU blend nonwovens.

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Table I. Mechanical Properties of Polyblends Electrospun as a Function of Blending Composition (PSF/PU, w/w) and All the Tests were Conducted for Five Samples, and the Averaged-Valued were Reported; (a) 90/10, (b) 80/20, (c) 20/80, and (d) 0/100

	Young's Modulus (MPa)		Yield Stress (MPa)		Tensile Strength (MPa)		Strain (%)	
	Avg.[a]	SD[b]	Avg.[a]	SD[b]	Avg.[a]	SD[b]	Avg.[a]	SD[b]
(a)	1.4	0.12	0.2	0.01	0.4	0.01	70	1.02
(b)	3.1	0.05	0.4	0.02	2.5	0.03	320	8.39
(c)	1.5	0.04	0.4	0.01	4.4	0.02	410	4.75
(d)	1.2	0.1	-	-	9.9	0.07	880	6.40

[a]Avg.: Average of five samples. [b]SD: Standard deviation.

References

(1) D. Wang, W. K. Te, and K. Li, *J. Membr. Sci.*, **204**, 247 (2002).
(2) J. E. Yoo, J. H. Kim, Y. Kim, and C. K. Kim, *J. Membr. Sci.*, **216**, 95 (2003).
(3) J. E. Gray, P. R. Norton, R. Alouno, C. L. Marolda, M. A. Valvano, and K. Griffiths, *Biomaterials*, **24**, 2759 (2003).
(4) Y. A. Demchenko, M. Stadenovsky, Z. Sedlakova, I. Sloufova, J. Baldrian, and M. Ilavsky, *Eur. Polym. J.*, **39**, 437 (2003).
(5) G. I. Taylor, *Proc. R. Soc. London A.*, **280**, 383 (1964).
(6) M. S. Khil, H. Y. Kim, Y. S. Kang, H. J. Bang, D. R. Lee, and J. K. Doo, *Macromol. Res.*, **13**, 62 (2005).
(7) N. Bhattarai, D. I. Cha, S. R. Bhattarai, M. S. Khil, and H. Y. Kim, *J. Polym. Sci.; Part B: Polym. Phys.*, **41**, 1955 (2003).
(8) P. Gibson, H. Schreuder-Gibson, and D. Rivin, *Colloid Surfaces A*, **187**, 469 (2001).
(9) Y. J. Ryu, H. Y. Kim, K. H. Lee, H. C. Park, and D. R. Lee, *Eur. Polym. J.*, **39**, 1883 (2003).
(10) K. H. Lee, H. Y. Kim, Y. M. La, D. R. Lee, and N. H. Sung, *J. Polym. Sci.; Part B: Polym. Phys.*, **40**, 2259 (2002).
(11) K. H. Lee, H. Y. Kim, H. J. Bang, Y. H. Jung, and S. G. Lee, *Polymer*, **44**, 4029 (2003).
(12) M. S. Khil, D. I. Cha, H. Y. Kim, I. S. Kim, and N. Bhattarai, *J. Biomed. Mater. Res. Part B: Appl. Biomater.*, **67**, 675, (2003).
(13) K. H. Lee, H. Y. Kim, M. S. Khil, Y. M. Ra, and D. R. Lee, *Polymer*, **44**, 1287 (2003).
(14) D. I. Cha, H. Y. Kim, K. H. Lee, Y. C. Jung, J. W. Cho, and B. C. Chun, *J. Appl. Polym. Sci.*, **96**, 460 (2005).
(15) A. C. Pierre, *Introduction to Sol-Gel Processing*, Kluwer Academic Publisher, Boston, 1998.
(16) H. Fong, I. Chun, and D. H. Reneker, *Polymer*, **40**, 4585 (1999).
(17) A. F. Turbak, *Nonwovens: Theory, Process, Performance, and Testing*, Tappi Press, Atlanta, 1993.
(18) K. Lee, B. Lee, C. Kim, H. Kim, K. Kim, and H. Kim, *Macromol. Res.*, **12**, 441 (2005).