

Preparation and Characterization of a Nanoscale Poly(vinyl alcohol) Fiber Aggregate Produced by an Electrospinning Method

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ABSTRACT: Nanoscale poly(vinyl alcohol) (PVA) fiber (100–500 nm) aggregates were prepared with an electrospinning technique. Additionally, a chemical crosslinking method was used to crosslink the nanoscale PVA fiber aggregates. Differential scanning calorimetry, wide-angle X-ray diffraction, and scanning electron microscopy techniques were employed to characterize the PVA fiber aggregates. The different crosslinking densities of the PVA fiber aggregates were obtained through the control of the weight percentage of glyoxal to PVA. The crosslinking densities due to heat treatment and chemical crosslinking were studied. The influence of heat treatment could be neglected in contrast to chemical crosslinking when the curing temperature was 120 °C. The primary factor that affected the crosslinking density was the volume of the chemical crosslinking agent. The results showed that the properly crosslinked PVA fiber aggregates had better antiwater solubility and mechanical properties than the non-crosslinked PVA fiber aggregates. © 2002 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 40: 1261–1268, 2002

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INTRODUCTION

Poly(vinyl alcohol) (PVA), a water-soluble polyhydroxy polymer, is the largest volume synthetic resin produced in the world. The excellent chemical resistance, physical properties, and complete

biodegradability of PVA resins have led to their broad practical applications.^{1–5}

Nanoscale materials can be rationally designed to exhibit novel and significantly improved physical, chemical, and biological properties, phenomena, and processes because of their size.⁶ Electrospinning is a process that produces continuous polymer fibers with nanoscale diameters through the action of an external electric field imposed on a polymer solution or melt.⁷ The morphology of fibers depends on the process parameters, includ-

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ing the solution concentration, applied electric field strength, deposition distance, and deposition time.^{8–10} Nonwoven fabrics composed of electrospun fibers have a large specific surface area and a small pore size in comparison with commercial textiles,¹¹ making them excellent candidates for use in filtration, biomedical materials,¹² and membrane applications.

Even though PVA has good mechanical properties in the dry state, its applications are limited by its high hydrophilicity.^{1,13,14} PVA fiber aggregates can be readily crosslinked for improved water resistance. Linear polymers can be joined by other chains at points along their lengths to make crosslinked structures; the chemical crosslinking of linear polymers may provide feasible for the improvement of mechanical properties and anti-water solubility.¹⁵ Because the crosslinking agent is normally activated by heating, the material does not soften and melt when heated further.¹⁶ A limitation on the selection of PVA fiber aggregate crosslinking agents for practical use is that they must be applied to fabrics via padding from aqueous solutions, followed by heat curing, which causes polymer crosslinking reactions to occur.

All multifunctional compounds capable of reacting with hydroxyl groups can be used to obtain three-dimensional networks in PVA fiber aggregates.^{12,17,18} Glyoxal is regarded as a good crosslinking agent with an important connection to permeation.¹⁹ Glyoxal has been heated with purified PVA fiber aggregates in the presence of acid catalysts such as phosphoric acid, sulfuric acid, and hydrogen chloride. Because a glyoxal molecule can form four linkages to PVA chains, glyoxal may be regarded as a tetrafunctional crosslinking agent, whereas formaldehyde is difunctional.¹⁹

However, crosslinked PVA fiber aggregates are difficult to find in periodicals and monographs. The purpose of this work was to prepare crosslinked nanoscale PVA fiber aggregates and characterize their physical and mechanical properties.

EXPERIMENTAL

Materials

PVA425 (number-average molecular weight = 65,000; 96% hydrolyzed) was obtained from Celanese Ltd. Glyoxal (40% aqueous solution), phosphoric acid (85% aqueous solution), and tetrahydrofuran were purchased from Aldrich. These chemicals were used without further purification. Distilled water was used as a solvent.

rahydrofuran were purchased from Aldrich. These chemicals were used without further purification. Distilled water was used as a solvent.

Preparation of the Crosslinked Fiber Aggregates

A PVA solution was prepared from PVA powder and distilled water at 80 °C with vigorous stirring. The concentration of the PVA solution tested ranged from 8 to 16 wt %. A schematic of the electrospinning process is shown in Figure 1. The PVA solution was placed in a syringe. The syringe was then clamped to a ring stand that was above a grounded tubular layer. The tubular layer not only revolved on its own axis but also moved right and left continuously. The tubular layer was covered by a piece of aluminum foil. The power supply was connected to the metal syringe tip. The voltage ranged from 7 to 19 kV, and the tip-to-collector distance (TCD) ranged from 6 to 14 cm. The droplet instantly disintegrated into fibers that were drawn to the tubular layer.

For the preparation of the crosslinked PVA fiber aggregate, a 10 wt % PVA solution was prepared. Glyoxal and phosphoric acid were added after the PVA powder dissolved entirely. The weight percentage of glyoxal to PVA ranged from 0 to 10 wt %. The pH value of the PVA solution was controlled within 2–3 with phosphoric acid. The voltage was 19 kV, and the TCD was 8 cm.

PVA fiber aggregates were put into an oven; the curing temperature was 120 °C, and the curing time was 5 min. The crosslinked PVA fiber aggregates were purified by extraction with tetrahydrofuran in a Soxhlet apparatus for 24 h and dried at 70 °C *in vacuo* for 24 h.

Thermally treated samples were prepared, but without the addition of glyoxal and phosphoric acid. The heat-treatment temperature ranged from 120 to 180 °C, and the heat-treatment time ranged from 2 to 300 min.

Characterization Techniques

Scanning Electron Microscopy (SEM)

The morphology and diameter of PVA fiber aggregates were determined with SEM. A small section of the fiber mat was placed on the SEM sample holder and sputter-coated with gold (Denton Desk-1 sputter coater). An Amray 3000 SEM with an accelerating voltage of 20 kV was employed for the SEM photographs.

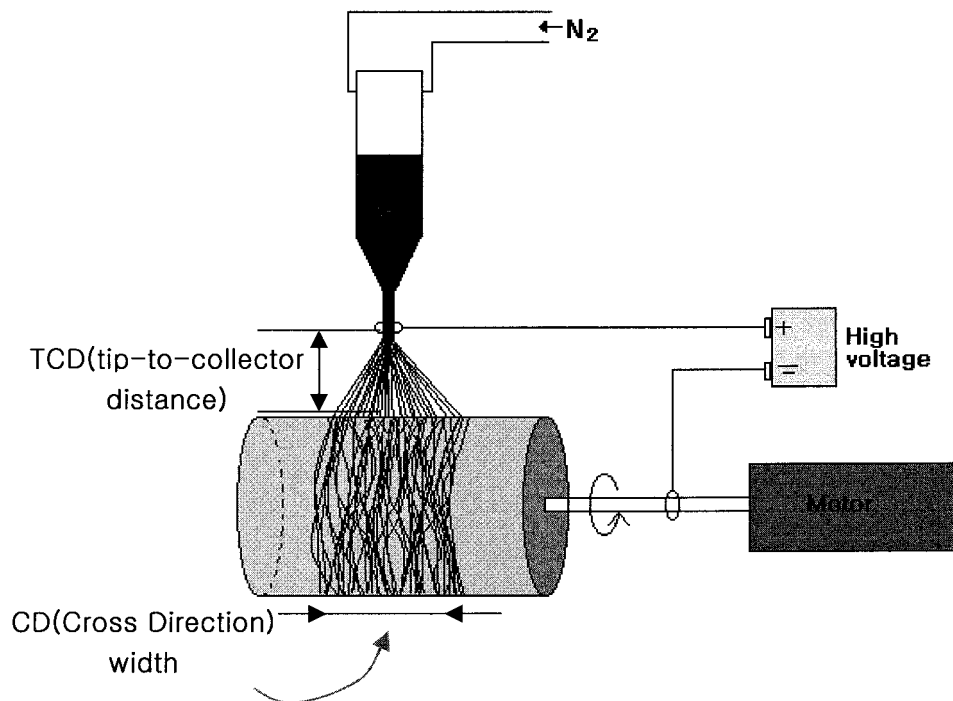


Figure 1. Schematic of the electrospinning process.

Differential Scanning Calorimetry (DSC)

The thermal behavior of noncrosslinked and crosslinked (to different degrees) PVA fiber aggregates was studied with a DSC technique. DSC was performed with a DuPont 2100 thermoanalyzer under a nitrogen atmosphere. DSC traces were recorded between 30 and 250 °C at a heating rate of 10 °C/min.

Wide-Angle X-Ray Diffraction (WAXD)

The measurement of the crystallinity was carried out at room temperature with a Philips diffractometer, with a Geiger counter, connected to a computer. The diffraction scans were collected at $2\theta = 5\text{--}44^\circ$.

Determination of the Water Absorbency of the PVA fiber aggregates

The water content of the PVA fiber aggregates after swelling was calculated with the expression $W_a = (W_b - W_c)/W_c$, where W_a was the water uptake per gram of PVA fiber aggregate and W_b and W_c were the weights of PVA fiber aggregate after swelling and subsequent drying, respectively. The time duration for swelling was 48 h. The excess water on the swollen fiber aggregate

was wiped up with filter paper. Each sample for swelling was checked 10 times.

Mechanical Properties

The mechanical properties of PVA fiber aggregates were determined with a Instron 4301 (Automated Materials Testing System 1.23 series IX). The extension rate was 100 mm/min at 22 °C. Samples were prepared in the cross direction and machine direction (2 cm wide, 15 cm long, and 60–170 μm thick).

RESULTS AND DISCUSSION

Preparation and Crosslinking of the Nanoscale PVA fiber aggregates

To choose suitable electrospinning conditions for thinner diameter and uniform PVA fibers, we performed a series of experiments on electrospinning conditions, including concentration, voltage, and TCD. The average diameter of a PVA fiber was increased from 260 to 400 nm with the PVA concentration increasing from 8 to 16 wt % (voltage = 19 kV; TCD = 8 cm). The high-concentration solution showed high viscosity and high surface

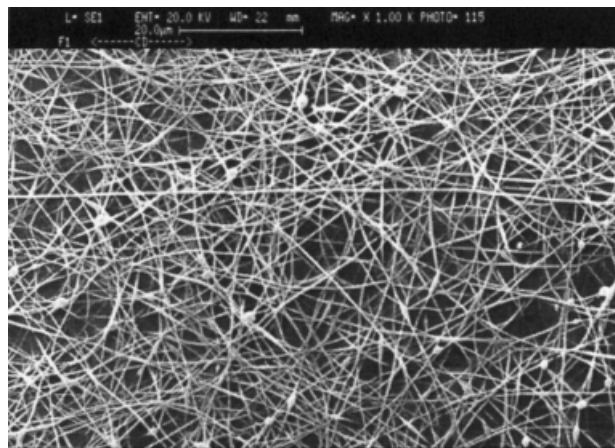


Figure 2. SEM image of the PVA fiber aggregate (concentration = 10 wt %; TCD = 8 cm; voltage = 19 kV; glyoxal to PVA = 6 wt %).

tension. The split ability was reduced with increasing surface tension. The electrospinning fiber had some elasticity before the solvent evaporated. The chance of contraction was increased with increasing TCD. As a result, the average diameter of a PVA fiber was slightly increased from 260 to 330 nm with TCD increasing from 6 to 14 cm (voltage = 19 kV; concentration = 10 wt %). The electrostatic force gradually increased with increasing voltage. The split ability of a droplet was reinforced by the increasing electrostatic force. The average diameter of a PVA fiber was slightly decreased from 310 to 270 nm with the voltage increasing from 7 to 19 kV (TCD = 8 cm; concentration = 10 wt %).

Electrospinning conditions, including the concentration (10 wt %), TCD (8 cm) and voltage (19 kV), were used to obtain thinner and regular PVA fibers. Nanoscale PVA fiber aggregates were produced through electrospinning of a PVA solution (10 wt %) with a crosslinking agent. Figure 2 shows a representative image of a PVA fiber aggregate. The fiber aggregate contained 6 wt % glyoxal to PVA. The frequency distribution of the fiber diameter is presented in Figure 3. The average diameter of the fibers was about 280 nm. The amount of glyoxal added to the PVA solution was very small. Therefore, the surface tension was not changed with the addition of glyoxal. The influence of the concentration of glyoxal on the diameter of the nanofibers could be neglected.

The curing process was necessary for activating the crosslinking agent. The curing conditions (120 °C and 5 min) were used because glyoxal was not stable at high temperatures. To distinguish

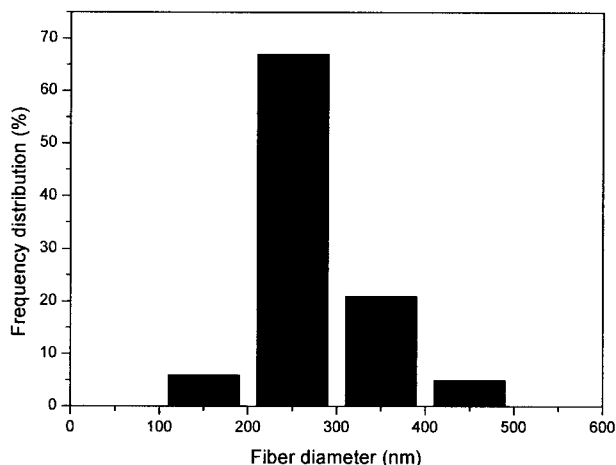


Figure 3. Frequency distribution of the PVA fiber diameter (concentration = 10 wt %; TCD = 8 cm; voltage = 19 kV; glyoxal to PVA = 6 wt %).

the influences of heat treatment and chemical crosslinking agents, we performed a series of heat-treatment experiments. When the heat-treatment temperature was greater than 150 °C, the fiber aggregate became yellow, and the brittleness of the fiber aggregate increased because of thermal degradation and oxidation.

DSC

DSC is a useful technique for investigating the curing reactions of crosslinkable polymers. Figure 4 shows that the melting temperature decreased with increasing heat-treatment temperature and time, suggesting a large influence of the heat treatment on the fiber aggregate. The melting

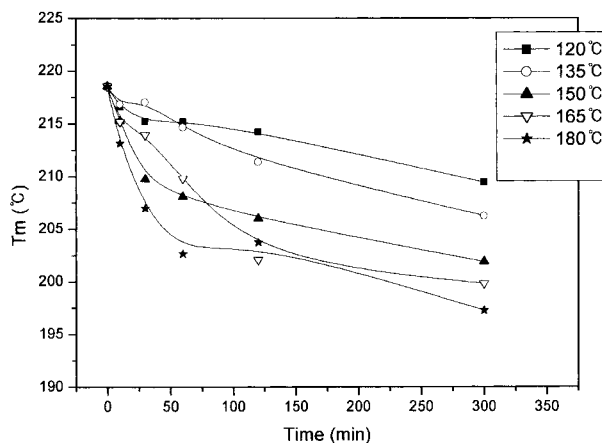


Figure 4. Melting temperature (T_m) as a function of the heat-treatment temperature and time.

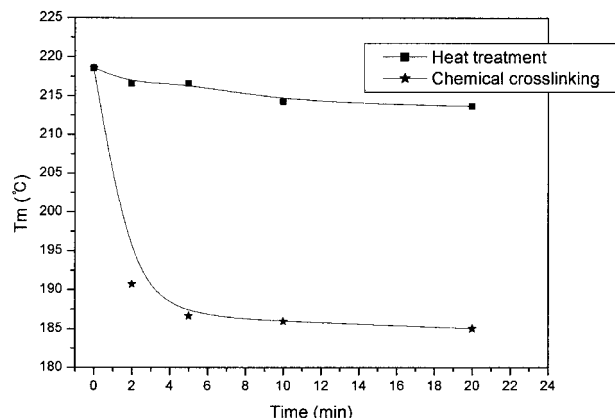


Figure 5. Melting temperature (T_m) of the heat-treated PVA fiber aggregate and chemically crosslinked (2 wt % glyoxal) PVA fiber aggregate as a function of the curing time (curing temperature = 120 °C).

temperature of PVA fiber aggregates decreased from 218 to 198 °C with the heat-treatment time increasing from 0 to 300 min with a heat-treatment temperature of 180 °C. Meanwhile, the melting temperature decreased from 210 to 198 °C with the heat-treatment temperature increasing from 120 to 180 °C with a heat-treatment time of 300 min. The melting temperatures of the heat-treated PVA fiber aggregates and chemically crosslinked (2 wt % glyoxal) PVA fiber aggregates as a function of the curing time (curing temperature = 120 °C) are presented in Figure 5. The melting temperature sharply decreased with increasing curing time for the chemically crosslinked sample, showing that the melting temperature was strongly influenced by chemical crosslinking in comparison with that for heat treatment. The melting temperature of PVA fiber aggregates decreased from 214 (heat treatment) to 180 °C (chemical crosslinking) for a curing time of 20 min. Figure 6 present DSC thermograms over a temperature range of 30–250 °C for PVA fiber aggregates with different weight percentages of glyoxal to PVA. As shown in Figure 6(a,b), after electrospinning, the melting temperature increased because the molecular orientation in the fiber aggregate was higher than that in the PVA powder. A rapid decrease in the enthalpy of fusion and the melting temperature suggested that the crystallinity and perfection of the crystal structure were reduced with the degree of crosslinking increased [Fig. 6(b–g)]. Moreover, the melting point disappeared when PVA fiber aggregates were crosslinked properly [Fig. 6(g)].

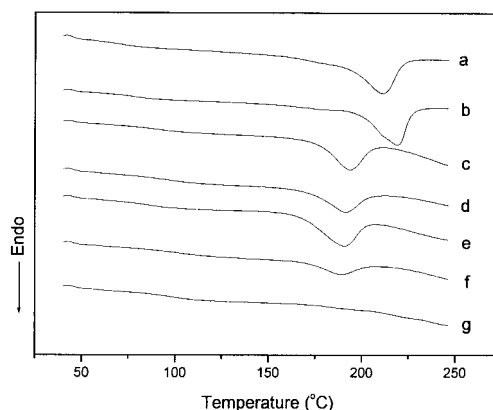


Figure 6. DSC thermograms from 30 to 250 °C for PVA: (a) PVA powder and (b–g) PVA fiber aggregates crosslinked with 0, 2, 4, 6, 8, and 10 wt % glyoxal, respectively.

WAXD

The crystalline properties of electrospinning fiber and crosslinked fiber aggregates may also be of primary importance when we consider the materials for commercial applications. Figure 7 shows WAXD patterns of PVA. Compared with those of the PVA powder [Fig. 7(a)], the reflections of the fiber pattern [Fig. 7(b)] were relatively broad and strong. Meanwhile, the WAXD pattern of the PVA powder also contained numerous higher order reflections that could not be seen in the fiber pattern. The broad and strong nature of the PVA fiber pattern reflections indicated that the crystalline microstructure in the electrospinning fiber aggregate was significantly greater than that in the PVA powder.

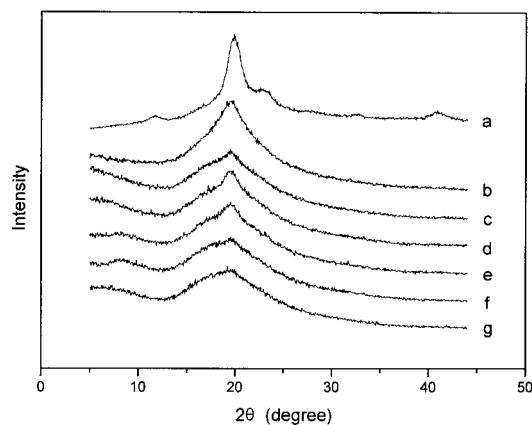


Figure 7. WAXD patterns of PVA: (a) PVA powder and (b–g) PVA fiber aggregates crosslinked with 0, 2, 4, 6, 8, and 10 wt % glyoxal, respectively.

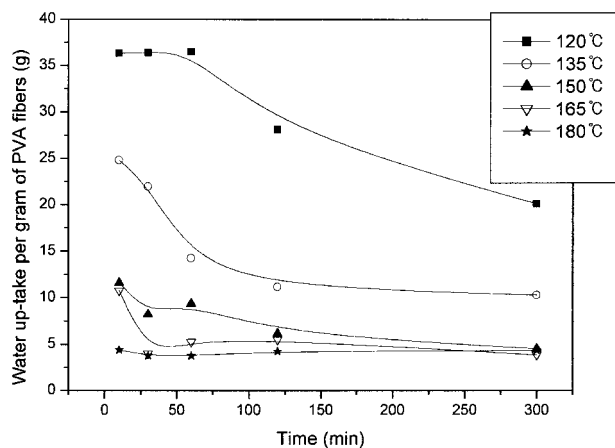


Figure 8. Water uptake per gram of the PVA fiber aggregate with different heat-treatment temperatures and times.

The WAXD patterns of PVA fiber aggregates with different weight percentages of glyoxal to PVA are presented in Figure 7(b–g). The reflections of the crosslinked PVA fiber aggregates were broader and weaker with the increasing weight percentage of glyoxal to PVA. There was no significant difference in the reflections after the PVA fiber aggregates were crosslinked with 6 wt % glyoxal, and PVA fiber aggregates remained crystalline. However, the sample with the highest crosslinking density was thoroughly amorphous according to the DSC results [Fig. 6(g)]. The reason that PVA fiber aggregates maintained their crystallinity may be that the pseudohexagonal²⁰ ordering was retained after crosslinking even in the amorphous samples.

Swelling Behavior

A characteristic property of permanent networks is their ability to swell in suitable solvents. If a network is immersed in a solvent that is miscible with the polymer chains of the network, the solvent is imbibed, and the network swells.¹⁶ Water was a suitable medium because PVA was soluble in water.²¹ PVA became insoluble in water for a sufficiently large degree of crosslinking. The swelling, expressed as grams of water uptake per gram of PVA fiber aggregate, was used as a measure of the crosslinking density.

The water uptake of PVA fiber aggregates is presented in Figure 8 with different heat-treatment temperatures and times. The water content in the fiber aggregates decreased with increasing

temperature and time for the fiber aggregates treated, but there was no evident difference with increasing heat-treatment time when the temperature was greater than 150 °C. The difference between curves of 120 and 180 °C was evident because of the influence of the heat treatment. The influence of the heat treatment gradually increased with increasing heat-treatment temperature and time. Figure 9 shows that the water content in the fiber aggregates obviously decreased with the increasing weight percentage of glyoxal to PVA. The number of hydroxyl groups of PVA decreased as the weight percentage of glyoxal to PVA increased; as a result, the water uptake decreased with the increasing weight percentage of glyoxal to PVA.

During the swelling test, some part of the PVA fiber aggregate was dissolved in water because the crosslinking was not proper. Figure 10 shows that the weight loss decreased with increasing heat-treatment temperature and time. Similar results can be observed in Figure 8. The weight loss of the PVA fiber aggregates with different weight percentages of glyoxal to PVA is shown in Figure 11. The weight loss of PVA fiber aggregates obviously decreased with the increasing weight percentage of glyoxal to PVA.

The total water content decreased with the increasing weight percentage of glyoxal to PVA, indicating an increase in the crosslinking density of the PVA fiber aggregates, which made the polymer structure more rigid and compact.²² In a comparison of Figures 9, 8(a), 11, and 10(a), the

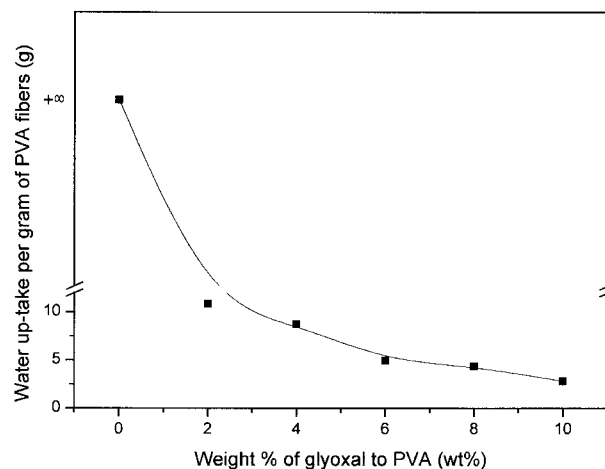


Figure 9. Water uptake per gram of the PVA fiber aggregate with different weight percentages of glyoxal to PVA (curing temperature = 120 °C; curing time = 5 min).

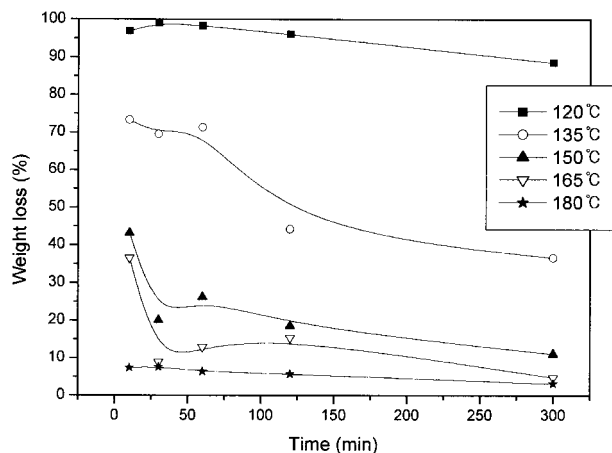


Figure 10. Weight loss of the PVA fiber aggregate with different heat-treatment temperatures and times.

influence of heat treatment can be neglected, in contrast with chemical crosslinking. The primary factor that affected the crosslinking density was the volume of the chemical crosslinking agent.

Mechanical Properties

Some of the fascination with the behavior of polymers comes from the large changes in physical properties and the wide range of mechanical behaviors displayed at easily accessible temperatures and under easily accessible conditions.¹⁶ The tensile strength and elongation of the crosslinked PVA fiber aggregates are listed in Figures 12 and 13, respectively. The tensile strength of the PVA fiber aggregates increased with the increasing weight percentage of glyoxal

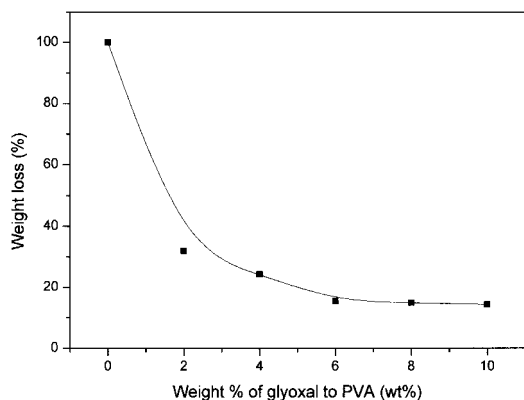


Figure 11. Weight loss of the PVA fiber aggregate with different weight percentages of glyoxal to PVA (curing temperature = 120 °C; curing time = 5 min).

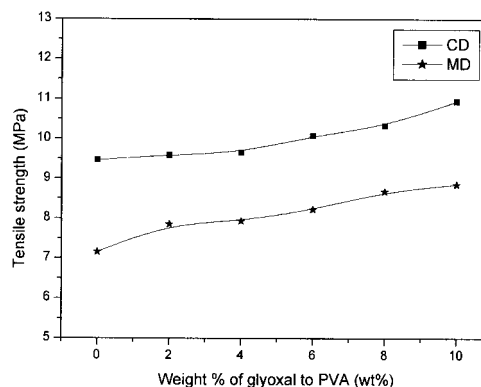


Figure 12. Tensile strength as a function of the weight percentage of glyoxal to PVA (CD = cross direction; MD = machine direction).

to PVA, whereas the elongation decreased. The difference in the tensile strengths and elongations between the cross direction and machine direction was slight because the tubular layer was moved right and left continuously. The linear polymer chains in the noncrosslinked fiber aggregates easily slid by one another via an outer force. Therefore, they had low tensile strength and high elongation. However, for the entirely three-dimensional crosslinked PVA fiber aggregates, the chains were tightly fettered. Sliding was difficult, so they had high tensile strength and low elongation.

CONCLUSIONS

Crosslinked PVA fiber aggregates with average diameters of about 280 nm were successfully pro-

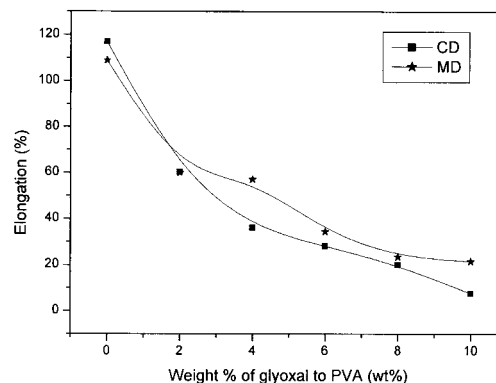


Figure 13. Elongation as a function of the weight percentage of glyoxal to PVA (CD = cross direction; MD = machine direction).

duced with electrospinning. The volume of the chemical crosslinking agent was the primary factor affecting the crosslinking density. The results showed that the properly crosslinked PVA fiber aggregates had better antiwater solubility and mechanical properties than the noncrosslinked PVA fiber aggregates.

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