

Improvement of the Water Resistance of Atactic Poly(vinyl alcohol) Nanowebs by a Heat Treatment

Sung Jun Lee,¹ Se Geun Lee,² Hoyoung Kim,¹ Won Seok Lyoo³

¹Advanced Nano-Material Research Team, Daegu Gyeongbuk Institute of Science and Technology, Daegu 700-742, Korea

²Polymer Gel Research Cluster Center, Kyongsan 712-749, Korea

³Division of Advanced Organic Materials, School of Textiles, Yeungnam University, Kyongsan 712-749, Korea

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ABSTRACT: Nanoscale materials can be rationally designed to exhibit significantly changed physical, chemical, and biological properties because of the extremely small dimensions. Therefore, atactic poly(vinyl alcohol) (a-PVA) nanowebs by an electrospinning technique have very high water solubility because of their nanoscale in comparison with microscale materials such as fibers and films. In this study, a-PVA nanowebs were prepared via electrospinning under suitable conditions to form PVA webs with uniform nanofibers (fiber average diameter = 200 ± 50 nm), not a bead or bead-and-string morphology. Furthermore, to improve the water resistance of the water-soluble a-PVA nanowebs, the PVA nano-

webs were heat-treated at various heat-treatment temperatures. The melting temperature of the heat-treated PVA nanowebs shifted toward a lower temperature with an increase in the heat-treatment temperature, and this indicated that micro-network domains formed. Moreover, with the exception of a PVA nanoweb treated at an excessive heat-treatment temperature, the heat-treated PVA nanowebs showed higher crystalline and mechanical properties than a pure PVA nanoweb. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3430–3434, 2007

Key words: a-PVA; electrospinning; heat-treated

INTRODUCTION

Poly(vinyl alcohol) (PVA) is generally prepared through the saponification of poly(vinyl ester) precursors such as poly(vinyl acetate) and poly(vinyl pivalate) because vinyl alcohol rearranges to give its tautomer, acetaldehyde, which cannot be polymerized.¹ PVA is typically a water-soluble polymer that is not toxic to humans and is biodegradable. It has been used as coatings for textiles, stabilizers in industry, polarizing films, sizers, adhesives, biomaterials, drug delivery systems, contact lenses, and nanomaterials, and its uses have expanded.²

Electrospinning for the preparation of ultrafine polymer fibers has been drawing great attention because of their various applications in separation filters, wound-dressing materials, tissue scaffolds, sensors, and so forth.^{3–8} It is obviously desirable to reduce the diameter of ultrafine fibers as much as possible to obtain outstanding properties such as a high specific surface area and high porosity. In elec-

trospinning, a polymer solution is ejected from a capillary by a strong electrostatic force and deposited as a nonwoven, fibrous mat on an electrically grounded target. As this jet travels through the air, the solvent evaporates, leaving behind ultrafine polymer fibers. As one of the most extensively studied polymers for electrospinning, PVA has been widely used with and without the addition of another polymer.^{9–12} In fundamental studies, PVA solutions have been electrospun to investigate the effects of processing parameters, such as the spinning voltage, solution flow rate, and distance between the needle tip and the ground electrode, on electrospinning and the effects of solution properties, such as the solution viscosity, conductivity, dielectric constant, and surface tension, on the structure and morphology of electrospun PVA fibers. The solution properties are several of the factors influencing the transformation of a polymer solution into ultrafine fibers. Above a certain concentration, fibers without beads are electrospun, and thinner fibers are obtained from a polymer solution with a higher net charge density. Reduced surface tension favors the formation of fibers without beads.⁹

In this study, using electrospinning, we prepared water-soluble atactic poly(vinyl alcohol) (a-PVA) nanowebs. Then, to improve the water resistance of the PVA nanowebs prepared, the nanowebs were heat-treated at four different temperatures. The structure and properties of the PVA nanowebs were

Correspondence to: W. S. Lyoo (wslyoo@yu.ac.kr).

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investigated with scanning electron microscopy (SEM), differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), Instron instrumentation, and measurements of the degree of solubility.

EXPERIMENTAL

Materials

a-PVA was obtained from DC Chemical Co., Ltd., (Seoul, Korea) and used as received. The number-average degree of polymerization, syndiotactic dyad content, and degree of saponification of PVA used in this study were 1700, 52.3%, and 99.9%, respectively.

Preparation of the PVA nanowebs

PVA was dissolved in water at 90°C for 2 h and kept there for 30 min to ensure homogenization. Then, the PVA aqueous solution was electrospun at a polymer concentration of 9 g/dL, an applied voltage of 25 kV, and a tip-to-collector distance (TCD) of 15 cm, which were the electrospinning conditions used to form a fibrous material obtained in a previous study.⁹ PVA nanowebs prepared by electrospinning were treated in a vacuum oven at 150, 170, 190, and 210°C for 3 h.

Characterization of the PVA nanowebs

The fiber morphology and fiber diameter of the PVA nanowebs were determined with SEM. A small section of the fiber mat was placed on an SEM sample holder and sputter-coated with argon (E-1030, Hitachi, Tokyo, Japan). An accelerating voltage of 15 kV was employed to take the photographs.

The crystal melting temperature of the PVA nanowebs was measured with DSC (DSC 7, PerkinElmer, Norwalk, CT) with a sample weight of 10 mg and at a heating rate of 10°C/min from 20 to 300°C under a nitrogen atmosphere.

WAXD scans were obtained with nickel-filtered Cu K α radiation (26 kV, 6 mA; D/Max-2500, Rigaku, Tokyo, Japan). The measurement of the crystallinity was carried out at room temperature with a Philips diffractometer (with a Geiger counter) (Eindhoven, The Netherlands) connected to a computer. The diffraction scans were collected at $2\theta = 5\text{--}50^\circ$.

For the mechanical properties, the nanowebs were subjected to a tensile test with an Instron 4301 with a 2-kg load cell. The measurements proceeded in air at room temperature at a tensile speed of 100 mm/min, and the values of the tensile strength were calculated. The nanoweb samples were cut into pieces 100 mm long and 10 mm wide. The reported tensile

strength of the PVA nanowebs was the average value of 10 specimens.

The degree of solubility of the PVA nanowebs in hot water at 90°C after 5 min was calculated as follows:

$$\text{Degree of solubility} = 1 - (W_a/W_b) \quad (1)$$

where W_a is the weight of the dried PVA nanoweb after the hot-water treatment and W_b is the weight of the dried nanoweb before the hot-water treatment.

RESULTS AND DISCUSSION

Extensive chain entanglements are necessary to produce electrospun fibers, the result being that lower solution concentrations lead to electrospaying rather than spinning. In a previous study,⁹ the concentrations of PVA were determined to assist in choosing the minimum concentrations for spinning. We found earlier that a PVA concentration greater than 7 g/dL is necessary to obtain electrospun nanofibers, and this appears to correspond to the onset of significant chain entanglements in the Brookfield viscosity. PVA nanowebs with a concentration of 7 g/dL exhibited a bead-and-string morphology because of the insufficient stretching of the polymer jet during electrospinning. As the concentration of PVA was increased, the morphology of the PVA nanowebs changed from a bead-and-string morphology to a completely fibrous structure, as shown in Figure 1. In addition, the prepared PVA nanowebs had a regular morphology with a fiber diameter distribution of 200 ± 50 nm.

Various experimental values for the melting point of PVA have been reported and summarized.^{13–15} They vary widely and range from 220 to 267°C. When PVA is heated gradually without a diluent, decomposition takes place, and hence the exact determination of the melting point is difficult. Also, the glass-transition temperature of PVA is determined on the basis of measurements of changes in the volume, specific heat, elongation, dielectric loss, elastic properties, polarized infrared, nuclear magnetic resonance, and so forth.¹⁶ Although experimental values vary widely, they are roughly classified into two temperature groups: about 70°C and about 85°C. Figure 2 presents DSC thermograms of a pure PVA nanoweb and heat-treated PVA nanowebs. A broad endothermic peak with a peak maximum of about 80°C is present in all cases and is attributed to the traces of water in the samples and their glass-transition temperatures. The peak maximum temperature and endothermic heat flow of the pure and heat-treated PVA nanowebs are tabulated separately (Table I). The second peak, with a maximum above 210°C, is associated with the melting of the polymer.

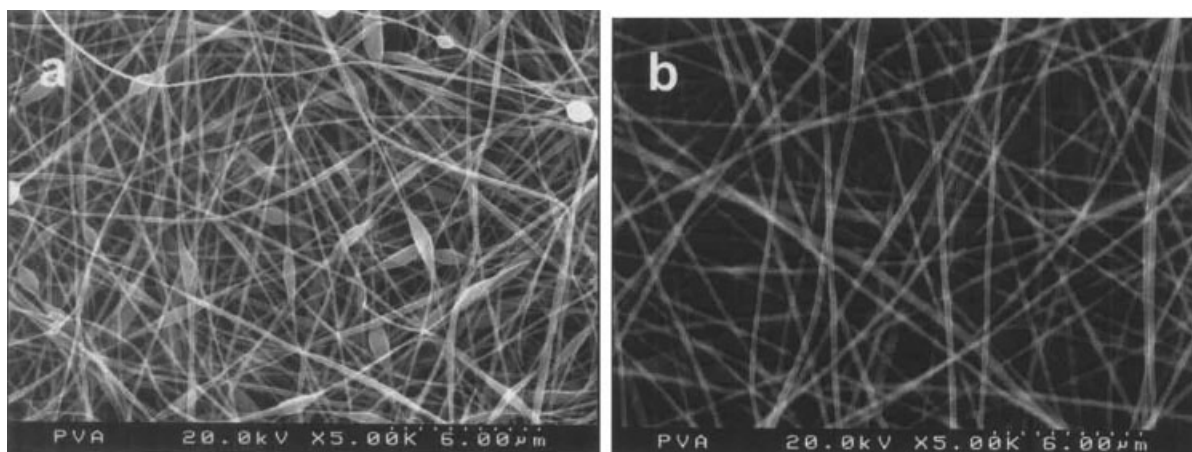


Figure 1 SEM photographs of a-PVA nanowebs electrospun at an applied voltage of 25 kV and a TCD of 15 cm with different polymer concentrations: (a) 7 and (b) 9 g/dL.

In the DSC thermogram, the melting temperature of pure PVA was observed to be about 229.2°C. The melting temperature of the heat-treated PVA nanowebs shifted to a low temperature with an increasing heat-treatment temperature. The last melting temperature was about 216°C when the heat-treatment temperature was 190°C. This indicated that the ordered association of the PVA molecules was reduced by the formation of micronetwork domains. On the other hand, in the case of a PVA nanoweb treated at 210°C, an increase in the melting temperature and a significant decrease in the enthalpy were shown. This was mainly due to the decomposition of PVA by excessive heat treatment at the onset temperature of the melting of PVA.

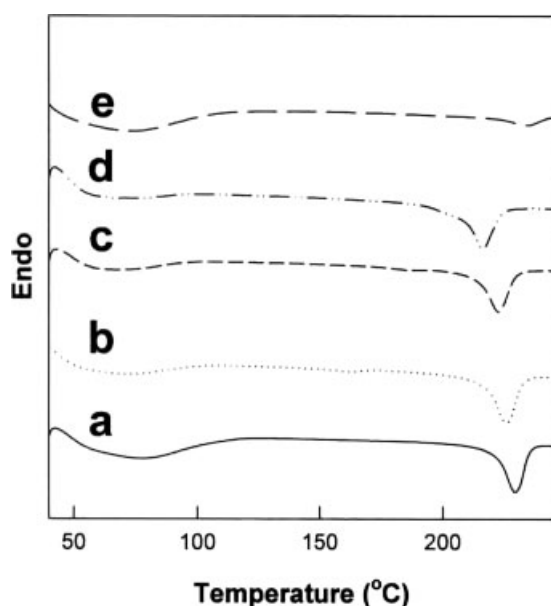


Figure 2 DSC thermograms of a-PVA nanowebs at different heat-treatment temperatures: (a) before the heat treatment, (b) 150°C, (c) 170°C, (d) 190°C, and (e) 210°C.

WAXD patterns of the PVA nanowebs are shown in Figure 3. The intensities of the peaks corresponding to the 100 plane at 10° and to the 101 plane at 20° increased with the heat treatment of the PVA nanowebs, and this indicated that crystallization commonly accompanied the heat treatment of the PVA nanowebs. In addition, the other peaks, including the 100, 001, and 200 plane peaks, were much sharper than those of a pure PVA nanoweb. This explains the fact that larger crystals in the lateral direction could be formed in the heat-treated PVA nanowebs.

Figure 4 shows the tensile strength of PVA nanowebs as a function of the heat-treatment temperature. A higher temperature did not always lead to better mechanical properties for the PVA nanowebs. The tensile strength at first increased gradually to a maximum with an increasing heat-treatment temperature and then decreased, and a PVA nanoweb treated at 170°C, the crystallization temperature of PVA, showed greater tensile strength. In contrast, a PVA nanoweb treated at 210°C, the onset temperature of the melting of PVA, was brittle because of the decomposition of the PVA nanoweb, so the tensile strength could not be measured.

TABLE I
Melting Parameters of a-PVA Nanowebs
Determined by DSC

Heat-treatment temperature (°C)	Heat of fusion (ΔH) (cal/g)	Crystal melting temperature (°C)
Before the heat treatment	68.8	229.2
150	68.9	225.6
170	60.8	222.5
190	74.9	216.1
210	15.3	233.5

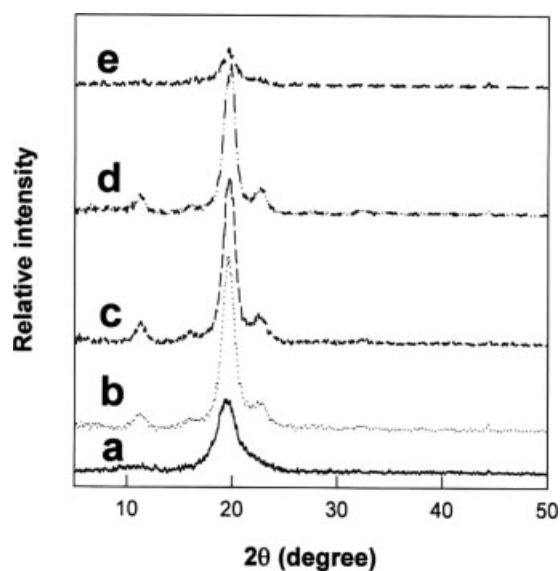


Figure 3 WAXD patterns of a-PVA nanowebbs at different heat-treatment temperatures: (a) before the heat treatment, (b) 150°C, (c) 170°C, (d) 190°C, and (e) 210°C.

The degree of solubility of the heat-treated PVA nanowebbs was calculated from weight changes after the treatment of the nanowebbs in hot water. In contrast to regular PVA materials, PVA nanowebbs have higher solubility because of their nanosize. Therefore, in the case of a pure PVA nanoweb, the degree of solubility could not be measured. On the other hand, in the case of heat-treated PVA nanowebbs, higher maintenance was shown. This clearly shows that a heat treatment can largely improve the water resistance of PVA nanowebbs. This phenomenon is closely related to the fact that the micronetwork

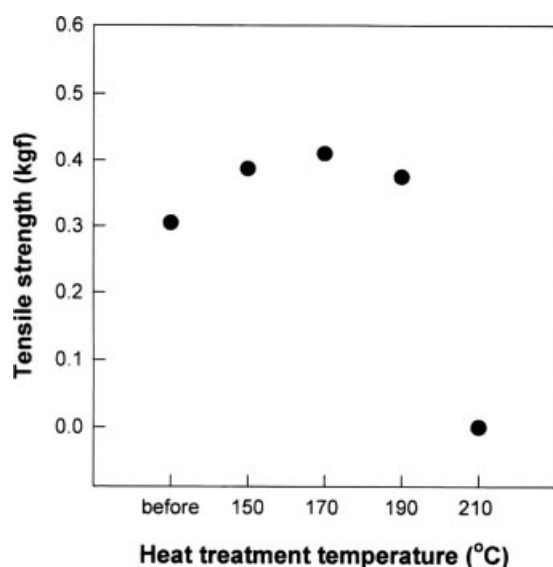


Figure 4 Tensile strengths of a-PVA nanowebbs at different heat-treatment temperatures.

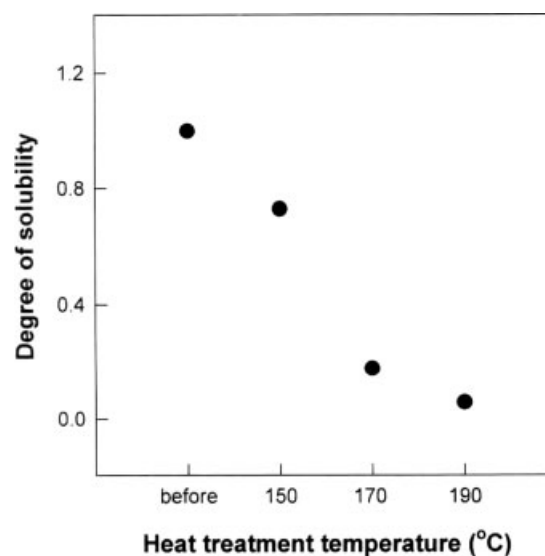


Figure 5 Changes in the degree of solubility with the heat-treatment temperature for PVA nanowebbs.

domains act as crosslinks. The results in Figure 5 clearly reveal that more micronetwork domains are formed in PVA nanowebbs during the heat treatment, and this agrees with the fact that there is a greater increase in the degree of solubility and water resistance of heat-treated PVA nanowebbs.

CONCLUSIONS

Ultrafine PVA fibers without beads were obtained through the electrospinning of a 9 g/dL PVA aqueous solution. Then, to improve the water resistance of the PVA nanowebbs, they were heat-treated at temperatures up to the glass-transition temperature of PVA. SEM showed that the average diameter of the fibers was about 200 ± 50 nm. Also, the heat-treated PVA nanowebbs showed crystalline and mechanical properties superior to those of a pure PVA nanoweb. However, for a PVA nanoweb treated at an excessive heat-treatment temperature, decreases in the thermal stability, crystallinity, and mechanical properties were found because of the decomposition of PVA. It can be concluded that a heat treatment at the proper temperature is required to improve the water resistance of PVA nanowebbs. In the near future, we will report on the preparation of crosslinked PVA nanowebbs with various crosslinking techniques.

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