

NOTE

Electrospun poly(vinyl alcohol) nanofibers: effects of degree of hydrolysis and enhanced water stability

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INTRODUCTION

Poly(vinyl alcohol) (PVA) is a highly hydrophilic, nontoxic and biocompatible semicrystalline polymer with excellent properties such as strength, water solubility, gas permeability and thermal characteristics. PVA is available in a variety of degrees of hydrolysis (DH) because it is derived from the hydrolysis (or alcoholysis) of poly(vinyl acetate) (PVAc).^{1–3} The properties of PVA are therefore affected by DH. A PVA with DH between 87 and 89% has lower mechanical and water resistance than a PVA with DH between 98 and 99.9%. Consequently, the potential to interact with other polar polymers would be expected to vary as a function of DH. In recent years, electrospinning has become of great interest, not only because it can produce polymer fibers with diameters in the range of nano- to a few micrometers using polymer solutions or melts but also because it has the advantage of being a simple, conventional method with which a wide range of porous structures can be produced, as well as being inexpensive as compared with conventional methods.^{4–8} The electrospinning of the PVA solution has been extensively studied for the preparation of ultrafine separation filters, biodegradable mats and inorganic fibers. The dissolution of PVA depends on the nature of the solvent, the temperature and the extent of hydrolysis in the polymer. Depending on the rheological characteristics of the solution, electrospinning of a polymer solution can produce a variety of structures, mostly including beads, beaded fibers and fibers.^{9,10} Various solution parameters affecting the morphology and diameter of electrospun PVA fibers, such as the solution concentration, molecular weight,¹¹ pH,¹² salt,¹³ surfactant molecules¹⁴ and so on, have been investigated. However, the effect of DH on the morphology and diameter of electrospun PVA fibers has been less studied. In addition, PVA forms excellent nanofibers through electrospinning, but its applications are limited by its high hydrophilicity, through which it dissolves immediately on contact with water. Therefore, PVA fibers have been modified by either chemical¹⁵ or physical¹⁶ crosslinking to improve

their mechanical properties and water resistance. In this study, we report the effects of DH on the morphology and diameter of electrospun PVA fibers and also explore the water resistance of electrospun PVA/poly(acrylic acid) (PAA) composite fibers through heat treatment.

EXPERIMENTAL PROCEDURE

Materials

PVA with various degrees of hydrolysis (DH=88, 96 and 99.9% hydrolyzed) and the same degree of polymerization=1700 was kindly provided by Kuraray Co. Ltd, Tokyo, Japan. The PVA solution with a DH of 92% was separately prepared by mixing the same weight ratio (1:1, v/v) of two PVA solutions with a DH of 88 and 96%. PAA with a molecular weight of 250 kDa was purchased from Wako, Osaka, Japan. All chemicals were of analytical grade and were used without further purification. Distilled water was used as the solvent.

Electrospinning

A high-voltage power supply (Har-100*12, Matsusada Co., Tokyo, Japan), capable of generating voltages up to 100 kV, was used as the source of the electric field. The PVA solutions dissolved in distilled water were supplied through a plastic syringe attached to a capillary tip with an inner diameter of 0.6 mm. The copper wire connected to a positive electrode (anode) was inserted into the polymer solution, and a negative electrode (cathode) was attached to a metallic collector. The voltage was fixed at 10 kV. The distance between the capillary tip and the collector was fixed to be 15 cm, and the plastic syringe was placed at an angle of 10° from the horizontal direction. The concentration of PVA solutions was in the range of 8–12 wt%. To improve the solubility of the PVA polymer, the PVA solution was heated to about 80 °C so as to disrupt the strong intra- and interchain bonding that may exist in PVA polymers. PVA/PAA composite fibers were obtained using the same strategy. Briefly, PVA/PAA solutions for electrospinning were prepared by blending the PVA solution with the PAA solution at various PAA weight fractions (ϕ_{PAA}). The concentrations of both the PVA and the PAA solutions were controlled to be ca. 12.0 wt%. All solutions were electrospun onto a rotating metallic collector at room temperature under identical conditions.

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Measurement

The conductivity and surface tension of PVA solutions were measured using a conductivity meter (G-series, CM-40G, TOA Electronics Ltd, Aichi, Japan) and a Wilhelmy plate method with a tensiometer (CBVP-Z, Kyowa Interface Science Co. Ltd, Saitama, Japan), respectively. Viscosities were measured using a viscometer (DV-1, Brookfield Co., Stoughton, MA, USA) with spindle No. 63 at 100 r.p.m. at room temperature. Fiber morphology, average fiber diameter and distribution of the electrospun PVA fibers were characterized using scanning electron microscopy (SEM, VE-8800, Keyence Co., Tokyo, Japan) on samples sputtered with Palladium-Platinum.

RESULTS AND DISCUSSION

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. Therefore, a low surface tension is desirable in electrospinning, as it reduces the critical voltage (V_c) needed for the ejection of the jet from the Taylor's cone. The surface tension of aqueous PVA solutions exhibits a marked dependence on the DH of the PVA, which may result in an altered spinnability. For instance, Wnek and colleagues¹⁴ reported that the addition of small amounts of Triton surfactant improves the electrospinnability of fully (>99%) hydrolyzed PVA, probably because of lowered surface tension and retarded PVA gelation, and therefore affords reproducible electrospinning. Figure 1 (top) shows SEM images of PVA fibers electrospun from the solution with various DH. The concentration of the PVA solution was 8.0 wt%, which is the

minimum polymer concentration for fiber formation in our study. Below this critical value, the application of voltage resulted in electrospaying or bead formation, primarily because of a Rayleigh instability. At a given concentration, the fiber diameter and interfiber spacing increased with increasing DH of the PVA. The average diameters of the PVA fibers electrospun from the solutions with different DH of 88, 92, 96 and 99.9% were determined to be 190, 200, 220 and 470 nm, respectively. The fiber diameter increased exponentially with respect to the DH of the PVA (Figure 1, bottom). In addition, in the case of DH=99.9%, poor spinnability was observed because of a combination of higher surface tension and the tendency of PVA to undergo gelation through a strong hydrogen bonding.

To investigate the effects of DH on the spinnability of PVA, PVA solutions with various DH were prepared, and solution properties, such as viscosity, electrical conductivity and surface tension, were studied. Figure 2 shows changes in (a) viscosity and (b) surface tension of PVA solutions with various DH as a function of solution concentration. As seen in Figure 2a, viscosity rapidly increased at a PVA concentration of 10 wt%, and this is responsible for the topological restrictions on molecular motion resulting from the fact that the chains cannot pass through each other, as well as being strongly dependent on the DH of the PVA. In aqueous solutions, it can be considered that the inter- and intramolecular interactions between the polar hydroxyl groups in the PVA molecules occur through hydrogen bonding and therefore influence the rheological properties

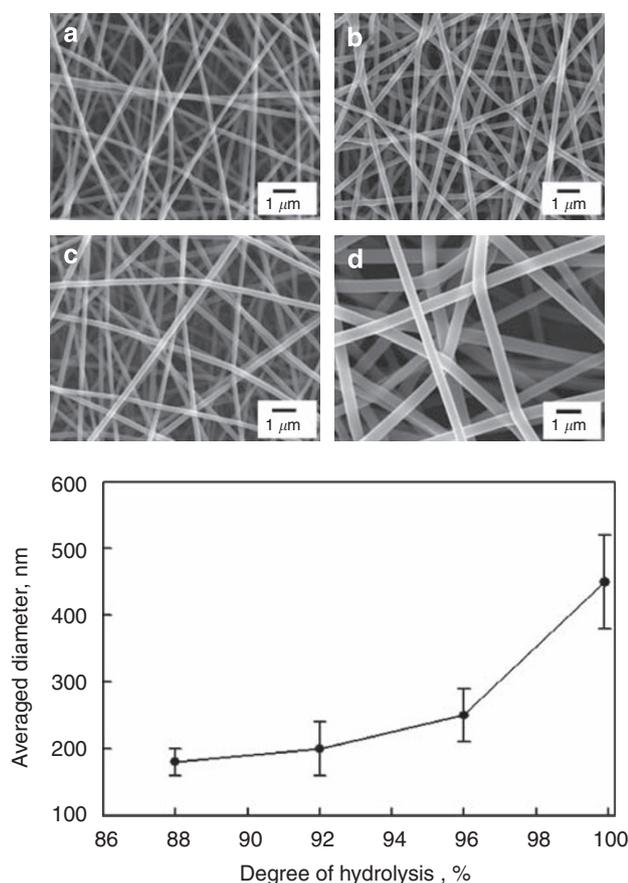


Figure 1 SEM images of electrospun PVA fibers with DH of (a) 88%, (b) 92%, (c) 96% and (d) 99.9% (top), and fiber diameters of the corresponding electrospun PVA fibers (bottom). The concentration of the PVA solution was 8.0 wt%.

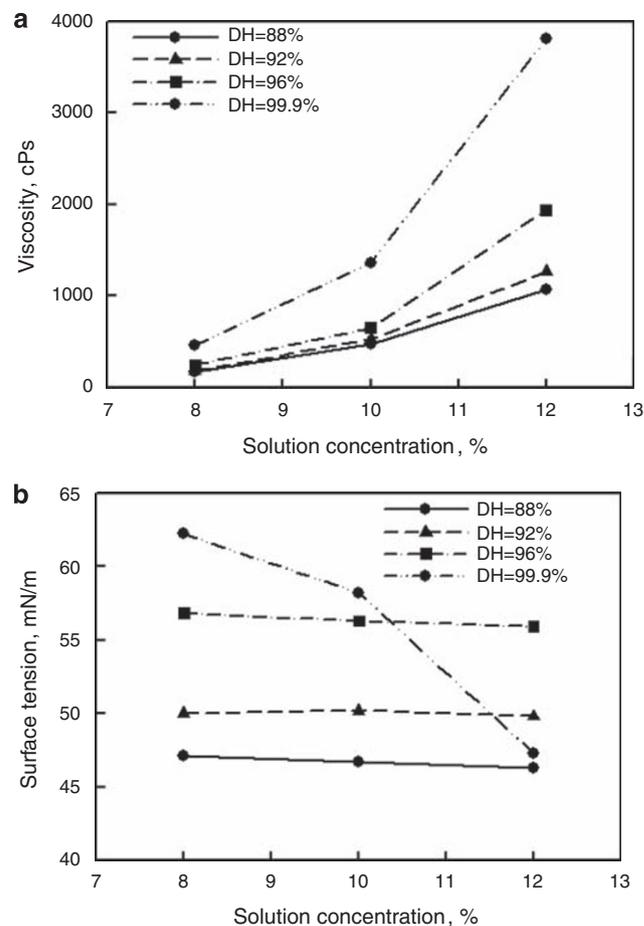


Figure 2 Changes in the (a) viscosity and (b) surface tension of PVA solutions with different DH as a function of solution concentration at room temperature.

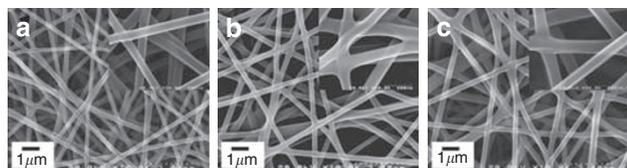


Figure 3 SEM images of PVA/PAA composite fibers electrospun from solutions with various ϕ_{PAA} . The concentration of both PVA and the PAA solutions was 8.0 wt%. (a) $\phi_{\text{PAA}}=0.25$, (b) $\phi_{\text{PAA}}=0.50$ and (c) $\phi_{\text{PAA}}=0.75$.

of the PVA solutions. Moreover, the surface tension of PVA solutions at a constant concentration markedly increased with increasing DH of the PVA, whereas the surface tension was not affected by the solution concentration of the PVA (Figure 2b). Specifically, in the case of DH=99.9%, the decreased surface tension at higher concentration may be due to the formation of strong intra- and interchain bonding in PVA chains, giving rise to physically gelling structures.¹¹ As expected, the average diameter of the electrospun PVA fibers (DH=88%) increased with increasing solution concentration of the PVA, and this value was found to be 190, 280 and 350 nm for the solution concentrations of 8, 10 and 12 wt%, respectively.

In addition, PVA/PAA composite fibers were prepared by the electrospinning of PVA/PAA blend solutions with different PAA weight fractions (ϕ_{PAA}). Compared with electrospun pure PVA fibers, electrospinnability was markedly improved, probably because of a dramatically decreased surface tension, which is discussed later. Figure 3 shows SEM images of PVA/PAA composite fibers electrospun from solutions with various ϕ_{PAA} . The concentration of both the PVA and PAA solutions was fixed at 8.0 wt%. As seen in Figure 3, the resultant PVA/PAA composite fibers were rather uniform, and the fiber diameter and its distribution increased with increasing ϕ_{PAA} in the PVA/PAA blend solutions. However, in the case of pure PAA, many beads were observed, and the distribution of the fiber diameter was much broader (data not shown). By contrast, the PVA/PAA blends exhibited better electrospinnability than did pure PAA. The average diameters of the PVA/PAA composite fibers electrospun from the blend solutions with different ϕ_{PAA} values of 0.25, 0.50 and 0.75 were determined to be 300 ± 80 , 290 ± 90 and 220 ± 50 nm, respectively. Figure 4 shows the viscosity of the PVA/PAA blend solutions as a function of ϕ_{PAA} . As seen in Figure 4, viscosity initially increased dramatically, then reached a maximum at $\phi_{\text{PAA}}=0.50$, which is close to a molar ratio of $[-\text{OH in PVA}]/[-\text{COOH in PAA}] \cong 1.0$ (here, $\phi_{\text{PAA}} \approx 0.60$), and finally decreased. As a result, the change in solution viscosity can be considered as the $-\text{OH}$ groups in PVA forming an intermolecular complex with the $-\text{COOH}$ groups in PAA through hydrogen bonding. It may therefore be expected that the strongest interactions between PVA and PAA occur at around $\phi_{\text{PAA}}=0.5-0.6$, and thereby bring about the highest viscosity.

Not surprisingly, as-spun pure PVA fibers are readily soluble in water at room temperature. Therefore, to improve the water resistance of electrospun PVA fibers, PVA/PAA blend solutions with different ϕ_{PAA} values were electrospun, and the resulting PVA/PAA composite fibers were heat treated at 100°C for 1 h. Figure 5 shows SEM images of PVA/PAA composite fibers after contact with pure water for 1 h, followed by vacuum drying. As seen in Figure 5, interestingly, for the PVA/PAA composite fibers with $\phi_{\text{PAA}}=0.5$, the fibrous morphologies were completely conserved, indicating a dramatically enhanced water resistance of the corresponding PVA/PAA composite fibers.¹⁷ This indicates that chemical crosslinking between PVA and PAA that occurred through an ester formation between the $-\text{OH}$ groups in

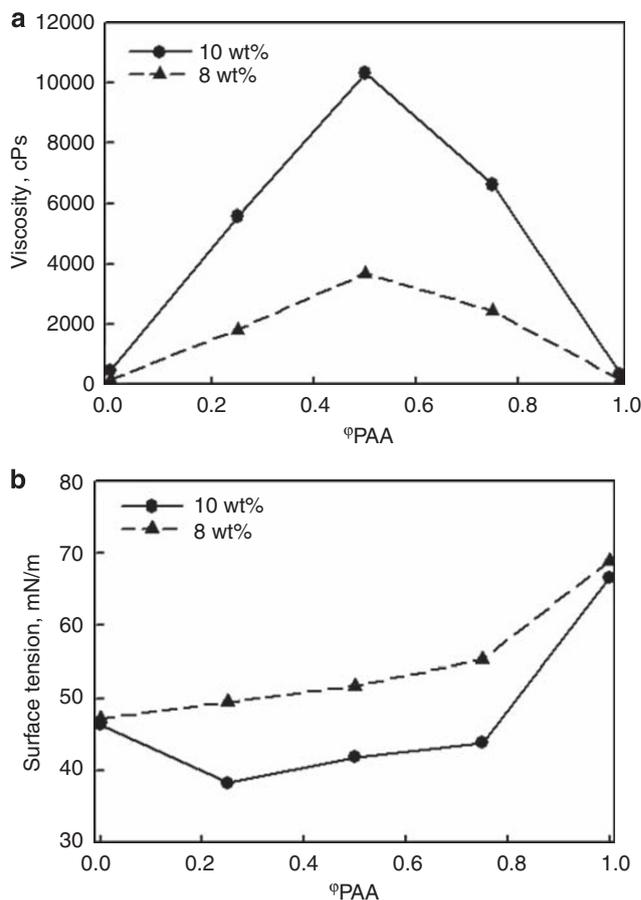


Figure 4 Changes in the (a) viscosity and (b) surface tension of PVA/PAA blend solutions as a function of ϕ_{PAA} . The arrow indicates the ϕ_{PAA} value for the formation of stoichiometric hydrogen bonding between the $-\text{OH}$ in PVA and the $-\text{COOH}$ in PAA.

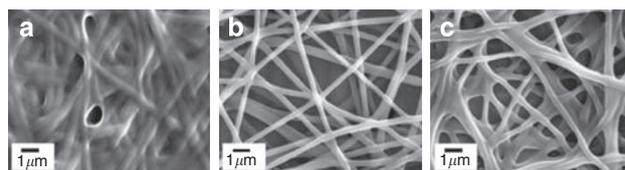


Figure 5 SEM images of PVA/PAA composite fibers after contact with water for 1 h, followed by vacuum drying. (a) $\phi_{\text{PAA}}=0.25$, (b) $\phi_{\text{PAA}}=0.50$ and (c) $\phi_{\text{PAA}}=0.75$.

PVA and the $-\text{COOH}$ groups in PAA during heat treatment at 100°C for 1 h, which was confirmed by the Fourier transform infrared (FT-IR) analysis (Figure 6). Even though the FT-IR spectrum of heat-treated PVA/PAA composite fibers ($\phi_{\text{PAA}}=0.75$, Figure 6b) shows a considerable amount of $-\text{OH}$ groups (3450 cm^{-1}) left in the polymers, it can be clearly seen that the $-\text{C}=\text{O}$ stretching vibration at 1640 cm^{-1} becomes stronger after heat treatment. This indicates that the $-\text{C}=\text{O}$ stretching vibration (1715 cm^{-1}) is normally shifted to the right (lower frequencies) through an ester ($-\text{C}(\text{O})\text{O}$) formation between the $-\text{OH}$ groups in PVA and the $-\text{COOH}$ groups in PAA. Similar results were also observed for other samples.

The water stability of the heat-treated PVA/PAA composite fibers was also affected by ϕ_{PAA} in the PVA/PAA blend solutions. In the case of PVA/PAA composite fibers with $\phi_{\text{PAA}}=0.25$ and 0.75 , the typical porous structures and fiber morphologies in the electrospun nanofiber

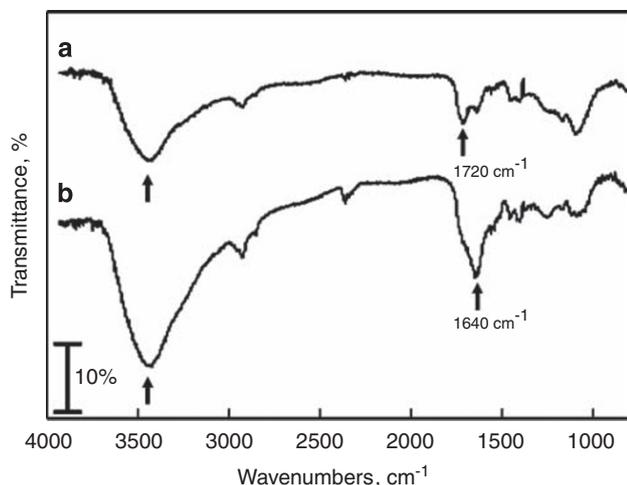


Figure 6 Fourier transform infrared spectra of PVA/PAA composite fibers ($\phi_{\text{PAA}}=0.75$) (a) before and (b) after heat treatment at 100 °C for 1 h.

disappeared because of partial swelling of excess amounts of either PVA or PAA on contact with water, suggesting that the degree of crosslinking was smaller than that of PVA/PAA composite fibers with $\phi_{\text{PAA}}=0.5$. It was concluded that water resistance increased by heat treatment and also depended on ϕ_{PAA} . Here, it should also be noted that extensive heat treatment at longer times and higher temperatures can also result in degradation of the resultant PVA/PAA composite nanofibers.

CONCLUSION

In summary, we examined the effects of the DH of PVA on electrospinning and also explored an enhanced water resistance of electrospun PVA/PAA composite fibers through heat treatment. We found that, at a constant concentration of PVA solution (~ 8 wt%), the average diameter of the electrospun PVA fibers increased with increasing DH, and these values were found to be ~ 190 , 200, 220 and 470 nm for the PVA solutions of DH of 88, 92, 96 and 99.9%, respectively. Moreover, the solution viscosity of PVA in water rapidly increased from 10 wt% of the PVA concentration and strongly depended on the DH of the PVA. In addition, the water resistance of heat-treated PVA/PAA composite fibers was dramatically enhanced and was also affected by ϕ_{PAA} in PVA/PAA blend solutions.

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