Reactive Electrospinning of Poly(vinyl alcohol) Nanofibers

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ABSTRACT: We aim to couple the electrospinning in-line with solution chemistry to fabricate novel crosslinked polymer nanofibers. Poly(vinyl alcohol) (PVA) was used as a model polymer due to its high amount of hydroxyl groups. To obtain ideal parameters for electrospinning, pure PVA was explored primarily. To gain crosslinked fibers, PVA was first crosslinked partially with glutaraldehyde (GA) followed by transferring this precursor to a long hot tube which was used as reactor and then electrospun right before gelation. The preheating time and tube-passing time were determined with viscometer and rheometer. The reactive as-spun fibers could maintain their original morphology after water immersion due to their high crosslinking degree. The thermal stability and mechanical property of reactive as-spun fibers were improved drastically compared with pure and GA vapor crosslinked PVA fibers. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 1067–1073, 2012

Key words: reactive electrospinning; poly(vinyl alcohol); nanofiber; crosslinking

INTRODUCTION

Electrospinning provides a simple and versatile way to fabricate very fine continuous polymer fibers that form a nonwoven structure. The membrane-like nanofibrous mats exhibits good tensile strength, high porosity, and thus lightweight. In the case of water-soluble polymer such as poly(vinyl alcohol) (PVA) and poly(2-hydroxyethyl methacrylate), they need crosslinking to improve their water resistance. The general strategy to obtain crosslinked fibers is first electrospin to obtain pure fibers and then further crosslinking.[1–5] This strategy has its disadvantages such as time consuming, only surface crosslinking, and difficult handle. The general method of crosslinking PVA includes chemical crosslinking such as glutaraldehyde (GA) treatment,[6–8] electron beam or gamma irradiation,[9] and physical crosslinking such as heat treatment or annealing.[1] Qin and

Wang[10] first add maleic acid into PVA solution to prepare precursor and then form crosslinked PVA fibers by electrospinning. Recently, reactive electrospin PVA using GA as a chemical crosslinker combined with hydrochloric acid as a catalyst was used by Tang et al.[11]

The objective of our research is to couple the electrospinning in-line with solution chemistry to fabricate novel crosslinked polymer nanofibers. The general methodology is that the mainstream solution contains only soluble polymers, whereas the initiators (catalyst, crosslinker, etc.) are added *in situ*, i.e., through an in-line "reactor," near the outlet of the electrospinning capillary. The polymerization and gelation occur right before and during the electrospinning process. To reach high reaction rate or crosslinking degree, hot and long capillary is designed because high temperature and long time are favorable to reaction. The crosslinking time can be determined roughly with viscometer and rheometer. When compared with two-step method, the processibility of electrospinning and mechanical property of our fibers would be greatly improved. In the study, the PVA was used as model polymer due to its high amount of hydroxyl groups. The pure PVA was first explored to obtain ideal parameters for electrospinning. In the case of reactive electrospinning, the PVA solution was mixed with GA and preheated at 50°C in a flask for a certain time. During above process, the PVA was partially crosslinked. This precursor was flowed through a long metal tube (capillary) at 70°C for further crosslinked
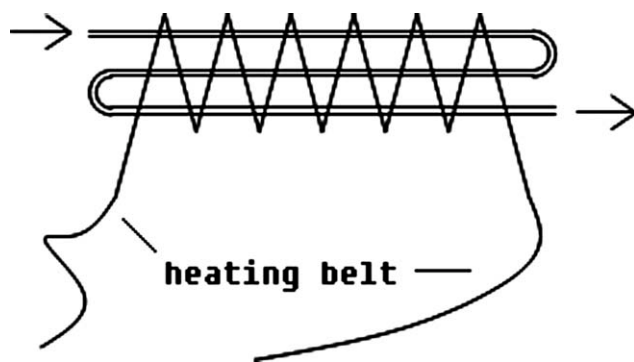
Figure 1 Schematic drawing of capillary for electrospinning.

and then electrospun. The pure PVA fibers were crosslinked with GA vapor and used as control. The water-resistance property of fibers was measured using water immersion test. The thermal stability was determined using a thermo-gravimetric analysis (TGA). The mechanical property of fibers was tested with a dynamic mechanical analysis (DMA).

EXPERIMENTAL

Materials and device

PVA powder (M_w = 78,000 g/mol, 98% hydrolyzed) was purchased from Polysciences. Trition X-100 was obtained from Fisher scientific. A total of 25% GA aqueous solution was provided by Sigma chemical.

A new capillary for reactive electrospinning was designed and constructed as shown in Figure 1. When compared with conventional espsin, our capillary is a long metal tube wrapped with a heating belt. The metal tube can be heated by heating belt and used as "reactor." The temperature of tube can be controlled by thermo-sensor, and the tube-passing time can be adjusted by flow rate and tube length.

Electrospinning of pure PVA nanofibers

The viscosity of PVA solution was first measured to find the appropriate concentration for electrospinning. Series concentrated of PVA solution were prepared by dissolving PVA powder in distilled water

at 80°C under constant stirring. The effect of concentration on viscosity was explored using viscometer. Triton X-100 was added with the concentration of 1 w/w % to reduce surface tension. This mixture was stirred further for 15 min before electrospinning.

Reactive electrospinning of PVA nanofibers

A total of 25% GA was used to crosslink PVA solution at a theoretical crosslinking degree of 100%. The calculated GA was added and stirred for 10 min at room temperature. Then, about 6 mL of mixture was transferred to viscometer at 50°C. The viscosity was recorded every 10 min to obtain viscosity–time (η–t) curve. A little mixture was also dropped onto rheometer to test gel time at 50°C. The viscosity of mixture would increase largely due to crosslinking. From viscosity–time curve, the gel time could be determined, respectively. On the basis of above proposal, we plan to preheat PVA/GA mixture in a flask at 50°C for a certain time (denoted as preheating time) and then transfer to a long metal tube at 70°C for in-line electrospinning. The time of the mixture flowing through the tube is denoted as tube-passing time. After that, the PVA/GA mixture would reach high crosslinking degree (before gelation). Therefore, preheating and tube-passing time should be first explored using the viscosity–time curve. In this study, 8% PVA solution was preheated at 50°C in a flask within oil bath for 1 h. Then, this precursor passed through the long metal tube at 70°C for tube-passing time and electrospun. To minimize falling drops at the tip of syringe, the syringe was tilted at 15° from the horizontal.

Vapor crosslinking of pure PVA fibers

The crosslinking process was carried out according to the method established by Zhang et al.[12] In brief, in a sealed desiccator containing 10 mL of 25% aqueous GA solution, the fibers were crosslinked in the GA vapor at room temperature for 2 days. After crosslinking, the fibers were dried at 60°C in vacuum for 24 h. The descriptions of above samples were listed in Table I.

TABLE I
Description of Samples in This Article

Samples	Voltage (kV)	TCD[a] (cm)	Flow rate (mL/h)	Description
Pure PVA	30	15	1.0	12% Pure PVA
Reactive as-spun PVA	30	12	1.0	8% PVA mixed with GA, preheated for 1 h
Vapor crosslinked PVA	30	15	1.0	12% Pure PVA crosslinked with GA vapor

[a] Distance between tip and collector.

Water immersion test

To determine the solubility of crosslinked PVA fibers, the gravimetric method was used. The fibers listed in Table I were immersed in water at 37°C for 24 h and then dried at 80°C for 48 h with vacuum oven. The weight loss was calculated according to initial weight and residual weight. The images of fibers after immersion were observed with scanning electron microscopy (SEM).

CHARACTERIZATIONS

Viscosity measurement

The viscosity of PVA solution was measured using Brookfield LVT viscometer equipped with a small-sample thermostated adapter, spindle, and chamber SC4-18/13R. The temperature was maintained during the measurements using a thermostatically controlled tank. During the crosslinking procedure, viscosity was recorded as the function of time.

Rheological property of PVA solution

The gelation process was monitored with an ARES Rheometer using dynamic time sweep mode. The crosslinking process occurred over the 1 mL mixture solution of PVA and GA on the parallel plate (diameter 15 mm) under the conditions of a time sweep at 50°C, with a 1.3-mm gap, 10% strain, and frequency sweep at 0.1–10 rad/s. The crosslinking was monitored for 4 h by observing the viscous modulus and the elastic modulus.

Morphology of PVA fibers

The morphology and diameter of PVA fibers were determined with SEM. A Hitachi-2100 SEM with an accelerating voltage of 15 kV was used for the SEM photographs.

Thermo-gravimetric analyses

TGA measurements were carried out with a TA instruments Q600 TGA operated from 50 to 600°C at a rate of 10°C/min in the atmosphere of nitrogen.

Dynamic mechanical analysis

The mechanical properties of PVA fibers were determined using a TA Instruments Q800 DMA. For DMA test, the specimens was cut along the nano-fiber winding direction with a typical size of 20 mm (length) × 6 mm (width) and a thickness of about 0.06 mm. The DMA multistress mode and strain sweep were used. From the stress–strain curve, the
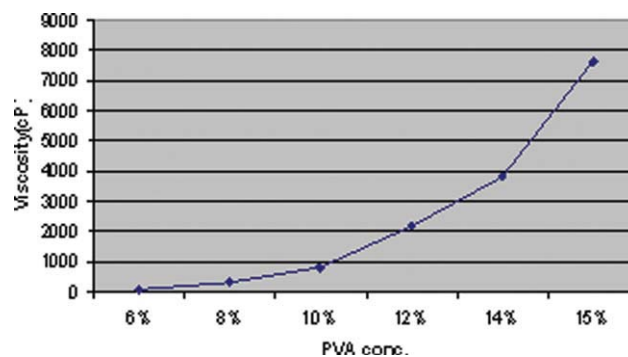
Figure 2 Effect of concentration of PVA solution on viscosity.

slope was calculated as elastic modulus. The test temperature was 30°C for all the experiments.

RESULTS AND DISCUSSION

The term "reactive electrospinning" was first proposed by Kim et al.,[13] where crosslinking occurred simultaneously during the electrospinning process. Ji et al.[14] selected poly(ethylene glycol)diacrylate as crosslinker to prepare crosslinked hyaluronic acid with dual-syringe reactive electrospin. Herein, we first crosslinked PVA partially, then put them into a long and hot tube for further curing, and finally electrospun right before gelation to obtain high crosslinked fibers.

Electrospinning of pure PVA nanofibers

The viscosity of PVA solution was first measured to find the appropriate concentration for electrospinning, and the results are shown in Figure 2. The viscosity of PVA solution increases very slowly up to 12 wt %, and thereafter increases rapidly. The solution concentration is one of the most significant parameters to control the electrospun fiber morphology. Figure 3 shows SEM micrographs of the fibers electrospun with series of concentration solutions. For the low polymer concentration of 8% and 10%, a large number of beads and bead-fibers appear [Fig. 3(a,b)]. Beads disappear at the concentration of 12% and the diameter of obtained fibers is 278 nm ± 80 nm [Fig. 3(c)]. Finally, the parameters for electrospinning are fixed as follows: 12 wt % (concentration), 30 kV (voltage), 15 cm (the distance between tip and receiver), and 1 mL/h (flow rate). It is noted that a small amount of Triton X-100 can promote electrospinning. Wang et al. and Yao et al. explored the effect of surfactant concentration on the electrospinning.[2,3] In this study, 1% Triton X-100 was used.
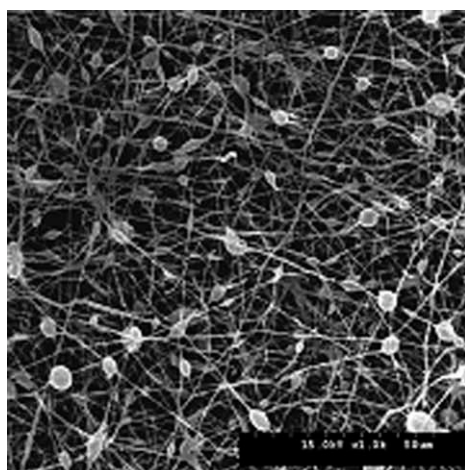
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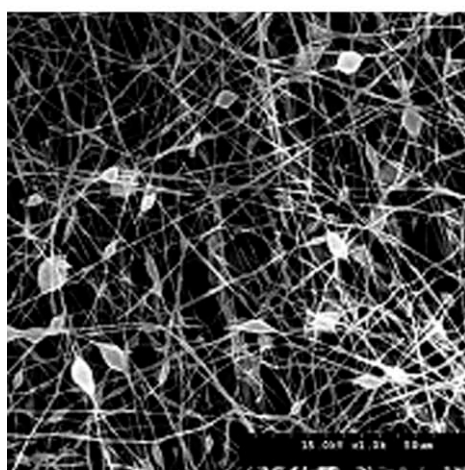
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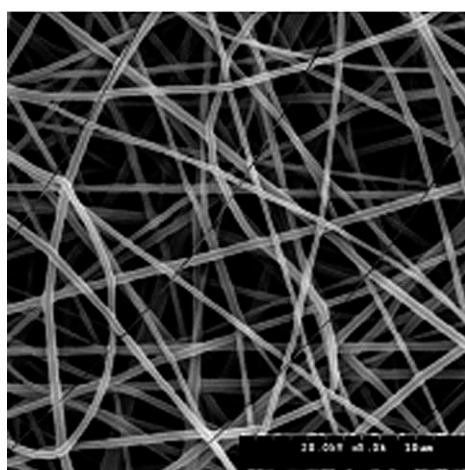
(c)

Figure 3 SEM images of PVA fibers by electrospinning at different concentration. (a) 8% PVA, 1% Triton X-100, 0.5 mL/h, 15 cm, ×1000; (b) 10% PVA, 1% Triton X-100, 0.5 mL/h, 15 cm, ×1000; (c) 12%, 1% Triton X-100, 0.5 mL/h, 15 cm, ×5000.
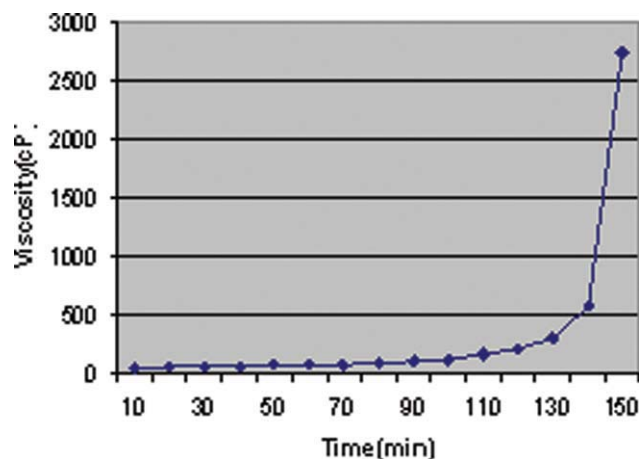

Figure 4 Viscosity of 8% PVA solution at theoretical crosslinking degree of 100% as the function of time at 50°C.

Reactive electrospinning of PVA nanofibers

Even though PVA has a good mechanical property in the dry state, its applications are limited by its high hydrophilicity. PVA fiber can be readily cross-linked for improved water resistance. Crosslinking agents including GA and glyoxal were usually used as chemical crosslinker. A total of 8% PVA solution (lower than 12%) was chosen to react with GA to prepare precursor because the viscosity would increase during crosslinking. The viscosity of PVA solution during this procedure was recorded with viscometer. Figure 4 shows viscosity results as the function of time. In the beginning time of 100 min, the viscosity increased slowly. However, the viscosity increased largely after the time of 120 min. For the easy handle and evaporation reduction, the temperature and preheating time were fixed at 50°C and 1 h, respectively. After the preheating time was fixed, the tube-passing time should be decided further. The precursor was prepared in the flask within oil bath at 50°C for 1 h. About 6 mL of this precursor was transfer to viscometer at 70°C to test gel time. According to our data (not shown), the further gel time was about 20 min, therefore the tube-passing time should shorter than this time in case of gelation. The hot tube-passing time can be controlled by the flow rate and the metal tube length. In our study, tube-passing time was about 10 min. Finally, the precursor was transferred to syringe and flowed through the hot metal tube at 70°C for electrospinning. The parameter of reaction electrospinning was optimized and listed: 12 cm (distance between receptor and tip), 30 kV (voltage), 1.0 mL/h (flow rate), and 200 rpm (rotary speed). Figure 5 shows the SEM image of crosslinked fibers. It was observed that the fibers were deposited as a randomly oriented state, forming highly porous structures, which were held
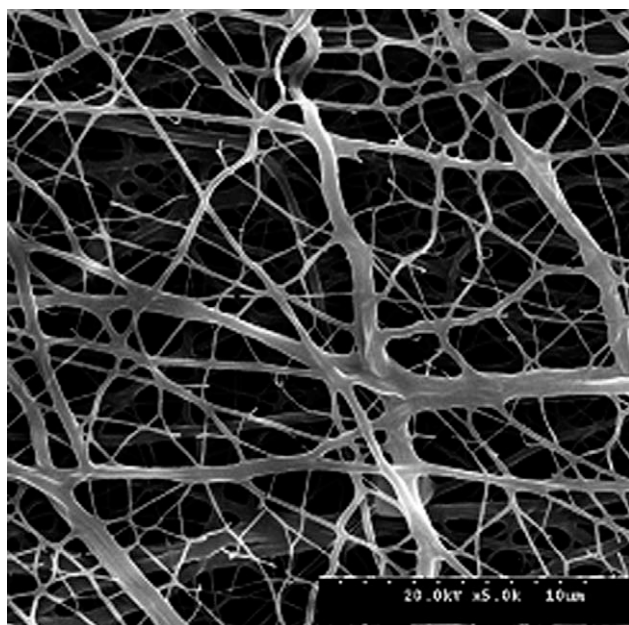
Figure 5 SEM image of reactive as-spun PVA fiber (×5000).

together by connecting sites such as crossing and bonding between the fibers. The diameter was not uniform compared with pure fibers.

The gelation process was also monitored rheologically by rheometer. Figure 6 shows the rheological property of 8% PVA solution at theoretical crosslinking degree of 100% at 50°C. Both of the storage modulus and loss modulus increased over the entire time range. However, the storage modulus ($\acute{G}$) increased more quickly than that of loss modulus (G'') due to gelation. The storage modulus overpassed the loss modulus at the time of 7000 s (117 min). This gel time is much closer to the value that tested with viscometer (2 h). It is noted that gap is
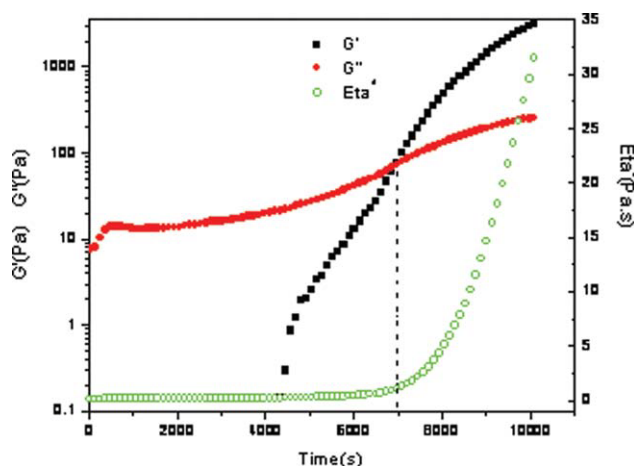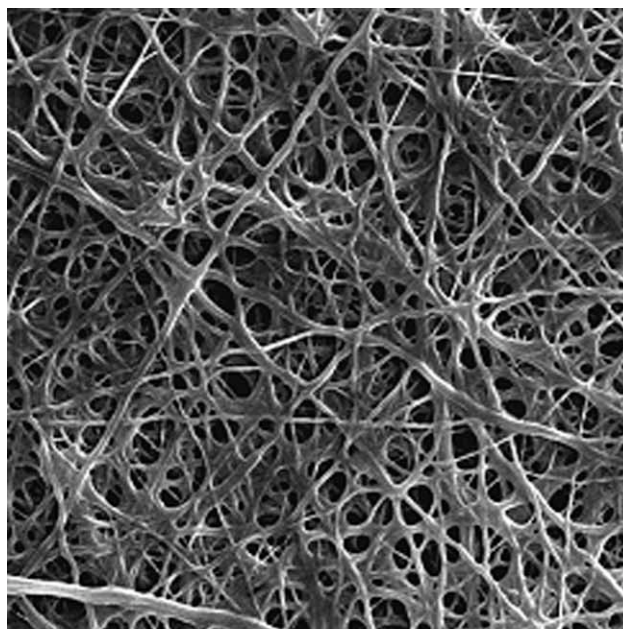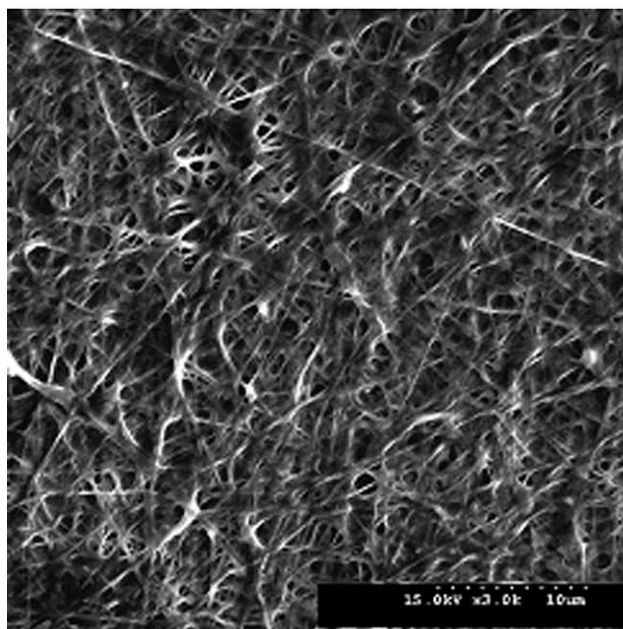

Figure 6 Rheological property of 8% PVA solution at theoretical crosslinking degree of 100% at 50°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
The Rate of Weight Loss after Water Immersion at 37°C for 24 h

	Rate of weight loss (%)
Pure PVA	100
Vapor crosslinked PVA	64.7
Reactive as-spun PVA	24.7

(a)

(b)

Figure 7 SEM images of fibers after water immersion at 37°C for 24 h: (a) Reactive as-spun PVA fibers, ×3000, and (b) GA vapor crosslinked PVA, ×3000.

<table>
<tr><td colspan="2" align="center">TABLE III
Elastic Modulus of Electrospun PVA Mats by DMA</td></tr>
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Sample	Elastic modulus (MPa)
Pure PVA	235 ± 38
Vapor crosslinked PVA	261 ± 36
Reactive as-spun PVA	1139 ± 145

important for rheometer due to evaporation. During the test process, the cap was used to reduce evaporation.

Water immersion test

To test solubility of fibers, the mats were immersed in water at 37°C for 24 h. The rate of weight loss was calculated and shown in Table II. The pure PVA mats were dissolved in water immediately. For the vapor-crosslinked fibers, the weight loss was high up to 64.7%, which indicated that vapor cross-linking method was low efficient. In the case of reactive as-spun mats, the weight loss was only 24.7%, which indicated that most of PVA fibers were cross-linked. After immersion, the morphology of reactive as-spun fibers hardly changed [Fig.7(a)], which indicated that crosslinked fibers could maintain their backbone due to high crosslinking degree. However, for the GA vapor crosslinked PVA fibers, most of fibers were entangled together [Fig.7(b)], which indicated that vapor crosslinked PVA fibers could not maintain their backbone due to low crosslinking degree.

Dynamic mechanicalanalysis

The conventional method for mechanical test is using a universal test machine. The specimen should
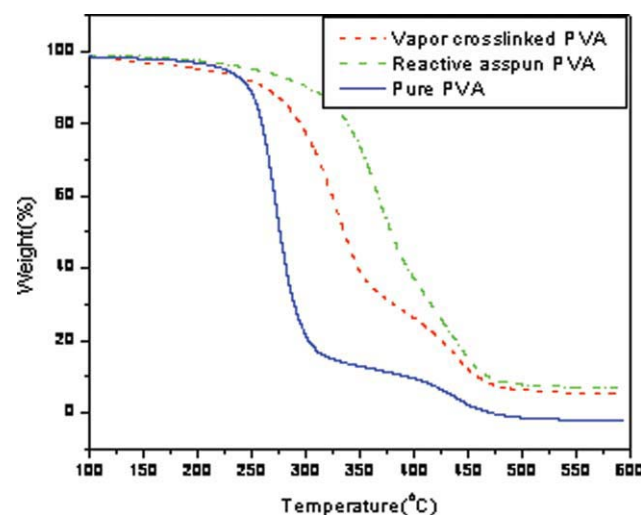

Figure 8 Thermo-gravimetric analyses curve of pure and crosslinked PVA fiber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

<table>
<tr><td colspan="3" align="center">TABLE IV
Thermogravimetric Data of PVA Fibers</td></tr>
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	T_i (°C)[a]	T_{max} (°C)[b]
Pure PVA	247	275
Vapor crosslinked PVA	287	329
Reactive as-spun PVA	326	366

[a] T_i, onset of the curve weight loss versus temperature.
[b] T_{max}, the maximum weight loss temperatures.

be prepared according to ASTM standard. In general, the electrospun mat is very thin and has low tensile strength. In addition, DMA instrument is more sensitive to load compared with universal test machines. Therefore, using DMA for mechanical test can reduce test error and increase precision. Herein, DMA was used to test mechanical property of fibers. From the stress–strain curve, the slopes were calculated as elastic modulus and are listed in Table III. Vapor crosslinked PVA mats have a little higher elastic modulus than pure PVA mats, which indicated that crosslinking degree was very low. The elastic modulus of reactive as-spun mats was increased high up to 385%, which was drastically improved compared with other mats.

Thermal analysis

The TGA curves of linear and crosslinked fibers are shown in Figure 8. The thermal analysis data obtained by TGA are summarized in Table IV. Pure PVA fiber was decomposed at 247°C. In the case of reactive as-spun fiber, it was decomposed at 326°C. It indicated that the thermal stability of PVA fiber was improved drastically. When compared with pure PVA, vapor crosslinked PVA had a relatively higher decomposition temperature (T_i). As shown in Figure 8, the TGA curves displayed a two-step degradation mechanism. The maximum weight loss temperatures (T_{max}) for the low temperature step obtained from the differential thermo-gravimetric traces was summarized in Table IV. The weight loss in the low temperature range may correspond to the breaking of ester linkage, whereas the weight loss in the high temperature ranges to the degradation of the main chain.[15]

CONCLUSIONS

In summary, nanofibrous PVA were prepared in-line with solution chemistry through reactive electrospinning technique. These fibers have a good water resistant property, a high mechanical strength, and a high thermal stability. The reactive electrospinning technique has the potential of industrial applications. Reactive electrospinning in-line with photochemistry is ongoing.

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