

Selective Chemical Absorbance in Electrospun Nonwovens

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ABSTRACT: The absorbance of liquids and compounds with various degrees of hydrophilicity into electrospun fabrics and conventional fabrics was measured. Electrospun cellulose and poly(lactic acid) fabrics had comparable fiber diameters and pore spacings between fibers. Woven cotton and polyester [poly(ethylene terephthalate)] fabrics had pore spacings between fibers 10–20 times larger than the electrospun fabrics. The absorbance of liquids and chemicals with various degrees of water/octanol solubility onto the hydrophobic [poly(ethylene terephthalate) and poly(lactic acid)] and hydrophilic (cellulose and cotton)

fabrics was compared. Both the surface chemistry of the fibers and the pore size in the fabrics were found to affect the liquid uptake, with smaller pores and similar chemistry resulting in the greatest liquid absorbance. The absorbance of chemical compounds also increased with decreasing fabric pore size, increasing surface-to-volume ratio, and compatible surface chemistry of the fabric. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2363–2370, 2007

Key words: dyes/pigments; fibers; hydrophilic polymers; polyesters

INTRODUCTION

Electrospinning is a method of producing fibrous polymer mats with fiber diameters in the range of 0.05 μm to several tens of micrometers.¹ Unlike conventional fiber-forming methods that rely on mechanical forces to push a spinning solution through a tiny orifice or spinneret, electrospinning uses electrical force to pull a fiber from the surface of a charged droplet.² The electrospun fibers can be collected as a randomly laid nonwoven fabric with an exceptionally large surface-to-mass ratio, a high porosity, and a small pore size.^{1,2} The small diameter of electrospun fibers leads to large specific surface areas in electrospun fabrics. This high surface area has been shown to provide increased absorbency over other textile fabrics.³

Electrospinning cellulose acetate has been widely reported. Liu and Hsieh³ prepared ultrafine fibrous cellulose membranes by electrospinning cellulose acetate. They found that a 2 : 1 acetone/dimethylacetamide mixture was the most versatile mixing ratio because it allowed continuous electrospinning of cel-

lulose acetate concentrations between 12.5 and 20%. A study by Son et al.⁴ reported that ultrafine cellulose acetate fibers were obtained through the electrospinning of cellulose acetate/acetone at concentrations above 17 wt % until the tip of the needle was blocked by the evaporation of acetone. They also noted that through the electrospinning of cellulose acetate, acetone, and water, long, ultrafine cellulose acetate fibers were continuously generated at a water concentration of 10–15 wt %. Although the electrospinning of cellulose acetate was patented in 1934,⁵ many problems are still challenging researchers, such as the blockage caused by cellulose acetate precipitation at the needle tip during the electrospinning process.

Electrospinning poly(lactic acid) (PLA) has also been widely explored. Zeng et al.⁶ studied ultrafine fibers electrospun from biodegradable polymers. They prepared poly(L-lactide) fibers from chloroform, chloroform/acetone (3 : 1 v/v), and chloroform/acetone (1 : 1 v/v) solvent systems. They found that fibers from a chloroform solution had a rough and pitted surface, with diameters ranging from 500 nm to 3 μm . The fibers had a significantly smoother surface and smaller diameter when they were electrospun from a mixed solvent of chloroform and acetone.

The composition of the binary solvent system used for making the spinning solution has been shown to have a great influence on the structure and properties of the fiber. Leenslag and Pennings⁷ reported

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that compared to pure chloroform spun PLA fibers, PLA fibers spun from a chloroform/toluene mixture had a porous structure. This was attributed to a more rapid phase separation in the presence of toluene, a poor solvent for PLA. Horacek and Kalisek⁸ reported that the viscosity of poly(L-lactide) in all mixed solvents was lower than that in chloroform; that is, there was always a lower level of the polymer/solvent interaction. All mixed systems were inclined to phase-separate when spun. The kinetics of phase separation mainly depended on the volatility gradient between the solvent (chloroform) and the nonsolvent.

There are two approaches to incorporating chemical substances into electrospun nonwoven fabrics: incorporating the substance into the individual fibers as they are manufactured or using the nonwoven fabric to absorb the substance like a sponge. The first approach involves incorporating the substances into the spinning solution so that they are incorporated within the nanofibers. This method, however, can be successful only if the substance to be incorporated into the fibers can be dissolved or dispersed in the same solvents as the nanofiber-forming polymer. The concentrations of the chemical and polymer are limited.

The second approach, using the nonwoven fabrics to absorb substances like a sponge, takes strong advantage of the tailorable pore size and chemistry of electrospun mats. Liu and Hsieh³ took this approach when they investigated the electrospinning of cellulose acetate membranes. Mats converted completely to cellulose were shown to absorb water 10 times as much as conventional cellulose absorbents. The research reported here explores the enhanced absorbency of electrospun nonwoven fabrics.

In this study, absorbent nonwoven fabrics from biodegradable and renewable polymers were developed by electrospinning. The two polymers used in this study were PLA and cellulose acetate. To improve the continuity of electrospinning cellulose acetate, we cooled the solution temperature to 5°C and used an acetone/water mixed-solvent system to dissolve cellulose acetate. By dissolving PLA in a chloroform/acetone mixed-solvent system, we made pitted fibers, which further increased the surface-area-to-volume ratio. The absorption capacity and selectivity of the chemicals by these electrospun nonwoven fabrics were tested with distilled and deionized water, mineral oil, and dyes with known logarithmic values of the octanol/water partition coefficient (K_{ow}).

EXPERIMENTAL

Materials

PLA [weight-average molecular weight (M_w) = 143,000, weight-average molecular weight/number-average

molecular weight (M_w/M_n) = 1.8] was obtained from Cargill Dow LLC (Minnetonka, MN). Cellulose acetate (acetyl concentration = 29.8%, M_n = 30,000) was purchased from Aldrich Chemical Co. (Milwaukee, WI) Chloroform (EM Science, Gibbstown, NJ), analytical-reagent-grade acetone (J. T. Baker, Phillipsburg, NJ), and *N,N*-dimethylformamide (Mallinckrodt Laboratory Chemicals, Phillipsburg, NJ) were used without further purification. Distilled deionized water was produced in our laboratory with a Mega-Pure MP-1 system. Mineral oil was purchased from Sigma-Aldrich Corp. (St. Louis, MO). The direct dye (Rit Scarlet 5 dye, Rit, Indianapolis, IN) was obtained from a grocery store. The disperse red dye (005 Spectrasperse Rubine 3BA; M_w = 330.35, $\log K_{ow}$ = 3.14) and fluorescent dye (D-820 Savannah Yellow; M_w = 333, $\log K_{ow}$ = 3.68, non-ionic) were gifts from Dr. Alan G. Taylor. Plain woven 100% polyester [poly(ethylene terephthalate) (PET)] and 100% cotton fabrics were obtained from Test Fabrics, Inc. (West Pittston, PA).

Sample preparation

Electrospinning

The apparatus used for electrospinning is shown in Figure 1. The high-voltage supply (Gamma High Voltage Research, Ormond Beach, FL), syringe pump (Harvard Apparatus, Holliston, MA), and spinning chamber were enclosed in boxes built of 0.5-in. polyethylene with clear polycarbonate doors on the front. The boxes provided electrical isolation between the syringe pump and the high voltage applied to the syringe needle. Additionally, the boxes isolated the spinning chamber from ambient air currents in the laboratory. The solution was added in a 5-mL glass syringe with a 24-gauge (o.d. = 0.59 mm) stainless steel needle (Hamilton Co., Reno, NV). The needle was connected to the high-voltage source. A grounded counter electrode was connected to a copper plate, which acted as a collector. For cellulose acetate electrospinning, the glass syringe was chilled

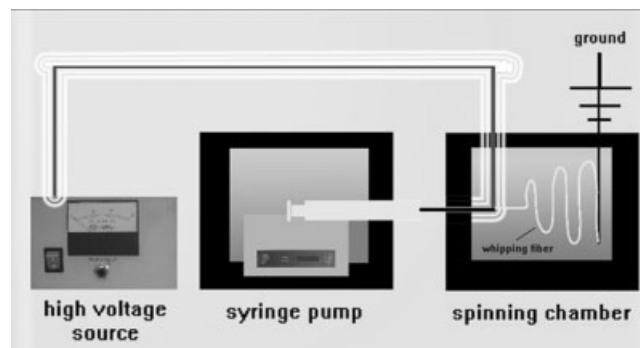


Figure 1 Apparatus used for electrospinning.

during the electrospinning process. Because the high-voltage supply would ground to any electrically conductive elements of a cooling system and this would result in shorting of the system and failure of the spinning process, only insulating materials were used. Flexible tygon tubing was connected to a circulating chiller (Isotemp refrigerated circulator, Fisher Scientific, Pittsburgh, PA) and wrapped around the entire length of the glass syringe. To compensate for the poor thermal conductivity of the tubing, the system was allowed to equilibrate for at least 15 min.

Deacetylation of cellulose acetate

The deacetylation process was conducted in a 0.05M NaOH/EtOH solution, which was constantly stirred (400 rpm) for 1 h at room temperature. The hydrolyzed nonwoven fabrics were then rinsed in deionized water, and pH paper was used to confirm complete rinsing. After air drying, the hydrolyzed nonwoven fabrics were dried under a vacuum at 60°C overnight.

Partition coefficient of Rit Scarlet 5

The partition coefficient of the direct dye (Rit Scarlet 5) in water/1-octanol mixtures was determined with the shake-flask method.⁹ A Beer–Lambert law plot was constructed for each phase of the two-phase water/1-octanol mixtures.

Fabric characterization and absorbance

Characterization

The change in the chemical structure of cellulose acetate fibers during deacetylation was analyzed with Fourier transform infrared (FTIR) spectroscopy. The morphology of the electrospun fibers and the dyed nonwoven fabrics before and after the controlled release procedure was observed on a scanning electron microscope.

An 1100-AEHXL capillary flow porometer (Porous Media, Inc., Ithaca, NY) was used in this study to measure the pore size and distribution of the electrospun nonwoven fabrics. Fabric samples were cut into 3 cm × 3 cm squares. Samples were tested first with air and then with Galwick oil. Galwick oil was obtained from the porometer manufacturer specifically for use in porosity measurements.

Mineral oil and water absorbance

The absorption of water and mineral oil into the fabrics was studied through the measurement of the change in the fabric weight with time when in contact with liquid. Fabric samples cut into 0.5 cm × 3 cm rectangles were attached to small copper-wire hooks with an adhesive and allowed to dry at room

temperature at least 12 h. The prepared samples were then hung from a Cahn electrobalance (TRI/Princeton Wettability Apparatus, Princeton, NJ), and a stepping motor was used to raise a beaker of either distilled and deionized water or mineral oil until a difference in the balance reading indicated that the sample had come into contact with the liquid. Weight measurements were recorded with the software in 1-min increments until the liquid appeared to reach the full, 3-cm height. All measurements were performed in triplicate.

Absorbance of dyes into fabrics

Four types of fabrics were used in this research: 100% polyester woven fabrics, 100% cotton woven fabrics, cellulose nonwoven fabrics deacetylated from the electrospun cellulose acetate nonwoven fabrics, and electrospun PLA nonwoven fabrics. A direct dye (Rit Scarlet 5) and a disperse dye (Disperse Red 5) were applied to these four fabrics. The dye bath concentration was fixed at 20% owf with a liquor ratio of 100 : 1. In the dyeing process, each fabric was incubated in a dye bath at room temperature for 24 h while being shaken on a platform shaker (Inova 2300 platform shaker, New Brunswick Scientific, Edison, NJ) at a speed of 200 rpm. After dyeing, the fabrics were first dried in ambient air until most of the water was gone, and then they were dried under a vacuum (Isotemp 282 A vacuum oven, Fisher Scientific) at 40°C for 24 h. To measure the dye concentration on the fabrics, 1 mL of a dye solution/suspension was removed from the dye bath before and after the dyeing process. By suitable dilution as required (1 mL of the solution diluted to 50 mL in a 50-mL volumetric flask), the visible absorbance of the dye bath was measured with a Perkin-Elmer Lambda 35 ultraviolet–visible (UV–vis) spectrometer (Norwalk, CT). With the calibration curves for the dyes, the dye concentration of the dye bath before and after the dyeing process was calculated. The difference between the dye concentration of the dye bath before and after the dyeing was the dye concentration absorbed into the fabric.

RESULTS AND DISCUSSION

Formation of nonwoven fabrics from hydrophilic and hydrophobic fibers

The electrospinning parameters and the fiber characteristics are presented in Table I.

Electrospun PLA nonwoven fabrics

The PLA fibers electrospun from a chloroform/acetone (3 : 1 v/v) mixture had a pitted surface morphology (Fig. 2). This was attributed to a more rapid phase separation in the presence of the poor solvent

TABLE I
Electrospinning Parameters and Fiber Characteristics

Sample	Cellulose acetate	PLA
Polymer concentration (wt %)	17	8
Solvent	17/3 (v/v) acetone/water	3/1 (v/v) chloroform/acetone
Driving voltage (kV)	10	15–18
Working distance (cm)	12	14
Flow rate	2.5 mL/h	0.01 mL/min
Average fiber diameter (μm)	2	2

(acetone). The average diameter of the PLA fibers produced was around 2 μm .

Electrospun cellulose nonwoven fabrics

Previous researchers³ noticed that when only acetone was used as the solvent for cellulose acetate, the tip of the needle was easily blocked because of the rapid evaporation of acetone. In this study, to improve the continuity of the electrospinning process, two steps were used: (1) an acetone/water mixed-solvent system was used to dissolve cellulose acetate, and (2) during the electrospinning process, the cellulose acetate solution was cooled to 5°C. These two steps enhanced the continuity of electrospinning the cellulose acetate fibers. Figure 3 shows the flat fiber structure of cellulose acetate. The electrospun cellulose acetate fibers had a flat structure, and the average diameter of the fibers was around 2 μm .

The cellulose nonwoven fabrics were obtained by deacetylation of electrospun cellulose acetate nonwoven fabrics. After 1 h of deacetylation, the FTIR spectra of the electrospun mat confirmed that acetate groups had been removed (Fig. 4). The intensities of the characteristic absorbance peaks—1745 ($\nu_{\text{C=O}}$), 1375 ($\nu_{\text{C-CH}_3}$), and 1235 cm^{-1} ($\nu_{\text{C-O-C}}$), which were attributed to the vibration of the acetate group—dis-

appeared after 1 h of deacetylation. On the other hand, the absorbance peak at 3600 cm^{-1} ($\nu_{\text{O-H}}$; not shown) increased. A spectrum of a pure cellulose sample is included for comparison. The acetate peaks are not evident for the pure cellulose. Differences between the spectra of the pure cellulose and the regenerated cellulose electrospun membrane were expected and resulted from differences in the crystalline polymorphs of the two samples. The pure cellulose sample had a cellulose I crystalline polymorph, whereas the deacetylated cellulose acetate had a cellulose III crystalline polymorph.

The morphology of the cellulose nonwoven fabrics was observed with scanning electron microscopy (SEM). Figure 5 shows that the cellulose fibers that were deacetylated for 1 h from cellulose acetate fibers had a twisted and flat structure. Compared with that of the cellulose acetate fibers, the average diameter of the cellulose fibers did not change after 1 h of deacetylation. The average diameter of the cellulose fibers was around 2 μm .

Pore structures of the fabrics

Pore sizes for the four fabrics are presented in Table II. The two electrospun samples had similar mean pore sizes, although the standard deviation of the measured pore sizes from the mean was larger for the cellulose fabric. The two conventional woven fabrics, however, had mean pore diameters 10–20 times larger than the electrospun fabrics. During absorption processes, pores act as capillaries, pulling liquid into the fabric via capillary action. The capillary action can be described by the following equation:¹⁰

$$h = 2T \cos \theta / \rho g r$$

where h is the height (m), T is the surface tension (J/m^2 or N/m), θ is the contact angle, ρ is the density of the liquid (kg/m^3), g is the acceleration due to gravity (m/s^2), and r is the radius of the tube (m).

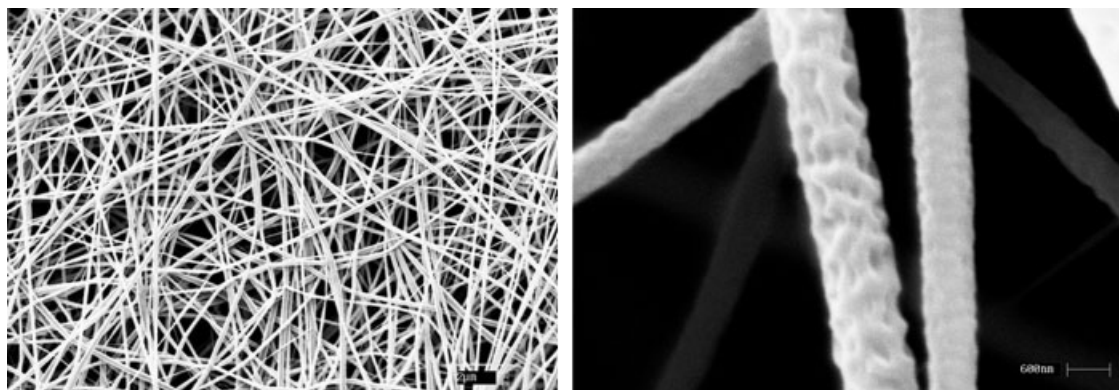


Figure 2 SEM photographs of electrospun PLA nonwoven fabrics: [8 wt % PLA/chloroform–acetone (3 : 1 v/v), M_w of PLA = 143,000, polydispersity index = 1.8].

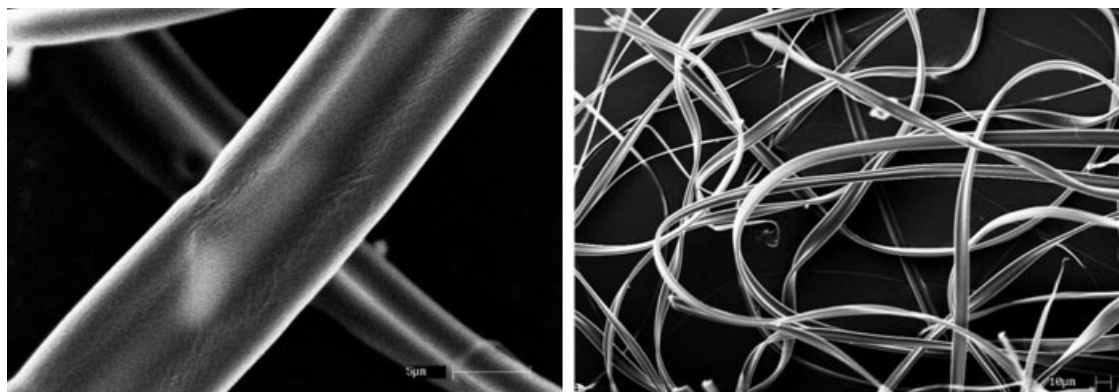


Figure 3 SEM photographs of electrospun cellulose acetate nonwoven fabrics [17 wt % cellulose acetate/acetone–water (17 : 3 v/v), M_n of cellulose acetate = 30,000, 39.8 wt % acetyl content].

The pore size corresponds to the radius of the tube, and the compatibility between the liquid and the fiber is expressed as $\cos \theta$. When the liquid wets the fiber surface, $\cos \theta$ will approach 1. A combination of a compatible liquid and a small pore radius is expected to result in increased liquid absorbance. In addition to the intrafiber pore size, nanoscale surface roughness, such as pitting on the electrospun PLA fiber surface, has been shown to amplify wetting behavior.¹¹ Increased effective hydrophobicity and increased wettability in mineral oil are expected. The water contact angle, measured by the sessile drop method, on PLA films has been reported to be 82° .¹² The contact angle measured on electrospun PLA nonwoven fabric in our laboratory was 124° , however.¹³ The water contact angle on the woven cellulose fabric and electrospun cellulose nonwoven fabric was 0° , as expected. The contact angle of water on PET has been reported to be 82° by the sessile drop method¹⁴ and 79° by the Wilhelmy balance method.¹⁵ The effects of the increased

hydrophobicity of the PLA fiber resulting from surface pitting is evident in the water absorbance results. When bulk PLA and PET have similar water contact angles, the smaller pore size of the electrospun nonwoven fabric is expected to result in greater water absorbance rather than the observed decrease in the water absorbance.

Mineral oil and water absorbance

Both woven and electrospun fabrics had typical wicking behavior, with initial rapid absorbance followed by slower absorbance (Fig. 6). Similar curves for the mass uptake of liquid have been reported for electrospun and melt-blown nonwoven fabrics. PLA has more hydrophilic sites than PET, and the PLA electrospun fabric has lower water absorbance than the PET fabric.

Dye absorbance by the four fabrics

A commonly used partition coefficient is K_{ow} , which is the ratio of a chemical's concentration in octanol to its concentration in water at equilibrium in a closed system composed of octanol and water.¹⁶ For organic chemicals, $\log K_{ow}$ ranges from -3 to 7 . When $\log K_{ow}$ exceeds 2 , substances are considered hydrophobic.¹⁷

The partition coefficient of the direct dye (Rit Scarlet 5) in water/1-octanol was determined by UV–vis spectroscopy. The $\log K_{ow}$ value of Rit Scarlet 5 was 1.5 , so the direct dye was hydrophilic in nature. The $\log K_{ow}$ value of the disperse dye was 3.14 , so it was hydrophobic.

Table III shows the absorbance of the two types of dyes by different fabrics. These experiments do not represent a true textile dyeing process in which the conditions are optimized for the diffusion of dye into fibers. In this case, the dye was used as a marker for the selective absorbance of chemicals onto the fiber surface. The morphology of the elec-

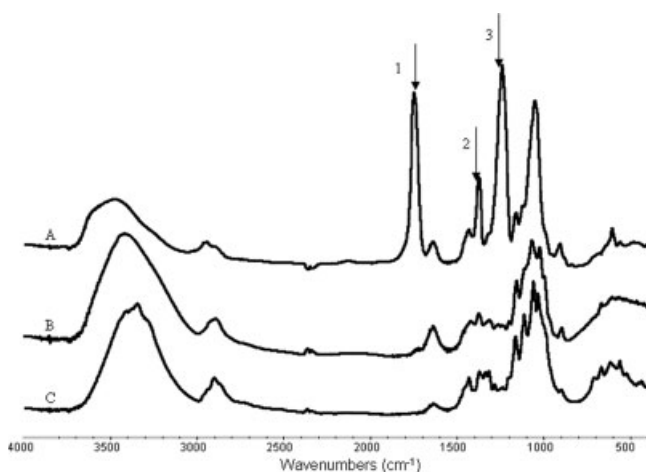


Figure 4 Changes in the FTIR spectra during the deacetylation of cellulose acetate fibers.

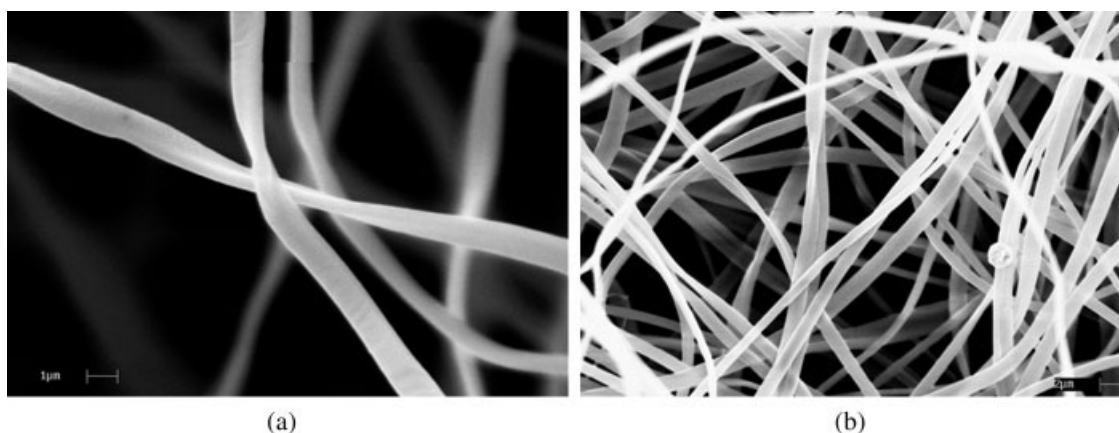


Figure 5 SEM photographs of cellulose nonwoven fabrics (deacetylated from cellulose acetate nonwoven fabrics for 1 h).

trospun nonwoven fabrics saturated with the disperse dye was observed with SEM (Fig. 7). Figure 7(a) shows that the disperse dye agglomerated on the cellulose fibers. The apparent contact angle between the disperse dye and the surface of the cellulose fibers was small. This indicated that the affinity between the disperse dye and the cellulose fibers was low. Figure 7(b) shows the morphology of the electrospun PLA nonwoven fabrics with the disperse dye before the release procedure was conducted. There were two forms of the disperse dye absorbed onto the PLA fibers: (1) the disperse dye was spread between the PLA fibers, and (2) big agglomerates of the disperse dye on the surface of the PLA fibers were observed. The contact angle between the disperse dye and the fiber was large. A good affinity between the PLA fibers and the disperse dye was indicated.

The amount of the direct dye taken up by the cellulose nonwoven fabrics was 128.9 mg/g of fabric, which was larger than that taken up by the electrospun PLA nonwoven fabrics (13.4 mg/g of fabric), by the 100% cotton woven fabrics (47.4 mg/g of fabric), and by the 100% polyester woven fabrics (23.6 mg/g of fabric). The cellulose nonwoven fabrics took up much more direct dye than the electrospun PLA nonwoven fabrics did. The 100% cotton woven fabrics took up more direct dye than the 100% polyester woven fabrics did. As expected, the direct dyes (hydrophilic) had higher affinity to the cellulosic fabrics (hydrophilic) than the hydrophobic fabrics. In this case, with the dye completely dissolved in the water bath, the relationship between

the dye uptake, hydrophilicity, and capillary (pore) size was easily seen. Both the greater hydrophilicity and the smaller pore size resulted in increased absorbance.

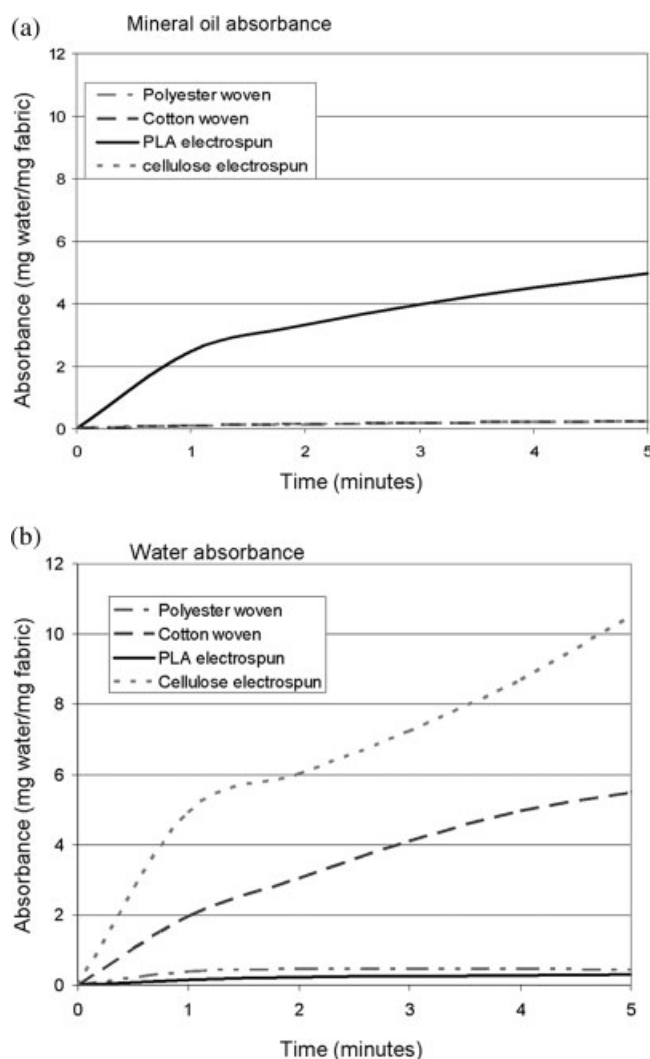


Figure 6 Absorbance of water and mineral oil by (a) woven and (b) electrospun fabrics.

TABLE II
Mean Flow Pore Diameter of the Fabrics

Sample	Mean flow pore diameter (μm)
Cellulose nonwoven fabric	3.8 ± 1.6
PLA nonwoven fabric	3.6 ± 0.7
Cotton woven fabric	36.9 ± 2.3
Polyester woven fabric	75.3 ± 6.7

TABLE III
Dye Absorbance by the Fabrics

Dye absorbance	Amount of direct red dye absorbance (mg/g of fabric)	Amount of disperse red 5 dye absorbance (mg/g of fabric)
100% polyester woven fabric	23.6	6.5
100% cotton woven fabric	47.4	5.4
Electrospun cellulose nonwoven fabric	128.9	25.4
Electrospun PLA nonwoven fabric	13.4	163.2

The electrospun PLA nonwoven fabrics took up 163.2 mg of disperse dye per gram of fabric, whereas the cellulose nonwoven fabrics took up 25.4 mg of disperse dye per gram of the fabric. The amounts of the disperse dye absorbed by the 100% polyester woven fabrics and the 100% cotton woven fabrics were 6.5 and 5.4 mg/g of fabric, respectively, indicating that the affinity of the disperse dye to both fibers was nearly equal under these conditions. Two competing conditions are likely to have contributed to the dye absorbance in this case. First, the hydrophilic cotton fiber has a high affinity for the water carrying the disperse dye. The polyester, on the other hand, has a greater affinity for the dye itself. The increased absorbance of the disperse dye by the electrospun cellulose fabric can be attributed to increased capillary action of the carrier water into the fabric. Figure 7(a) clearly indicates that the disperse dye forms balls and agglomerates to minimize contact with the cellulose surface on drying. No affinity between the dye and the fiber surface is evident. The increased hydrophobicity and small interfiber pore size of the PLA electrospun fabric, however, resulted in a dramatic increase in the disperse dye absorbance. Figure 7(b) confirms that the disperse dye is incorporated differently into the PLA electrospun nonwoven fabric than the cellulose electrospun nonwoven fabric. Here the dye has spread over the fiber surfaces,

creating intimate contact between the dye molecules and the PLA fibers.

CONCLUSIONS

The decreased fiber size and pore size found in electrospun PLA and cellulose nonwoven fabrics corresponded to increased absorbency. A smaller fiber diameter resulted in a larger surface area and hence an increased ability to absorb. Additionally, the small fiber size and pitted surface morphology of the PLA electrospun fabrics resulted in greater hydrophobicity than that reported for bulk PLA materials. The affinity for both the dye and the bath liquid influenced the absorbance of dye chemicals from aqueous baths. Future experiments will explore sustained release and further tailoring of the surface chemistry and morphology of fibers to selectively absorb and release chemicals.

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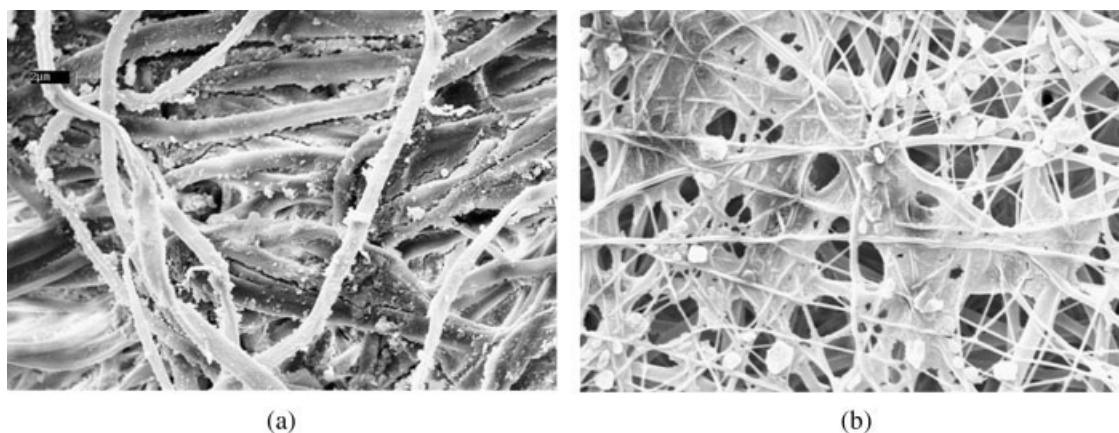


Figure 7 SEM photographs of electrospun nonwoven fabrics saturated with the disperse dye: (a) cellulose nonwoven fabrics and (b) PLA nonwoven fabrics.

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