

Characterization of PVOH Nonwoven Mats Prepared from Surfactant-Polymer System via Electrospinning

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Received May 18, 2005; Revised August 11, 2005

Abstract: The electrospinning process is a fascinating method to fabricate small nanosized fibers of diameter several hundred nanometers. Surfactant-polymer solutions were prepared by adding poly(vinyl alcohol) (PVOH) to distilled water with cationic, anionic, amphoteric, and non-ionic surfactants. Average diameter of the electrospun PVOH fibers prepared from PVOH solution was over 300 nm, and was decreased to 150 nm for the mixture of PVOH/amphoteric surfactant. To explain the formation of ultrafine fiber, the characteristic properties in a mixture of PVOH/surfactant such as surface tension, viscosity, and conductivity were determined. In this paper, the effect of interactions between polymers with different classes of surfactants on the morphological and mechanical properties of electrospun PVOH nonwoven mats was broadly investigated.

Keywords: surfactant-polymer system, electrospinning, morphology, point-bonded structure, interaction.

Introduction

Poly(vinyl alcohol) (PVOH) has been available since about 1924. Today, much of the PVOH produced is used in a variety of industry areas, including chemical engineering, pharmaceuticals, textiles, medical devices, and food additives.^{1,2} Although the physical properties of PVOH vary with the degree of crystallinity that is heavily dependent on the degree of hydrolysis and the average molecular weight of the polymer, PVOH is well known as a semi-crystalline hydrophilic polymer with excellent properties³ such as the strength, water solubility, gas permeability, and thermal characteristics. Especially, PVOH has been widely used as synthetic fiber because of its good mechanical properties. It has been produced in a form of staple, monofilament, and multi-filament by traditional methods such as melt, dry, and wet spinning. Fiber diameter produced by these methods ranges from 10 to 300 μm .

In recent years electrospinning is receiving alluring attention as a useful method to prepare fibers ranging from 50 to 500 nm in diameter. The electrospinning process was first studied by Zeleny⁴ in 1914 and patented by Formhals⁵ in 1934. Taylor established the equilibrium shape of suspended meniscus at a critical voltage in 1964.⁶ It is well

established in many literatures⁷⁻⁹ that the morphological properties of the electrospun fibers strongly depend on the processing parameters such as solution conditions (viscosity, surface tension, and electric conductivity), tip-to-collector distance, and applied electric field strength.

A surfactant usually contains both hydrophobic and hydrophilic part within a molecule^{10,11} and acts as surface active agent that can greatly influence on the chemical properties at the interface. The driven force for a surfactant to adsorb at an interface is to lower the free energy of that phase boundary.^{12,13} Therefore, when that boundary is covered with surfactant molecules, the surface tension is reduced. The primary classification of surfactants is made on the basis of the charge of the polar head group. Traditionally, there are four types: anionic surfactant; cationic surfactant; amphoteric surfactant with polarity (negative and the positive charge); and non-ionic surfactant with no electrical net charge.¹⁴

The objectives of this study are to prepare ultra-fine nanofibrous mats from PVOH-surfactant solutions via electrospinning, to measure the mechanical properties, and to observe the morphological change of the resulting mats. In order to elucidate the reason that the formation of ultra-fine fibers in the presence of surfactant was favored, solution properties of polymer-surfactant systems were systematically characterized.

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Experimental

Materials. The PVOH with a molecular weight (M_w) of 65,000 was purchased from Dong Yang Chemical Co. (South Korea). Cationic (stearyl trimethyl ammonium chloride) and anionic (dodecyl benzene sulfonate ammonium salt) surfactants were obtained from KCI Ltd. (South Korea). Non-ionic (nonyl phenol) surfactant was obtained from Hannong Chemical Co. (South Korea). Amphoteric surfactant (lauryl betaine) supplied from IC Chemical Co. (South Korea) was used as received. The characteristics of four kinds of surfactant are shown in Table I.

Preparation of Polymer Solution. A 10% (w/v) PVOH solution was prepared by distilled water (DW) and gently stirred at 80°C until complete dissolution of polymer occurred. Then, each surfactant was incorporated into the PVOH solution. The ratio of the PVOH solution/surfactant was 100/0, 99.9/0.1, 99.5/0.5, and 99/1% (v/v), respectively. The PVOH solutions prepared were stirred for 1 h at room temperature and then used for electrospinning.

Electrospinning Setup. The apparatus used in the electrospinning process is as follows: high voltage power supply (CPS-60 k02v1, Chungpa EMT, Co., Korea) was used to supply voltage in a range of 0-50 kV. A 5 mL syringe used in these experiments had a capillary tip diameter of 1 mm, and the syringe was tilted approximately at 5° from the horizontal. The anode was directly inserted into the polymer solution in the syringe. The cathode was connected to the collector. The electrospinning conditions of voltage and tip to collector distance (TCD) were fixed at 15 kV and 12 cm, respectively. The electrospun PVOH mats were separated from the collector and dried under vacuum for 24 h at room temperature.

Characterization. The surface tension of polymer solution was measured by the Wilhelmy ring method using a tension meter (K100, Krüss Co., Germany) at 25°C. The platinum ring was cleaned with a butane torch. The viscosity of polymer solution was measured by a digital viscometer (Model DV III, Brookfield Co., USA) with spindle No. 62 at 100 rpm at room temperature. Electric conductivity of polymer solution was also analyzed by an electric conduc-

tivity meter (G series, CM-40G, TOA Electronics Ltd., Japan) at room temperature.

The morphology of the resulting mats was examined with a scanning electron microscopy (SEM, GSM-5900, Jeol Co., Japan) after gold sputtering. The average diameter and the diameter distribution were obtained from an image analyzer (Image-proplus, Media Cybernetics Co., USA).

The mechanical properties of electrospun PVOH/surfactant nonwoven mats were measured by a universal testing machine (UTM, AG-5000G, Shimadzu Corp., Japan). The extension rate of the cross head is 10 mm/min. All samples were measured in the form of dumbbell-shaped model according to ASTM D638.

Results and Discussion

Polymer Solution Characterization. The electrospinning technique is regarded as an important process for applying natural and synthetic materials in various areas.^{7,15-17} It is well known that various parameters such as solution concentration, ionic salts content, and applied electric field strength, affect on the mechanical and morphological properties of electrospun mats.^{7,8} Figure 1 shows dynamic surface tension (mN/m) of PVOH solution with 0.1, 0.5, and 1.0% (v/v) of surfactant content, respectively, for each surfactant (anionic, cationic, amphoteric, and non-ionic surfactant) at room temperature. The surface tension of PVOH solution alone was about 44 mN/m. The surface tension in a mixture of PVOH and anionic surfactant as a function of surfactant content decreased from 40.5 to 36.5 mN/m, but that in a mixture of PVOH and cationic surfactant was not significant with increasing of surfactant content. Although cationic surfactant is more added to that solution, this implies that surface activity of the surfactant remains constant. This surface behavior is regarded as an evidence for the polymer-

Table I. General Characteristics of Surfactants Used in This Study

Samples	Charge	Appearance	Electric Conductivity
Stearyl Trimethyl Ammonium Chlorid	Cationic	Paste	-
Dodecyl Benzene Sulfonate Ammonium	Anionic	Liquid	2.29 S/m
Lauryl Betaine	Amphoteric	Liquid	4.81 S/m
Nonyl Phenol	Non-ionic	Liquid	1.1×10^{-4} S/m

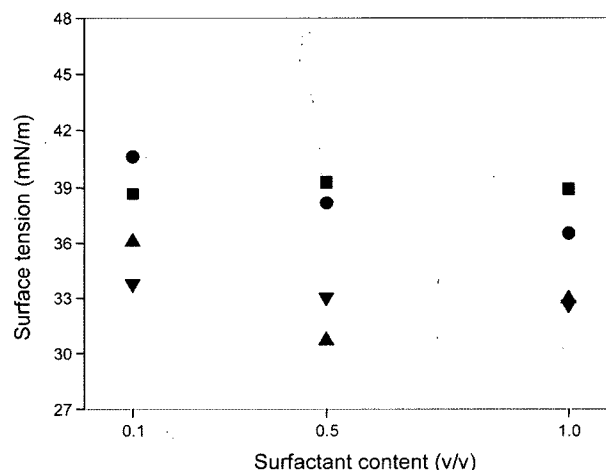


Figure 1. Dynamic surface tension of mixtures of PVOH and surfactant as a function of surfactant content at 25°C (■ : Cationic, ● : Anionic, ▲ : Amphoteric, ▼ : Non-ionic surfactant).

surfactant interaction. It is recognized that the main driving force of this kind of interaction results from the association of surfactant molecules with the dispersed polymer molecules in order to increase the surfactant micelle stability.¹⁴ On the other hand, nonionic surfactant micelles are relatively stable and their stabilities did not further increase as associate with polymers. As expected, the mixtures of PVOH and surfactant had lower surface tension than PVOH solution itself in all cases.

The viscosity in the mixture of PVOH/surfactant as a function of surfactant content at room temperature shows in Figure 2. The viscosity of the PVOH solution was about 430 cPs. The viscosity of the solution as a function of surfactant content for both a mixture of PVOH/non-ionic surfactant and a mixture of PVOH/amphoteric surfactant was constant. On the other hand, the viscosity of the solution in both a mixture of PVOH/anionic surfactant and PVOH/cationic surfactant increased with increasing surfactant content.

These results may be explained by the fact that above a critical surfactant concentration, known as the critical aggregation concentration (CAC), some ionic surfactants can bind cooperatively to nonionic polymers. This cooperative binding driven by electrical or hydrophobic interactions results in the formation of polymer-surfactant complexes in the solution. Shirahama *et al.*¹⁸ and Cabane^{19,20} proposed a structural model for these complexes, afterward conformed by NMR and neutron scattering experiments.²¹ The strength of the surfactant-polymer interaction is dependent upon the chemical properties of the polymer and surfactant. An added surfactant interacts strongly with the hydrophobic groups (alkyl group) of the polymer, leading to a strengthened association between polymer chains and thus to an increased viscosity. As regards aggregate structure in these systems, the pearl-necklace model,¹⁹ with the surfactant

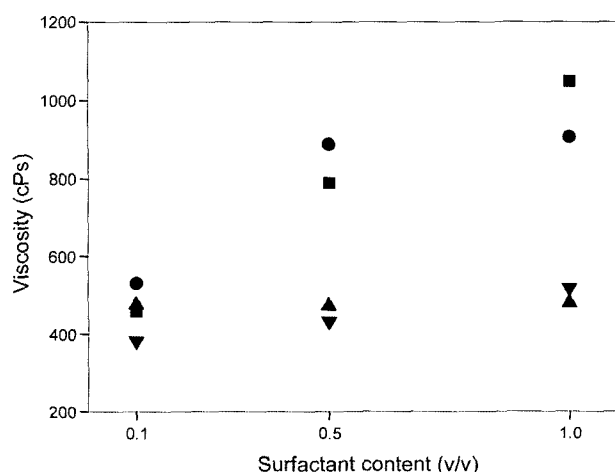


Figure 2. Viscosity of PVOH solutions with four different classes of surfactants as a function of the surfactant content at 25 °C (■ : Cationic, ● : Anionic, ▲ : Amphoteric, ▼ : Non-ionic surfactant).

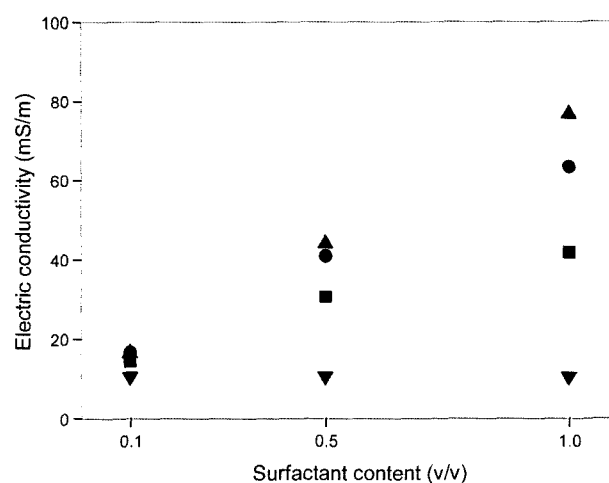


Figure 3. Electric conductivity in mixtures of PVOH and each class of surfactant as a function of surfactant content at 25 °C (■ : Cationic, ● : Anionic, ▲ : Amphoteric, ▼ : Non-ionic surfactant).

forming discrete micellar-like cluster along the polymer chain, has received wide acceptance for the case of mixed solutions of ionic surfactants and nonionic homopolymer.

Figure 3 shows the electric conductivity in mixtures of PVOH and each type of surfactant. The electric conductivity of PVOH solution alone was 10 mS/m. For a mixture of PVOH and cationic, anionic, and amphoteric surfactants, respectively, the electric conductivity of polymer solutions increased with increasing surfactant content, except a mixture of PVOH and non-ionic surfactant. A non-ionic surfactant did not affect the electric conductivity in a mixture of PVOH solution due to their non-electric property.

Characterization of Electrospun Fibers. The aqueous characteristics of PVOH-surfactant solution were discussed in previous section. Aqueous characteristics of PVOH such as viscosity of polymer solution, electric conductivity, and dynamic surface tension depended upon the content and types of surfactants. It is obvious that some of PVOH solution in the presence of surfactants have an influence upon morphological properties of PVOH nonwoven mats during the electrospinning.

Figure 4(a-e) shows the SEM images of PVOH nonwoven mats prepared from a mixture of PVOH/surfactant via electrospinning. The diameter of electrospun fibers decreased when surfactants were incorporated into PVOH solution. The average diameter of fiber in PVOH solution alone was about 300 nm. Considering the morphology in detail, the PVOH nonwoven mats in a mixture of PVOH and amphoteric or anionic surfactant have much more bonding points than those in PVOH solution alone and the former also have more junctions and bundles of fibers than the latter. Furthermore, in the case of cationic surfactant, junctions and bundles of fibers increased as the surfactant content increased. It was already reported in many

literatures^{8,23} that the mechanical properties of nonwoven mats increase with increasing of junctions and bundles of fibers. Fiber diameter of the electrospun nonwoven mats prepared from mixture of PVOH/amphoteric surfactant (Figure 4(d-1, d-2)) were much thinner comparing to the others. The average diameter of fibers from PVOH/amphoteric surfactant decreased from 300 up to 150 nm due to the higher conductivity. Zong *et al.*²² reported that calcium ion added as processing parameter affects on the diameter of P(D,L-lactide) and P(L-lactide) nanofibers. As a similar case, when the amphoteric surfactants dissolve in medium, they exist in a zwitterion state, which can simultaneously

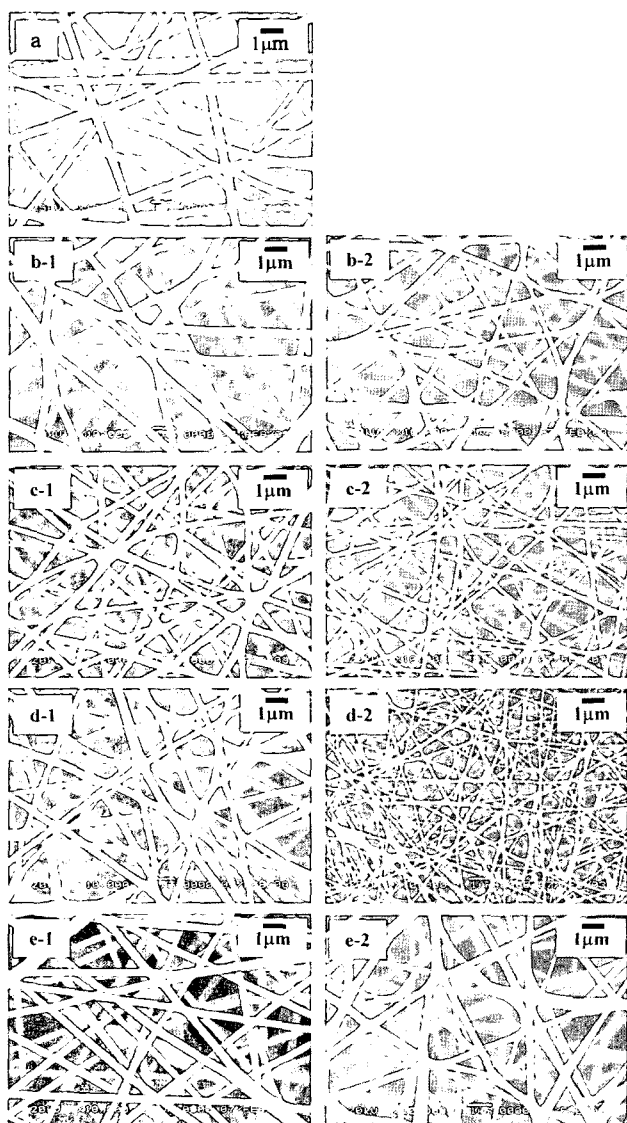


Figure 4. SEM images of the electrospun PVOH nonwoven mats prepared from various PVOH-surfactant systems: (a) PVOH solution; (b) PVOH-cationic surfactant solution; (c) PVOH-anionic surfactant solution; (d) PVOH-amphoteric surfactant solution; and (e) PVOH-non-ionic surfactant solution (1: 0.1% (v/v), 2: 1% (v/v)).

act as a cation and an anion. The zwitterion produces electrolyte materials, exhibiting the high conductivity.

As a consequence, the average fiber diameters from mixtures of PVOH/surfactant, except for PVOH/nonionic surfactant, decreases with the amount of added surfactant as shown in Figure 5.

Mechanical Properties. Mechanical properties of electrospun nonwoven mats from PVOH solution and PVOH-surfactant system are shown in Table II. Herein, the basis weight of the PVOH/cationic surfactant nonwoven mats was $3.0 \pm 0.1 \text{ g/m}^2$, while that of PVOH/nonionic surfactant nonwoven mats was $9.2 \pm 0.1 \text{ g/m}^2$.

However, the electrospun nonwoven mats from the solution of PVOH alone, PVOH/anionic surfactant, and PVOH/amphoteric surfactant could not measure the mechanical properties due to the properties of fuzz (in the case of PVOH alone and PVOH/anionic surfactant) and stiffness (in the case of PVOH/amphoteric surfactant). Although the basis weight of PVOH/nonionic surfactant nonwoven mats was higher than that of PVOH/cationic surfactant nonwoven mats, the mechanical properties of the latter were

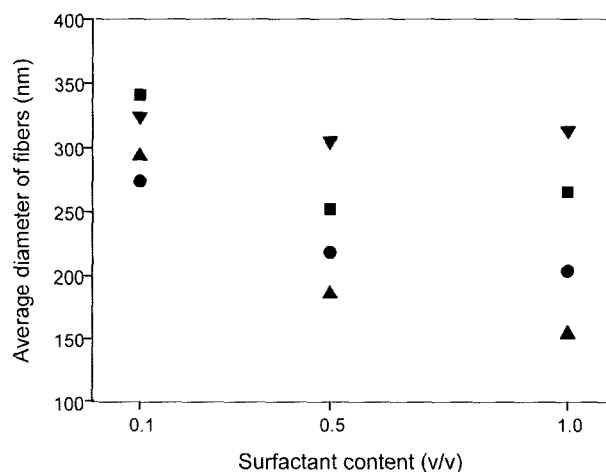


Figure 5. Average fiber diameter from mixtures of PVOH and each class of surfactant as a function of surfactant content at 25 °C (■: Cationic, ●: Anionic, ▲: Amphoteric, ▼: Non-ionic surfactant).

Table II. Mechanical Properties of Electrospun Nonwoven Mats from PVOH/ Surfactant (1 wt%, v/v) Solutions

Sample	Tensile Strength (MPa)	Elongation at Break (%)
Pure PVOH	-	-
Cationic	11.8	529
Anionic	-	-
Amphoteric	-	-
Non-ionic	3.9	191

more excellent than those of the former. These results describe the fact that the mechanical behavior of electrospun nonwoven mats mainly depend on the morphology and bonding structure of fibers^{22,23} such as the arrangement and orientation between fibers. Tensile strength of PVOH nonwoven mats in the presence of cationic surfactant was 11.8 MPa and elongation at break was 529%.

Moreover, we subsequently investigated the mechanical properties of electrospun fibers from two different cationic surfactant contents with 0.1 and 1 wt% (v/v) to more clearly describe the effect of surfactant addition. Figure 6 shows the effect of surfactant content on the mechanical property of electrospun nonwoven mats. When we compare Figure 4(b-1, b-2) with Figure 6, we easily find the difference of both the morphology and mechanical property of them. Thus, as the surfactant content increases, electrospun nonwoven mats have more point-bonded junctions. The mechanical property of final electrospun nonwoven mats becomes substantially higher.

Figure 7 shows SEM images of electrospun nonwoven mats from mixtures of PVOH/nonionic surfactant and

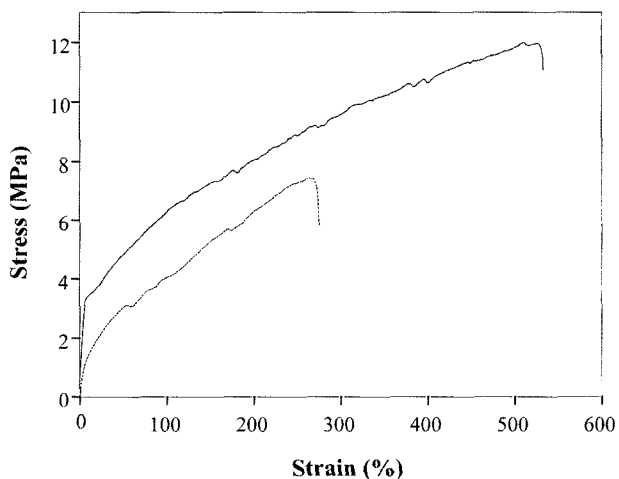


Figure 6. Stress-strain curves of electrospun nonwoven mats from PVOH solution with 0.1(dot) and 1 wt%(v/v)(solid) of cationic surfactant content, respectively.

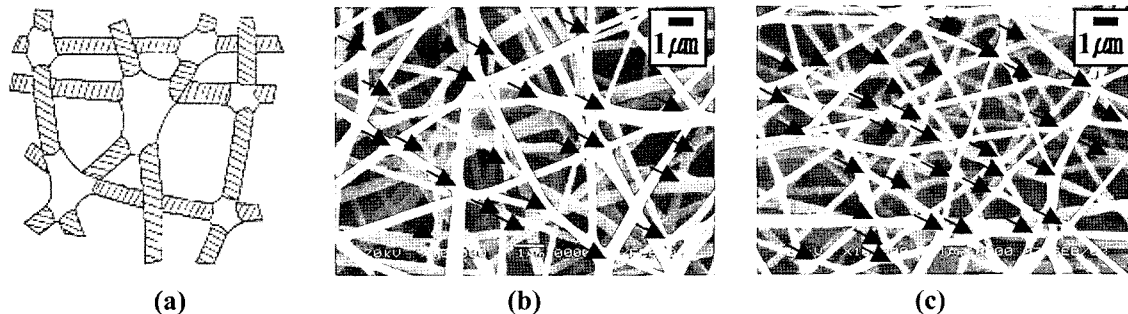


Figure 7. Schematic diagram of (a) pointed bonding structure and SEM images of electrospun nonwoven mats from mixtures of (b) PVOH-nonionic surfactant (1% (v/v)) and (c) PVOH-cationic surfactant (1% (v/v)). Arrows indicate bonding points.

PVOH/cationic surfactant, respectively. The arrows indicate point-bonded junctions in the electrospun nonwoven mats. The electrospun nonwoven mats from PVOH/cationic surfactant solution have more point-bonded junctions than those from the PVOH/non-ionic surfactant solution. This result indicates that the morphology of electrospun mats from PVOH/surfactant system, such as the fiber diameter and the frequency of point-bonded junctions, varies with type of surfactant, thereby affecting mechanical property.

Conclusions

In the present work, nanofibrous nonwoven mats from PVOH-surfactant solutions were successfully prepared by electrospinning. The fiber diameter of PVOH mats remarkably decreased from 250 to 150 nm as the amphoteric surfactant content within the range of 4% (v/v) increases, while the average diameter of fibers slightly decreased as the cationic and anionic surfactant content increases. However, the non-ionic surfactant did not give any effect on the fiber diameter of PVOH nonwoven mats. In conclusion, the morphological and mechanical properties of them prepared are affected by the type and content of surfactant.

Acknowledgements. This work was supported by the Regional Research Center Program of the Korean Ministry of Education & Human Resources Development through the Center for Healthcare Technology Development.

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