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Electrospinning and Solution Properties of Nafion and Poly(acrylic acid)

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ABSTRACT: In this study, the electrospinning performance and solution properties of Nafion and its blend with another polyelectrolyte, poly(acrylic acid) (PAA), were investigated. Attempts to electrospin pure Nafion at various polymer concentrations (5−35 wt %), solvents, neutralization, and electrospinning conditions resulted in electrospraying rather than electrospinning. However, a polymer solution blend (5 wt %) of Nafion and PAA resulted in beaded fibers at 8 wt % PAA and smooth electrospinning above 12% PAA. Fiber sizes of the blend increased from 90 to 600 nm with increasing PAA content. Dynamic light scattering on pure Nafion solutions in various solvents reveals large aggregates (i.e., dispersion) of various sizes due to polymer backbone and ionic interactions. The lack of sufficient polymer chain entanglement evidenced by low viscosity and aggregate formation in Nafion solutions prohibits fiber formation during electrospinning. The addition of PAA to Nafion modifies the ionic strength of the solvent resulting in suppressed aggregate formation, increased viscosity, and subsequently enhanced polymer chain entanglement. Coincidentally, the onset of suppressed aggregate formation in the blend solution coincides with the electrospraying−electrospinning transition (8% PAA). In addition, thermal treatment enhances water stability of the electrospun blend fibers.

Introduction

Polyelectrolytes have been explored in a variety of applications, including drug delivery,[1] antimicrobial agents,[2] chemical and biological protective clothing,[3−4] and biomimetic actuators.[5] More specifically, the anionic polyelectrolyte Nafion has been widely used as a proton exchange membrane in fuel cells.[6,7] In addition, applications for Nafion include electrochemical devices, chlori−alkali production, metal-ion recovery, water electrolysis, batteries, sensors, and superacid catalysts.[8−10] Commercially, Nafion is available in several forms, such as extruded films of various thicknesses and equivalent weights, as dispersions in water/alcohol solutions, and in pellet form. Scaling down Nafion on the size scale of nanometers is expected to increase its efficacy for many of the applications listed above by providing ultrahigh specific surface areas. Recent results by Snyder and Elabd[11,12] demonstrate the impact of Nafion in nanofibrous form on improving fuel cell performance.

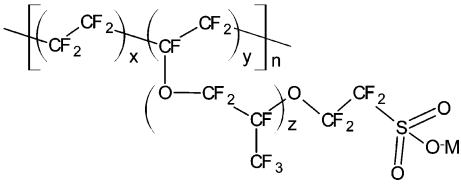

Figure 1. Molecular structure of Nafion.

Electrospinning is one technique that produces polymer fibers with nanometer-sized diameters with the use of electrostatic forces.[13−15] To date, few investigations have reported Nafion in nanofibrous form.[11,12,16] In this spinning process, a high voltage is applied to a polymer solution, forcing the solution out through a metal spinnerette and deforming the pendent drop at the tip of the spinnerette into a conical shape referred to as the “Taylor cone”. Above a critical voltage, electrostatic forces overcome the surface tension of the solution, and an electrified polymer jet is formed. The jet is then elongated and whipped continuously by electrostatic repulsion until it is deposited on the grounded collector in the form of a randomly interconnected fibrous mat. Fiber formation by electrospinning depends on the polymer solution properties and the spinning parameters. Similar to traditional fiber spinning processes (e.g., melt spinning), electrospinning also requires a proper viscosity (i.e., sufficient chain entanglement) of the polymer solution to form fibers. Therefore, in addition to having the proper polymer solution concentration, polymers with linear or lightly branched structures are usually desired, while those with highly branched or star-shaped architectures should be avoided. Unlike other fiber spinning processes, the electrostatic driving force in electrospinning indicates that the conductivity of the polymer solution is another important factor for spinning performance.

While most polymers are neutral in nature, polyelectrolytes are of fundamental significance in electrospinning due to the electrostatic charges along its polymer backbone.[17−20] Polyelectrolytes exhibit higher conductivities compared to neutral polymers and a high net charge density in aqueous solutions.[17,18] Results have shown that the addition of a polyelectrolyte to an aqueous neutral polymer solution increases the conductivity significantly, resulting in a smoother electrospinning performance and smaller fibers.[17,20] Polyelectrolytes exhibit rodlike conformation in salt-free aqueous solution due to electrostatic repulsion between the charged groups. In the presence of salt, polyelectrolytes exist as random coils since the repulsive interactions are screened. Therefore, the viscoelastic behavior and electrospinning performance of polyeletrolytes are dependent on salt concentration in solution.[17−20] McKee et al.[17] found that the scaling behavior of a cationic polyelectrolyte in the semidilute entangled regime shifted from polyelectrolyte ($\eta_{sp} \sim C^{1.5}$) to neutral polymer behavior ($\eta_{sp} \sim C^{3.75}$) in the high salt limit. Moreover, the minimum concentration for fiber formation decreased with an increase in salt concentration.

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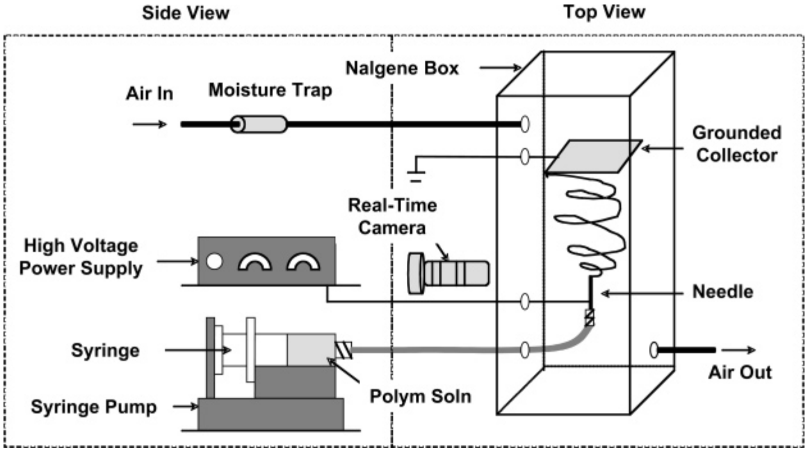
Scheme 1. Electrospinning Apparatus



Electrospinning Nafion is of importance in this study. Chemically, Nafion has a fluorocarbon backbone with perfluoroether side chain and sulfonic acid pendant group (Figure 1). In its charged state, the sulfonic acid (SO_3^-) can either be hydrolyzed with a hydronium ion (H_3O^+) or neutralized with a cation (M^+). As a result of electrostatic interactions between ion pairs, these ionic groups will aggregate to form tightly packed regions referred to as ion clusters.[8,9] The incompatible fluorocarbon backbone and ionic clusters exist as phase-separated regions in the polymer. This unique molecular structure with branched architecture and superacid pendant groups suggests different solution properties and electrospinning characteristics compared to other polyelectrolytes.

In this work, the solution properties and electrospinning performance of Nafion and its blend with another polyelectrolyte, poly(acrylic acid) (PAA), were investigated. The main focus was to understand how formation of fibers and the resulting fiber structure are affected by the nature of the polymer solution. Therefore, the effects of the solution properties and blend polymer on the morphology, size, and structure of the fibers were investigated. The influence of the blend polymer on the solution properties of Nafion was particularly stressed. The water stability of the Nafion−PAA nanofibers was also explored through thermal treatment for potential applications in water-rich environments.

Experimental Section

Materials. Nafion (1100 EW, 5 wt % in a 3/1 volume ratio of isopropyl alcohol/water) was purchased from Ion Power, Inc. (Liquion) and was used as received. PAA ($M_v = 450\,000$), *N*,*N*-dimethylformamide (DMF; 99%), methanol (≥99.8%), isopropyl alcohol (≥99.5%), and cesium chloride (99.9%) were all purchased from Aldrich and used as received. Ultrapure deionized, reverse osmosis (RO) water (resistivity ∼ 16 MΩ cm) was used as appropriate.

Electrospinning. Electrospinning was performed with Nafion, PAA, and Nafion−PAA blend solutions at various polymer compositions. Nafion solutions in DMF were prepared by adding a specific amount of DMF to the 5 wt % commercial solution and boiling off the alcohol and water. Nafion/methanol solutions were produced by dissolving a Nafion film (cast from commercial solution) in methanol at room temperature. The Nafion solutions with 0.1 M CsCl were prepared by first dissolving a specified amount of CsCl in 3/1 isopropyl alcohol/water, then mixing the commercial Nafion solution with a proper amount of the CsCl solution, and stirring until homogeneous. Nafion−PAA blend solutions were prepared by mixing 5 wt % of PAA in 3/1 isopropyl alcohol/water with 5 wt % Nafion commercial solution at desired weight ratios.

Scheme 1 shows a schematic diagram of the electrospinning apparatus used in this study. It consists of a high-voltage power supply (Glassman High Voltage Inc., Series EL), syringe pump, syringe, needle (i.d. = 0.047 in.), and grounded collector (aluminum foil). The needle was connected to the high-voltage supply, which can generate positive DC voltages up to 50 kV. The spinning distance, which is the distance between the tip of the needle and the collector, was in the range of 10−25 cm. Positive voltages applied to polymer solutions were in the range of 10−25 kV. The solution flow rates were controlled with a syringe pump ranging from 0.5 to 5 mL/h. All electrospinning experiments were carried out at room temperature (∼24 °C) and at relative humidities below 30%, which was maintained by supplying dry air to the enclosed electrospinning chamber.

Characterization. The conductivity and viscosity of polymer solutions were measured using a conductivity meter (Mettlor-Toledo MC126) and a Brookfield digital viscometer (Model HDBT), respectively, at ambient temperature (∼24 °C). The morphology of electrospun fibers was observed using a scanning electron microscope (SEM, Phillips/FEI XL30) after platinum coating (Denton Desk II sputtering system, 40 mA, 30 s). The average diameter was determined by analyzing 20 fibers in each micrograph with a UTHSCSA Image Tool.

Dynamic Light Scattering. Solutions of 5 wt % Nafion and Nafion−PAA blend were diluted with the corresponding solvents to 5 mg/mL. The dynamic light scattering (DLS) measurements were carried out on a nanoparticle size analyzer (Brookhaven 90Plus). A solid-state laser (35 mW at $\lambda = 678$ nm) was used as the light source. The incident beam was vertically polarized with respect to the scattering plane. All measurements were made at 25 °C.

The CONTIN program available on the 90Plus was used to determine size distributions, $G(\Gamma)$, from the measured autocorrelation function. For a diffusive process, Γ is given by $\Gamma/q^2 = D$, where D is the translational diffusion coefficient. Thus, a distribution of Γ, such as $G(\Gamma)$, can be related to a diffusion coefficient or to an effective hydrodynamic radius (R_h) through the Stokes−Einstein relationship: $R_h = k_BT/(6\pi\eta D)$, where k_B and η are the Boltzmann constant and solvent viscosity, respectively.

Results and Discussion

Electrospinning of Pure Nafion. Nafion solution is commercially available at 5 wt % in a cosolvent of isopropyl alcohol and water (∼3/1 volume ratio). Electrospinning of this solution produced a stable polymer jet under proper spinning conditions but produced beads on the aluminum foil target (Figure 2). Increasing the solution concentration to 20 wt % by boiling off a specified amount of solvent resulted in no improvement to fiber formation. Electrospinning of Nafion was also evaluated in methanol and DMF over a broad range of concentrations,

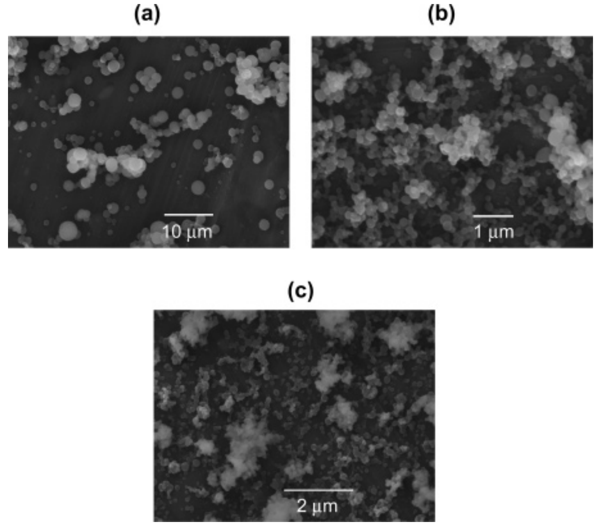


Figure 2. SEM images of electrosprayed Nafion at (a) 10 wt % in 3/1 isopropyl alcohol/water cosolvent, (b) 25 wt % in DMF, and (c) 15 wt % in methanol.

Table 1. Electrospinning of Nafion

polymer	solvent	concn (wt %)	electric field (kV/cm)	observation
Nafion	isopropyl alcohol/water	5−10	15−17/20	beads
	DMF	25−35	16/20	beads
	methanol	10−15	10−13/20	dense film or beads
Nafion−CsCl	isopropyl alcohol/water	15	12/20	beads

Table 2. Physical Properties of Nafion, Water, and Solvents

	γ [a] (mN/m)	η [b] (cP)	δ (cal/cm^3)$^{1/2}$
Nafion			10.1, 16.7 [c]
water	72.8	0.89	23.4 [d]
DMF	37.0	0.80	12.1 [d]
methanol	22.9	0.05	14.5 [d]
isopropyl alcohol	23.0	2.04	11.5 [d]

[a] Surface tension at 20 °C. [b] Viscosity at 25 °C. [c] Cohesive energy density.[9] [d] Hildebrand solubility parameter.[22]

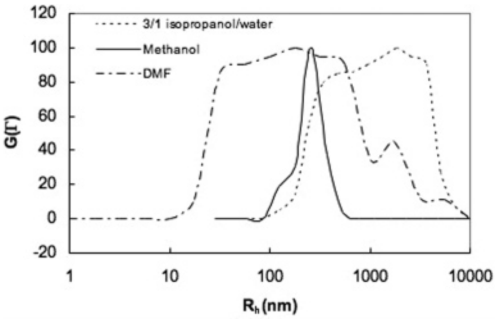


Figure 3. Hydrodynamic radii R_h distributions of Nafion in different solvents, 5 mg/ mL, obtained at 25 °C and at a scattering angle $\theta = 90°$.

10−35%. Similar observations were obtained in these solvents, where only beads were collected. In other words, varying polymer concentration, solvent, neutralization, and electrospinning conditions all resulted in electrospraying and not electrospinning of pure Nafion (Table 1).

Solution Properties of Pure Nafion. Electrospinning fiber formation from polymer solutions depends highly on the solution properties, such as viscosity, surface tension, and net charge density. For instance, electrospinning of cellulose acetate in a 2/1 acetone/dimethylacetamide cosolvent produces fibers at surface tensions around 26 dyn/cm and viscosities between 1.2 and 10.2 P.[21] High viscosities prohibit the electrospinning by the instability of flow, which is caused by the high cohesiveness of solution. At low viscosities, only droplets are formed due to the lack of chain entanglement. Surface tension of the polymer solution also directly affects the polymer jet formation, since the electrostatic forces in electric field must overcome the surface tension of the solution to form a polymer jet. The solvents that were used in electrospinning pure Nafion have surface tensions (γ) between 22.9 and 43.8 mN/m (Table 2). The observation of a smooth polymer jet in electrospinning suggests that these surface tensions are desirable for electrospinning. However, viscosity measurements show that a 5 wt % Nafion solution in a 3/1 isopropyl alcohol/water cosolvent has a viscosity of 6 cP. This value is similar to those of pure solvents (e.g., 2.04 cP for isopropyl alcohol; Table 2) and is much lower than those of common linear polymers in solution (e.g., 296 cP for 5 wt % PAA in 3/1 isopropyl alcohol/water cosolvent). Increasing the concentration to 10 wt % only raised the viscosity to 8 cP. Similarly, 5 wt % amounts of Nafion in methanol and DMF have viscosities of 8 and 10 cP, respectively. The abnormally low viscosities indicate the lack of polymer−polymer interactions in Nafion solutions and prompt a more in-depth investigation of Nafion solution properties.

Compared to the membrane structure of Nafion, little is known about the nature and structure of Nafion solutions. A colloidal dispersion structure has been suggested for Nafion solutions from studies using small-angle neutron scattering (SANS), small-angle X-ray scattering (SAXS),[23] and electron spin resonance (ESR).[24] These experiments have revealed that rodlike aggregate structures exist in Nafion solutions with polar solvents, such as water, methanol, and DMF. The aggregate size of Nafion has been investigated by dynamic light scattering, where multimodal and bimodal particle sizes were observed in various solvents, including water, methanol/water, ethanol/water, isopropyl alcohol/water, and DMF.[25−28] Typically, the small particle sizes (<100 nm) corresponded to the single molecular chains, noting that the molecular mass of Nafion is approximately 10^5−10^6 Da. Medium (∼500 nm) and large (>1 μm) particles were also observed and relate to Nafion aggregates. The medium particles were assigned to a primary rodlike aggregate, which is formed by the hydrophobic interaction of fluorocarbon backbone, and the large particles are assigned to larger (secondary) aggregate particles, which are formed by the ionic interactions of the primary aggregates.

The aggregate size distributions in Nafion solutions were also investigated in this study with dynamic light scattering. Figure 3 shows a few typical distribution curves of the apparent hydrodynamic radium (R_h) obtained from CONTIN analysis of the light scattering data for 5 mg/mL Nafion solutions. In a 3/1 isopropyl alcohol/water cosolvent, bimodal particle sizes were observed, one corresponding to the medium particles of 200 nm to 1 μm and the other related to large particles greater than 1 μm. In DMF, small particles of R_h < 100 nm appeared, while the large particles of R_h > 1 μm became less apparent. Nafion in methanol showed a narrow distribution of particle sizes at 100−200 nm. These results suggest that appreciable amounts of both primary and secondary aggregates exist in isopropyl alcohol/water cosolvent, while single molecules, primary aggregates and less secondary aggregates exist in DMF. In methanol, Nafion only exists in the form of primary aggregates. In other words, the secondary aggregates, which form through ionic interactions are partially suppressed in DMF and are not present in methanol.

According to Flory−Huggins theory, solvents, which have similar solubility parameters (δ_2) to the polymer (δ_1), are thermodynamically preferred for the formation of single molecular chains. The cohesive energy density (solubility parameter) of Nafion has been determined experimentally from swelling measurements.[29] There are two distinct swelling envelopes corresponding to two cohesive energy densities: one at 10.1 (cal/cm^3)$^{1/2}$ has been ascribed to the fluorocarbon backbone of Nafion, while the other at 16.7 (cal/cm^3)$^{1/2}$ has been tentatively attributed to the ionic side chain. Table 2 shows that isopropyl alcohol and DMF have a better solubility with the fluorocarbon backbone of Nafion, while methanol has a better solubility with Nafion ionic groups. The dissolution of the fluorocarbon backbone of Nafion in DMF suppresses the formation of primary aggregates and facilitates the existence of single molecular chains. Similarly, the interaction of ionic portion of Nafion with methanol prohibits the formation of secondary aggregates. Water reduces the solubility of fluorocarbon backbone, while isopropyl alcohol enhances interactions between ionic groups. Consequently, both primary and secondary aggregates exist in the isopropyl alcohol/water cosolvent.

DLS studies reveal that aggregates exist in all three solvents used in electrospinning. These aggregates are apparently the crucial reasons for no fiber formation. In the electrospinning process, although stable polymer jets were still observed under proper spinning conditions, probably, as a result of the electrostatic forces in Nafion, the aggregate formation reduces chain entanglements and hinders electrospinning fiber formation. Adding 0.1 M salt (e.g., NaCl or CsCl) to the Nafion solution has proved to suppress the formation of large aggregation by shielding the electrostatic interactions between the ionic groups of Nafion. [27] However, similar to the Nafion−methanol solution, the primary aggregates prevent enough chain entanglement for fiber formation. To enhance chain entanglement, a linear polymer was added to the Nafion solution and the electrospinning and solution properties were investigated. The amphiphilic polymer, PAA, was selected, considering that it can be dissolved in both aqueous and organic solvents. In addition, the carboxylic acid groups add functionality to the electrospun fiber, not only enabling cross-linking of the fiber but also enhancing fiber accessibility to other functional agents.

Electrospinning of Nafion−PAA Blends. Electrospinning of PAA has been successfully demonstrated in water and DMF.[18−19] This work shows that continuous and uniform fibers were also obtained from 5 wt % PAA in 3/1 isopropyl alcohol/water cosolvent (Figure 4f). This PAA solution was blended with a 5 wt % commercial Nafion solution at various weight ratios to investigate the effects of PAA content on the electrospinning performance and fiber morphologies.

Smooth electrospinning was obtained at a PAA content above 12%. Below this content, stable polymer jets were also observed, but were blocked occasionally. As shown in Table 3, at a constant feeding rate of 1 mL/h, the optimal electrospinning conditions for Nafion−PAA blends at >12% PAA move to lower voltages and shorter spin distances with an increase of PAA content. PAA content also reveals a significant impact on the fiber morphologies (Figure 4). At a PAA content below 8%, only beads were collected on aluminum foil. Beaded fibers were observed as PAA content approached 8%, while fiber mats with few beads/defects were obtained at a 12% PAA content. As the amount of PAA increased to above 25%, defect-free fiber mats were obtained.

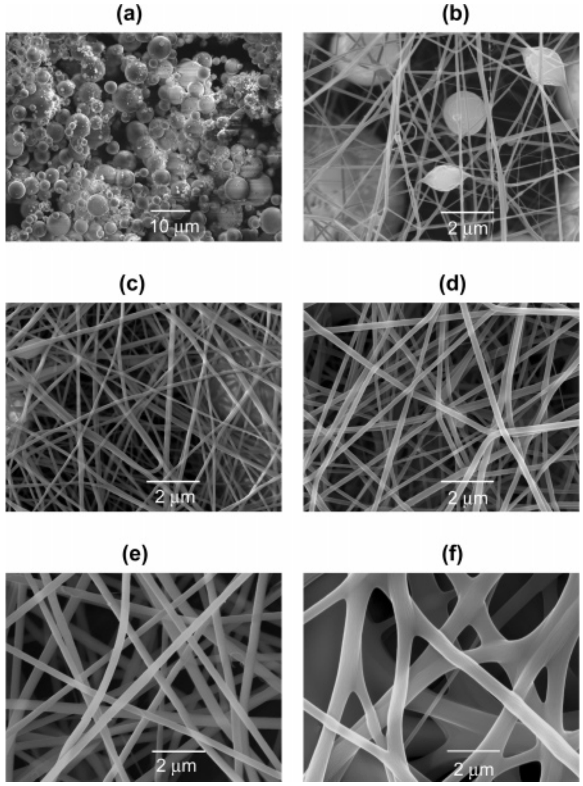


Figure 4. SEM images of Nafion−PAA electrospun fibers with a PAA content of (a) 5, (b) 8, (c) 12, (d) 25, (e) 66, and (f) 100%.

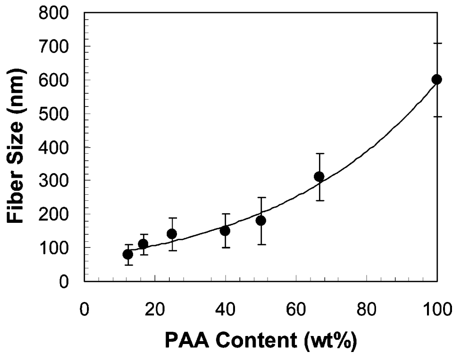


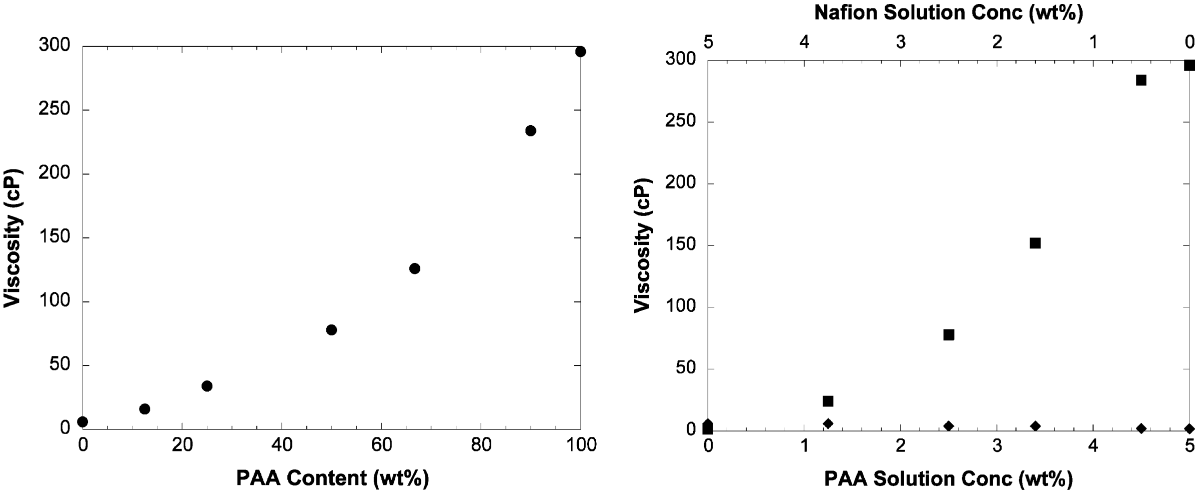
Figure 5. Effect of PAA content on fiber size of electrospun Nafion−PAA.

Table 3. Electrospinning of Nafion−PAA Blend Solution

PAA content (%)	electric field (kV/cm)	observation
100	16/18	fiber mat
66	10/20	fiber mat
50	12/24	fiber mat
25	17/25	fiber mat
16	18/28	fiber mat, few beads
12	15/25	fiber mat, few beads
8	15/24	beaded fibers
5	16/21	beads

The beaded fibers at 8% PAA have an average fiber diameter of 90 nm (Figure 5). Fiber size increased steadily and became more uniform with increasing PAA content, approaching 300 nm at 66% PAA. The pure PAA fibers electrospun from 5 wt % solution in 3/1 isopropyl alcohol/water cosolvent had an average diameter of 600 nm.

Solution Properties of Nafion−PAA Blends. The increase of fiber sizes results from changes in the solution properties.



(a) **(b)**

Figure 6. Viscosity (at 24 °C) of (**a**) Nafion−PAA blends (●) and (**b**) pure Nafion (◆) and pure PAA (■). All polymers were dissolved in a 3/1 isopropyl alcohol/water cosolvent, and the pure Nafion and pure PAA in (b) correspond to solution concentrations similar to the blend solutions in a at each specified PAA content.

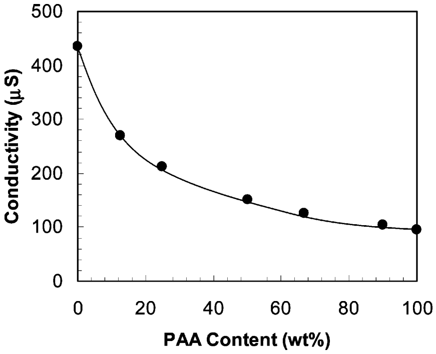


Figure 7. Conductivity of Nafion−PAA blend solutions in 3/1 isopropyl alcohol/water at 24 °C.

With an increase in PAA content, an increase in viscosity and a decrease in conductivity were observed (shown in Figures 6a and 7). Both changes give rise to the formation of larger fibers.[18]

At first glance, the improvement in spinnability of Nafion with the addition of PAA appears to be related solely to the increase in solution viscosity, which may result from enhanced chain entanglement. The significance of chain entanglement in electrospun-fiber formation has been recognized by several investigators.[17,30] An entanglement concentration is defined as the transition between the unentangled and entangled semidilute regimes and marks the solution concentration at which chains overlap sufficiently to form topologically constrained entanglements. In electrospinning, continuous fibers are only obtained above this concentration. Beaded fibers form near this transition, while only beads are observed below this concentration.

Due to the aggregate formation of Nafion in solution, the lack of chain entanglement results in no fiber formation. The improvement in spinnability with the addition of the linear polymer PAA suggests enhanced chain entanglement. This enhancement is not sufficient below 8% PAA content, at which beaded fibers were observed; therefore, this may be regarded as the required entanglement content. Defect-free fibers were formed at PAA contents of 25% or higher. This is consistent with previous observation that defect-free fibers are formed at concentration above 2.5 times entanglement concentration.[17,30] These observations appear to be consistent with the increase in blend solution viscosity shown in Figure 6a.

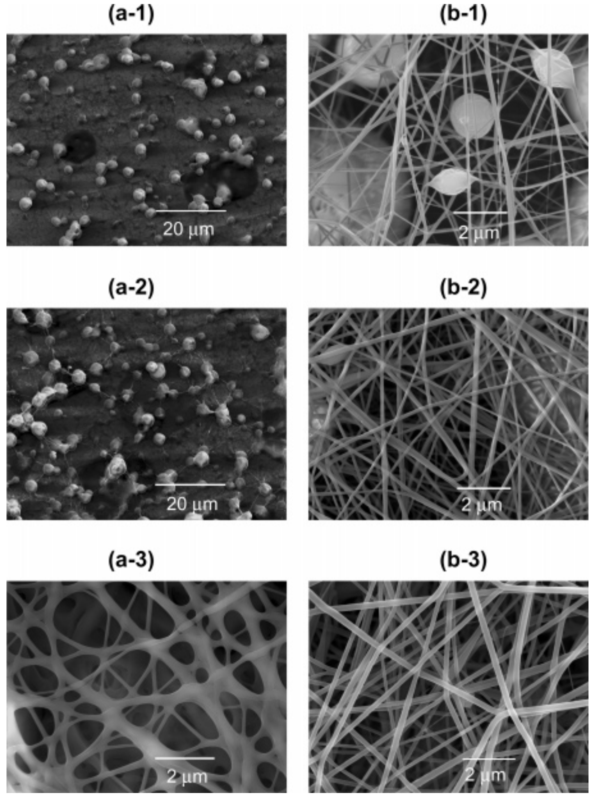


Figure 8. SEM images of electrospun PAA in 3/1 isopropyl alcohol/water at the following solution concentrations: (a-1) 0.42, (a-2) 0.625, and (a-3) 1.25 wt %. Nafion−PAA blends in 3/1 isopropyl alcohol/water with the following PAA contents: (b-1) 8, (b-2) 12, and (b-3) 25%. The total polymer concentrations of Nafion−PAA blends were 5 wt % in 3/1 isopropyl alcohol/water. The PAA concentrations in the blends are equal to those of the pure PAA solutions, respectively.

To understand the effect of viscosity on electrospinning in more depth, pure PAA solutions were electrospun at similar concentrations to the PAA in Nafion−PAA blends at low contents (8, 12, and 25%). The results are shown in Figure 8. At concentrations of 0.42 and 0.625 wt %, PAA does not electrospin (Figure 8a-1,-2) although their viscosities are similar to the Nafion−PAA analogues (Figure 6a (8 and 12% PAA)

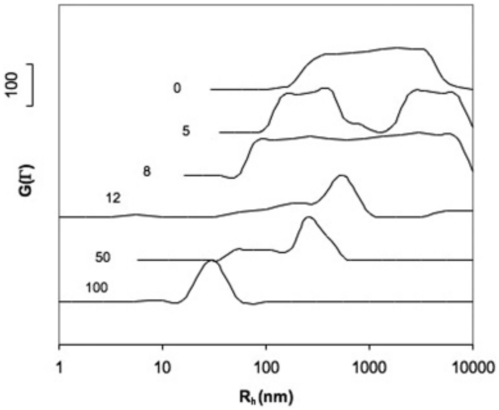


Figure 9. Hydrodynamic radii R_h distributions of Nafion−PAA blends in 3/1 isopropyl alcohol/water, 5 mg/mL, obtained at 25 °C and at a scattering angle $\theta = 90°$. The numbers on the graph represent the weight percent content of PAA in the blends. The distributions are offset here for legibility.

and Figure 6b). At a higher concentration of 1.25 wt %, PAA electrospins (Figure 8a-3) but results in larger fibers and a broad distribution of sizes compared to its Nafion−PAA analogue (25% PAA; Figure 8b-3). This may be a result of lower solution conductivity at this viscosity (Figure 7). These results suggest that viscosity alone does not contribute to the electrospinnability of the Nafion−PAA blends. In fact, in the Nafion−PAA blends, not only does PAA improve the electrospinnability of Nafion but Nafion also enhances the fiber formation of PAA at low concentrations.

To understand the effect of PAA on improving the spinnability of Nafion further, the solution properties (aggregate sizes) of the blend solution were examined by dynamic light scattering (Figure 9). A DLS study of 1 mg/mL PAA solution in isopropyl alcohol/water showed a narrow distribution of hydrodynamic radii with an average value of 36 nm. This is related to the length of a single PAA polymer chain (M_v = 450 000). As described previously, Nafion in isopropyl alcohol/water cosolvent exists in two types of aggregate sizes, 200 nm to 1 μm and above 1 μm, respectively. In the 5 mg/mL blend solution, two sizes of aggregates were still clearly observed at 5% PAA. As PAA approaches the suggested entanglement content of 8%, particle sizes below 100 nm were detected and a broader size distribution was observed. A further increase in PAA content resulted in the disappearance of large aggregates above 1 μm. Instead, a narrow distribution of 500 nm to 1 μm medium particles and a broad distribution of 50−500 nm small particles were observed at 12% PAA. At 50% PAA, the medium particle sizes reduced to 200−700 nm, and the range of 50−200 nm small particles enlarged. Apparently, the existence of PAA suppresses the formation of secondary aggregates (>1 μm) at 12% or higher PAA content. There are two distributions: one at sub-hundred-nanometer region corresponds to PAA single chains; the other at 200−700 nm corresponds to primary aggregates of Nafion. Comparing pure Nafion and PAA DLS data shows that Nafion (a sulfonic acid containing polymer) does not behave similar to typical polyelectrolytes in solution, resulting in a higher level of difficulty for electrospinning. Unlike PAA (linear architecture), Nafion has a branched architecture with a fluorocarbon backbone and superacid pendant groups terminating each branch. This results in an aggregate formation in solution, unlike typical linear polyelectrolytes, which dissolve in a good solvent. The lack of chain entanglement due to this aggregate formation results in its inability to electrospin. Breaking up this aggregate formation in complex polyelectrolytes like Nafion appears to be the key to electrospinnability.

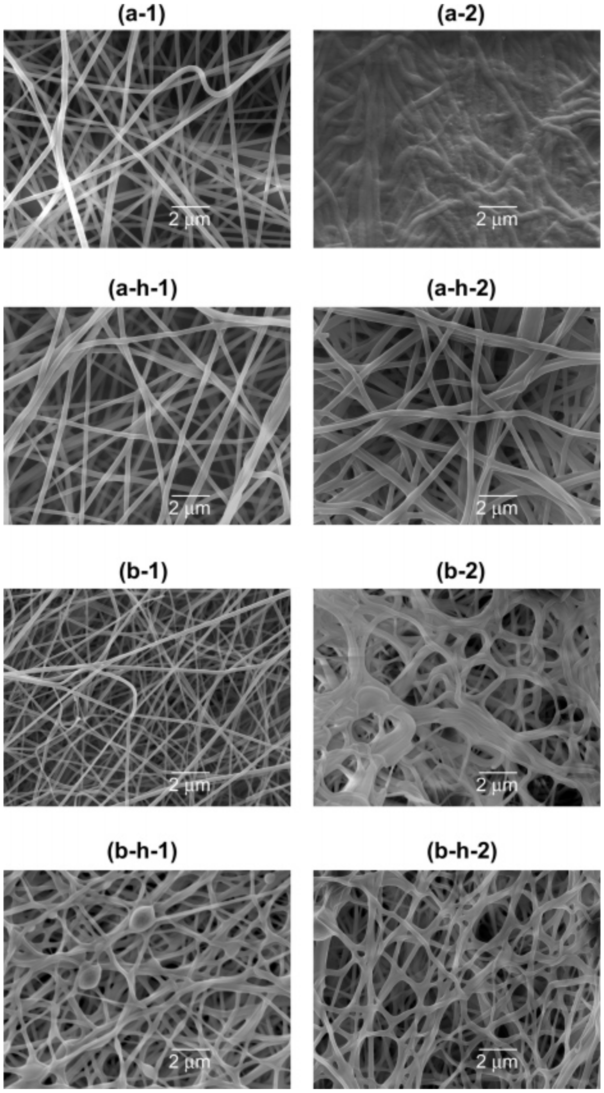


Figure 10. SEM images of Nafion−PAA electrospun fibers with a PAA content of (a) 50 and (b) 16%: (h) heat treated at 140 °C for 10 min; (1) imaged before water exposure; (2) imaged after 3-day water exposure.

A possible reason for the suppression of the Nafion aggregate structure could be the increased ionic strength of the solvent in the presence of the polyelectrolyte PAA. The increased ionic strength is demonstrated by the enhanced electrical conductivity from 5.5 μS for deionized water to 94.5 μS for PAA/isopropyl alcohol/water mixture. As described previously, a strengthened ionic environment screens the electrostatic interactions of ionic clusters in Nafion resulting in a more extended form of the polymer chains or more chain entagelment. Therefore, although the same suppression effect was obtained by mixing inorganic salt (e.g., NaCl) with Nafion, enough chain entanglement for electrospinning was only achieved by using a polyelectrolyte as the ionic strength modifier. In addition to the modified ionic strength, the fact that fiber formation of PAA was improved in Nafion−PAA blends suggests that there might be other unknown reasons for the enhanced spinnability of both Nafion and PAA.

Water Stability. Parts a-1 and a-2 of Figure 10 show that the Nafion−PAA fiber mat at 50% PAA loses its fibrous structure after a 10 min immersion in deionized water at room temperature. This is accompanied by a 43.5% decrease in mass. The mass loss suggests that the water-soluble PAA component dissolves out of the mat. The remaining Nafion component swells and fuses into a dense film after exposure to water. Thermal treatment of the fiber mat at 140 °C for 10 min reduces the lateral area by nearly 50% but resulted in no significant change to the fiber mat morphology (Figure 10a-h-1). The fibrous structure was still retained after immersing in water for 3 days (Figure 10a-h-2). In other words, the water stability of the mat was significantly enhanced after thermal treatment. The fiber size after water immersion increased by ~50% as a result of polymer swelling.

At a lower PAA content (16%), the fiber mat retained most of its fibrous structure after 10 min water immersion. Fibers on the outer layer of the mat fused together, probably due to dissolution of PAA and swelling of Nafion. However, a porous structure was still clearly observed (Figure 10b-2). After thermal treatment of the mat, more distinct fusion of the fibers was observed compared to the fiber mat at 50% PAA (Figure 10b-h-1). But no further change in the fiber mat morphology or mass or in the porous structure was observed after exposing the thermally treated mat to water for 3 days (Figure 10b-h-2).

Nafion alone exhibits a thermal history, where annealing significantly alters its solubility in water and alcohols.[9] Also, thermal treatment above the glass transition temperature of PAA (T_g = 106 °C) can induce a dehydration reaction of the carboxylic acid groups, resulting in covalent cross-links among the PAA chains. However, FTIR-ATR spectroscopy of the fiber mats (data not shown) was not conclusive in showing evidence of covalent cross-linking due to thermal treatment. The relaxation of polymer chains of both PAA and Nafion at high temperatures may have caused the fiber mat to shrink. The more distinct fusion behavior at higher Nafion content may result from the melting of small and imperfect crystallites in Nafion.[31]

Thermal treatment demonstrates one feasible approach to enhance the water stability of the electrospun blend fibers. Although possible anhydride cross-links may not be stable in aqueous environments over time, the carboxylic acid functional groups in PAA provide a potential avenue for a variety of cross-linking methods, which could be explored according to the application of the electrospun fiber.

Conclusions

Electrospinning branched polyelectrolytes with superacid (sulfonic acid) pendant groups (e.g., Nafion) were demonstrated in this study. This process required blending Nafion with another polyelectrolyte, PAA—a linear polymer with carboxylic acid groups. The addition of PAA promotes sufficient entanglement for proper electrospinning evidenced by solution properties, such as increased ionic strength and subsequently suppressed aggregate formation and increased viscosity. Solution viscosity, however, does not appear to be the sole reason for Nafion electrospinnability. Electrospinning pure Nafion solutions will require modifying solution properties to suppress aggregate formation (dispersion-to-solution transition) and enhance polymer chain entanglement. Unlike typical polyelectrolytes, understanding aggregation and polymer chain entanglement for sulfonated polymers in solution would be of interest for future studies. Additionally, in this study, the thermal treatment of Nafion−PAA electrospun fibers resulted in substantial improvement in the water stability of the fiber mat due the thermal history of Nafion. Water insoluble nanometer-sized fibers (ultrahigh specific surface areas) of polyelectrolytes containing sulfonic acid could have a significant impact on a variety of applications, including fuel cells.

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