Electrospinning Fabrication and Characterization of Poly(vinyl alcohol)/Waterborne Polyurethane Nanofiber Membranes in Aqueous Solution

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ABSTRACT: Poly(vinyl alcohol) (PVA)/waterborne polyurethane (WBPU) nanofiber mats were prepared using electrospinning method with aqueous solutions. Scanning electron microscopy (SEM), X-ray diffraction (XRD), thermal gravimetric analyzer (TGA), and tensile strength testing machine (ZWICK) were used to characterize the morphology and properties of the PVA/WBPU nanofiber mats. The results showed that the morphologies of PVA/WBPU nanofiber mats changed with the total solid concentration and the mass ratio of PVA/WBPU in the spinning solution. The tensile strength and thermal stability of the fibers could be significantly affected by the WBPU contents. The electrospun PVA/WBPU membranes showed higher water uptake, which would have potential applications in wound dressings. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2337–2345, 2011

Key words: poly(vinyl alcohol); waterborne polyurethane; electrospinning; nanofiber mat

INTRODUCTION

Polyurethane (PU) is a segmented polymer with a microphase-segmented morphology, which displays highly elastomeric behaviors. PU is also a functional polymer, and its properties can be tailored by adjusting their compositions. For example, PU has been widely used in coatings, adhesives, binders, air filters, protective textiles, sensors, and medical industries, such as wound-dressing materials and antimicrobial filter.[1–5] Recently, numerous studies on the electrospinning of PUs have been conducted. PU nanofiber mats exhibit good mechanical properties with excellent tensile strength over 10 MPa and high strain of more than 300%. Electrospun PU mats can be used as high-performance air filters, protective textiles, wound dressing materials, sensors, etc.[6–15] Shah et al.[13] developed elastomeric biodegradable segmented amino acid-based PUs by the structural modification of poly(L-tyrosine). Rockwood et al.[14] prepared aligned and unaligned biodegradable PU culture substrates by electrospinning, and Khil et al.[15] made a nanofibrous PU membrane by electrospinning and investigated its performance as a wound dressing.

Although PUs have excellent properties, the preparation of these materials requires a large amount of volatile organic solvent. Many countries have restricted the production of solvent based PU due to pollution concerns. For this reason, the development of waterborne polyurethane (WBPU) formulations has been an active research area.[14–18] In the preparation of WBPU, water is the only material that needs to be evaporated during the drying process. Therefore, the manufacture of WBPU eliminates the use of toxic and flammable chemicals and does not generate polluted air or waste water.[19,20] Nowadays, a great interest on the research and development of WBPU has been rising cross many different industries.

Poly(vinyl alcohol) (PVA) is a semicrystalline hydrophilic polymer with good chemical and thermal stability. Also, it is a nontoxic material with high biocompatibility and water permeability. These properties have led to the use of PVA in a wide range of

applications in the medical, cosmetic, food, pharmaceutical, and packaging industries.[21–23] Especially, PVA has been used in fiber and film products for many years. Ultrafine PVA fibers, which may have different potential applications than microfibers, cannot be produced by conventional spinning techniques.[24–26] Moreover, our group reports several cases of electrospun PVA blend nanofibers with improved fiber properties. Blending chitosan oligosaccharide, montmorillonite with either medium molecular weight or high-molecular weight-PVA, the composite nanofibers with improved mechanical and thermal properties were obtained.[27–31] During these works, we optimized the best conditions such as electrospinning voltage, collector speed, tip-target distance, and the solution parameters such as polymer concentration, viscosity, and feed mass ratio, high-performance PVA blend nanofibers were obtained.

Although many types of PVA nanofibers were prepared using electrospinning technique, PVA nanofibers blends with PU, especially WBPU, have not been reported yet. In this study, the PVA nanofiber mates containing different amounts of WBPU were successfully prepared using electrospinning technique. The effects of WBPU on PVA nanofiber formation and the properties were studied. Nanofibers were investigated using a series of characterization methods, including scanning electron microscopy (SEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and tensile strength tester. The result indicates that the elasticity of WBPU Nanofiber web is better than pure PVA. It is therefore expected that the electrospun PVA/WBPU nanofiber mats can exhibit a better performance than PVA nanofiber mats for wound dressing material due to their increased elasticity.

EXPERIMENTAL

Materials

PVA with P_n = 1700 (fully hydrolyzed, degree of saponification = 99.9%) was obtained from DC Chemical Co., Seoul, Korea. Doubly distilled water was used to prepare polymers solutions. Poly(1,4-butanediol adipate) diol (M_w = 2000), tetramethylxylene diisocyanate (TMXDI, Cytec Industries), di-n-butyltin diluate(DBTDL, Aldrich), and triethylamine (TEA, Fluka) were used as received without further purification. Dimethylol propioinc acid (DMPA, Tokyo Kasei Kogyo, Japan) was used as internal emulsifier and heated to 60°C under vacuum for 48 h to remove water and dissolved gases before use.

Synthesis of WBPU

The prepolymer was prepared in a 1000-mL four-necked glass flask equipped with a thermometer, a stirrer, a reflex condenser, and carried out at 80°C under nitrogen atmosphere. The polyol, TMXDI, and DMPA were added in a glass reactor. The reaction mixture was allowed to react until the theoretical NCO content was reached. The TEA was then added to the reaction mixture to neutralize the carboxyl groups of the NCO-terminated PU prepolymer. After 30 min of the neutralization reaction, distilled water was added to the reaction mixture under vigorous stirring. The chain extender was added to avoid the reaction between the unreacted NCO groups and the water. Finally, the solvent-free NCO-terminated prepolymer (solid contents 35%) was obtained. The polymerization reaction procedure and chemical structures are illustrated in Scheme 1.

Electrospinning of PVA/WBPU nanofiber mats

PVA was dissolved in doubly distilled water at 80°C under magnetic stirring for 2 h followed by cooling to room temperature. The PVA/WBPU solution was prepared by mixing of PVA and WBPU aqueous solutions at total solid concentration of 10 and 15% with different mass ratios (10/0, 9/1, 7/3, 5/5, 3/7, and 1/9). During the electrospinning process, high-voltage power (CHUNGPA EMT Co., Seoul, Korea; model CPS-60K02VIT) was applied to the PVA/WBPU solution in a syringe via an alligator clip attached to the syringe needle. The applied voltage was adjusted to 15 kV. The solution was delivered to the blunt needle tip via syringe pump to control the solution flow rate. Fibers were collected on an electrically grounded aluminum foil placed at 15 cm distance to the needle tip in the thickness of 30 μm. The above spinning conditions were found being the best condition to make nanofiber mats used PVA polymer in our recently reports.[27–31]

Characterizations

The viscosity measurement for PVA/WBPU emulsions was performed with a Brookfield DV-II+ viscometer (Brookfield Engineering Lab., Middleboro, MA) at 25°C. The morphology and property characterizations of electrospun PVA/WBPU nanofibers were investigated with a field-emission scanning electron microscope (FE–SEM) (JEOL, model JSM-6380) after gold coating, and tensile strength was determined by the ZWICK Z005 testing machine (Zwick GmbH, Germany). XRD (Philips model X'Pert APD) with the Cu Kα radiation with wavelength of 0.154 nm. The scanning rate was 2°/min ranging from 10° to 30° (2θ). The thermal behavior of PVA/WBPU nanofiber mats was studied with TGA techniques (model Q-50) from TA
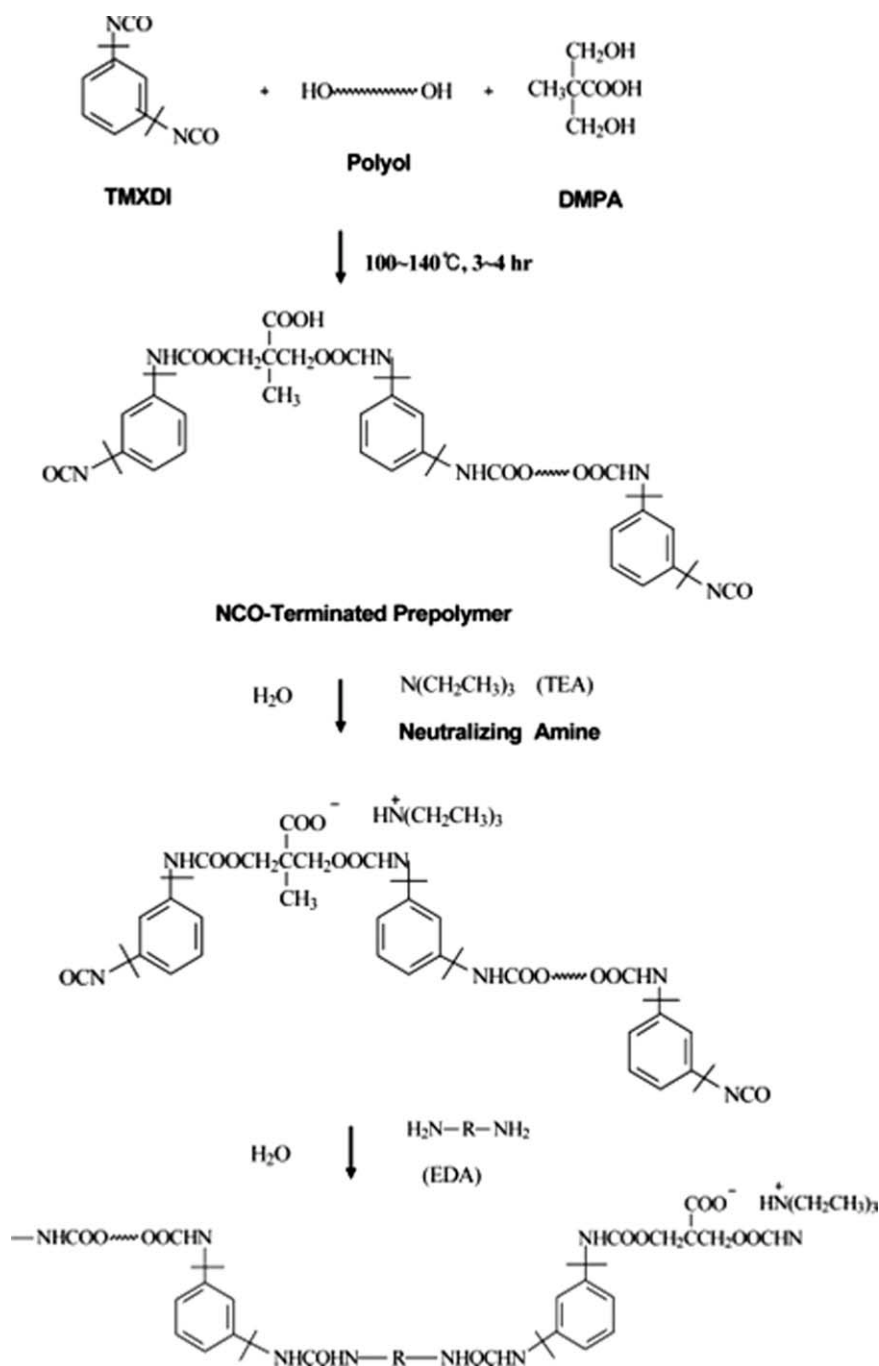
Scheme 1 Schematic diagram for the synthesis of WBPU.

instruments, USA. Elctrospun PVA/WBPU membranes were cut into pieces in 2 × 2 cm and weighed in an electronic balance with a 0.1-mg resolution. After incubation in distilled water at room temperature for 2 h, the samples were weighed again immediately after removing them from water and absorbing surface water with a piece of filter paper. The water uptake of the electrospun membranes was calculated using the following equation:

$$Water\,uptake(\%) = (m_1 - m_0)/m_0 \times 100$$

where m_0 and m_1 were the masses of the membranes before and after the incubation of the samples in water, respectively.

RESULTS AND DISCUSSION

Morphology

To examine the effect of solution viscosity on the morphologies of nanofibers, blend nanofibers from various solution conditions were prepared. The

TABLE I
The Formulation of PVA/WBPU Emulsion and Their Viscosity (cps)

Blend ratio (PVA/WBPU)	Total polymer concentration (%)	
	10	15
10/0	2026	2789
9/1	1538	1787
7/3	1183	1401
5/5	735	995
3/7	355	616
1/9	319	587

formulation of PVA/WBPU emulsions and their viscosity are listed in Table I. It can be seen that the viscosity of the emulsions generally decreased as WBPU contents were increased. For example, the viscosity of the emulsion decreased from 2026 to 319 when the ratio was increased from 10/0 to 1/9. Changing the total polymer concentration and the mass ratio of PVA to WBPU could alter the fiber diameter and morphology very effectively as shown in Figures 1 and 2. A series of nanofiber mats were made at a fixed applied voltage (15 kV) and tip-to-collector distance (15 cm) with a total solid concentration of 10 and 15 wt % and
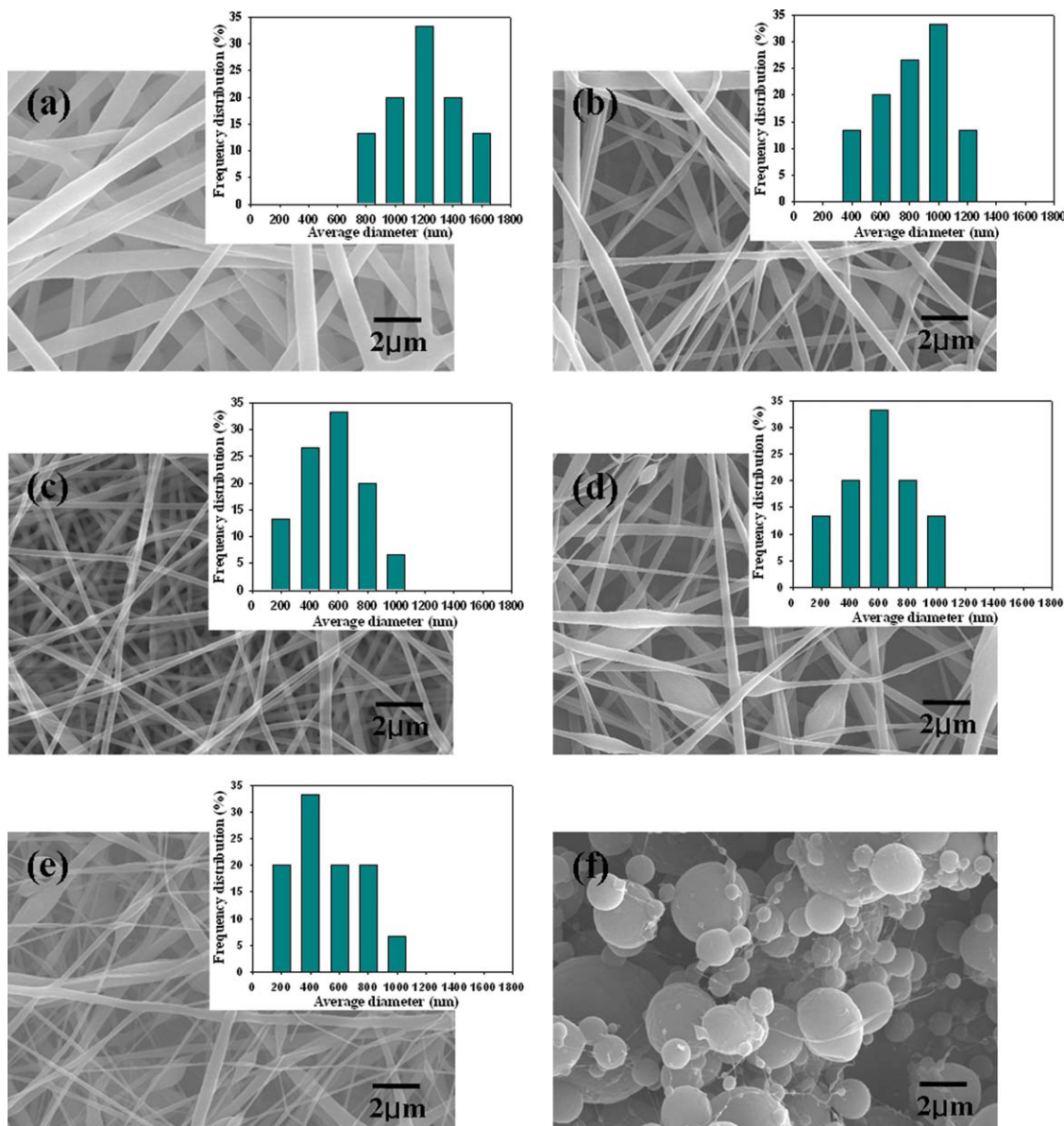

Figure 1 FE–SEM images of PVA/WBPU nanofibers that electrospun with various mass ratios of (a) 10/0, (b) 9/1, (c) 7/3, (d) 5/5, (e) 3/7, and (f) 1/9 (total polymer concentration = 10 wt %, TCD = 15 cm, and applied voltage = 15 kV). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
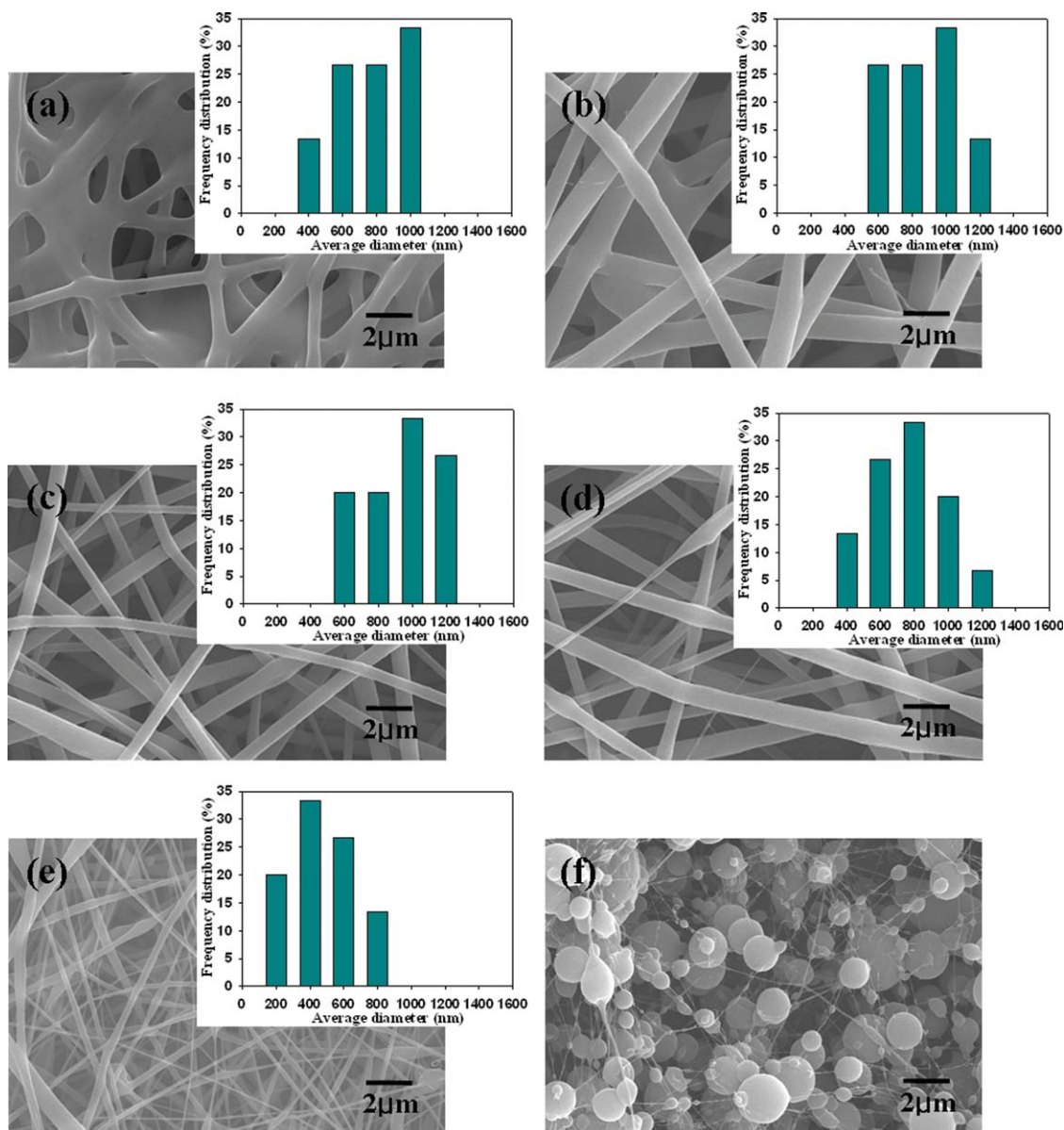
Figure 2 FE–SEM images of PVA/WBPU nanofibers that electrospun with various mass ratios of (a) 10/0, (b) 9/1, (c) 7/3, (d) 5/5, (e) 3/7, and (f) 1/9 (total polymer concentration = 15 wt %, TCD = 15 cm, and applied voltage = 15 kV). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PVA/WBPU mass ratios of 10/0, 7/3, 5/5, and 3/7, respectively.

1. At the 10 wt % total solid concentration: homogeneous fibers with average diameters around ∼ 550 nm were obtained for pure PVA solution [Fig. 1(a)]. With increasing WBPU contents, fibers connected by some beads were found as shown in Figure 1(b–e), respectively. In case of 1/9 blend ratio, uneven particles were found. It should be noted that, when PVA/WBPU mass ratio in the blend solution is higher than 3/7, the viscosity of the solution is too low to be electrospun.

2. At the 15 wt % total solid concentration: a similar trend of morphological change as that of total polymer concentration of 10 wt % was observed (Fig. 2). On the other hand, at a lower WBPU mass ratio (up to 50%), fiber diameters were thicker than that obtained with 10 wt % of total solid content. Comparing the SEM images shown in Figures 1 and 2, it was found that there was no bead formed for the sample with an equal concentration of PVA and WBPU. It was noted that the diameter of fibers and the formation of beads are strongly influenced by the viscosity of the solution.[32]
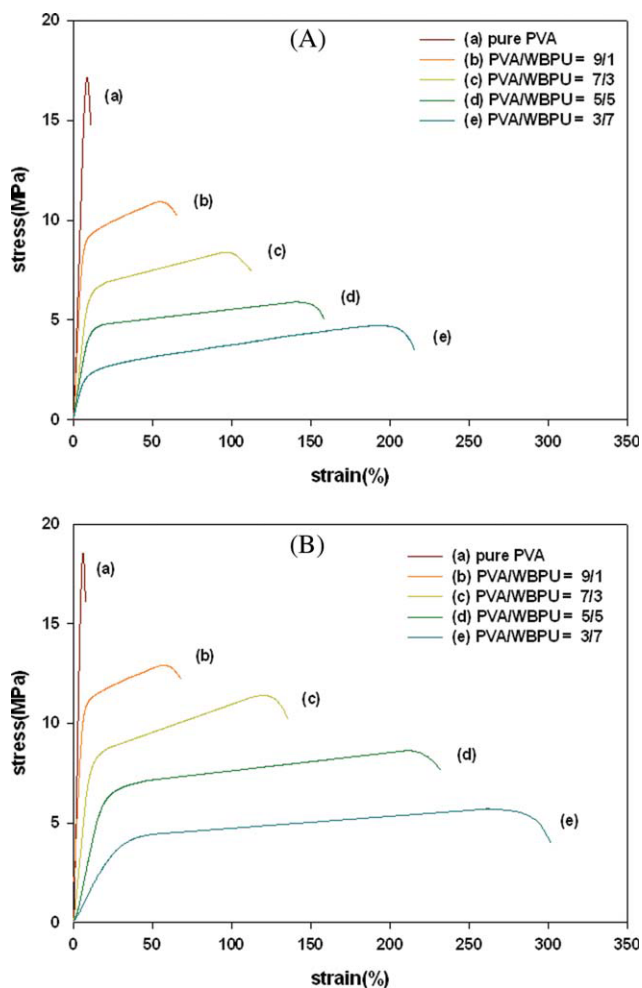
Figure 3 Stress–strain curve of PVA/WBPU nanofibers that electrospun with various mass ratios at (a) 10 and (b) 15 wt % total polymer concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

It can be concluded that the concentration and mass ratio of the PVA/WBPU blend solutions were two important parameters that had remarkable effects on the morphology of the electrospun nanofiber mats.

Tensile property

Figure 3 shows the stress–strain curves of the PVA/WBPU nanofiber mats. Stress–strain analysis was carried out at room temperature in a material testing station (Zwick Z005) using standard procedures (ASTM D 882) at the extension rate of 10 mm/min. All the nanofiber mats show a nonlinear elastic behavior in the low-stress region and plastic deformation at higher stress. In the case of PVA/WBPU nanofibers, their tensile strength and elongation were dramatically changed compared to the pure PVA nanofiber.[33] It was noted that although the tensile

strength of PVA nanofiber mats was lower than that of the WBPU blend nanofibers, their elongation was improved as much as about 60–260%. It is believed that the improvement of mechanical properties of the PVA/WBPU nanofiber mats is due to the enhancement of elasticity PVA nanofiber itself.

XRD data

The X-ray diffraction (XRD) patterns of the PVA/WBPU electrospun nanofiber mats are presented in Figure 4. The pure PVA fiber mat shows a significant crystalline peak at about 19.3°, which is because of the occurrence of strong inter- and intramolecular hydrogen bonding.[34] The other side, XRD diffraction pattern of WBPU, indicates that it is a typical amorphous material, that is, no diffraction peak was obtained. As the amount of WBPU in the PVA/WBPU blend fibers was increased, the intensity of the diffraction peak at about 19.3° became lower and broader. This suggested that the crystallinity of
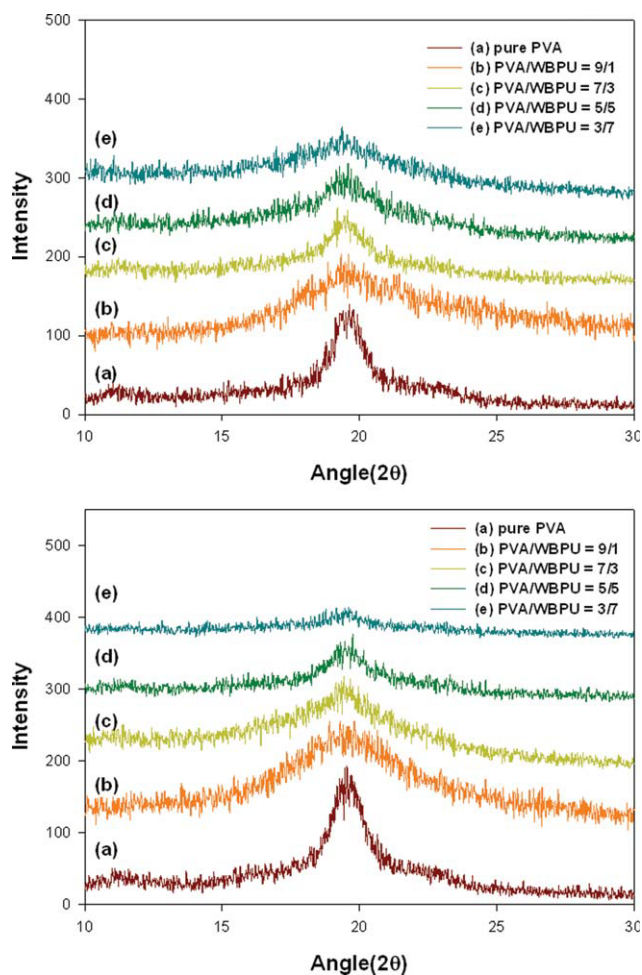

Figure 4 XRD data of PVA/WBPU nanofibers that electrospun with various mass ratios at (a) 10 and (b) 15 wt % total polymer concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5 TGA data of PVA/WBPU nanofibers that electrospun with various mass ratios at (a) 10 and (b) 15 wt % total polymer concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
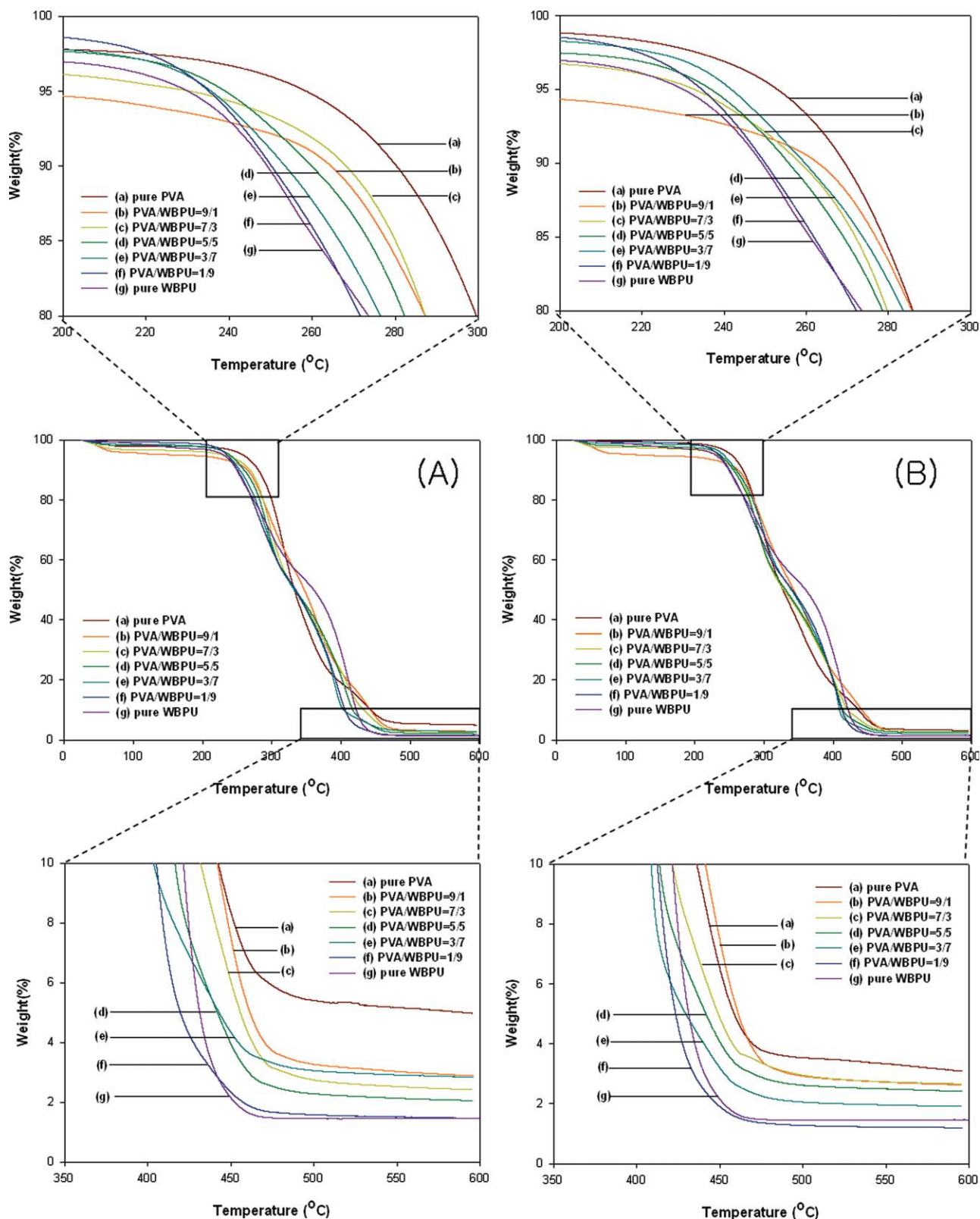
Figure 6 Water uptake of PVA/WBPU nanofibers that electrospun with various mass ratios at (a) 10 and (b) 15 wt % total polymer concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
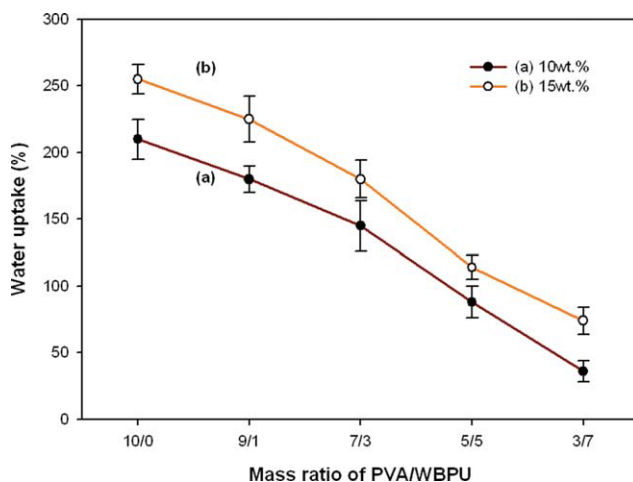
PVA/WBPU fibers with higher amounts of WBPU [(a)–(e)] was lower than that of the electrospun PVA fiber.

Thermal properties

Thermal stability of electrospun PVA/WBPU nanofibers was measured using TGA in nitrogen atmosphere. The TGA thermograms shown in Figure 5 indicate that the fiber mats with various PVA/WBPU mass ratios and total solid concentrations have different decomposition temperatures. The actual depolymerization temperature depends on the structure, molecular weight, and conformation of the polymer. Meanwhile, the curves in Figure 5[A(g)] and B(g) represent the bulk WBPU, and the curves in Figure 5[A(a),B(a)] were obtained from pure PVA. Three weight loss peaks were observed in the TGA curve for bulk PVA [(a) line]. The first peak at 25–60°C was due to moisture vaporization, the second peak at 260–380°C was due to the thermal degradation of PVA, and the third peak at 430–460°C was due to the byproduct formation of PVA during the TGA thermal degradation process. WBPU [(g) line] displays a slower initial and then a rapid degradation process. The weight loss peaks from 180 to 360°C and 360 to 550°C correspond to the soft and hard segments degradation. Other curves with different mass ratios of PVA/WBPU show the same trend of thermal stability. It can be seen that although the thermal degradation temperature of WBPU is not as high as that of the PVA, higher thermal properties could be obtained with a higher mass ratio of PVA in the PVA/WBPU blend nanofiber mats.

Water uptake

Figure 6 illustrates the variation of the water uptake of the electrospun PVA/WBPU membranes with different mass ratios, which suggests that the water uptake increased from 36 to 210 wt % and 74 to 255 wt % when the mass ratio of PVA/WBPU was changed at 10 wt % and 15 wt % total polymer concentration, respectively. Because PVA is an excellent water soluble polymer, the water uptake of the electrospun PVA/WBPU membranes could get higher with the increasing amount of PVA. However, the better nanofibrous morphology of the electrospun PVA/WBPU membranes with higher PVA amount, which exhibited higher surface-to-volume ratio and porosity, could be the main reason to make their water uptake increase. The electrospun PVA/WBPU membranes with higher water uptake would have potential applications in wound dressings.

CONCLUSIONS

Ultrafine PVA/WBPU submicron fibers were produced by the electrospinning method in aqueous solution. The nanofibers were characterized by FE–SEM, XRD, TGA, and tensile strength testing machine. The polymer concentration and mass ratios were the important factors influencing the electrospinnability and the morphology of the electrospun nanofiber mats. The elongation of PVA/WBPU nanofibers was improved as much as about 60–260% comparing to the pure PVA nanofibers. The results suggested that the optimum fabrication conditions for PVA/WBPU nanofiber are 15 wt % of total solid concentration with a mass ratio from 7/3 to 5/5. At these conditions, higher strength of and enhanced elasticity of electrospun nanofiber was obtained. Furthermore, higher thermal properties could be obtained with a higher mass ratio of PVA in the PVA/WBPU blend nanofiber mats. The electrospun PVA/WBPU membranes could have potential applications in wound dressings because of their higher water uptake.

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