Water Absorption and Mechanical Properties of Electrospun Structured Hydrogels

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ABSTRACT: Electrospun nanofibers are made when electrostatic forces overcome the surface tension of a polymer solution, causing an electrically charged jet to be ejected; as the jet travels through the air, the solvent evaporates, leaving behind an electrically charged fiber, which can be collected in the form of a nonwoven sheet. A superabsorbent was added to a polymer solution containing an elastomer (concentrations = 0–85%). The mixture was electrospun, producing nanofibers in which the superabsorbent particles were held in place with nanoscale elastic fibers. The nanofibers were tested for absorbency in water and synthetic urine. Fluid absorption by the nanofibers led to the formation of structured hydrogels. Increases in the weight gain from water absorption ranged from 400 to 5000%. The linear dimensions of samples cut from the nonwoven sheet were measured; wetting the superabsorbent increased the thickness dimension of the sheet dramatically and produced a smaller change in the plane of the sheet. The rate of water absorption was calculated; the samples containing 0–70% superabsorbent reached essentially their maximum absorbency within 5 s. The excellent strength and elasticity of the wet samples make these structured hydrogels ideal for many uses, including wound care, drug delivery, and sanitary goods. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 427–434, 2005

Key words: hydrogels; nanocomposites; swelling

INTRODUCTION

A large number of polymers can be used to produce nanofibers; however, the beauty of it all is the unending number of possible combinations that have yet to be examined. Molecular additives can be used to alter the characteristics of the fibers, or as in this study, two polymers can be combined to produce the desired traits. Through a combination of a superabsorbent polymer with an elastomer, a fiber can be produced that is strong and elastic but also absorbs copious amounts of water. Lightly crosslinked polymer networks, called *gels*, of polymer chains made up of polyelectrolytes containing carboxylate anions and sodium cations are often superabsorbent. A difference in the osmotic pressure results from the concentration of ionic groups present in the gel network; this is the driving force behind the polymer gel's superabsorbency.[1] The crosslinked chains cannot be separated and dispersed in water, and this limits the amount of swelling possible.[2] Superabsorbent polymers are hydrogels capable of absorbing up to 100 times the volume of the original polymer.[1,3,4] Having been used in diapers for more than 30 years, superabsorbents are now being used to make water-swellable rubbers, water-blocking tapes, and soil additives.[3,5] Other more specialized uses have also been found, including artificial snow,[6,7] drilling fluid additives,[8] polymer concrete suited for repairing cracks,[9] dew-preventing coatings,[10] and sealing composites in long-distance cable.[11] More general uses for superabsorbents can be found in agriculture,[12–14] horticulture,[12,15] firefighting,[16] and drug delivery.[17,18]

The concept of electrospinning has been around for almost 100 years;[19] however, recent advances in the field have spawned a renewed interest in the applications of this technology. The most notable property of electrospun nanofibers is their exceedingly high ratio of surface area to volume, a result of their small diameter. The length of electrospun nanofibers is often many kilometers and is limited only by choices in the manufacturing process. Nanofibers are finding many different applications, including separation membranes, wound-dressing materials, artificial blood vessels, nanocomposites, and nonwoven fabrics.[20] Although this list is impressive, it is certainly not all-encompassing.

Electrospinning produces polymer fibers with diameters ranging from nanometers to a few micrometers. A polymer solution or melt is electrically charged with a high-voltage power supply. The polymer solution is spun from a container, which has a nozzle with

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a diameter in the submillimeter range. As the applied electrostatic force increases, the drop at the end of the nozzle is charged. The electrical and surface tension forces cause the charged drop to adopt a conical shape known as the Taylor cone.[21] Once the electric field surpasses a critical value, an electrically charged jet of the solution is ejected from the tip of the cone toward the grounded target plate.[22] The jet elongates and dries in flight. The dry nanofiber is collected on the target plate. A typical charged jet elongates in a straight line for some distance and then bends in response to electrical forces and develops a spiral path. Every segment of the jet along the spiral path continues to elongate, bend, and become thinner until it dries and solidifies. After bending begins, the trajectory of every segment of the jet is not along, but nearly perpendicular to, the path of the jet.

In this study, superabsorbent polymers and elastomeric copolymers were combined during the electrospinning process to generate superabsorbent electrospun nanofibers, which were capable of absorbing and retaining large amounts of fluid while maintaining their mechanical integrity and strength. The maximum absorbency of water by the superabsorbent electrospun nanofibers was determined along with their capacity to absorb synthetic urine. The rate at which the absorption occurred was also established. A comparison was made between the absorbency of the nanofibers and thin films. The reduction of the superabsorbent capacity due to the electrospinning of the superabsorbent polymers into nanofibers was ascertained. A tensile stress test was performed to measure the amount of stress and strain that a water-swollen nanofiber was able to support without mechanical failure.

EXPERIMENTAL

Materials

Tecophilic polymer was purchased form Thermedics, Inc. (Wilmington, MA) Waterlock (A-180) superabsorbent polymer was purchased from Grain Processing Corp. (Muscatine, IA) Tetrahydrofuran (THF), urea, sodium chloride, sodium sulfite, and sodium phosphate were purchased from Fisher Co. (Fairlawn, NJ) Ammonium chloride was purchased from Mallinckrodt, Inc. (St. Louis, MO), and ethanol was purchased from VWR (Buffalo Grove, IL). Double-sided conducting tape was purchased from SPI Supplies (West Chester, PA). The Labquake Shaker was manufactured by Labindustries, Inc.

A diagram of the electrospinning apparatus is shown in Figure 1. The direct-current power supply (D-ES 30PN/M692) was purchased from Gamma High Voltage Research (Ormond Beach, FL). Cones manufactured by Wilton Industries (Woodridge, IL)
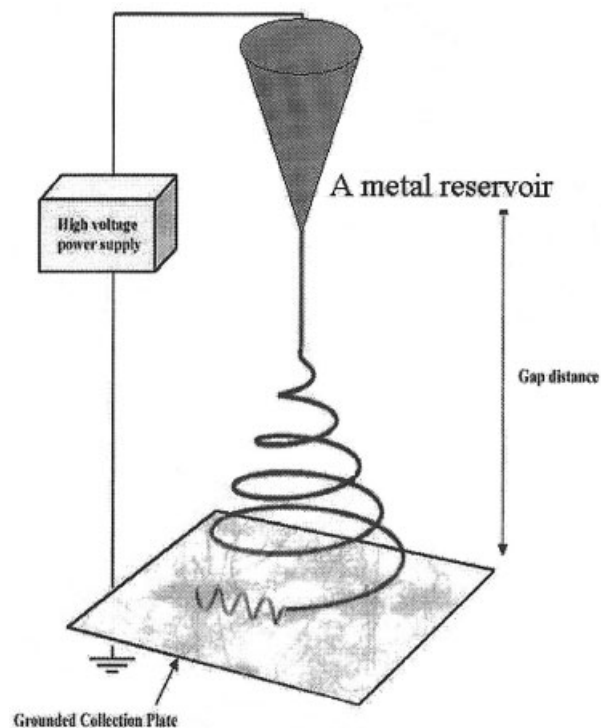

Figure 1   Diagram of the electrospinning apparatus.

for use in pastry decorations were used as fluid reservoirs. A copper grounded plate (30 cm × 30 cm) was used as the target for collecting the fibers.

Methods

The polymer solutions were spun from a conical metal reservoir, and the gap distance was varied with the use of a laboratory jack. The metal cone was suspended with copper wire that was connected to the power supply. Aluminum foil covered the target plate; to facilitate the removal of the fibers, the nanofibers were collected on a square of polyester netting that was placed on top of the aluminum foil. The polymer solutions, with a viscosity similar to that of honey, usually spun well. The diameter of the hole at the tip of the metal conical reservoirs was either about 1 or 1.5 mm. A larger hole was chosen for the higher viscosity solutions. The voltage and gap distance were also varied to produce the best fibers at the highest rate.

Solution preparation

The stock polymer solution was a 14% (w/w) solution of Tecophilic polymer in ethanol and THF (80:20). This solution was prepared as follows. Tecophilic was initially dissolved in excess THF and then concentrated by evaporation; ethanol was added to the solution to produce the desired concentrations. The next step was

to suspend the superabsorbent polymer, Waterlock or sodium (poly)acrylate (SPA), in ethanol and then add the Tecophilic solution. The mixture needed to be inverted each time before it was spun to resuspend the superabsorbent. Various concentrations of Waterlock with respect to Tecophilic were used: 0, 7, 30, 47, 71, 85, and 95 wt %. A solution of 50:50 (w/w) SPA/Tecophilic was prepared as well.

Synthetic urine was prepared by the addition of the following to distilled water: 25 g of urea, 9 g of sodium chloride, 2.5 g of sodium phosphate, 3 g of ammonium chloride, and 3 g of sodium sulfite. Once all were dissolved, additional distilled water was added until the total volume was equal to 1 L.

Solution spinning

The viscosity of the Waterlock/Tecophilic solutions was such that the appropriate metal conical reservoir had a hole with a diameter of about 1 mm. The samples were all spun at a gap distance of 37 cm with a voltage of 30 kV at room temperature. The SPA/Tecophilic solution was spun at a voltage of 30 kV with a 30-cm gap distance with a cone that had a hole with a diameter of approximately 1.5 mm. About 25–30 g of a solution was required to produce a fibrous mat with a thickness of approximately 1 mm and an area of 100 cm^2, with a dry weight of approximately 2 g. The fibers were then removed from the polyester netting and cut into 1.5-cm squares to be tested for absorbency. The diameters of the nanofiber segments varied from 500 to 1500 nm. The thickness of the nonwoven sheet varied also, but in most cases, samples with a thickness of about 10 mm were used.

Scanning electron microscopy (SEM) micrographs

A fiber sample was placed on double-sided conducting tape, which was attached to the sample holder. The sample was coated, with ion sputtering, with a very thin layer of a Pd alloy. This very thin metal layer made the surface electrically conducting, but it did not alter the fine features of the sample. A JEOL JEM-5310 scanning electron microscope (Peabody, MA) was used and operated at 25 kV and 60 μA.

Absorbency tests

The superabsorbent electrospun nanofibers were tested for the absorbency of both water and synthetic urine. The procedure for testing was to first weigh the fiber sample and record the dry weight as well as the initial dimensions. The fiber sample was then placed in a beaker containing either water or synthetic urine and was removed after 5 s. The wet sample was placed on a paper towel, and the excess water was allowed to drain off. The sample was then weighed and mea-
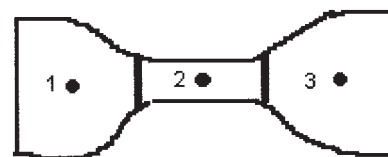
Dumbbell Type 5-D638

Figure 2 Dumbbell (type 5-D638).

sured. This process continued, with the weight and size taken after immersion for 0.16, 0.5, 1, 2, 5, and 10 min. Finally, the fiber was immersed for at least 24 h to reach equilibrium absorbency. The absorbency was defined as follows:

$$Q = (W_2 - W_1)/W_1 \qquad (1)$$

where Q is the absorbency, W_1 is the initial weight, and W_2 is the weight of the fiber when wet.

Dimensional analysis

The structured hydrogels underwent dimensional changes throughout the water absorption process. These changes occurred in the thickness of the sample and in the area. To analyze the changes, we used an equation to determine the wet-to-dry ratio for the area and thickness. The wet-to-dry ratio was defined as follows:

$$R_{\text{Twd}} = T_w/T_d \quad \text{or} \quad R_{\text{Awd}} = A_w/A_d \qquad (2)$$

where R_{Twd} is the wet-to-dry ratio for thickness, T_w is the thickness of the sample after maximum water absorption, T_d is the thickness of the dry fiber sample, R_{Awd} is the wet-to-dry ratio for area, A_w is the area of the sample after maximum water absorption, and A_d is the area of the dry fiber sample

Fiber strength

Ideally, a superabsorbent not only is capable of absorbing fluids rapidly but also can sustain mechanical forces while wet. Mechanical tests were performed that measured the amount of stress and strain that the fibrous mat was able to endure before it broke. An Instron 5567 mechanical testing machine (Canton, MA) was used. Dumbbells (type 5-D638), shown in Figure 2, were cut from the fibrous mat. The thickness of the fibrous mat was measured in three places. Two black lines were placed 10 mm apart to mark the area in which the elongation was measured. The area between the two black lines was wet with water at least 1 min before the test was conducted because the absorbency tests showed that 95% of the total water gain
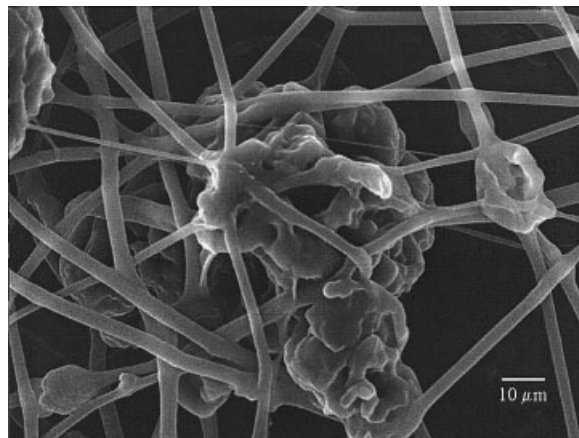
Figure 3 SEM image of the electrospun nanofibers before wetting (original magnification = 1000×).

Figure 4 SEM image of the dehydrated structured hydrogel after wetting and drying (original magnification = 1000×).

was achieved after 5 s. The parts labeled 1 and 3 were not wetted and served as attachments to the grips of a tensile testing machine.

The thickness measurements were made at the second spot on the dry sample. Three samples of each of the different ratios of Waterlock/Tecophilic (0, 7, 30, 50, 70, and 85%) were run. All tensile force measurements were made with the grips separating at 50 mm/min.

Residue tests

A test was conducted to determine the total amount of the superabsorbent material, or residue, lost from the nanofiber matrix after it reached equilibrium absorption. Each sample taken from the fibrous mat was weighed and then was placed in a vial containing water and shaken with a Labquake shaker (Berkeley, CA) for 24 h. The sample was then removed, and the water from the beaker was transferred to an aluminum dish of known mass. The aluminum dish was placed in an oven until all of the water had evaporated. It was then weighed to determine the amount of residue that remained. All superabsorbent electrospun nanofibers containing Waterlock were tested for residuals.

RESULTS AND DISCUSSION

Morphology of the structured hydrogels

SEM micrographs were taken of the structured hydrogels in two different states. The first micrograph shown in Figure 3 shows the original electrospun structured hydrogel before the sample was wet. The second micrograph (Fig. 4) shows the structured hydrogel after water absorption occurred and the sample was dehydrated *in vacuo*. The dry absorbent particles
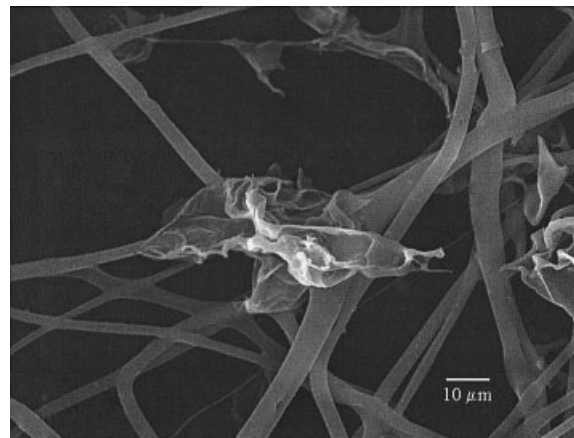
were more like torn and tangled sheets after wetting and drying.

Absorbency tests

The absorbency tests were performed in both water and synthetic urine. Four samples of each of the Waterlock/Tecophilic combinations were tested, and the average absorbency of the four samples at equilibrium was calculated. Figure 5 shows a graph of the equilibrium absorbency of water by structured hydrogels that contained 7–85 wt % superabsorbent.

The structured hydrogels did not absorb as much water as pure Waterlock in powder form. Despite this, they are desirable for many important applications. The producers of the Waterlock superabsorbent indicate that it can absorb up to 160 mL of water/g of
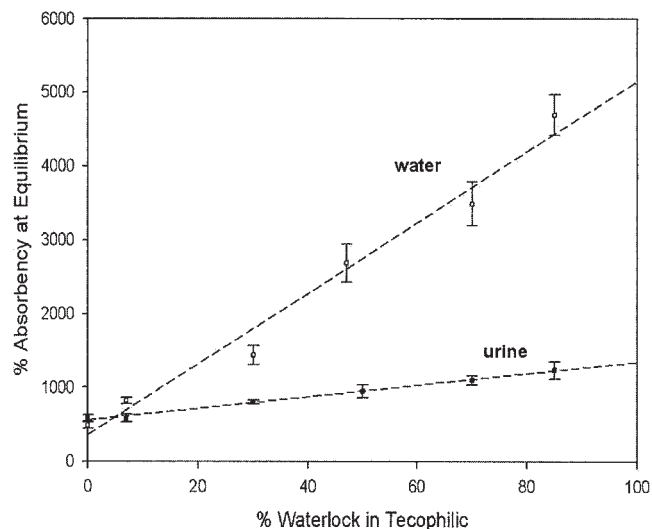

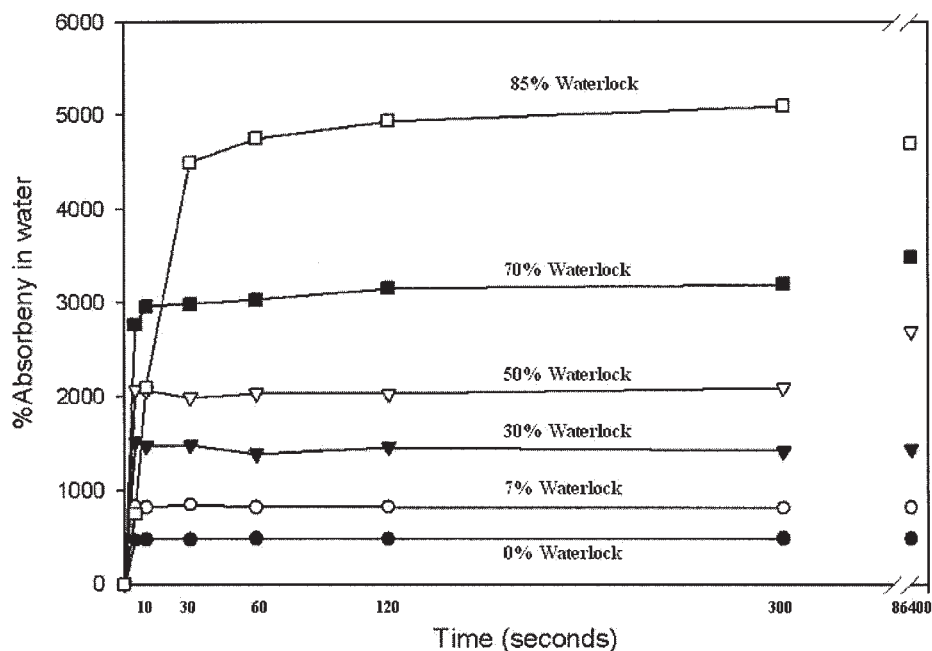**Figure 5** Absorbency in (○) water and (●) synthetic urine.

Figure 6 Rate of absorption of the structured hydrogels.

polymer. The experimental data from the graph in Figure 5 extrapolate to only 90 mL of water/g of polymer, a 44% decrease. This decrease can be attributed to the mechanical restraint of the crosslinked nanofibers, which appear to limit the amount of swelling possible.

The same procedure was followed for the absorbency tests in urine. Figure 5 also shows the results of the absorbency tests in synthetic urine. As expected, the absorbency of water by structured hydrogels was greater than that of synthetic urine.

Figure 5 shows that the nanofibers containing 7% superabsorbent had results very similar to those of nanofibers made up of only Tecophilic polymer (identified as 0% Waterlock in Tecophilic on the graph). Also, the increase in the absorbency with increasing amounts of the superabsorbent was not as great for the synthetic urine as for the water. Figure 5 compares the absorbency in water and in synthetic urine.

SPA absorbency tests

The nanofibers spun with 50:50 SPA/Tecophilic were also tested for water absorbency. The nanofibers were unable to retain the superabsorbent during swelling. As they swelled, the superabsorbent particles detached from the nanofiber matrix and separated from the nanofibers. The loss of superabsorbent from the nanofibers was unacceptable; the residual concentration was greater than 20%. Further research needs to be conducted to produce nanofibers containing SPA with improved residuals.

Rate of water absorption

Figure 5 shows only the absorbency at equilibrium. Determining the rate of absorption is interesting as well. In most cases, a rapid rate of absorption is desired. The graph in Figure 6 illustrates the rate at which the structured hydrogels absorbed water. Within 5 s, the 0, 7, and 30% Waterlock samples reached essentially their maximum absorbency. As the amount of Waterlock was increased, the rate at which the structured hydrogels absorbed decreased. The 50 and 70% samples absorbed greater than 75% of their maximum absorbency after 5 s. The 85% sample required 30 s to reach 96% of its maximum absorbency.

Dimensional changes in the structured hydrogels resulting from Waterlock concentration variations

For every sample, the dimensions were measured when it was dry and when it was saturated with water. Figure 7 shows that as the amount of Waterlock in the hydrogels increased, so did the wet-to-dry ratio for the thickness. The wet-to-dry ratio for the area did not change significantly with the Waterlock concentration. This indicates that the nanofibers containing no Waterlock only expanded in length and width. The addition of a superabsorbent allowed the nanofibers to increase in the length, width, and thickness when they were wet.

Tensile stress testing

As stated earlier, the Tecophilic polymer provided strength and elasticity for the structured hydrogels,
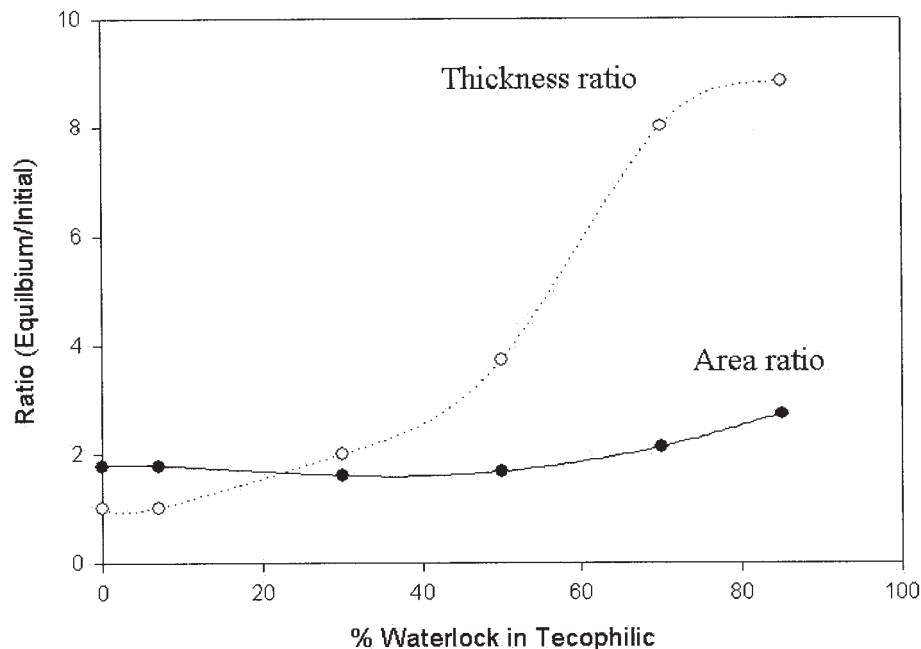
Figure 7 Change in the area and thickness during swelling.

whereas Waterlock did not. The higher the Waterlock concentration was, the weaker the structured hydrogels became, as shown in Figure 8. The structured hydrogels containing large amounts of Waterlock, that is, 70 and 85%, were not mechanically strong. Both broke below 0.5 MPa. Those with no Waterlock at all or only 7% did not break until the stress had reached 2–3 MPa. The 70 and 85% Waterlock samples also had

the lowest strain at their breaking point. For both, the strain was around 600%. Samples containing lower concentrations of Waterlock all broke around 900%.

Figure 9 compares the strength of dry Tecophilic nanofibers and wet Tecophilic nanofibers. As expected, the nanofibers were stronger when dry; dry Tecophilic nanofibers were able to withstand a stress of almost 9 MPa, whereas the wet nanofibers only
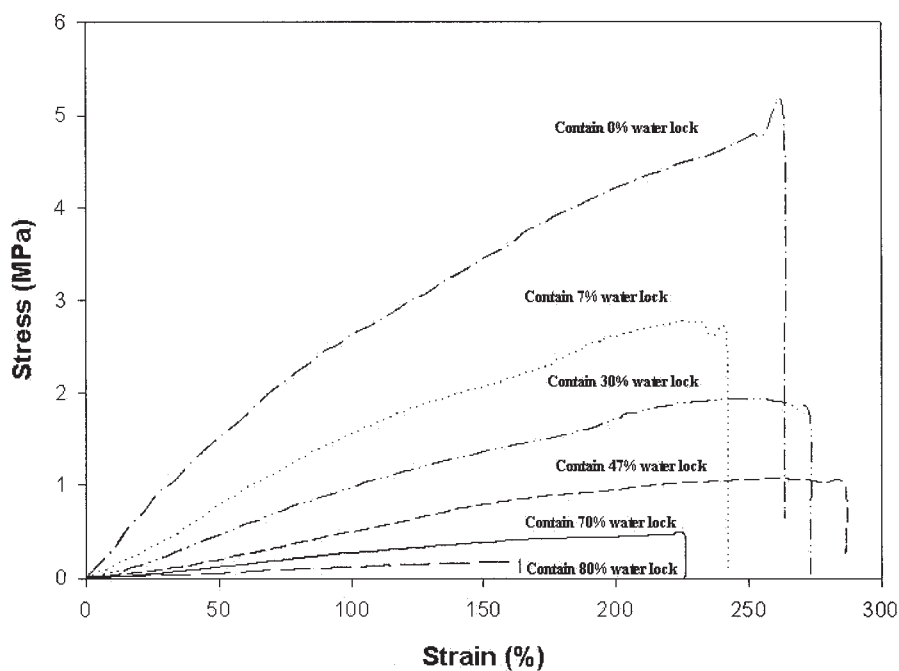

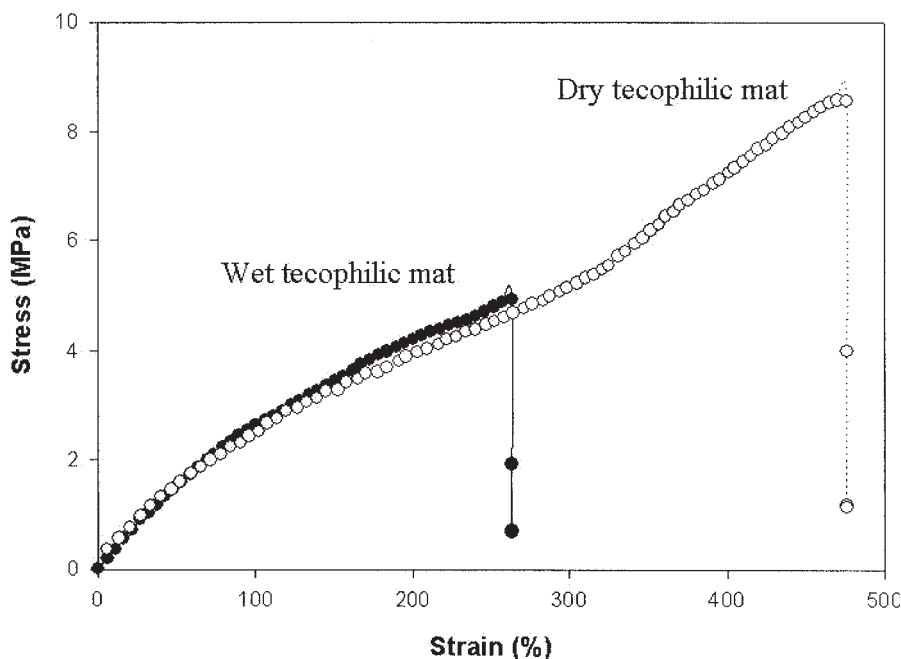**Figure 8** Tensile stress test data for the structured hydrogels.

Figure 9 Tensile stress test data for the Tecophilic electrospun nanofibers.

withstood about 5 MPa. The dry Tecophilic nanofibers also withstood more strain, stretching to almost 5 times their original length. The wet Tecophilic nanofibers were only able to stretch by about 275%. A point-bonded structure was suggested to account for changes in the mechanical behavior, such as deformation, in electrospun mats.[23] Before the test was performed, the nanofibers destined to be the wet samples were initially placed in water, and the absorption of water resulted in the stretching of the network bonds. The wet Tecophilic nanofiber samples were already under some stress, and strain caused swelling (expanding) in the sample. The swelling (expanding) may have been the cause of the reduction of the tensile stress and strain in the wet Tecophilic nanofiber samples, whereas the moduli for both wet and dry nanofiber mats remained almost the same.

Residue tests

Residue tests were performed on all six samples. The residual percentage after 24 h ranged from 1.58 to 4.46%. This was an acceptable amount of release of the superabsorbent from the structured hydrogels. The Tecophilic elastomer was able to contain Waterlock within the nanofibers while still allowing the superabsorbent sufficient space to swell after becoming saturated with water.

CONCLUSIONS

Adding a superabsorbent to a polymer solution before electrospinning produced nanofibers capable of ab-

sorbing copious amounts of water while retaining a useful level of mechanical strength. Various amounts of the superabsorbent were added to the Tecophilic polymer solution (0, 7, 30, 47, 70, and 85%). The samples were cut from the fibrous mats and were tested in both water and synthetic urine for their absorption capabilities. Upon the absorption of water with the electrospun nanofibers, structured hydrogels were produced. The structured hydrogels absorbed 400–5000% in water and 500–1250% in synthetic urine. The rate of absorption was determined as well and turned out to be very impressive. Within 5 s, 0, 7, and 30% Waterlock samples absorbed essentially the maximum amount of water. The 50 and 70% samples absorbed more than 75% of their maximum within 5 s. Within 30 s, the 85% sample achieved 96% of its equilibrium absorption. The change in the dimensions upon the absorption of water by the hydrogels showed that Tecophilic was able to absorb in only two dimensions. The superabsorbent allowed a third dimensional change. As the amount of the superabsorbent increased, so did the ratio of the equilibrium thickness to the initial thickness. The structured hydrogels were flexible and strong, as indicated by the results of the stress–strain tests. The combination of these characteristics makes these structured hydrogels superior for any application that requires the hydrogel to be both strong and capable of absorbing large amounts of fluid very quickly.

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