Electrospinning of Poly(vinyl alcohol) and Poly(4-styrenesulfonic acid) for Fuel Cell Applications

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ABSTRACT: Electrospun fibers of poly(vinyl alcohol) (PVA) and PVA/poly(4-styrenesulfonic acid) (PSSA) were obtained. By varying PVA to PSSA weight ratios, various fiber sizes and shapes were observed. The fiber diameters ranged from 176 to 766 nm, and the largest fibers were obtained from 15 wt % aqueous PVA solution. The effect of solution viscosity on fiber morphology was discussed. The presence of PSSA in electrospun fibers was confirmed by Fourier Transform Infrared spectroscopy. The PVA fibers were thermally stable up to 250°C, and the PVA/PSSA fibers were stable up to approximately 150°C. The water stability of the fibers was improved by heat-treatment at 120°C. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2594–2600, 2012

Key words: conducting polymers; fibers; fuel cell; membranes; polyelectrolytes

INTRODUCTION

Polymer electrolyte membrane fuel cells have received a lot of attention as power sources for vehicles and electronic devices due to their high efficiency and environmental friendly properties.[1,2] The current polyelectrolyte membranes (PEMs) used are generally based on hydrated sulfonated polymers. Among these, perfluorosulfonic acid membranes, such as Nafion®, have drawn much interest because of their chemical and electrochemical stabilities. Nafion® is prepared by the free radical initiated copolymerization of tetrafluoroethylene (TFE) and a perfluorovinyl ether containing a sulfonyl fluoride.[3] The major drawbacks of using Nafion® as PEM include the high cost of perfluoroether comonomers and the safety concerns of TFE in its synthesis.

Poly(4-styrenesulfonic acid) (PSSA) has been considered as a promising choice for PEM because of its low cost and relative high proton conductivity. A composite material of PSSA and phosphotungstic acid prepared by solvent-casting method showed an extremely high proton conductivity of 1×10^{-2} S/cm at 180°C under dry nitrogen flow.[4] However, small molecules may leach out from the conventional cast membrane, leading to a decrease in proton conduction, and possibly membrane instability. To address this issue, electrospinning has been introduced.[5]

Electrospinning is a simple method to produce fibrous materials with diameters ranging from nanometers to micrometers. A high voltage is applied to a polymer solution, and a conical drop called the Taylor cone is formed at the tip of a needle. Once electrostatic forces overcome the surface tension of the solution, a polymer jet is produced. The jet is elongated and later deposited on a grounded collector. Tamura and Kawakami[6] have recently found that when nanofibers were introduced to the membrane, the gas permeability could be controlled. It was reported that electrospinning of Nafion® solution was challenging due to aggregation of ionic groups;[7] however, on addition of poly(vinyl alcohol) (PVA), sprayable solutions were obtained.[8] PVA has several properties that make it an attractive material for fuel cell applications such as controllable physical properties, hydrophilic properties, and excellent methanol barrier.[9] In addition, PVA has a high density of hydroxyl groups that provide crosslinking sites for crosslinking through irradiation, chemical, or thermal treatments.[10]

In this work, electrospun fibers of PVA and PSSA were first prepared and characterized. The effect of weight ratio of PVA to PSSA on solution properties, shape, and size of the fibers was studied. Surface morphology was characterized using scanning

electron microscopy. Thermal property and water stability of the fibers were also investigated.

EXPERIMENTAL

Materials

PVA (95% hydrolyzed, average MW 95,000) was purchased from Acros Organics (Pittsburgh, PA). PSSA (MW 75,000, 18 wt % in water) was purchased from Aldrich (St. Louis, MO). All chemicals were used as received.

Fiber preparation by electrospinning

Electrospinning was performed with PVA, PSSA, and PVA/PSSA solutions with varying polymer compositions. Aqueous 10 wt % PVA solution was prepared by dissolving PVA powder in deionized (DI) water at 80°C with constant stirring for 3 h. The solution was cooled to room temperature before addition of PSSA aqueous solution. The blended PVA/PSSA solutions were stirred overnight to ensure adequate mixing before electrospinning process.

The polymer solution was loaded into a plastic syringe equipped with a 23-gauge stainless steel needle, connected to a high-voltage supply (DEL High-Voltage (0–100 kV), DEL Electronics Corp.). The polymer solutions were spun at a flow rate of 0.5 mL/h using a syringe pump (TERUMO Terufusion Syringe pump TE-331, Japan). A piece of flat aluminum foil was placed 20 cm below the tip of the needle and used to collect the fibers. The positive voltage applied was 19.4 kV. All experiments were performed at room temperature. The electrospinning apparatus is shown in Figure 1.

Characterization

Surface morphology was studied using a scanning electron microscope (LEO 1450VP, UK). The average diameters of the fibers were determined by analyzing 200 fibers in each micrograph. The viscosity of polymer solutions were measured at room temperature at a shear rate of 20 rpm using a digital viscometer (Brookfield, model DV-II). Fourier Transform Infrared (FTIR) spectra were measured on a PerkinElmer FTIR spectrometer (spectrumOne) measuring in the range of 4500–500 cm^{-1}. Thermogravimetric–differential thermal analysis was performed using Pyris Diamond TG/DTA (Perkin Elmer Instrument) with a heating rate of 10°C/min from 50 to 500°C under nitrogen. X-ray diffraction (XRD) data was obtained on a Bruker D8 ADVANCE diffractometer using monochromatic CuKα radiation. Glass transition temperature was obtained by differential scanning calorimetry (DSC) using a Perkin–Elmer Pyris 1
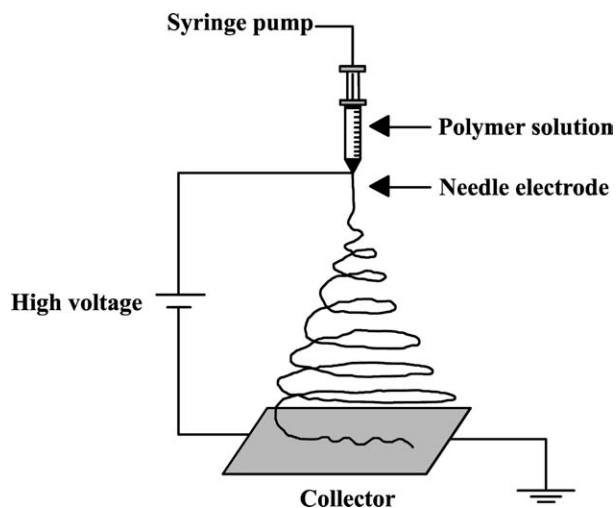

Figure 1 Schematic diagram of the electrospinning apparatus.

DSC. Sample was analyzed with a heating rate of 10°C/min from room temperature to 180°C under nitrogen flow.

RESULTS AND DISCUSSION

Electrospinning of polymer solutions

The electrospinning of PSSA solution at a voltage of 19.4 kV resulted in no fiber formation. To improve the spinnability, 10 weight % (wt %) PVA aqueous solution was added to the PSSA solution at different amounts. The final wt % PVA in PVA/PSSA blends was calculated by dividing the weight of PVA by the sum of the weights of PVA and PSSA. The weight percentages of PVA in this study were 0, 67, 75, 80, 86, 90, and 100. At low PVA contents, beaded fibers were observed (Table I). Fiber mats were obtained from the blended solutions with PVA content ≥ 75%. Electrospinning 10 wt % PVA solution in the absence of PSSA yielded no fiber, while increasing the PVA concentration to 15 wt %, PVA fibers were observed.

Refer to the SEM images in Figure 2, it could be seen that the fibers became smoother with increasing PVA content. The fiber diameter distributions are shown in Figure 3, and a plot of fiber size vs. PVA content is shown in Figure 4. The fiber size increased when wt % of PVA was increased. The trend still held even though the pure PVA fibers were prepared from a solution with a higher PVA concentration. The largest fibers were obtained from 15 wt % aqueous PVA solution with an average diameter of 766 nm.

Solution properties play important roles in the synthesis of fiber via electrospinning. Fiber formation depends highly on viscosity, charge density, and surface tension.[11–13] The viscosity of PSSA solution was 22.5 mPa s, measured at a shear rate of

TABLE I
Electrospinning of PVA/PSSA Blends

PVA content (wt %)	Voltage (kV)	Distance (cm)	Rate (mL/h)	Observations
0	19.4	20	0.5	Solution droplets
67	19.4	20	0.5	Beaded fibers
75	19.4	20	0.5	Fiber mat
80	19.4	20	0.5	Fiber mat
86	19.4	20	0.5	Fiber mat
90	19.3	20	0.5	Fiber mat
100[a]	15.5	20	0.5	Fiber mat

[a] 15 wt % PVA solution.

20 rpm. A drastic increase in viscosity was observed when PVA was introduced to the PSSA solution, shown in Figure 5. The improvement in spinnability of PSSA with PVA could be related to the increase in viscosity of the polymer solution, which may result from enhanced chain entanglement.[7] Sufficient chain entanglements are required to maintain the continuity of the jet during electrospinning. The spinnability of 15 wt % aqueous PVA solution could be attributed to the three orders of magnitude increase in the solution viscosity compared with that of 10 wt % aqueous PVA solution.

When PVA contents were ranging from 75% to 90%, it was found that the fiber size increased with decreasing solution viscosity. The observed trend was opposite from previous reports, where fiber size increased with increasing viscosity,[14,15] suggesting that viscosity was not the dominant factor governing the fiber size in this concentration regime. Besides viscosity, solution conductivity also affected electrospinnability of polymer solution. Because electrospinning
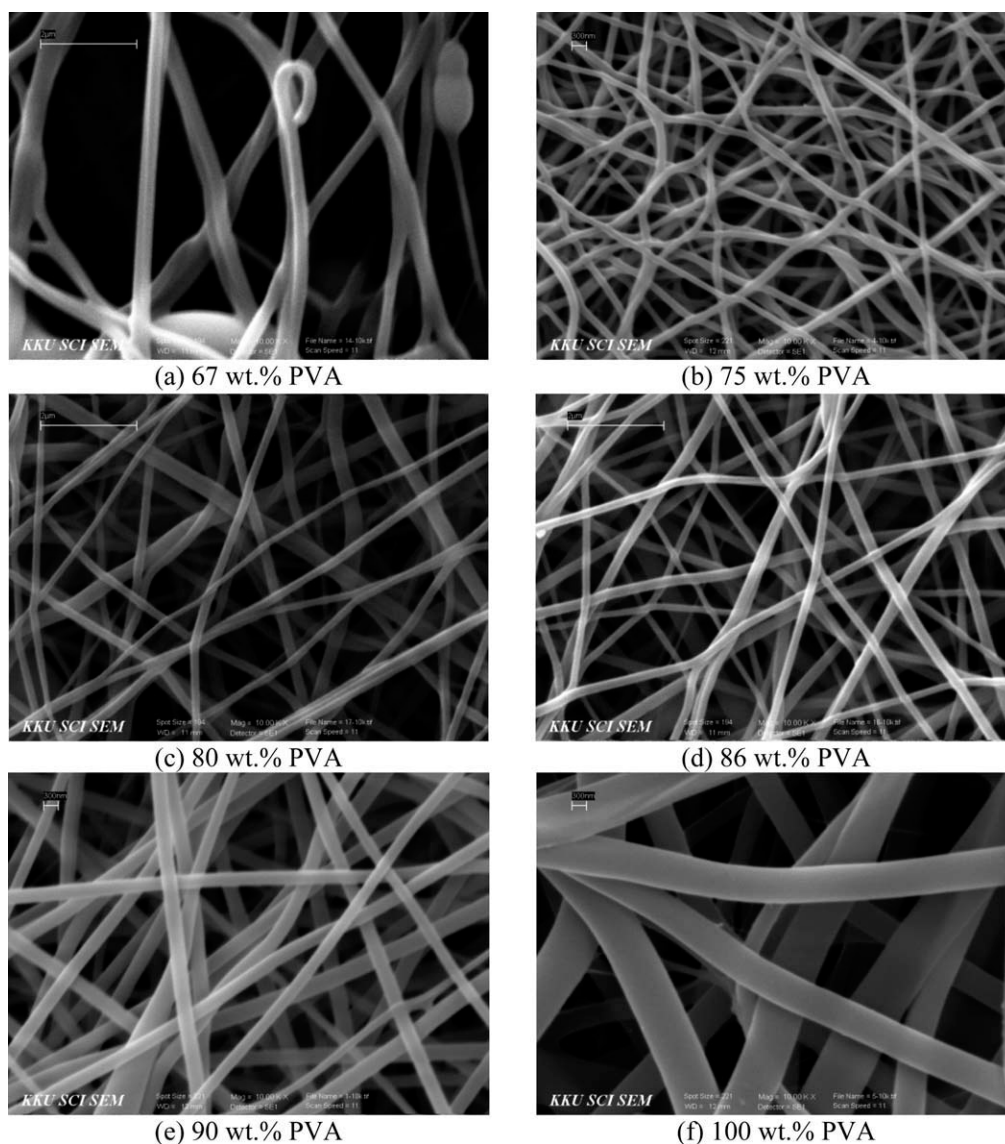

Figure 2 SEM images (10k magnification) of electrospun PVA/PSSA blends at various PVA compositions. (a) 67 wt %, (b) 75 wt %, (c) 80 wt %, (d) 86 wt %, (e) 90 wt %, and (f) 100 wt %.
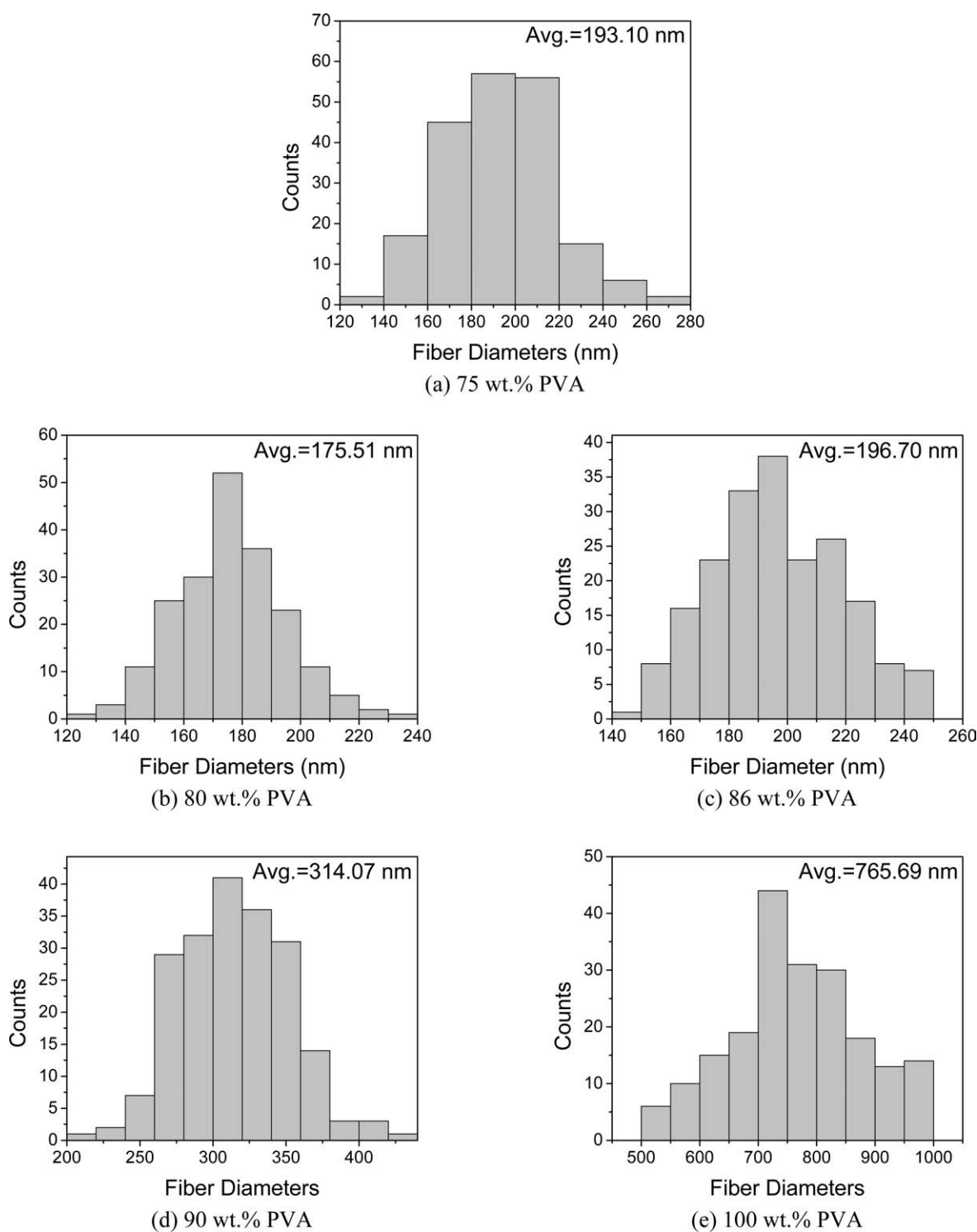
Figure 3 Size distributions of the electrospun fibers. Fibers prepared from (a) 75 wt %, (b) 80 wt %, (c) 86 wt %, (d) 90 wt %, and (e) 100 wt % PVA.

involves stretching of the solution caused by repulsion of the charges at its surface, the extent of solution elongation is changed by varying the charge density. PSSA is a polyelectrolyte containing sulfonic acid groups; therefore, at high PSSA content, i.e., low PVA content, there would be a strong repulsion between the negative charges within and among the polymer chains. This repulsion led to a good solution stretching which resulted in smaller fiber sizes.[16]

Considering the case where 67 wt % PVA was introduced, beaded fibers were formed from a combination of high solution viscosity and high conductivity. This observation implied that besides the repulsive forces, surface tension also affected the
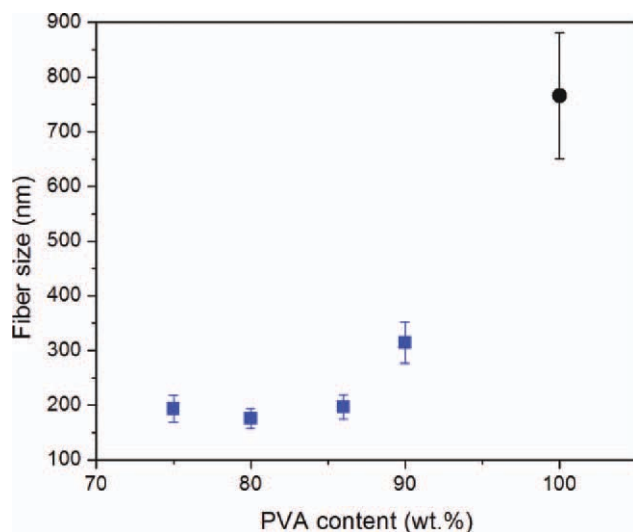
Figure 4 Effect of PVA content on fiber size. From blends prepared from 10 wt % PVA solutions (■) and from pure 15 wt % (●) PVA solution [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

shape of the fibers. At an initiation stage of the electrospinning process, it is necessary for charged solution to overcome its surface tension to form a polymer jet. The surface tension may cause the formation of beads along the jet.[17] Zhu et al.[18] reported that in the electrospinning of aqueous PVA solution, PVA behaved as a surfactant and the increasing amount of PVA resulted in the decrease of surface tension. Therefore, the beaded fibers obtained from 67 wt % PVA solution could be attributed to the high surface tension, and possibly the strong hydrogen bonding between the large amount of sulfonic acid groups of PSSA and hydroxyl groups of PVA and water.[19]
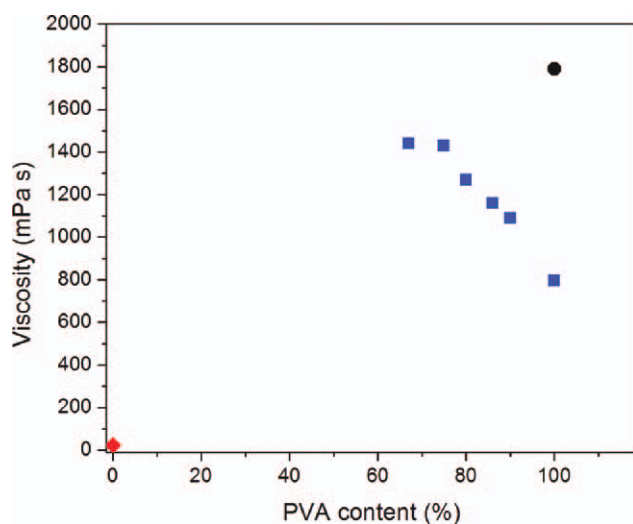

Figure 5 Viscosity of PSSA solution (◆), PVA/PSSA blends, and pure PVA. (■) and (●) denote solutions prepared from 10 wt % and 15 wt % aqueous PVA solutions, respectively [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].
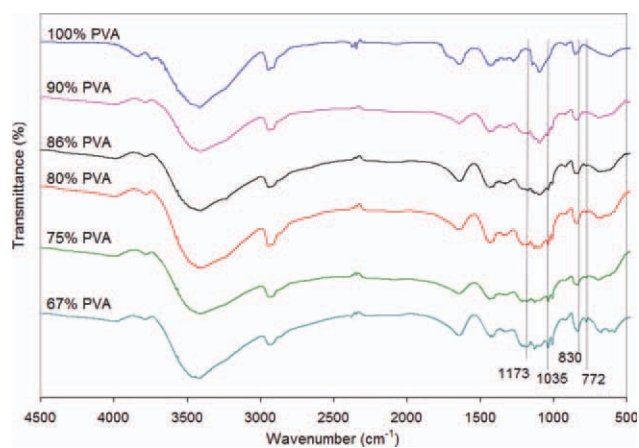
Figure 6 FTIR spectra of PVA and PVA/PSSA fibers [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

Fiber compositions

FTIR spectra were used to confirm the presence of PSSA in the electrospun fibers. As shown in Figure 6, the characteristic peaks of PVA at 3400, 1417, and 1090 cm^{-1} were designated to O-H stretching, O-H bending, and C-OH stretching, respectively.[20] On introduction of PSSA, new peaks at 1173, 1035, 830, and 772 cm^{-1} were observed. The peaks at 1173 and 1035 cm^{-1} were assigned to the S=O asymmetric and symmetric stretches.[20] The wagging vibrations of C-H in 1,4- and 1,2-substituted benzene rings of PSSA were shown at 830 and 772 cm^{-1}, respectively.[21] In comparison with the O-H peak of pure PVA fiber (3400 cm^{-1}), the O-H peak of PVA/PSSA fibers slightly shift to higher wavenumbers, indicating the formation of hydrogen bonds between -OH of PVA and -SO$_3$H of PSSA.[22] The heat-treated 90% PVA fibers were also characterized using FTIR.
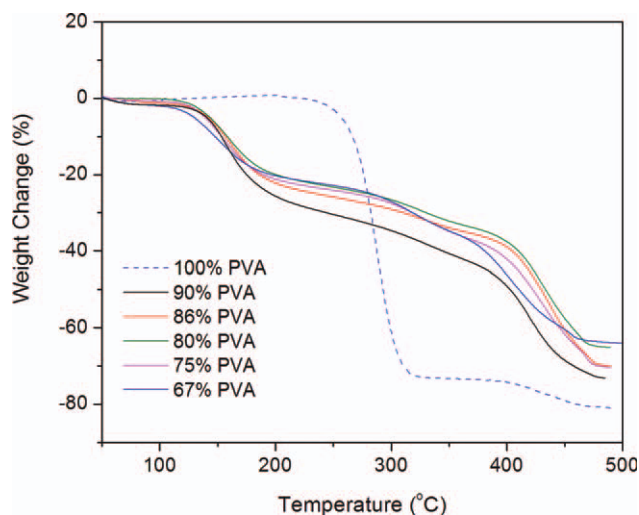

Figure 7 TG thermograms of electrospun fibers [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].
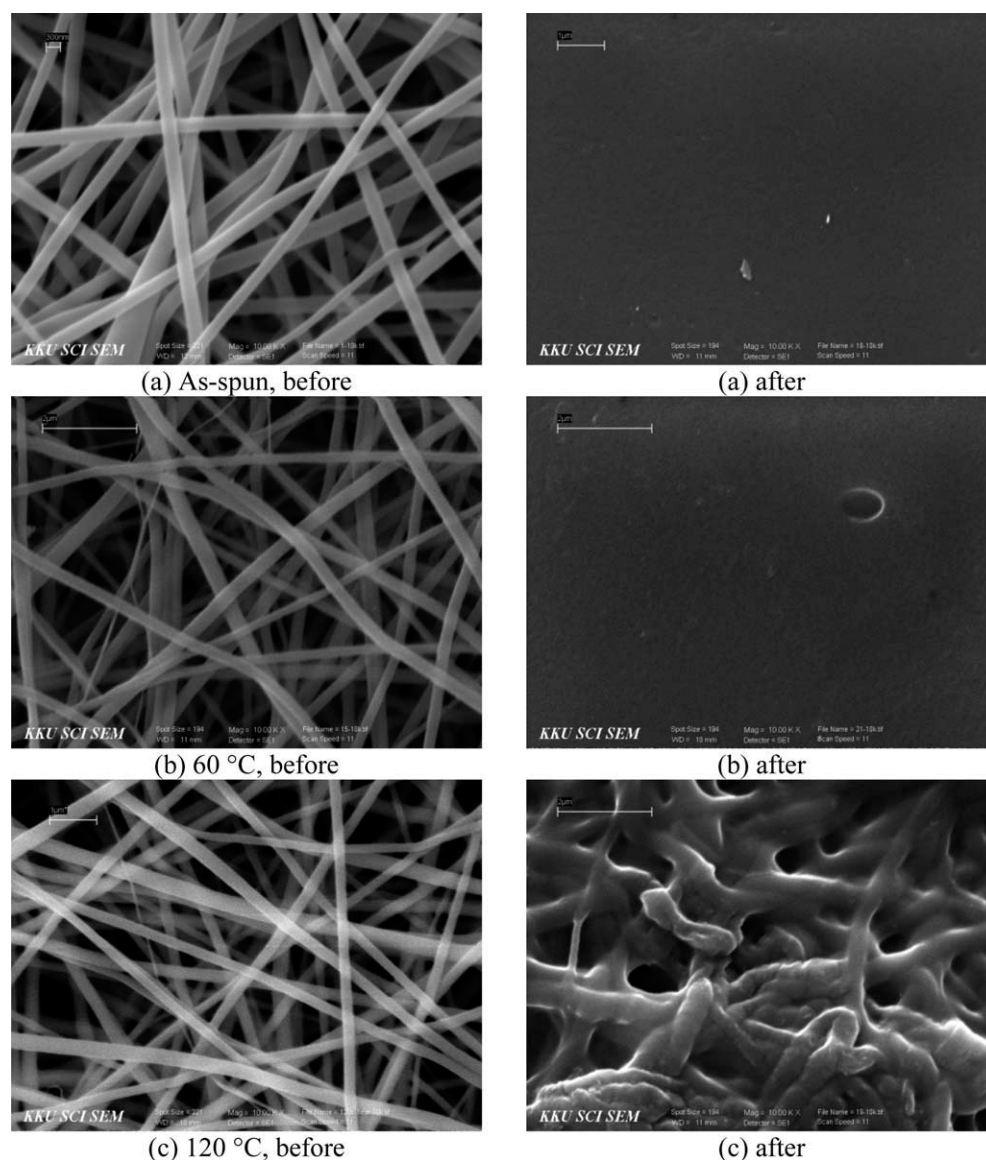
Figure 8 SEM images of fibers prepared from 90 wt % PVA before (left) and after (right) immersion in DI water at room temperature for 24 h. (a) As-spun fiber (no heat treatment), (b) heat-treated at 60°C for 10 min, and (c) heat-treated at 120°C for 10 min.

Comparing with the unheated fibers, no change in IR spectra was observed. The absence of the characteristic peaks at 1680 and 1200 cm^{-1}, corresponding to C=O and C-O stretching modes, suggested that there was no C-O-C formation between the hydroxyl group of PVA and carboxyl group of PSSA.[23]

Thermal analysis

Thermogravimetric analysis results were shown in Figure 7. The fibers prepared from all blended solutions showed similar thermal property. Similar to previous reports on the thermal property of PVA-PSSA blend membranes, TG thermograms of the obtained PVA/PSSA fibers showed three main degradation stages; thermal dehydration, thermal desulfonation, and thermal oxidation.[24–26] The first weight loss of about 20% between 50 and 190°C was attributed to the loss of the absorbed water on the fiber, indicating the hygroscopic nature of sulfonic acid groups. The second loss between 190 and 400°C was likely due to the loss of sulfonic acid groups of PSSA by desulfonation. The third weight loss region at above 400°C corresponded to the loss of polymeric main chain.[27,28] The pristine PVA fibers were thermally stable up to 250°C. The decompositions of PVA main and side chains were observed in the temperature range of 250–320°C.[29] It should be noted that polymeric membranes containing sulfonic acid groups are suitable for uses for fuel cell operating at temperatures $< 100°C$;[30] therefore, the electrospun PVA/PSSA fibers are considered thermally stable.

Water stability

It was reported earlier that the stabilization of PVA fiber against water could be improved by physically crosslinking the fibers with a thermal treatment.[31] Similarly, the obtained PVA/PSSA fibers containing 90 wt % PVA were heated for 10 min at two different temperatures, 60 and 120°C, and their stabilities against water were studied. It was found that the shape and size of the fibers did not change after heat treatments, Figure 8 (left). After immersing the fibers in DI water at room temperature for 24 h, drastic changes in fiber shape were observed, Figure 8 (right). With no heat treatment and a heat treatment at 60°C, the fiber mats became flat sheets after the immersion. On the other hand, with a heat-treatment at 120°C, a dense membrane structure was observed after the test, suggesting an improvement in water stability. XRD pattern of the untreated 90% PVA fiber showed a weak and broad peak at $2\theta \approx 20°$ (data not shown), corresponding to the (101) plane of PVA. Kang et al.[31] reported that the peak intensity of PVA fiber increased with increasing heat treatment temperature. However, on heat treatment, no changes in XRD pattern and intensity were observed in our study, suggesting that the crystallization of PVA was not additionally induced by heat. This could be due to the presence of PSSA, where an incorporation of PSSA was reported to lower the intensity of the peak at 20° of the PVA membrane.[25] The absence of strong phase separation was also supported by a single T_g value of about 140°C obtained from the 90% PVA fiber.

CONCLUSIONS

Electrospun fibers of PVA and PVA/PSSA were successfully synthesized. Fiber sizes and shapes were changed with changing the weight ratio of PVA to PSSA. The size highly depends on the solution viscosity, conductivity, and surface tension. The obtained PVA/PSSA fibers were thermally stable up to approximately 150°C. Although the water stability of the fibers was improved by heat-treatment at 120°C, we acknowledge that these fibers are not sufficiently stable for use as membranes in fuel cells. To achieve a membrane with good mechanical and water resistant properties, the uses of irradiation and chemical crosslinking are being explored.

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