Electrospinning and Stabilization of Fully Hydrolyzed Poly(Vinyl Alcohol) Fibers

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Fully (99+ %) hydrolyzed poly(vinyl alcohol) (PVA) was electrospun from water using Triton X-100 surfactant to lower the surface tension. The diameter of the electrospun PVA fibers ranged from 100 to 700 nm. Treatment of the PVA fiber mats with methanol for 8 h stabilized the fibers against disintegration in contact with water. In addition, the mats showed increased mechanical strength due to increased crystallinity following post-spinning treatment with methanol. We suggest that methanol treatment serves to increase the degree of crystallinity, and hence the number of physical cross-links in the electrospun PVA fibers. This may occur by removal of residual water within the fibers by the alcohol, allowing PVA−water hydrogen bonding to be replaced by intermolecular polymer hydrogen bonding resulting in additional crystallization. Potential applications of electrospun PVA include filters, precursors to graphitic fibers, and biomedical materials.

Introduction

Electrospinning is a straightforward, convenient, and inexpensive method of preparing polymer fibers at submicron scales.[1−7] In electrospinning, a high electric potential is applied to a polymer solution or melt (most typically a solution). The fibers are derived by charging a liquid typically to 5−30 kV vs a ground a short distance away, which leads to charge injection into the liquid from the electrode. The sign of the injected charge depends on the polarity of the electrode; i.e., a negative electrode produces a negatively charged liquid. The charged liquid is attracted to the ground electrode of opposite polarity, forming a so-called Taylor cone at the nozzle orifice as the polymer solution is drawn out by the electric field to form a liquid jet. As the solvent of the polymer jet evaporates, the jet solidifies and a polymer fiber is formed. In the past decade, substantial attention was drawn to electrospinning with research interests focusing on the theoretical foundation of the electrospinning process, including fiber initiation, jet instability, and the structure and morphology of the electrospun fibers.[1−6]

Of particular interest to us is the creation of fibrous polymers for a variety of applications including precursors to carbonaceous materials,[8] tissue engineering scaffolds,[9,10] and controlled drug delivery platforms.[11] Our laboratories have been especially interested in the electrospinning of poly(vinyl alcohol) (PVA) because it is an inexpensive material which is biocompatible. Furthermore, because PVA is not degradable in most physiological situations, it is useful for long-term or permanent scaffolds in tissue engineering. For example, PVA hydrogels have been utilized in regenerating artificial articular cartilage[12] and constructing an artificial pancreas.[13] Because PVA is derived from the hydrolysis (or alcoholysis) of poly(vinyl acetate), it is available in a variety of degrees of hydrolysis. We[14] and others[15−17] have electrospun partially (87−96%) hydrolyzed PVA from water, but we have been specifically

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(14) In some cases, the % hydrolysis of the PVA used in earlier studies is not clear. We find that 87−88% hydrolyzed PVA with number average MW of 124 000−186 000 (Aldrich) electrospins readily from 10% w/v water solution at a feeding rate of 0.5 mL/h; fiber diameters ranged from 100 to 300 nm. We also electrospun the 10 wt % of 96% hydrolyzed PVA with MW 85 000−146 000 (Aldrich) in water using a 2.5 kV/cm electric field. The average electrospun fiber diameter was about 200 nm.

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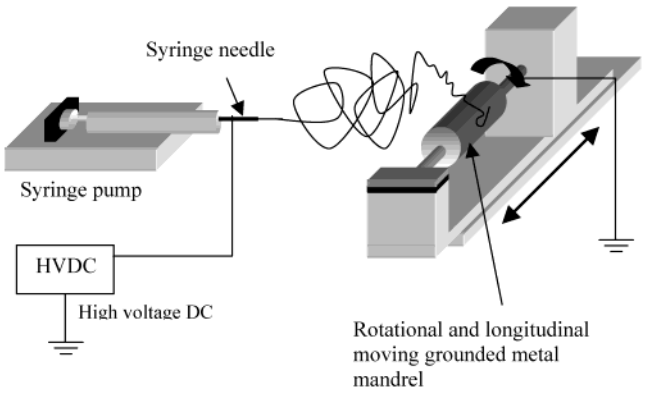

Figure 1. Schematic of electrospinning device.

interested in more completely (>99%) hydrolyzed PVA. Toward that end, we found that aqueous solutions of fully hydrolyzed PVA, at least under the conditions we routinely employ and without additives, will not electrospin; rather, sporadic electrospraying of droplets is observed. However, electrospinning was successfully accomplished with the use of a surfactant, and the details of this modification are discussed in the present paper. We also discuss a simple approach to stabilize the fibers against disintegration in water without the need for covalent cross-linking.

Experimental Section

Aqueous PVA solutions (10 wt %) were prepared by dissolving PVA powder (99+% hydrolyzed, number average MW 115 000 g/mol) (Aldrich Chemical, Milwaukee, WI) in deionized water at 80 °C with constant stirring for at least 12 h. When the solution was cooled to room temperature, Triton X-100 (Sigma-Aldrich, St. Louis, MO) in the concentration range between 0.03 and 1.5 v/w % was added. The mixture was stirred further for 10−15 min before electrospinning. The configuration of the electrospinning setup used in this study is shown in Figure 1. It consists of a syringe with a flat-end metal needle, a syringe pump for controlled feeding rates, a grounded cylindrical stainless steel mandrel, and a high-voltage DC power supply (Spellman, CZE 1000R, Spellman High Voltage Electronics Corp., Hauppauge, NY). In a typical electrospinning experiment, PVA solution was transferred into a syringe and delivered to the tip of the syringe needle by the syringe pump at a constant feed rate (0.7−2.0 mL/h). A 25-kV positive voltage was applied to the PVA solution via the stainless steel syringe needle. The subsequently ejected polymer fiber was collected on the rotating, cylindrical stainless steel mandrel, which was rotated and moved longitudinally simultaneously during the electrospinning process. The distance between the tip of the needle and the surface of the mandrel was about 10 cm. Electrospun PVA mats were stabilized against disintegration in water by treatment with methanol for several hours (8−24 h; 24 h is typical). Then, the methanol-treated PVA mat was dried in a ventilated hood at room temperature for 24 h.

Contact angles of PVA solutions were measured on hydrophobically modified glass microscope slides using a goniometer (NRL C. A. Goniometer, Ramé-Hart Inc., Mountain Lakes, NJ) to track changes in surface tension of 100% hydrolyzed PVA/Triton solutions as a function of surfactant concentration. The surfaces of glass microscope slides were modified using octadecyltricholorsilane (OTS) as follows. Glass slides were sequentially cleaned by ultrasonication in acetone (1 min), isopropyl alcohol (1 min), and 4:1:1 $H_2O/NH_4OH/H_2O_2$ (10 s), then immersed in a solution of 0.1 v/v % OTS in anhydrous toluene at 40 °C for 30 min. The slides were then rinsed with dried toluene 3× and dried at 110 °C for 20 min. In a contact angle measurement, a droplet of PVA solution was vertically placed on an OTS-modified glass slide from a fixed height, and the contact angle was directly measured from the focusing lens of the goniometer. Because OTS provided hydrophobic surfaces on the substrate, deionized water on the hydrophobic OTS surface has a relatively high contact angle (102°), and this angle was expected to decrease upon addition of surfactant.

Table 1. DSC Results on Electrospun PVA Mats Before and After Methanol Treatment

sample	electrospun mat without methanol soaking	electrospun mat soaked in methanol for 8 h	electrospun mat soaked in methanol for 24 h
T_m (°C)	229	232	231
ΔH (J/g)	72.4 ± 1.0	82.7 ± 2.1	81.6 ± 1.0
degree of crystallinity (%)	52.2 ± 0.7	59.7 ± 1.5	58.8 ± 0.8

The morphology of PVA mats was characterized using scanning electron microscopy (SEM) (JEOL JSM-820, JEOL (U.S.A.), Inc., Peabody, MA) and polarized light microscopy (Leica DM IRBE, Leica Microsystems AG, Wetzlar, Germany). For optical microscopy, PVA fibers were collected on a microscope glass slide during the electrospinning process. The slide was soaked in methanol for 1 h and then dried in air. A few drops of water were placed on top of the fibers (both untreated and treated) and examined simultaneously under light microscope before the water was evaporated.

Differential scanning calorimetry (DSC) (Perkin-Elmer Pyris DSC 1, PerkinElmer Instruments, Shelton, CT) was used to characterize the thermal properties of the electrospun PVA mats. A piece of PVA mat (5−10 mg) was placed in an aluminum sample pan and heated from 30 to 250 °C at 5 °C/min under N_2. A melting peak was observed at approximately 230 °C for all samples (Table 1). The degree of crystallinity was calculated by dividing ΔH by the heat required for melting a 100% crystalline PVA sample (ΔH_c = 138.6 J/g).[18]

The mechanical properties of the electrospun PVA mats were characterized using a dynamic mechanical analysis (DMA) instrument (Rheometrics RSA II, Rheometric Scientific Inc, Piscataway, NJ). For DMA tests, the specimens were cut into rectangular bars with a typical geometry of 6 mm wide, 21 mm long (between the grips), and 0.08 mm thick. The elastic modulus (E′) and loss modulus (E″) were obtained during a frequency sweep (1−100 rad/s) in tension at room temperature. The DMA tests were performed on the dry mats before and after methanol treatment under ambient conditions. A methanol-treated (24 h), water-swollen (over 10 days) mat was also studied, and water was constantly sprayed on the mat during the measurements to prevent dehydration of the sample.

Results and Discussion

PVA Electrospinning. Electrospinning occurs when the applied electrical voltage exceeds a critical electrical potential at which the electrostatic force overcomes the surface tension of the polymer solution. A droplet of polymer solution at the needle tip is deformed into a conical shape, the Taylor cone, from which a jet of polymer solution is initiated. Taylor[19] established the dependency of the critical potential of forming a cone at the end of a capillary tube according to

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$$\left(\frac{V_c}{H}\right)^2 = \frac{4}{L^2}\left(\ln\frac{2L}{R} - \frac{3}{2}\right)(0.117\pi\gamma R)$$

where V_c is the critical electrical voltage, H is the separation between the tip of the capillary and the ground, L is the length of the capillary, R is the radius of the capillary, and γ is the surface tension of the solution. From the above equation, one can see that the critical electric voltage of formation of a Taylor cone is proportional to the surface tension of the solution provided that H, L, and R are fixed. Thus, solutions with high surface tension require a higher voltage to initiate the Taylor cone and thus the fiber jets.

The surface tension of aqueous PVA solutions exhibits a marked dependence on the degree of hydrolysis of the PVA.[20] The rise of surface tension becomes more pronounced as the degree of hydrolysis approaches 100%. For example, the surface tension increases from 51 to 54 dyn/cm when the degree of hydrolysis is increased from 87 to 95%, and then sharply increases to ca. 69 dyn/cm when the degree of hydrolysis is ca. 99.5%.[20] The surface tension of pure water is ca. 73 dyn/cm. It seemed that the inability to electrospin 100% hydrolyzed PVA water solution was the result of its high surface tension, and that the critical electric field needed to overcome the surface tension to form a Taylor cone may be beyond the limit of our setup. To facilitate the electrospinning of 100% hydrolyzed PVA, a small amount of diluted Triton X-100, a nonionic surfactant, was used to lower the surface tension of the PVA solution.[21] When 25 kV was applied to the 100% hydrolyzed PVA/Triton solution with a ca. 10-cm needle tip to target distance, a fine jet of polymer was immediately ejected from the polymer droplet at the tip of the needle. Continuous PVA fibers were deposited on the rotating cylindrical stainless steel mandrel and collected in the form of a nonwoven, fibrous mat. Contact angle measurements on hydrophobically modified glass surfaces were used to monitor the efficacy of Triton X-100 to lower, and so adjust, the surface tension of 100% hydrolyzed PVA/water solutions. The contact angle of 10 wt % of 100% hydrolyzed PVA water solution without Triton X-100 was as high as that of pure deionized water, 101.2 ± 0.4°.[22] By addition of a small amount of surfactant, the contact angle of the 100% hydrolyzed PVA solution was significantly lowered (Figure 2). The contact angle of the aqueous 10 wt %, 100% hydrolyzed PVA solution decreased dramatically with an increase of Triton X-100 concentration and then leveled off when the surfactant concentration was about 0.3 v/w %, yielding a contact angle of about 60°. Further addition of surfactant has little effect on the contact angle of the polymer solution. The electrospinning feasibility of 100% hydrolyzed PVA/Triton solutions was examined at 2.5 kV/cm. When the surfactant to PVA concentration was below 0.06 v/w %, corresponding to a contact angle of about 86°, electrospraying of small droplets was dominant. Electrospraying resulted in the formation of combinations of isolated droplets and small pieces of PVA film, the latter presumably due to coalescence of wet droplets followed by evaporation of water. When the surfactant to PVA concentration was between 0.1 and 0.2 v/w %, corresponding to contact angle of 77−65°, electrospraying was accompanied by some electrospinning of fibers. Electrospinning began to dominate when the surfactant concentration was about 0.3 v/w %. The 100% hydrolyzed PVA solution electrospun particularly well when its contact angle was about 54−60°. The diameters of the resulting PVA fibers ranged from 100 to 700 nm, with the majority in the 300−500 nm range as observed by SEM in Figure 3a.[23]

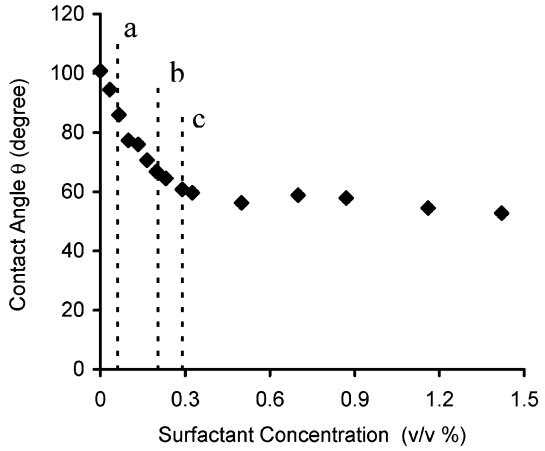

Figure 2. Effect of surfactant (Triton X-100) concentration with respect to PVA on contact angle of 100% hydrolyzed PVA solution on OTS surfaces. Electrospraying dominated in the region left of dotted line a. In the region between dotted lines a and b, electrospraying was still dominant but accompanied with some electrospinning. Electrospinning dominated in the region to the right of dotted line c.

Although we observe an empirical correlation between a decrease in surface tension and the onset of electrospinning, other factors may be in play, including the possibility of localized gel formation in the solutions interfering with electrospinning but which may be suppressed by the addition of surfactant.[24]

Stabilization of PVA Fibers Against Dissolution in Water. When an electrospun PVA mat (which is white because of light scattering from the fibrous structure) is immersed in water, the mat instantaneously shrinks and becomes a clear, gelatinous material. Thus, the unique nanofibrous structure of the electrospun material is lost in an aqueous environment. PVA can be chemically cross-linked with a variety of substances including glutaraldehyde, acetylaldehyde, or formaldehyde.[25,26] Recently, Ding et al.[17] prepared PVA nanofiber aggregates using the tetrafunctional cross-

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(21) Other surface-tension-lowering substances can also be used. For example, poly(ethylene glycol) monomethyl ether, MW = 550 g/mol, at a concentration of 10 v/w of >99% hydrolyzed PVA also promotes electrospinning.

(22) As the degree of hydrolysis decreases, the contact angle of the PVA solutions (10 wt %) decreases. The contact angles of 96% hydrolyzed PVA and 87−88% hydrolyzed PVA solution on OTS-modified glass were 82.5 ± 0.5° and 72.7 ± 0.3°, respectively.

(23) Occasionally, the fibers electrospun from PVA/Triton solution had "beads" along the polymer fibers, known as "beads-on-string" morphology.[5, 15] Bead formation could be essentially suppressed by adding a small amount of acetic acid to the PVA/Triton solution prior to electrospinning to afford smoother fibers. This is likely due to the increase of the net charge density of the polymer solution by addition of acetic acid. See also, for example: Jia, H.; Zhu, G.; Vugrinovich, B.; Kataphinan, W.; Reneker, D. H.; Wang, P. *Biotechnol. Prog.* **2002**, *18*, 1027. Ionic surfactants may be particularly useful for PVA electrospinning, and studies of their efficacy are in progress.

(24) We thank a reviewer for suggesting this possibility.

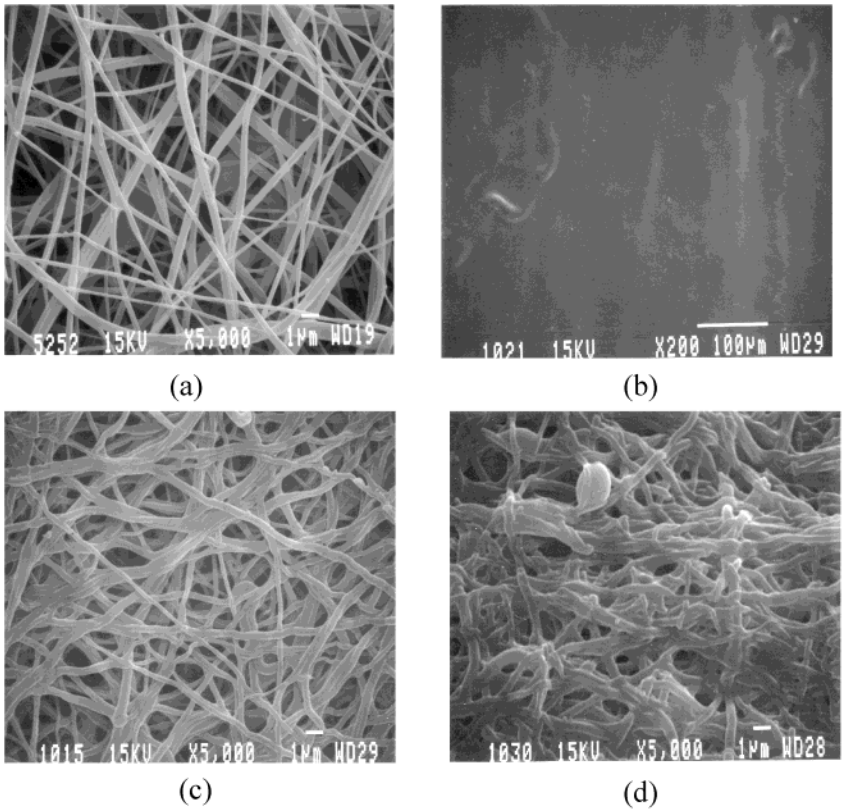

Figure 3. SEM photos of (a) original electrospun PVA mat without any methanol treatment; (b) mat of (a) after immersion in water for 1 h; (c) electrospun PVA mat after soaking in methanol for 24 h; (d) mat of (c) after 3 weeks of immersion in water.

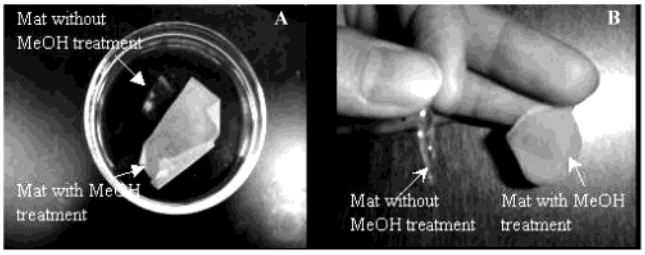

Figure 4. Comparison of electrospun 100% hydrolyzed PVA mat with and without methanol treatment in water. The methanol-treated mat had been in water for 3 weeks, whereas the mat without methanol treatment had been in water for 4 h: (a) in water; (b) without methanol soaking, the wet mat loses its physical integrity, whereas the methanol-treated wet mat is elastic.

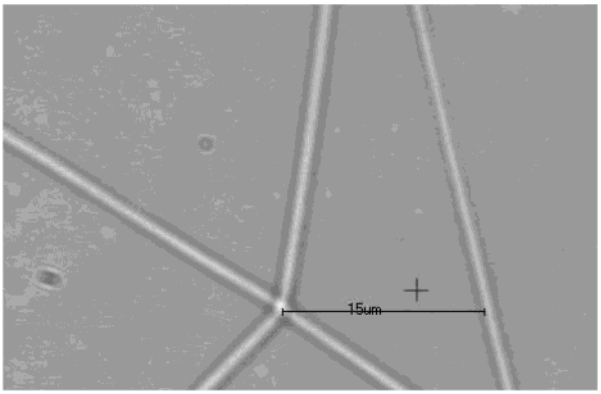

Figure 5. PVA fibers electrospun onto a glass microscope slide, soaked in methanol for 1 h, and immersed in water. Photo taken in water at the end of 3 days of continuous immersion.

linking agent glyoxal prior to electrospinning. We sought to avoid chemical cross-linking in order to mitigate the introduction of reactive species that could compromise biocompatibility. Approaches are known that produce physical hydrogels of PVA through partial crystallization, in particular the alternate freeze−thaw technique applied to PVA solutions.[27] However, we have found an apparently new and simple treatment to physically cross-link electrospun, 100% hydrolyzed PVA fibers using lower alcohols such as methanol. Soaking of an electrospun PVA mat in methanol for at least 12 h preserves the integrity of the mat when it is immersed in water. Scanning electron micrographs revealed that the fibrous morphology of an electrospun mat without methanol treatment was completely destroyed when the mat was immersed in water (Figure 3b). A methanol-treated mat (Figure 3c) appears to retain a significant degree of fibrous character even after 3 weeks of immersion in water (Figure 3d).

Figure 4 shows a visual comparison of a wet, electrospun PVA mat prior to and after methanol treatment. Without methanol treatment, even though the PVA electrospun mat does not dissolve in water, it completely loses its mechanical integrity, forming a soft, gelatinous mass (Figure 4). In contrast, the water-swollen, methanol-treated PVA mat remains as such (see also Figure 3d) and is elastic.[28] These observations can be verified with individual fibers by using a light microscope. As shown in Figure 5, methanol-treated (1 h) PVA fibers remain intact in contact with water after several days.

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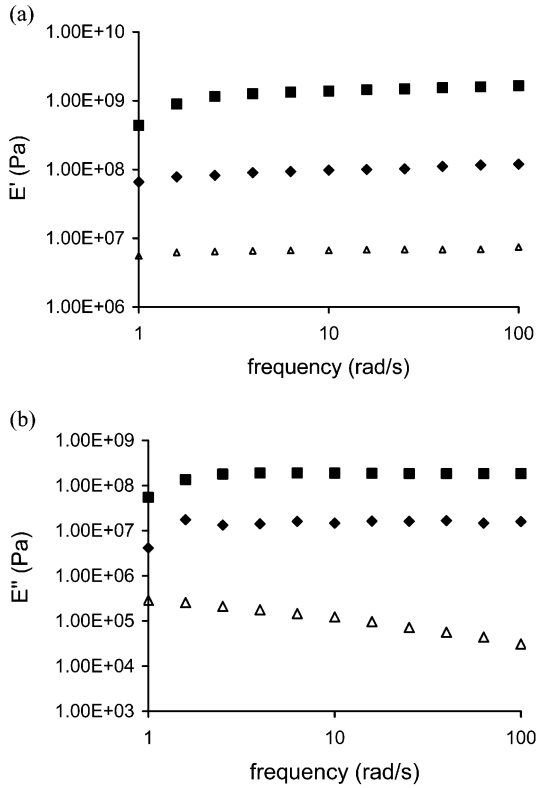

Figure 6. Storage modulus (a) and loss modulus (b) of electrospun PVA mats: dry mat without methanol treatment under ambient conditions (◆), dry mat after soaking in methanol for 20 h under ambient conditions (■), and water-swollen, methanol-treated (20 h) mat (△).

We speculated that methanol treatment served to increase the degree of crystallinity, and hence the number of physical cross-links in the electrospun PVA fibers. This may occur by removal of residual water within the fibers by the alcohol, allowing PVA−water hydrogen bonding to be replaced by intermolecular polymer hydrogen bonding resulting in additional crystallization. (Extraction of residual surfactant may also promote some local crystallization.) Toward that end, we determined the degrees of crystallinity for treated and untreated mats from DSC experiments, the results of which are summarized in Table 1. The original, 100% hydrolyzed PVA mat was partially crystalline with degree of crystallinity about 52%.[29] Soaking it in methanol affords an additional ca. 7% crystallinity, or an increase of about 13% relative to the initial amount. There is little dependence of the degree of crystallinity on methanol soaking time beyond about 8 h of immersion.[30]

(28) We find that soaking the mat in either 95% ethanol or rubbing alcohol, 70/30 v/v % 2-propanol/water, also stabilizes the mats. Such treatments do not appear to stabilize PVA with a lower degree of hydrolysis (e.g., 87%), presumably because crystallization is more difficult with acetate "defects."

Table 2. Elastic Moduli of Electrospun PVA Mats at 1 Hz

sample	electrospun mat without methanol soaking	electrospun mat soaked in methanol for 20 h
dry mat	93 ± 12 MPa	1331 ± 162 MPa
wet mat		6.7 ± 0.7 MPa

The results of dynamic mechanical testing of PVA electrospun mats are shown in Figure 6. The frequency sweep from 1 to 100 rad/s indicates that, in all cases, the elastic (or storage) modulus, E′, increases with frequency over the frequency range. This is a typical characteristic of the viscoelastic response of polymers. Note that data on wet PVA mats without methanol treatment are not available because these materials have essentially no mechanical integrity. Methanol treatment not only preserved the fibrous structure of the PVA mat but also significantly increased the mechanical strength of the mat. The elastic modulus of the dry mats increased by a factor of 10 after methanol treatment (Table 2). When immersed in water, methanol-treated PVA mats swelled significantly, thus softening the material yet affording the characteristics of a mechanically stable hydrogel.[31] It is also worth noting that the loss modulus, E″, of the wet, methanol-treated mat decreased with increasing frequency in contrast to the dry mats. Apparently, less energy per cycle is able to be dissipated by the methanol-treated, water-plasticized mats.

Conclusions

The addition of small amounts of Triton surfactant affords the reproducible electrospinning of fully hydrolyzed PVA. Importantly, the electrospun PVA fibers can be stabilized against disintegration in water by a simple soak in methanol. It is concluded that methanol treatment increases the degree of crystallinity of the PVA fibers, thereby increasing the number of physical cross-links responsible for fiber stabilization in water.

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(29) This is about 17% higher than the PVA film cast from the same solution. This increase of degree of crystallinity of the electrospun mat may be due to partial drawing of polymer chains during the electrospinning process that enhances the formation of crystallites. Studies on cast films with and without alcohol treatment are underway and will be reported elsewhere.

(30) We are working to establish the time scale for alcohol-induced stabilization of the PVA fibers. As indicated in Figure 5, experiments on thin mats electrospun onto glass microscope slides indicate that 1 h of treatment is effective. Additional experiments suggest that as little as 30 min of treatment is sufficient.

(31) When immersed in water, methanol-treated PVA mats exhibit properties of a hydrogel. The water uptake of the methanol-treated PVA mat (24-h methanol soak) was about 250%.