

# Wetting Behavior of Electrospun Poly(L-lactic acid)/Poly(vinyl alcohol) Composite Nonwovens

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Received 20 January 2008; accepted 28 June 2008

DOI 10.1002/app.28904

Published online 8 September 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Poly(L-lactic acid) (PLLA) fibers have been extensively studied for various applications. In this work, PLLA and poly(vinyl alcohol) (PVA) were prepared by coelectrospinning to form composite nonwoven materials. The structures and diameter distribution of the electrospun PLLA/PVA composite nonwovens were examined by atomic force microscopy (AFM) and scanning electronic microscope (SEM). The wetting behavior of the electrospun PLLA/PVA composite nonwovens was also investigated using static contact angles and dynamic water adsorption measurements. It was observed that the

addition of PVA in the electrospun PLLA/PVA composite nonwovens significantly altered the contact angles and water adsorption of the composite materials. It was also found that the increase in the content of PLLA led to the increase in the surface contact angle and decrease in water adsorption of the electrospun PLLA/PVA nonwoven materials. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3172–3177, 2008

**Key words:** adsorption; composites; fibers; morphology; nanotechnology

## INTRODUCTION

Fibers with diameters below 1000 nm are defined as nanofibers. Nanofibers, which have excellent properties such as high surface areas, small pores than regular fibers, have great potential in tissue scaffolds, filtration, protective clothing, nanocatalysis, and optical electronics.<sup>1</sup> Electrospinning is the most common technique for preparing polymer nanofibers, in which a thin polymer jet is ejected when the electrostatic force applied to the polymer liquid overcomes the surface tension of the polymer solution. The charged jet is elongated and accelerated by the electrostatic field, undergoing stretching, solvent evaporation and deposition on a substrate as a random fibrous web. Electrospun nanofibers usually have various fineness, orientation and surface morphology in the same nanofiber webs because of the various factors influencing the process.<sup>1,2</sup>

With the great efforts in ecological environment protection, various biodegradable polymers have

been created and studied. Poly(L-lactic acid) (PLLA) is one of the most promising biodegradable polymers owing to its mechanical properties, thermoplastic processibility, biocompatibility, and biodegradability.<sup>3</sup> With many unique features, PLLA has been increasingly used as commodity plastics in packaging, agricultural products and disposable materials. It also has great potential of applications in medicine, surgery and tissue engineering because of its biocompatibility and biodegradability.<sup>3,4</sup>

PLLA nanofibers have also attracted great attention in recent years because of its potential applications in medicine, tissue engineering and filtration.<sup>5</sup> To improve the surface properties of the PLLA materials, various techniques, such as plasma treatment, have been employed for the modification of the materials<sup>6</sup> to improve the wettability of PLLA fibers. In this study, poly(vinyl alcohol) (PVA) was added into the PLLA to form composite materials by coelectrospinning of PLLA and PVA. The composite materials were collected in fibrous structures, in which PLLA and PVA fibers were physically blended. PVA electrospun fibers were added into PLLA electrospun fibers to improve the wettability of the material due to the water adsorption properties of PVA. PVA has also been increasingly used to make nanofibers by electrospinning for various applications.<sup>7–9</sup> Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to observe the structures of the electrospun fibers. Static contact angle and water adsorption were measured to evaluate the wetting behavior of electrospun PLLA/PVA composite materials.

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Contract grant sponsor: Program for New Century Excellent Talents in University by Chinese Ministry of Education; contract grant number: NCET-06-0485.

Contract grant sponsor: Doctoral Program of Higher Education by Chinese Ministry of Education; contract grant number: 20060295005.

Contract grant sponsor: Jiangnan University; contract grant number: 206000-21050737.

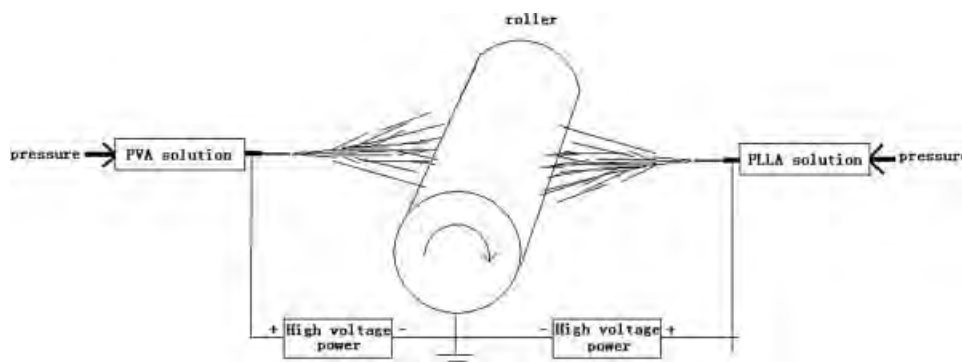


Figure 1 Setup of electrospinning.

## EXPERIMENTAL

### Materials preparation

PLLA chips ( $M_n$  83000) were obtained from Shenzhen Guanghua Weiye Enterprise, China and PVA1799 samples with molecular weight of 84,000–89,000 were obtained from Shanghai Kanghu Chemical. Both of them were used without further purification. Analytically pure dichloromethane was used as the solvent of PLLA and Formic acid with a purity of 88% as the solvent of PVA. These two solvents were purchased from Sinopharm Group Chemical Reagent, China. PLLA and PVA solutions were prepared at room temperature. The concentration of PLLA solution was 30% in mass and the concentration of PVA solution was 12% in mass.

### Electrospinning

The schematic view of the coelectrospinning setup is shown in Figure 1. PLLA and PVA solutions were placed in syringes (BD type, with a content of 20 mL) with evenly-chopped pinheads (a diameter of 0.7 mm) as the ejection capillary, pressed by a syringe pump (WZ-50C2, Zhejiang, China) to control the solution flow rate. Two high-voltage power suppliers (DW-P503-4AC, Tianjin, China) were used to contact needle tips and the roller for forming electrostatic fields. The electronically grounded roller ran clockwise to collect the composite fibers. The conditions of coelectrospinning were set as follows: voltage 15 kV, solution flow rate 1.0, 0.8, 0.5, 0.2 mL, collecting distance 15 cm for PLLA solution; voltage 18 kV, solution flow rate 0.2 mL, collecting distance 15 cm for PVA solution. The PLLA/PVA composite materials were obtained by collecting the fibers for 8 h.

### Structural characterization

The structures of electrospun PLLA/PVA nonwoven materials were observed by a scanning electronic microscope (SEM, Hitachi S-4800, Japan). The magnification was set as 10.0k. Atomic force microscopy

(AFM, CSPM4000, Benyuan Company) was applied to observe the surface morphology of the materials. Tapping mode was used in this study. All samples were scanned at room temperature in the atmosphere.

### Static contact angles

Static contact angles of the electrospun PLLA/PVA nonwoven materials were performed on a Drop Shape Analyzer (DSA100, Germany). The size of drop needle used was 1.8 mm in inner diameter, and the size of a droplet obtained was over 5 mm in diameter. When a droplet squeezed from the needle dropped onto the mats, which were placed on a horizontal plate, a picture was taken after 5 s and the contact angle was measured by the software. The samples were dried in a vacuum oven (DZF-6090, Shanghai, China) for 2 h before the contact angle test. All the samples were tested for at least two times, and an average was calculated as the static contact angle of the materials.

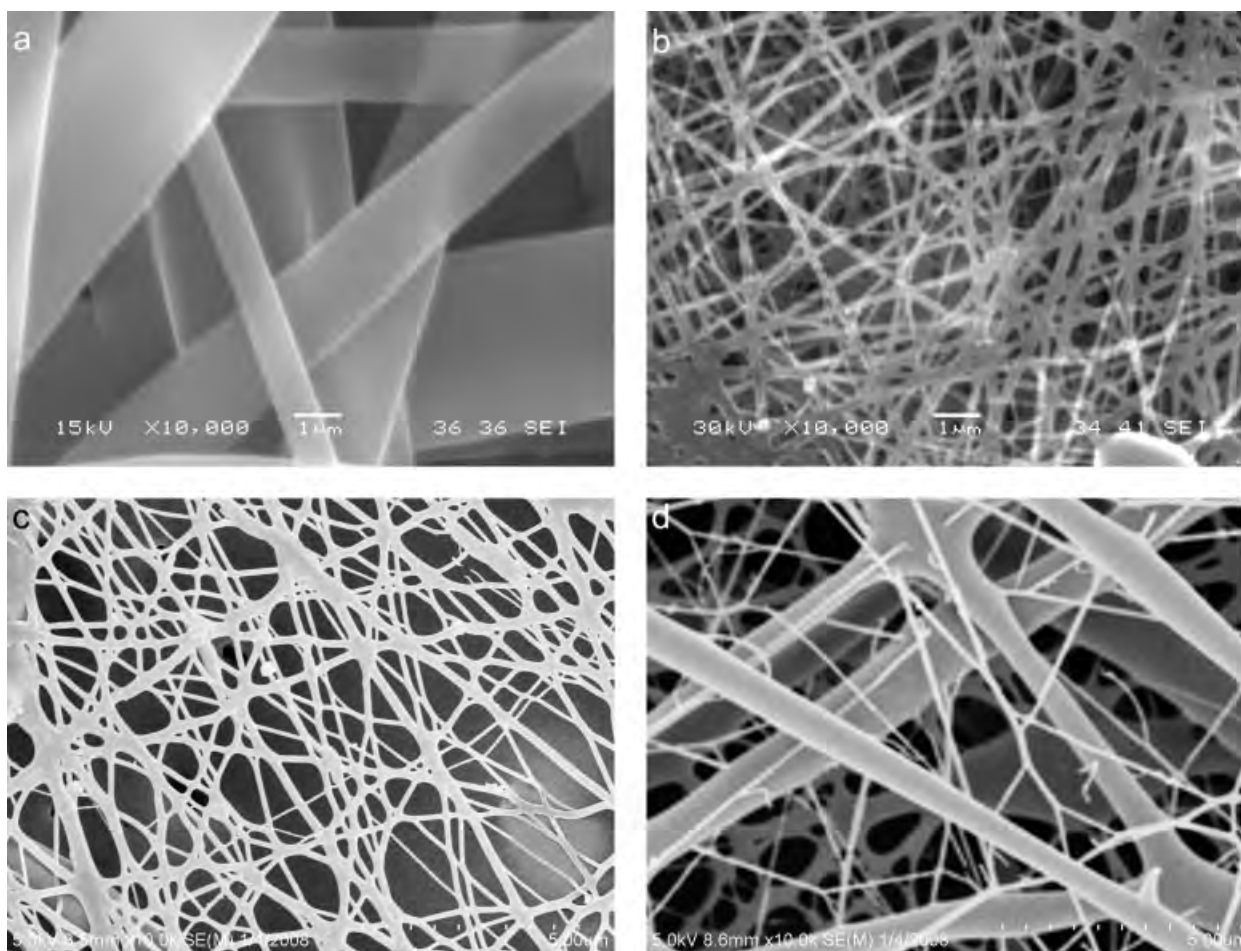
### Dynamic water adsorption

Water adsorption was measured using CDCA-100F Dynamic Contact Angle Tensiometer (Camtel, UK) under room temperature. Each sample was cut to a size of 1 cm × 4 cm with sharp scissors and dried in the vacuum oven for 2 h. When the specimen was immersed into water, the water weight adsorbed was detected and recorded. The dynamic water adsorption per unit mass was plotted as a function of time.

## RESULTS AND DISCUSSION

### Fibrous structures

The electrospun fibers form fibrous webs as shown in Figure 2. The SEM images clearly reveal that the electrospun PLLA fibers have larger diameters than those of electrospun PVA fibers. The electrospun PLLA fiber have diameters ranging from 900 to 5000 nm when



**Figure 2** SEM images of (a) pure PLLA 1.0 mL/h; (b) pure PVA 0.2 mL/h; (c) PLLA/PVA = 0.8/0.2; (d) PLLA/PVA = 0.2/0.2.

the flow rate for electrospinning is 1.0 mL/h, as presented in Figure 2(a). It is also observed that the change in the flow rate leads to the change of fiber diameters. When the flow rate of PLLA is lowered to 0.8 mL/h, the fiber diameters change in the range between 200 and 1500 nm, much lower than those of PLLA fibers electrospun at the flow rate of 1.0 mL/h, as illustrated in Figure 2(c). The further decrease in the flow rate down to 0.2 mL/h causes the decrease of PLLA fiber diameters to the range between 100 and 600 nm, as shown in Figure 2(d).

The image in Figure 2(b) reveals that the electrospun PVA fibers only have diameters between 150 and 400 nm. It is clearly observed that the increasing amount of the PVA nanofibers into the composite mat reduces the sizes of pores in the composite mat, which will affect the capillary effect of pores in the material.

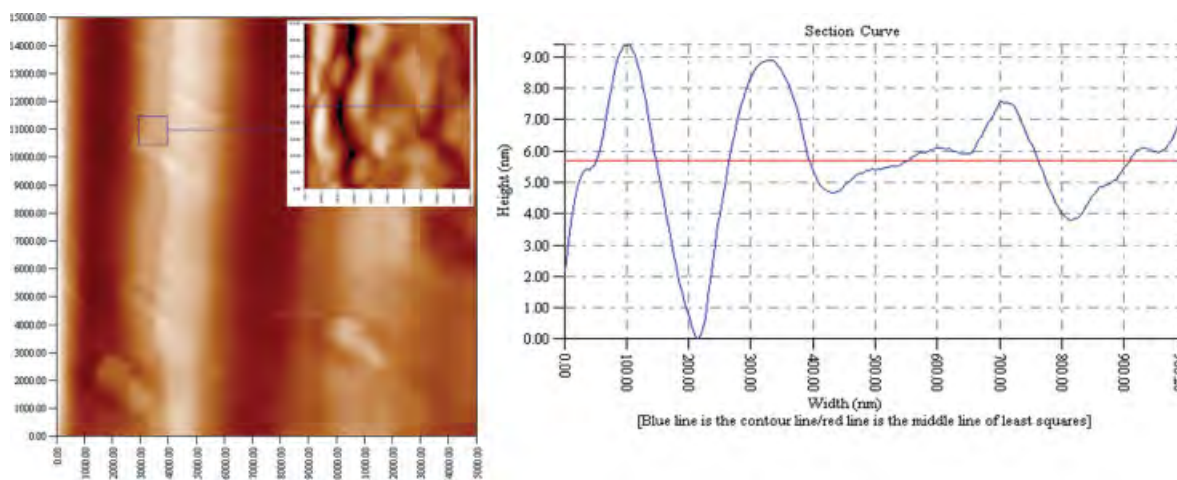
### Surface morphology

The roughness of the solid surface is one of the main reasons affecting the wetting behavior of a material.<sup>10,11</sup> The AFM images of electrospun PLLA/PVA

nonwoven materials are shown in Figures 3 and 4, in which the surface structures of the two kinds of electrospun fibers are revealed. The surfaces of the fibers are not smooth; therefore, a smaller range of 1000 nm × 1000 nm is also selected for comparison. From the small images, it can be seen that the surfaces are obviously rough, with a surface roughness  $R_a$  (Arithmetical mean deviation of the profile, arithmetical mean deviation of the absolute distance value between the profile points, and the middle line of least squares in the measure direction) of 1.56 nm for PLLA electrospun fiber and 1.35 nm for PVA electrospun fiber analyzed using the AFM software. It is also confirmed by the section analysis, which shows the section of the blue line in the images of 1000 nm × 1000 nm scan. In the pictures, the blue line is the contour line, and the red line is the middle line of least squares. The roughness is on the level of nanometer.

### Static contact angles

When a droplet is dropped on a smooth solid surface, if the droplet does not wet the surface completely, the



**Figure 3** AFM image of electrospun PLLA fiber and the section analysis. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

contact angle ( $\theta$ ) is formed between the vapor–liquid interface and the solid–liquid interface on the contacting point of the three phases.<sup>12</sup> It is an important index characterizing the wettability of a material.

Figure 5 shows the static contact angles measured. The pure PLLA electrospun fibers have a contact angle of 86.88°. The images in Figure 5 clearly reveal that the contact angle reduces as the content of PVA increases. The static contact angle is reduced to 51.17° when the flow rate of PLLA is lowered to 0.2 mL/h, as listed in Table I.

On a rough surface, if a drop is sufficiently large compared with the roughness scale, this apparent contact angle is related to the ideal contact angle by the Wenzel equation:

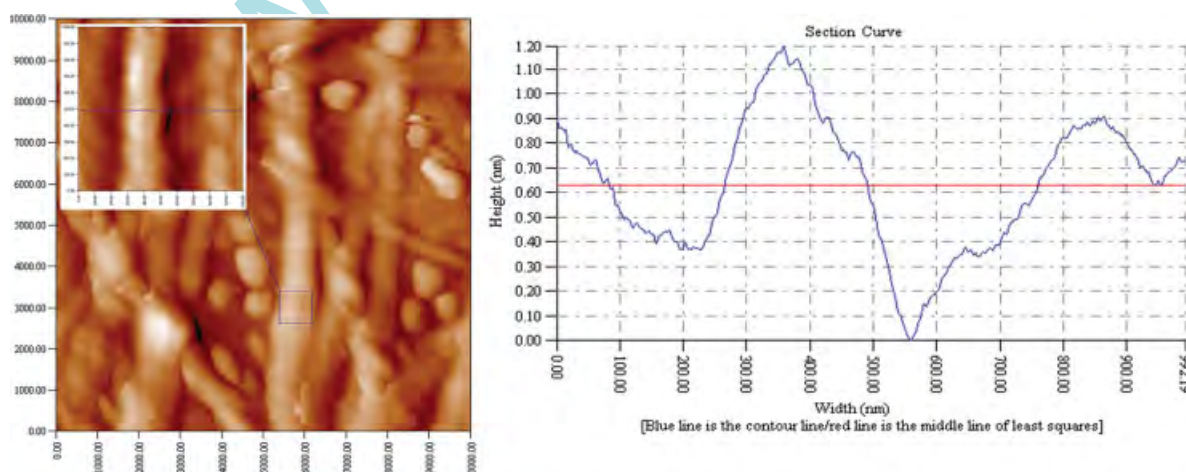
$$\cos \theta = R_f \cos \theta_0 \quad (1)$$

$\theta$  is the Wenzel contact angle, i.e., the apparent contact angle at the global energy minimum,  $\theta_0$  is the

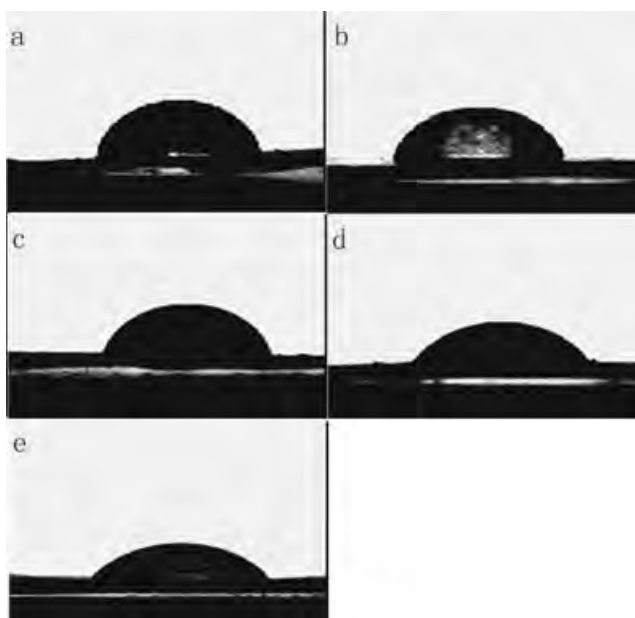
ideal contact angle, and  $R_f = A_{SL}/A_F$  is the roughness ratio, defined as the ratio between the true surface area  $A_{SL}$  and the apparent surface area  $A_F$  of the solid.<sup>13,14</sup> Surface roughness can increase the contact angle for hydrophobic materials ( $\theta_0 > 90^\circ$ ) and reduce the contact angle for hydrophilic materials ( $\theta_0 < 90^\circ$ ) oppositely. PLLA and PVA fibers have contact angles of less than 90°. Therefore an increase in the surface roughness can lead to a decrease of contact angles, enhancing the wetting ability of the electrospun PLLA/PVA nonwoven materials.

### Dynamic water adsorption

The results of dynamic water adsorption tests further reveal the changes of the wettability of the samples. When the pure PLLA electrospun fiber web immersed into water, the effect of the buoyancy of water pushes the materials upward since the wettability of PLLA is poor. Thus, the sample has a



**Figure 4** AFM image of electrospun PVA fibers and the section analysis. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



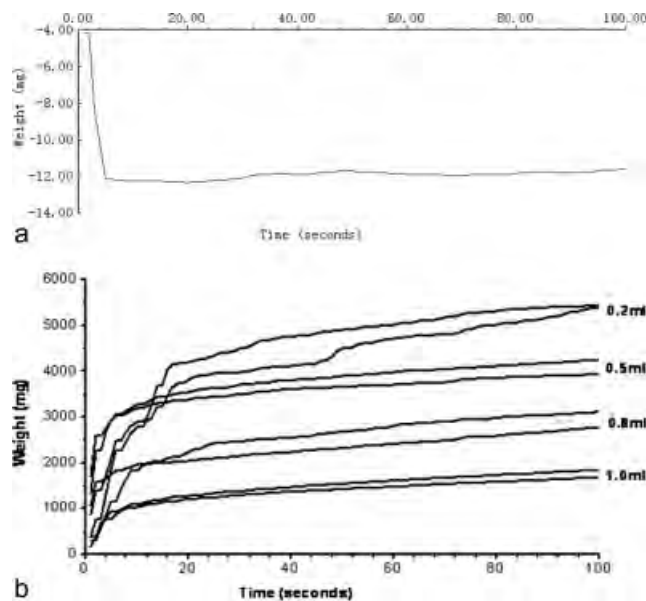
**Figure 5** Static contact angles of pure PLLA and electrospun PLLA/PVA nonwoven: (a) pure PLLA; (b) PLLA/PVA = 1.0/0.2; (c) PLLA/PVA = 0.8/0.2; (d) PLLA/PVA = 0.5/0.2; (e) PLLA/PVA = 0.2/0.2.

negative weight of water adsorption as presented in Figure 6(a). The negative weight of water adsorption means that the material will float on water. Although a prominent increase in the water adsorption can be observed for all the electrospun PLLA/PVA nonwoven materials in Figure 6(b). There are at least three distinct zones in each adsorption curve.<sup>15</sup> The first zone is regarded as the initial stage of water adsorption in the first few seconds. Then there is a transition zone when the rate of adsorption is gradually reduced. In the third zone the rate grows slowly and goes stable.

It can be that the composite mats produced with a flow rate of 1.0 mL PLLA solution have the lowest amounts of initial adsorption and total water adsorption. Both initial adsorption and total adsorption rise with reducing the flow rate of PLLA solution. The largest adsorption obtained with the flow rate of 0.2 mL PLLA solution is over 5000 mg which is almost three times of that in the case of a flow rate of 1.0 mL PLLA solution.

**TABLE I**  
Static Contact Angles of Electrospun Nonwovens

	Pure PLLA		PLLA/PVA		
Flow rate (mL)	0.8	1.0/0.2	0.8/0.2	0.5/0.2	0.2/0.2
Static contact angle (°)	86.88	82.85	78.87	61.06	51.17



**Figure 6** Water adsorption: (a) pure PLLA; (b) electrospun PLLA/PVA nonwoven.

It is well known that there are two key factors affecting the hydrophilicity of surfaces: surface chemistry and surface roughness.<sup>10,11</sup> Surface chemistry plays a key role in the wettability of electrospun PLLA/PVA nonwoven materials. The quantity and intensity of hydrophilic groups in the macromolecules have a great effect on the wettability of the fibers. Strong hydrophilic groups such as hydroxyl ( $-\text{OH}$ ), carboxyl ( $-\text{COOH}$ ), amidocyanogen ( $-\text{NH}_2$ ), can form chemical bonds with water molecules and improve the wettability of a material. A better wettability can be obtained with a higher ratio of PVA in the composite mat because PVA is a kind of hydrophilic polymer with hydroxys ( $-\text{OH}$ ) groups in the backbone chain. The results of static contact angle and dynamic water adsorption confirm this conclusion (Figs. 5 and 6).

Solid surface have a tendency of adsorbing something to reduce the surface energy. Wicking effect is another factor determining the wettability. The typical capillary pressure equation is as follows:

$$p = \frac{2\gamma_{LV} \cos \theta}{\bar{r}} \quad (2)$$

$\bar{r}$  is the equivalent radius of the capillary. It is derived from the eq. 2 that a smaller contact angle  $\theta$  and a smaller capillary radius will lead to a higher capillary effect. The capillary pressure increases when  $\bar{r}$ , the gap among fibers, reduces, which contributes to the water adsorption. Nanofibers have very large surface area to volume ratio (the ratio for a nanofiber can be as large as  $10^3$  times of that of a microfiber) and high porosity.

More nanofibers are added into the electrospun composite materials as the flow rate of PLLA solution decreases, which contributes to the water adsorption of the composite mats. The improvement in water adsorption is reflected in Figure 6.

### CONCLUSION

The electrospun PLLA/PVA nonwoven materials showed a better wettability than pure PLLA electrospun fibrous web, and the larger the ratio of PVA was, the better the wettability of the composite achieved. This was proved by tests of static contact angles and dynamic water adsorption. The reasons were also discussed from three aspects. Firstly, the hydrophilic group ( $-OH$ ) introduced by PVA had a strong affinity with molecules of water and made a great contribution to the improvement in the wettability of the composite. The micromorphology of electrospun PLLA/PVA nonwoven materials was of roughness, which led to a reduction of contact angles. Finally, the structures of electrospun composite materials e.g., smaller fiber diameters and pore sizes also contributed to the water adsorption through the capillary effect.

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