

Preparation and Characterization of Nanoscaled Poly(vinyl alcohol) Fibers via Electrospinning

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Abstract: Nanoscaled PVA fibers were prepared by electrospinning. This paper described the electrospinning process, the processing conditions, fiber morphology, and some potential applications of the PVA nano-fibers. PVA fibers with various diameters (50-250 nm) were obtained by changing solution concentration, voltage and tip to collector distance (TCD). The major factor was the concentration of PVA solution which affected the fiber diameter evidently. Increasing the concentration, the fiber diameter was increased, and the amount of beads was reduced even to 0%. The fibers were found to be efficiently crosslinked by glyoxal during the curing process. Phosphoric acid was used as a catalyst activator to reduce strength losses during crosslinking. Scanning electron micrograph (SEM) and differential scanning calorimetric (DSC) techniques were employed to characterize the morphology and crosslinking of PVA fibers. It was found that the primary factor which affected the crosslinking density was the content of chemical crosslinking agent.

Keywords: Electrospinning, Nanofiber, Poly(vinyl alcohol), Crosslinking, Glyoxal

Introduction

Poly(vinyl alcohol) (PVA) is a water-soluble polyhydroxy polymer and the largest volume for resin produced in the world[1]. The excellent chemical resistance, physical properties, and biodegradability have led PVA to broad practical applications[2].

It was well known that nanoscaled materials can be rationally designed to exhibit novel and significantly improved physical, chemical, and biological properties because of their size. Electrospinning is a process that produces continuous polymer fibers with diameters in the nano-scale through the action of an external electric field imposed on a polymer solution or melt[3]. In the electrospinning process, a polymer solution held by its surface tension at the end of a capillary tube is subjected to an electric field. Charge is induced on the liquid surface by an electric field. Mutual charge repulsion causes a force directly opposite to the surface tension. As the intensity of the electric field is increased, the hemispherical surface the solution at the tip of the capillary tube elongates to form a conical shape known as the Taylor cone. When the electric field reaches a critical value at which the repulsive electric force overcomes the surface tension force, a charged jet of the solution is ejected from the tip of the Taylor cone[4].

The morphology of the fibers was found depending on the process parameters; including solution concentration, applied electric field strength, deposition distance and deposition time[5]. Non-woven fabrics composed of electrospun fibers have a large specific surface area and

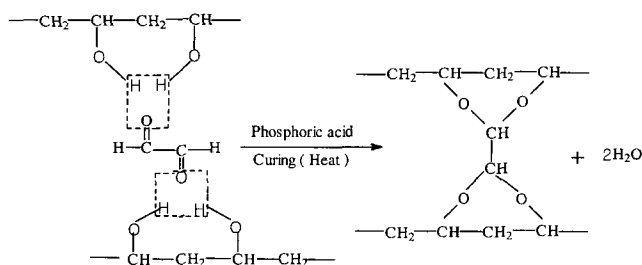
small pore size compared to commercial textiles, making them excellent candidates for use in filtration, biomedical materials[6] and membrane applications.

In spite of the fact that PVA has good mechanical properties in the dry state, its applications were limited by its high hydrophilicity[2,7,8]. PVA fibers can be readily crosslinked to improve mechanical properties and anti-water solubility [9,10]. The crosslinked nanoscaled PVA fibers can be used as filter paper to filtrate the solution with microscaled particles. Linear polymers can be joined by other chains at points along their length to make a crosslinked structure, chemical crosslinking of linear polymer may provide feasible methods for the improvement of the mechanical properties and anti-water solubility[9]. Because the crosslinking agent is normally activated by heating, after which the material does not soften and melt even if heated further[11]. A limitation on the selection of crosslinking agents for practical use is that they must be applied to fabric by padding from aqueous solution, followed by heat curing which causes polymer crosslinking reactions to occur.

Glyoxal was regarded as a good crosslinking agent used to have an important bearing on the permeation[12]. Glyoxal is heated with purified PVA nano-fibers in the presence of an acid catalyst such as phosphoric acid. Since a glyoxal molecule can form four linkages to PVA fibers, glyoxal may be regarded as a tetra-functional crosslinking agent, whereas formaldehyde is difunctional[12]. The reaction is represented in Scheme 1.

However, the crosslinked PVA nano-fibers are difficult to find in periodicals and monographs. The purpose of present work was to prepare the crosslinked nanoscaled PVA fibers, and investigate the factors to influence their morphology.

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Scheme 1. Chemical reaction crosslinking of PVA fibers.

Experimental

Materials

PVA425 (Mn, 65,000 hydrolysis 96 %) was obtained from Celanese Ltd. Glyoxal(40 % aqueous solution) and phosphoric acid(85 % aqueous solution) were purchased from Aldrich company. These chemicals were used without further purification. Distilled water was used as solvent.

PVA Solution Preparation

PVA solution was prepared from PVA powder, distilled water, glyoxal, phosphoric acid, at a temperature of 80 °C with vigorous stirring. The concentration of PVA solutions tested was 7, 9, 11, 13, and 15 wt%. The content of glyoxal to PVA was ranged from 2-8 wt%. PH value of PVA solution was controlled within 2-3 by adding phosphoric acid.

Electrospinning

The electrospinning apparatus is schematically shown in Figure 1. PVA solution was placed in a capillary tube. The capillary tube was then clamped to a ring-stand which was above a grounded tubular layer. The tubular layer was covered by a piece of aluminum foil. The power supply was connected to the metal syringe tip. The droplet instantly disintegrated into fibers which were drawn to the tubular

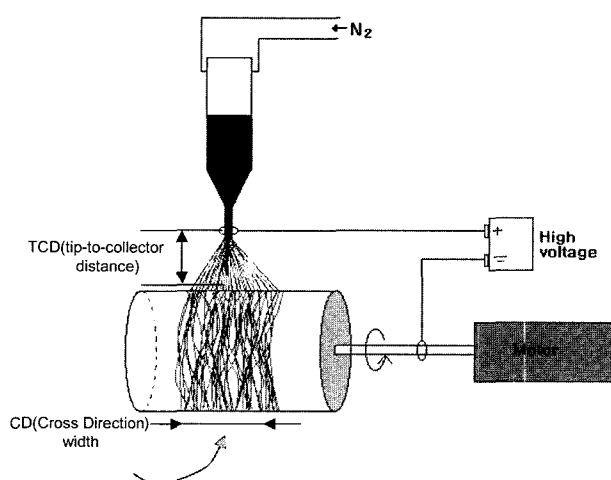


Figure 1. Schematic of the electrospinning process.

layer. The voltage was ranged from 7 to 19 kV. The distance from tip to collector was ranged from 4 to 12 cm. The critical voltage, CD (Cross Direction) width and throughput were checked during electrospinning.

Crosslinking of PVA Fibers

A desired thickness of PVA nano fibers was prepared under these conditions: voltage is 19 kV, concentration is 11 wt%, TCD is 8 cm. PVA fibers were put into the oven, and cured by crosslinking at 120 °C for 2-20 min. The crosslinked PVA fibers were purified by extraction with tetrahydrofuran in a Soxhlet apparatus for 24 h and dried at 70 °C under vacuum for 24 h. Thermally treated samples were prepared, but without the addition of glyoxal and phosphoric acid. The curing process is same to fibers with glyoxal and phosphoric acid.

Characterization of Electrospinning Fibers Morphology

The fiber morphology and fiber diameter of the electrospun PVA fibers were determined using scanning electron microscopy (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 using an accelerating voltage of 20 kV was employed to take the SEM photographs.

Characterization of the Thermal Behaviour of PVA Fibers

The thermal behaviour of non-crosslinked and crosslinked PVA fibers were studied by DSC (Du Pont 2100 thermo-analyzer) over the temperature range of 30-250 °C and at a heating rate of 10 °C/min.

Determination of the Water Absorbency of the PVA Fibers

The water content of the PVA fibers after swelling was calculated using the expression $W_a = (W_b - W_c)/W_c$, where W_a was the water up-take per gram of the PVA fibers, and W_b and W_c were the weight of the PVA fibers after swelling and subsequent drying, respectively. The time duration for swelling was 48 h. The excess water on the swollen fibers was wiped out with a filter paper. Each sample for swelling should be checked in 10 times.

Results and Discussion

Preparation of PVA Nano-fibers

Influence of Concentration

It has been observed in the electrospinning literature that solution concentration has a significant effect on the final size of particle[13]. For electrospinning, if the concentration was too low, the electrospinning process generated a mixture of fibers and droplet; if the concentration was too high, the solution proved extremely difficult to force through the syringe needle[14]. The solution viscosity and surface

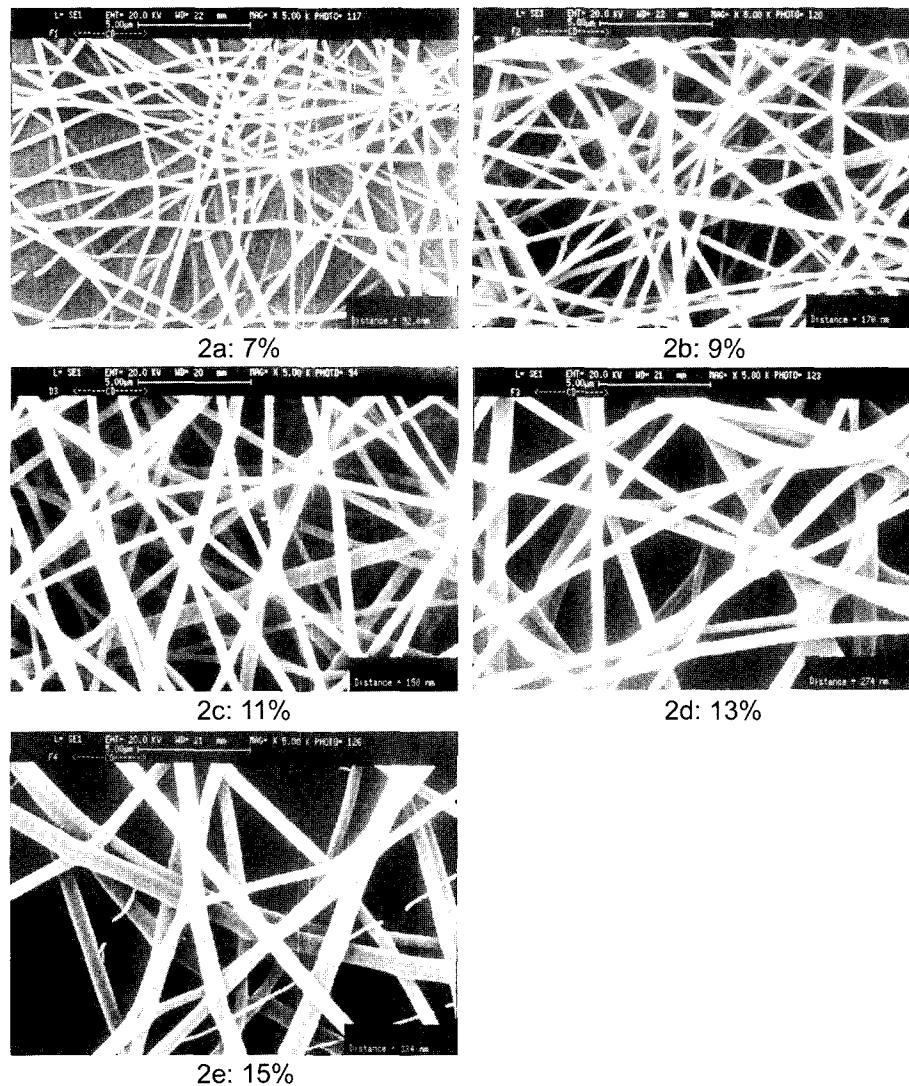


Figure 2. SEM of PVA fibers as a function of concentration. (voltage: 19 kV, TCD: 8 cm).

tension play an important role in determining the concentration of polymer solutions from which continuous fibers electrospun. The high concentration solution showed high viscosity and high surface tension. The split ability was reduced with increasing the surface tension.

Figure 2 showed the representative images of PVA fibers for solutions over the concentration range of 7 wt% to 15 wt%. The diameter distributions as a function of concentration were shown in Figure 3. As observed in Figures 2 and 3, the diameter of PVA fibers increased as the concentration increased. The electrospun beaded fibers are related to the instability of the jet of polymer solution[15]. The stability of polymer solution was enforced by increasing the concentration. As a result, the amount of beads was reduced. Increasing the concentration, the critical voltage was increased. It was shown in Figure 4. It illustrated the higher electrostatic force was needed with increasing the surface

tension during electrospinning process.

Influence of TCD (tip-to-collector distance)

The electrospinning fiber has some elasticity before evaporating the solvent. The chance of contraction was increased with increasing the TCD. Average diameter of PVA fibers as a function of TCD was shown in Figure 5. The diameter of fiber became slightly larger as the TCD increased. In Figure 6, the CD (Cross Direction) width increased with increasing the TCD in the range of 4 to 12 cm. It was confirmed that the droplet was split into cone during electrospinning process.

Influence of Voltage

The electrospay process could be sustained in a variety of modes characterized by the shape of the surface from which the liquid jet originated. These modes occurred at different

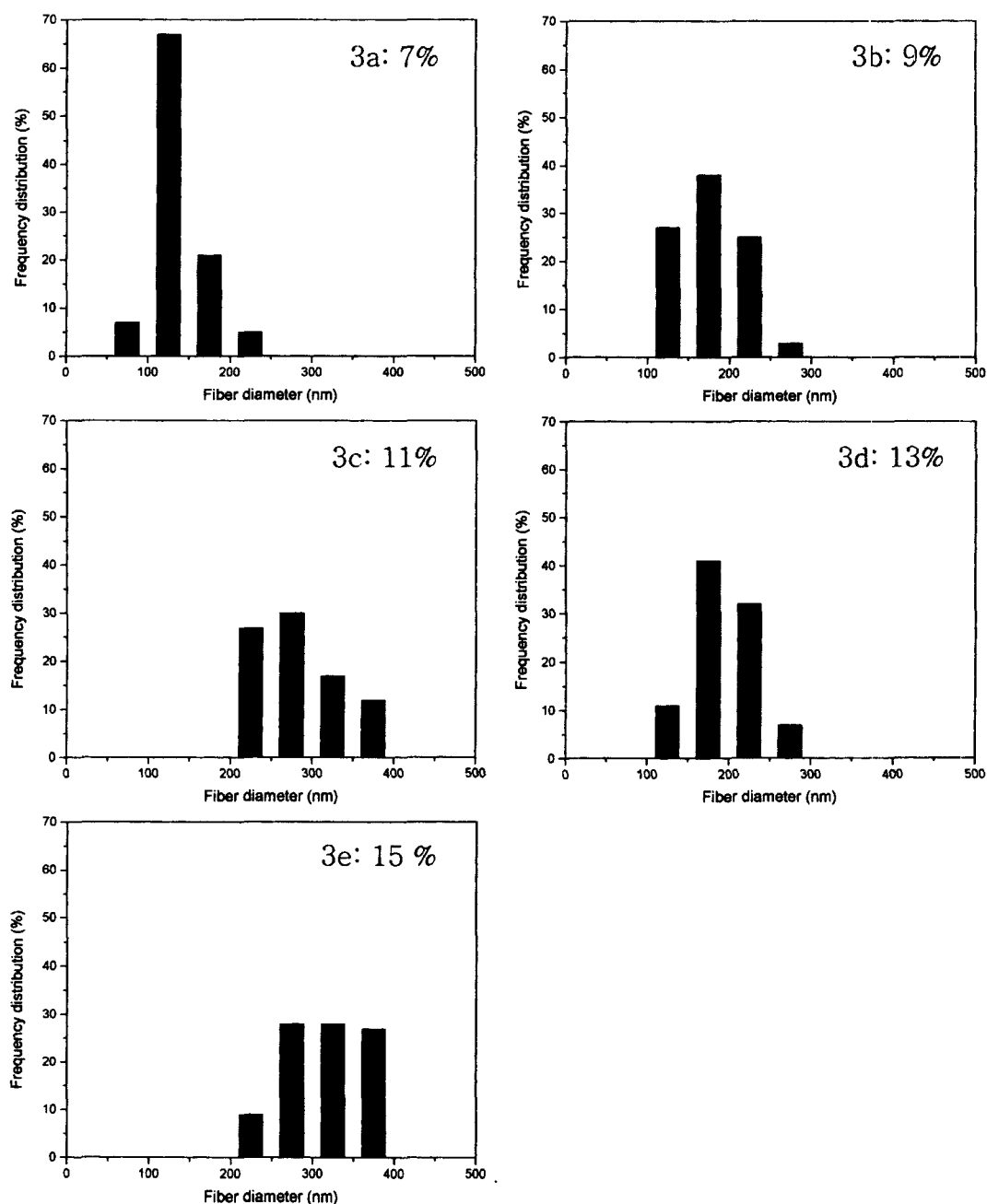


Figure 3. Frequency distribution of fiber diameter as a function of concentration. (voltage: 19 kV, TCD: 8 cm).

voltages and have significant effects on droplet size distribution and current transport[14]. It has been verified experimentally that the shape of the initiating drop changes with spinning conditions (voltage, viscosity, feed rate)[16]. It was known that the electrostatic force was gradually increased with increasing the voltage. The split ability of droplet was reinforced due to the increasing the electrostatic force. This influence was shown in Figure 7. Average diameter of PVA fibers is slightly decreased with increasing

the voltage. In Figure 8, the electrospinning throughput increased smoothly with increasing voltage from 7 to 19 kV. Increasing the voltage cause the rate at which solution was removed from the capillary tip to exceed the rate of delivery of solution to the tip needed to maintain the conical shape of the surface.

Differential Scanning Calorimetry (DSC)

DSC was a valuable technique for investigating the curing

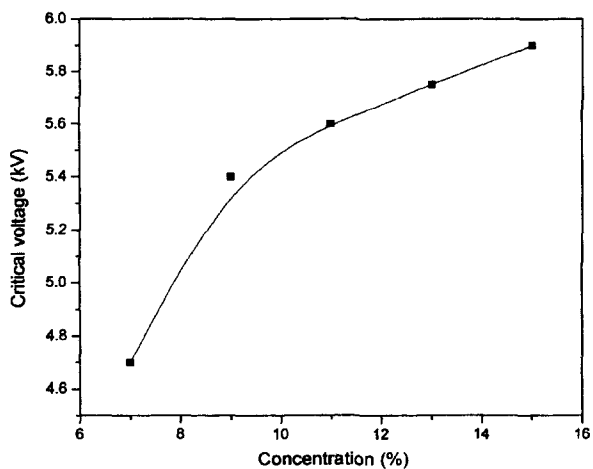


Figure 4. Critical voltage as a function of concentration. (voltage: 19 kV, TCD: 8 cm).

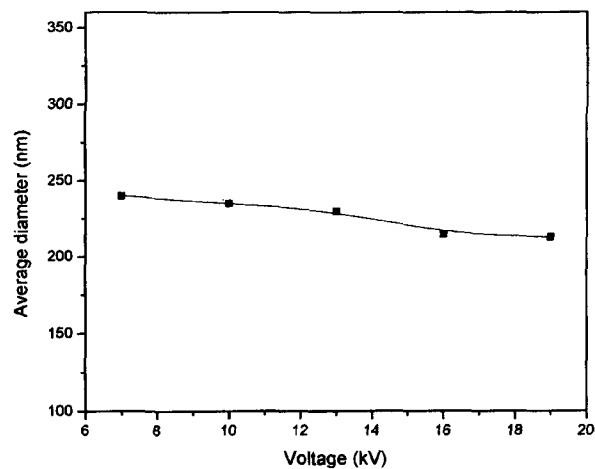


Figure 7. Average diameter as a function of voltage. (concentration: 11 wt%, TCD: 8 cm).

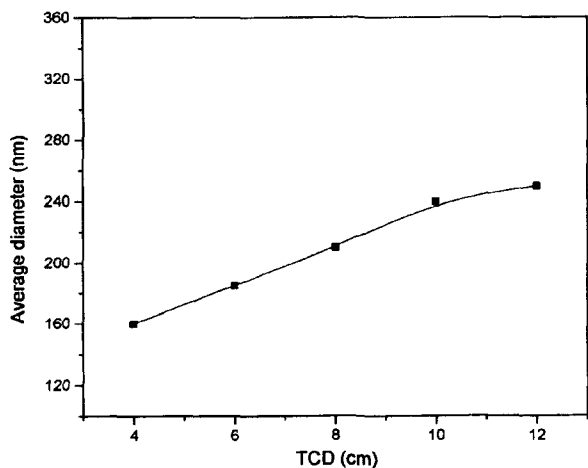


Figure 5. Average diameter as a function of distance. (concentration: 11 wt%, voltage: 19 kV).

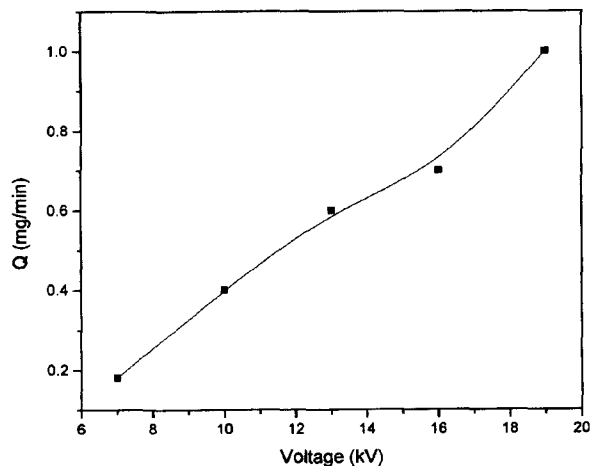


Figure 8. Throughput as a function of voltage. (concentration: 11 wt%, TCD: 8 cm).

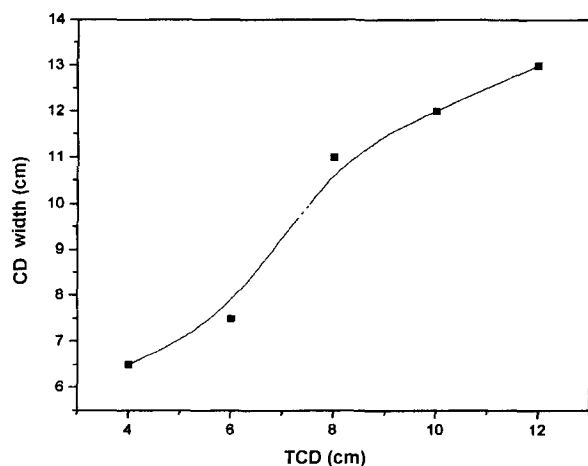


Figure 6. CD (Cross Direction) width as a function of distance. (concentration: 11 wt%, voltage: 19 kV).

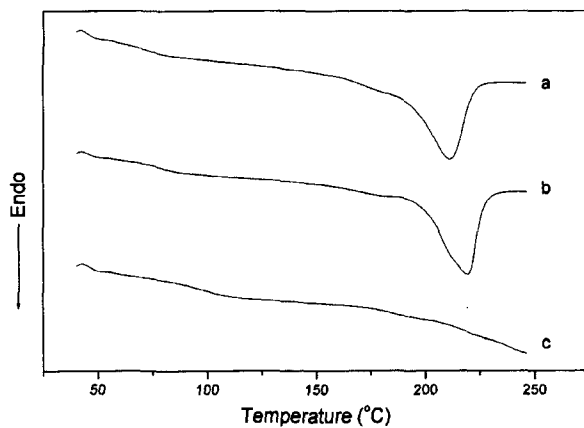


Figure 9. DSC thermograms for PVA. (a) PVA powder, from (b) to (c), PVA fibers crosslinked with glyoxal, in weight %, 0 and 8, respectively.

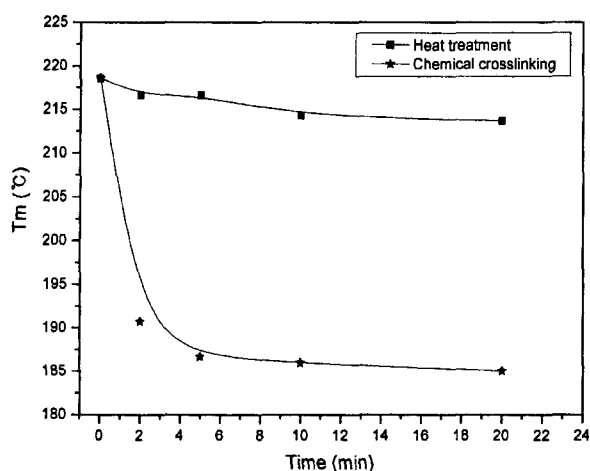


Figure 10. Melting temperature (T_m) of the heat treatment and chemical cross-linking (2 % crosslinking agent) PVA fibers as a function of curing time. The curing temperature is 120 °C.

reaction of crosslinkable polymers. Figure 9 presented the DSC thermograms over the temperature range 30 to 250 °C for PVA fibers. As shown in Figure 9a and 9b, after electrospinning, the melting temperature was increased due to the molecular orientation in fiber, and was higher than that in PVA powder[13]. The melting point and enthalpy of fusion disappeared when PVA fibers were crosslinked entirely (Figure 9c). The crosslinking conditions including concentration of crosslinking agent (8 wt%), curing temperature (120 °C) and curing time (5 min) were used to get entirely crosslinked PVA fibers. It suggested that the crystallinity and perfection of the crystal structure was reduced with increasing the degree of crosslinking. Melting temperature of the heat treatment and chemically cross-linked (2 wt% crosslinking agent) PVA fibers as a function of curing time (curing temperature 120 °C) were presented in Figure 10. The melting temperature was sharply decreased with increasing the curing time in chemical crosslinking, showing that the melting temperature was strongly influenced by chemical crosslinking as compared to that in heat treatment.

Swelling Behavior

A characteristic property of permanent networks is their ability to swell in suitable solvents. If a network is immersed in a solvent which is miscible with the polymer chains of the network, the solvent is absorbed and the network swells[11]. Water constituted a suitable medium, because PVA was soluble in water[8]. They became insoluble in water for sufficiently large degree of crosslinking. The swelling, expressed as gram of water up-take per gram of the PVA fibers, was used as a measure of the crosslinking density.

Figure 11 showed that the water content in fibers was obviously decreased with increasing the weight percent of

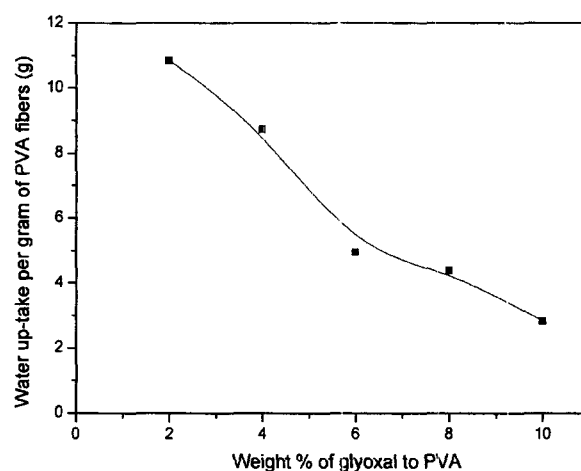


Figure 11. Water up-take per gram of PVA fibers with different weight % of glyoxal to PVA. The curing temperature is 120 °C, curing time is 5 min.

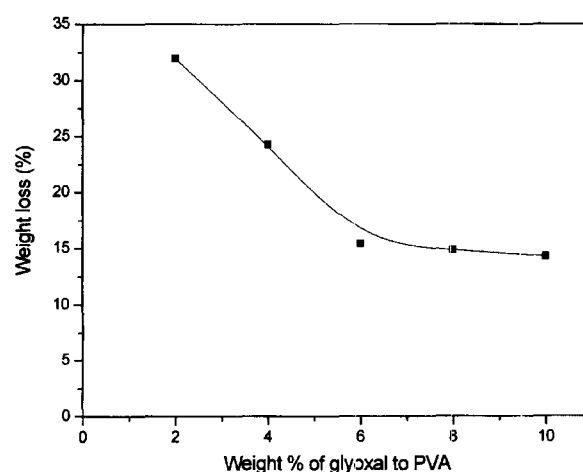


Figure 12. Weight loss of PVA fibers with different weight % of glyoxal to PVA. The curing temperature is 120 °C, curing time is 5 min.

glyoxal to PVA. The number of hydroxyl groups of PVA decreased as the weight percent of glyoxal to PVA was increased, as a result, the water up-take decreased with increasing the weight percent of glyoxal to PVA.

During the swelling test, some part of PVA fibers was dissolved in water due to the crosslinking was not entirely. The weight loss of PVA fibers with different weight percent of glyoxal to PVA was shown in Figure 12. The weight loss of PVA fibers was obviously decreased with increasing the weight percent of glyoxal to PVA.

Conclusion

PVA fibers with diameter of 50-250 nm were successfully prepared with using electrospinning technique. The diameter

of PVA fibers was largely influenced by solution concentration, voltage and tip-to-collector distance, respectively. After electrospinning, the morphology of PVA was greatly changed. The enthalpy of fusion and melting point disappeared when PVA fibers were crosslinked entirely. The volume of chemical crosslinking agent was found to be the primary factor which affect the crosslinking density. The results showed that the entirely crosslinked PVA fibers have better anti-water solubility than non-crosslinked PVA fibers.

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