Fabrication and Characterization of Poly-γ-glutamic Acid Nanofiber

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Received 11 August 2010; accepted 14 January 2011 DOI 10.1002/app.34176 Published online 19 April 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Poly- γ -glutamic acid (γ -PGA) is a natural polymer that is widely recognized as a component in the viscous filaments of fermented soybean (*natto*). γ -PGA is known for its superior biodegradability, biocompatibility and water retention characteristics. Crosslinked γ -PGA is commonly used as a hydrogel, but it is not used in the fiber form because it is soluble in water. In this study, we demonstrate the use of γ -PGA-Na for production of water insoluble γ -PGA nanofibers by electrospinning. This result was accomplished using an aqueous solvent

containing 10 wt % of an oxazoline component polymer as the crosslinking agent and by heat treatment. The crosslinking reaction was evaluated by solid-state NMR. The nanofiber webs showed a high level of moisture absorption capability while retaining their fibrous shape. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 150–158, 2011

Key words: electrospinning; poly-γ-glutamic acid; fiber; crosslinking ; mechanical properties

INTRODUCTION

The drive to become a low-carbon-consuming society has stimulated renewed interest in biopolymers. A well-known example of these non-petroleumdependent materials is poly- γ -glutamic acid (γ -PGA). γ -PGA is a polyamino acid commonly found as a component in the viscous filaments of fermented soybean (*natto*). It is produced under action of microbes such as *Bacillus species* and is known for its superior biodegradability, biocompatibility, and especially for its capacity for water retention and hydrophilicity.¹⁻⁴ γ -PGA, in a fibrous scaffold hydrogel composed of nanoparticles, has potential for use as a drug delivery carrier and in many biomedical applications, if it can be made water insoluble.

Various methods have been reported for insolubilization of γ -PGA, including the use of poly-ioncomplexes,^{5,6} copolymers,⁷ crosslinkers,^{8–13} and electron beam irradiation.¹⁴ As the fibrous nature of γ -PGA is evident in fermented soybean (*natto*), γ -PGA was converted to nanofibers by electrospinning.^{15–18} Electrospun γ -PGA is useful as a fiber mat for biomedical or tissue engineering applications.

The electrospinning method which is attractive for the processing of natural polymers are not suitable for processing at high temperature because it allows spinning to be carried out at room temperature.^{19–24} However, an organic acid (trifluoroacetic acid or 1,1,1,3,3,3-hexafluoro-2-propanol) is used as the solvent to make electrospun water -insoluble γ -PGA.^{15–18} This process is not suitable for mass production because these organic acids are expensive, harmful, and dangerous and thus should be recovered. For mass production of electrospun γ -PGA, it is therefore desirable to develop an aqueous base processing system.

It is well known that the Na salt of γ -PGA is used mainly as a precursor for hydrogel production via a basic aqueous processing system. Use of the γ -PGA Na salt permits change of the solvent in the system from an organic acid to a waterbased system, which in turn leads to process simplification, improvement in safety and reduction of cost in the production, and use of the nanofibers. Electrspun γ -PGA Na, however, remains soluble in water.¹⁶

In this study, we have developed an insolubilization method for γ -PGA Na nanofiber that is capable of retaining γ -PGA's fibrous shape even after water absorption. An oxazoline component polymer was selected as a crosslinking agent to react with the γ -PGA carboxyl groups in a ring-opening reaction under application of heat. The characteristics inherent to γ -PGA Na, such as moisture absorption and water absorption, were maintained through the formation of a nonwoven fabric web.

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Journal of Applied Polymer Science, Vol. 122, 150–158 (2011) $\ensuremath{\mathbb{C}}$ 2011 Wiley Periodicals, Inc.

Blending Conditions for the Electrospinning Solutions					
γ-PGA/OXA Weight ratio ^a	PGA-Na:OXA = 1:X Molar ratio ^b	Concentration (wt %)	Water (wt %)	Ethanol (wt %)	1 M HCl (wt %)
100/0	0.00	8	65	27	0
99.3/0.7	0.005	8	45	27	20
98/2	0.014	8	45	27	20
96/4	0.028	8	45	27	20
90/10	0.076	8	45	27	20
60/40	0.45	8	45	27	20
			65	27	0

TABLE I

^a nonvolatile matter.

^b carboxyl/oxazoline group of the polymer unit.

EXPERIMENTAL

Materials

 γ -PGA (γ -PGA HM-Na⁺ form ($M_w \approx 1.3 \times 10^6$ Da, carboxyl group content: 6.62 mmol/g), was manufactured by Vedan Enterprise (Taichung, Taiwan). The oxazoline component polymer (OXA; EPOCROS WS-700; $M_w = 4 \times 10^4$; aqueous solution with 25 wt % nonvolatile matter; oxazoline group content: 4.50 mmol/g) used as the crosslinking agent was manufactured by Nippon Shokubai (Tokyo, Japan). The hydrochloric acid (JIS special grade reagent, Kanto Chemical (Tokyo, Japan) was previously adjusted to a concentration of 1.0 *M*. The ethanol used was also a JIS special grade reagent manufactured by Kanto Chemical. A knitted fabric of 100% rayon, characterized by a thickness of 0.91 mm at 49 Pa pressure and an air resistance of 0.046 kPa·s/m, a collagen sponge with crosslinked by heat treatment at 140°C and 12 h (a thickness of 0.30 mm and 23 g/m²) were used as baseline samples for reference purposes.

Preparation of nanofiber

Solution

An ethanol/water/hydrochloric acid mix was used as the solvent. To produce the electrospinning solutions, an aqueous y-PGA solution and an aqueous OXA solution were mixed under agitation at a solid matter concentration of 8 wt %. Table I provides a summary of the mixing conditions for the spinning solutions (or spinning dope). The viscosity of the solutions was determined using a TVB-10 viscometer (Toki Sangyo).

Electrospinning and crosslinking

Electrospinning was carried out using an NS-LAB200S electrospinner (Elmarco) at an electrode distance of 100-120 mm and a voltage of 55-75 kV at 26°C and 20% relative humidity (RH). In this electrospinning system, solution was electrospun onto the polypropylene (PP) nonwoven (30 g/m²), which was moving at a winding velocity of 0.06 m/min for 3 h. The obtained γ -PGA web on the substrate material was then heated in a vacuum dryer at 120°C for 0, 0.25, 0.5, 1, and 12 h for crosslinking treatment. After heat treatment, the γ -PGA web was easily peeled off of the PP nonwoven by hand.

Characterization

Structural analysis

The structure of the γ -PGA fiber was analyzed by solid-state NMR (JNM-CMXP300 NMR, JOEL) using the pulse-mode CP-MAS method. The test conditions consisted of the following: 75 MHz measurement frequency; ¹³C measured nucleus; 90° pulse width (¹H) of 3.2 µs; 5 s waiting time after FID measurement; 5 mm sample tube diameter; and 6 kHz MAS rotating speed.^{25,26}

Insolubilization

The mass loss of the crosslinked γ -PGA fibrous membranes in water was determined gravimetrically. One hundred milligrams of γ -PGA fiber were placed in a 30 mL sample bottle; distilled water (20 mL) was then added and the mixture agitated with a shaker for 1 h. The distilled water was then exchanged. These operations were repeated three times, and then the insoluble matter was dried under vacuum at ambient temperature.

The weight loss of γ -PGA fiber was calculated using the following equation:

Weight loss (%) =
$$(1 - W_I/W_0) \times 100$$
, (1)

where $W_{\rm I}$ is the final dry weight of insoluble fibers (mg) and W_0 is the initial weight of the electrospun web.

Morphological observation

Crosslinked γ -PGA fibers were moistened, immersion-washed, and then freeze-dried. The morphology of the γ -PGA fiber was examined using a scanning electron microscope (SEM; 3D Real Surface View Microscope VE-8800, KEYENCE) at 20 kV accelerating voltage. Samples were sputter coated with gold. The fiber diameter was calculated from an average of 30 fibers in the image.

Moisture absorption/desorption characteristics

Moisture absorption/desorption behavior of a sample was evaluated through a series of ambient humidity change at $23 \pm 0.5^{\circ}$ C.

The electrospun γ -PGA web conditioned at 23 ± 0.5°C and 30 ± 2% RH (sample W_0) was set in a PP frame (40 × 40 mm, 0.2 mm thickness, 5 mm in width) and allowed to absorb moisture under an environment of 23 ± 0.5°C and 73 ± 2% RH for 20 h. Sample was then transferred to desorb moisture at 23 ± 0.5°C and 30 ± 2% RH for 20 h. During the experiment, the change in weight was monitored over time. Moisture regains, *M*1 and *M*2 were calculated as follows:

$$M_1 = (w_1 - w_0)/w_0 \times 100 \ (\%), \tag{2}$$

$$M_2 = (w_2 - w_0)/w_0 \times 100 \ (\%), \tag{3}$$

where w_0 : initial weight of sample W_0 conditioned at 30 ± 2% RH

 w_1 : weight after absorb moisture under an environment of 73 \pm 2% RH for 20 h

 w_2 : weight after desorb moisture at 30 \pm 2% RH for 20 h.

In addition, the water absorption/desorption isotherm at 25°C was determined using BELSORPaqua3 (Bel Japan).

Water absorbency characteristics

Water absorbency was detected by two different methods. One method involved immersion of samples in water, whereas the other required placement of a droplet of water on the samples to investigate the resulting wetness.

Method 1

 γ -PGA web (10 mg) was weighed and immersed in distilled water at 23 ± 0.5°C for 1, 5, 10, 15, and 30 min. After the appropriate amount of time, the sample was withdrawn from the water and water droplets were removed by light wiping, and then the weight of the sample after water absorption was determined by

Water absorbency
$$(\%) = (S_I - S_0)/S_0 \times 100$$
, (4)

where S_{I} and S_{0} are the weights (mg) of the wet samples and the dry samples, respectively.

Method 2

The γ -PGA web with the polyethylene frame was placed on a hot plate (10°C above the ambient temperature: (32.2°C) at 40 ± 1% RH). Ten microliters of water were placed on the center of the γ -PGA web drop-by-drop with a syringe. The change of the surface temperature, which characterizes the water absorption/diffusion and vaporization behavior of the γ -PGA web, was monitored over time in the central area where the water was being applied using an infrared-thermography instrument (TH9260 Thermotracer, NEC Avio Infrared Technologies).

Tensile tests

The tensile properties of the γ -PGA web were determined using the KES-G5S microtensile tester (Kato Tech). The specimen dimension was 10 mm in width and 0.2 mm in thickness. The gauge length was 10 mm. A crosshead speed of 12 mm/min was used. The tensile tests were carried out at 23°C under three different humidity conditions: 30, 75, and 100% RH, as well as in water. The strength and the elongation at break of the specimen and the modulus were determined from an average of 10 specimens.²⁷

RESULTS AND DISCUSSION

Evaluation of γ-PGA nanofibers

Structure changes with crosslinking

The CP/MAS ¹³C NMR spectra of γ -PGA, OXA, γ -PGA/OXA as spun and γ -PGA/OXA with heat treatment at various blend ratios are shown in Figure 1. The structural formulae of y-PGA, OXA and the estimated crosslinked derivatives are shown in Figure 2. For the sample spun from the γ -PGA/ OXA solutions, the intensity of the peak at 70 ppm derived from the -OCH₂- group of the oxazoline moiety varied according to the blending ratio of OXA. In the blend that was prepared without addition of hydrochloric acid, the α peak derived from the oxazoline group appeared as a shoulder at around 170 ppm [Fig. 1(c)]. This shoulder disappeared in the crosslinked derivative, which was prepared by adding hydrochloric acid and heating [Fig. 1(d)], and changed to the α' peak, which was similar to the peaks of the carboxyl and amide groups of γ -PGA. It was also found that of the two sharp peaks attributed to OXA, the intensity of the ε peak fell in the range of 40–45 ppm, which was significantly lower in the crosslinked derivative than in the blend. The change in peak intensity is considered to be due to the change in chemical shift $(\varepsilon \rightarrow \varepsilon')$ caused by the ring-opening reaction of the oxazoline group, as shown in Figure 2. Changes in peak intensity



Figure 1 CP/MAS ¹³C NMR spectra of (a) γ -PGA, (b) OXA, (c) Blended γ -PGA + OXA = 60 + 40 and crosslinked γ -PGA/OXA (d) = 60/40, (e) = 90/10, and (f) = 99.3/0.7.

corresponding to the chemical shift $(\delta \rightarrow \delta')$ of the methyl group in the neighborhood of the quaternary carbon and the chemical shift $(\beta \rightarrow \beta')$ caused by conversion of the tertiary amine in the oxazoline group to a secondary amine were also observed. The results indicate that crosslinking occurs by ring



Figure 2 Molecular structures of γ -PGA, OXA and crosslinked γ -PGA/OXA.



Figure 3 Weight loss for different ratios of γ -PGA. The solvent of the electrospinning solutopns. (a) water/ethanol/HCl and (b) water/ethanol.

opening of the oxazoline group by the carboxyl groups of γ -PGA.

Insolubilization

In Figure 3, the effect of the γ -PGA/OXA blend ratio on weight loss is shown for the samples that were treated with HCl and heated at 120°C for 1 h. It can be seen that the weight loss decreases as the OXA blending ratio is increased.

The crosslinked derivative was not obtainable without the addition of hydrochloric acid to the solution, even if OXA was blended at a level of 40 wt %. In other words, the addition of hydrochloric acid catalyzes the reaction between the OXA oxazoline groups and the γ -PGA carboxyl groups, producing a crosslinked γ -PGA derivative at a weight loss level of about 28%, even at an OXA blending ratio of only 4 wt %. The minimum weight loss was obtained for the sample with a blend ratio of γ -PGA/OXA = 60/40 wt %. At blend ratio of γ -PGA/OXA = 60/40 wt % and 90/10 wt %, the relationship between the heating time at 120°C and weight loss is depicted in Figure 4. The results show that heat treatment for 30 min is sufficient to complete the crosslinking reaction for the electrospun samples.

In Figure 5, SEM images of samples prepared with four different γ -PGA/OXA blend ratios are shown at three stages: (H) after 1 h of heat treatment, (M) conditioned at 73 ± 2% RH for 20 h and (W) freezedried samples after immersion in water. The fiber diameter for these samples is shown in Table II. An average fiber diameter of less than 200 nm was produced when the OXA blend ratio was lower than

Journal of Applied Polymer Science DOI 10.1002/app

- (b) 60 50 Weight loss [%] 40 30 20 10 0 0 120 240 360 480 600 720 Heating time (120°C)

·(a)

Figure 4 Effect of heating time on the weight loss of γ -PGA/OXA = 60/40 wt % web.

10 wt %. The fiber diameter was larger when OXA was blended at a blending ratio of 40 wt %. In Figure 6, solution viscosities were plotted against stirring time for OXA blend ratios of the 10 wt % and 40 wt %. The increase in viscosity remarkably occurred when the OXA blend ratio of 40 wt %. The difference in fiber diameter is probably due to continuation of the crosslinking reaction in the electrospinning solution.

The γ -PGA nanofiber without any blended OXA was readily dissolved by absorption of moisture in the air. When OXA was blended at 0.7 wt %, the sample was not completely dissolved by absorption of moisture and a fiber-like shape was observed [c-M in Fig. 5]. The fibrous shape was not retained after dipping in water, however, and the nanofiber converted to a gel-like mass [c-W in Fig. 5]. At 10 wt % OXA blend, the sample experienced a weight loss of 25% and the diameter of the freeze-dried fiber became slightly thinner because the fiber dissolved a little when dipped in water. This tendency is also observed as the weight loss as shown in Figure 3. This blend displayed a fibrous morphology though [b-W in Fig. 5], indicating that the sample retains its fibrous shape in water. Owing to a moisture swelling effect, an increase in fiber diameter was detected as shown in Table II.

The results confirmed that it is possible to prepare a fiber by electrospinning from an inexpensive and safe water/ethanol system using γ -PGA Na salt as the raw material. OXA was found to be a useful crosslinking agent for obtaining a water-insoluble γ -PGA nanofiber by heat-treating the as spun fiber.

Properties of γ-PGA nanofiber webs

Properties after moisture absorption/desorption

The hygroscopic characteristics of the γ -PGA nanofiber web were found to be dependent on the OXA blending rate. The capability to reabsorb moisture increases as the OXA blending rate decreases. The γ -PGA web is shown to exhibit very high moisture regain (*M*1) compared with rayon knitted fabric or



Figure 5 SEM images of nanofibers γ -PGA/OXA with γ -PGA/OXA ratios: (a) = 60/40, (b) = 90/10, (c) = 99.3/0.7, and (d) = 100/0 where the H images (top) were taken after crosslinking by heating for 1 h, the M images (center) were taken after absorption of moisture and the W images (bottom) were taken after dipping in water and freeze-drying.

70

TABLE II Fiber Diameters of γ-PGA/OXA Samples					
γ-PGA/ OXA ratio ^a (wt %)	(H) Heat treatment (nm)	(M) Absorption of moisture (nm)	(W) Water dip and freeze-dry (nm)	Viscosity (mPa·s)	
60/40 90/10 99.3/0.7 100/0	380 ± 140 150 ± 40 150 ± 50 150 ± 40	510 ± 180 260 ± 130 250 ± 30 -	300 ± 60 120 ± 40 -	31.8 42.6 56.4 110	

^a nonvolatile matter

collagen sponge, even at an OXA blending rate of 40 wt % (Fig. 7, Table III). Absorbed moisture was quickly desorbed in an atmosphere of 35% RH. The water absorption/desorption isotherm also shows a similar trend, indicating that the absorption amount is generally higher at low OXA blending rates (Fig. 8). The amount of absorption increases gradually at relatively low pressure in the absorption/desorption isotherm, indicating that it is an absorption in which the interaction with water is weak. In addition, the absorption amount apparently increases at a relative pressure of around 0.7–0.8, and the nanofiber exhibits hysteresis. The results suggest that the γ -PGA nanofiber web has mesopores wherein the adsorbed water is condensed.

During absorption of moisture, γ -PGA nanofiber webs with lower OXA blending rates experienced greater shrinkage. Area shrinkages of 81, 19 and 7% were observed for γ -PGA/OXA blends = 60/40, 90/ 10 and 99.3/0.7 wt %, respectively, when the γ -PGA web was moistened at 23 ± 0.5°C and 73 ± 2% RH for 20 h. The shrinkage may be associated with a change in shape of the γ -PGA nanofiber caused by swelling and partial solubilization due to moisture absorption.^{18,28}



Figure 6 Viscosity change of the electrospinning solutions at 23°C with γ -PGA/OXA blending ratios (a) = 60/40 and (b) = 90/10.



Figure 7 Moisture regain of crosslinked γ -PGA web comprised of crosslinked γ -PGA/OXA blended at ratios (a) = 60/40, (b) = 90/10, (c) = 99.3/0.7, (d) Rayon, and (e) Collagen.

Water absorbency and wetting behavior

In Figure 9, the water absorbency rates of the γ -PGA nanofiber webs are shown against immersion time in water. Water uptake occurs in less than 1 min for γ -PGA nanofiber webs, which is much faster than that of the knitted rayon fabric. The water absorbency of the γ -PGA web at equilibrium was more than 2300% for both the 10 wt % and 40 wt % OXA blends. These were the same level as the water absorbency of the collagen sponge. Samples with a 0.7 wt % OXA blend ratio, however, gradually changed to a gel in water.

When a droplet is applied on the sample surface, the water tends to sink into the hydrophilic web or diffuse between the fibers. In Figure 10, the temperature gradient on the surface, which can be seen in the infrared thermographs, shows how the water penetrated the sample and evaporated. The temperature measured at the center of the droplet on the γ -PGA nanofiber web is also shown in Figure 11. In the case of the 40 wt % OXA blended γ -PGA nanofiber web, water was diffused in less than 1 min

TABLE III Moisture Regain of Cross-Linked γ-PGA Web

	Moisture regain(%)		
γ-PGA/OXA ratio ^a (wt %)	M1	M2	M1 – M2
60/40	36.1	5.1	31.0
90/10	55.6	6.2	49.4
99.3/0.7	62.5	8.0	54.5
Rayon knitted fabric	11.8	8.2	3.6
Collagen sponge	23.3	2.9	20.4

^a nonvolatile matter.

Journal of Applied Polymer Science DOI 10.1002/app

m_{a,} mg/g

2500

2000

1500

1000

500

0

0

Figure 8 Absorption/desorption isotherm of the water with crosslinked γ -PGA webs. γ -PGA/OXA blending ratios (a) = 60/40, (b) = 90/10, and (c) = 99.3/0.7.

absorption

desorption

(a):

(C)

(b)

0.5

p/p0

followed by evaporation, with the nanofiber web returning to its initial state after 8 min. This phenomenon occurred much faster compared with the case of the rayon samples. On the other hand, the water did not spread, but remained localized for the nanofiber webs with an OXA blending ratio of 10 wt % and 0.7 wt %. These two γ -PGA webs displayed higher shrinkage when exposed to water. As a result, the space between the fibers was reduced and thus restricted water diffusion.



Figure 9 Water absorbency of crosslinked γ -PGA webs with γ -PGA/OXA blend ratios (a) = 60/40, (b) = 90/10, (c) = 99.3/0.7, (d) Rayon, and (e) Collagen.

Tensile properties

1

Typical tensile stress–strain curves of γ -PGA/OXA nanofiber webs are shown at four different moisture conditions (30, 75 and 100% RH and in water) in Figure 12. The tensile properties of the sample with a γ -PGA/OXA ratio of 99.3/0.7 wt % could not be obtained at 75 and 100% RH or in water because the sample was dissolved by moisture or water absorption. When the specimens were conditioned in the ambient humidity of 100% RH before the tensile test, stress, which is less than 1.8 ± 0.5 MPa , was observed for the sample γ -PGA/OXA blend at ratio 60/40 wt %. The slightly larger value of initial modulus obtained at



Figure 10 Thermographs of crosslinked γ -PGA webs after water absorption for webs with γ -PGA/OXA blend ratios: (a) = 60/40, (b) = 90/10, (c) = 99.3/0.7, and (d) Rayon. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 11 Temperature changes occurred by water evaporation on crosslinked γ -PGA/OXA webs and rayon fabric with γ -PGA/OXA blend ratios: (a) = 60/40, (b) = 90/10, (c) = 99.3/0.7, and (d) Rayon.

100% RH than that of 75% RH might be influenced by the additional stress caused by absorption. The webs in the dry state tended to be brittle, but they became softer when exposed to moisture and after water absorption (Fig. 12, Table IV). The tensile properties of the sample with γ -PGA/OXA = 60/40 wt % at 75% RH are similar to that of the skin (stress/strain: < 5 MPa/< 35%)²⁹ as listed in Table IV. Therefore when the sample absorbed water, strength became weak and further improvement is necessary.

CONCLUSIONS

 γ -PGA nanofibers were successfully prepared by electrospinning in a water/ethanol system. Using the water-soluble γ -PGA Na salt as a precursor material, introduction of an oxazoline component polymer (OXA) was found to be a useful crosslinking agent. The production of γ -PGA nanofibers from this system is attractive because it is inexpensive, nontoxic and crosslinkable by heating.



Figure 12 Stress–strain curves of crosslinked γ -PGA web (γ -PGA/OXA = 60/40) under different moisture conditions.

TABLE IV				
Tensile Properties	of Cross-Linked γ-PGA Web			

γ-PGA/OXA ratio ^a (wt %)	Humidity (%RH)	Modulus (MPa)	Stress (MPa)	Strain (%)
60/40	30	270 ± 70	23 ± 4	13 ± 4
	75	20 ± 2	6.3 ± 0.9	42 ± 2
	100	32 ± 5	7.3 ± 2.1	26 ± 7
	Water	11 ± 2	3.0 ± 0.7	30 ± 4
90/10	30	380 ± 120	28 ± 8	10 ± 3
	75	14 ± 2	2.6 ± 0.7	16 ± 3
	100	18 ± 5	1.5 ± 0.6	9.4 ± 4.4
	Water	1.5 ± 0.5	0.33 ± 0.24	15 ± 2
99.3/0.7	30	290 ± 90	5.8 ± 2.6	4.1 ± 1.2
	75, 100, water	_	_	_
Skin ^b	50	15-150	5–30	35–115

^a nonvolatile matter.

^b Ref. 29.

The weight loss of the γ -PGA/OXA nanofiber decreases as the blending ratio of OXA is increased. At a blend ratio of 10 wt %, the nanofibers retain their fibrous shape after moisture exposure or water absorption. The fiber diameter was less than 200 nm. Changes in fiber diameter were observed as a result of swelling.

The presence of OXA in electrospun γ -PGA and the crosslinking reaction of the oxazoline group with γ -PGA carboxyl groups was confirmed by solid-state NMR.

The tensile properties of γ -PGA/OXA nonwovens with 60/40 wt % are found to have modulus and elongation properties similar to that of the skin.

For the different γ -PGA/OXA blends, lower blend ratios of crosslinking agent resulted in higher absorption of moisture or water, with absorption levels about 14 and 8 times larger than that of the knitted rayon fabric, and about twice of the collagen sponge. With the interesting combination of mechanical and hygroscopic properties, γ -PGA in the form of a nanofiber web may be a promising candidate material for a broad array of applications ranging from agrichemical to biomedical products.

The authors express sincere thanks to Dr. Hidenori Okuzaki of the University of Yamanashi for his assistance in measuring the water absorption/desorption isotherm for this study.

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