

Preparation and Characterization of pH-Sensitive Hydrogel Fibers based on Hydrolyzed-Polyacrylonitrile/Soy Protein

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ABSTRACT: Novel smart hydrogel fibers were prepared from a blend of hydrolyzed-polyacrylonitrile (H-PAN) and Soy Protein (SP). The dynamic and static elongation/contraction behaviors were studied. It was discovered that H-PAN/SP hydrogel fibers consisted of a multiporous structure. With an increase in the content of SP, the hydrogel fibers exhibited excellent reversible pH-sensitive behavior. When the weight ratio of H-PAN to SP was 4 : 6, the hydrogel fibers showed the best response times at 1.35 s (elongation) and 0.63 s (con-

traction). Discontinuous volume phase transitions and hysteresis loops of the hydrogel fibers induced by changes in pH value were found. These results were found to be explainable in terms of the surface morphology and polyampholytic properties of H-PAN/SP hydrogel fibers. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1100–1108, 2008

Key words: hydrolyzed-polyacrylonitrile; soy protein; hydrogel fiber; pH-sensitive

INTRODUCTION

Hydrogels are formed with a three-dimensional network of polymer chains, where some parts are solvated by water molecules but the other parts are chemically or physically linked with each other.¹ Since Tanaka et al.^{2–7} put forward the Phase Transition Theory of hydrogel systems, more and more researchers have engaged in the investigation of the so-called “smart” or “intelligent” hydrogels, which demonstrate the ability of responding to various external factors (such as temperature, pH, electrical voltage, solvent composition, pressure, or ionic strength) and show a sudden or gradual change in their dynamic and equilibrium swelling properties. Because of the interesting property, smart hydrogels attract considerable attention on applications in a variety of fields (e.g., biomedical engineering, pharmaceutical, actuators and sensors, biomimetic engineering). It has been suggested that these hydrogels could be made into various forms (e.g., particle-like, film-like, fiber-like) and used as the basis for artificial organs,⁸ drug delivery systems,⁹ separation systems,¹⁰ or on–off switches.^{11,12}

As a special form, smart hydrogel fibers, which can reversibly elongate and contract in response to external stimuli, have been extensively investigated. Such behavior is partially similar to the contraction properties of natural muscle (the electrical signal from the nervous system triggers a series of chemical processes that lead to a volume change and a concomitant mechanical movement, developing mechanical energy), so a lot of researchers and technologists become interested in the development of “artificial muscle.”¹³ For example, Moschou et Al. prepared the artificial muscle material based on an acrylic acid/acrylamide hydrogel blended with a conductive polypyrrole/carbon black composite.¹⁴ Mao et al. prepared a solvent-sensitive hydrogel fiber by means of surface-grafting acrylonitrile onto cellulose fiber and consequent hydrolysis.¹⁵ However, among these hydrogel systems, pH-sensitive hydrogel fibers are studied most. Kuhn and Katchalsky in 1950s had already produced hydrogel fibers, which contracted in response to changes in pH,¹⁶ but slow response time of the fibers, in the order of minutes, inhibited their applications. During 1990s to early 2000s, a number of new gel systems were developed by novel methods and were studied deeply both on the morphology and static\dynamic response behaviors.^{17–21} Fei et al. prepared the thermoinduced pH-sensitive hydrogel fibers composed of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) and found that the higher the PAA content of the hydrogel the lower the jump point pH value in the static behavior and more microholes

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were formed, which greatly improved the response property.²⁰ Sun et al. prepared the pH-sensitive hydrogel fibers from chitosan/poly(propylene glycol) composite via solution spinning, which were then crosslinked by epichlorohydrin (ECH) and glutaraldehyde (GA). They studied the mechano-electro-chemical behavior of the hydrogel fibers and found that CS/PEG crosslinked by ECH is more sensitive than that by GA.²¹ Umemoto et al. produced the pH-sensitive hydrogel fibers from commercially available poly(acrylonitrile) (PAN) fibers, which can be changed by the preoxidation step from a linear chain structure to a planar network structure constructed with cyano groups and pyridine rings as a crosslinker. And the elongation/contraction response times of the hydrogel fibers were about 4 s and 2 s, respectively.¹⁸ And recently Spinks et al. fabricated the pH-sensitive chitosan/carbon nanotubes and chitosan/polyaniline/carbon nanotubes composite fibers with a wet spinning method and the response times were about 25 s.^{22,23} However, if we want these kinds of hydrogel fibers to be applied practically, the response times of elongation/contraction behavior still remain to be improved, when they are compared with natural muscle's response times (about 0.001 s).¹⁸

It is known that the swelling kinetics of the hydrogels is controlled by diffusion.³ To improve the response times, one approach is to reduce the size of hydrogels, and the second approach is to introduce multiporous structure into hydrogel.²⁴ Taking this into account, we make use of polyacrylonitrile (PAN) and soy protein (SP) as raw materials and a wet spinning method (although the electrospinning method²⁵⁻²⁷ has been developed, the hydrogel fibers are difficult to align) to prepare porous fine H-PAN/SP hydrogel fibers. PAN is the raw material of commercial acrylic fibers, which is easy to obtain the PAA/AM chemical structure by alkaline hydrolysis and can avoid the problem brought by the toxicity of residual monomers that are usually present in these synthetic gels. With the addition of SP, some kind of globin, the biocompatibility of hydrogel fibers can be improved partially furthermore. In addition, the dynamic and static elongation/contraction behaviors of the H-PAN/SP hydrogel fibers were well investigated. The results obtained were discussed in terms of the chemical structure of H-PAN, the morphological studies, and the polyampholytic properties of H-PAN/SP hydrogel. In this article, the pH-sensitivity of the hydrogel fibers was studied in detail.

EXPERIMENTAL

Materials

Polyacrylonitrile (PAN) powder of molecular weights 50,000 (M_w), which is used in the production

of commercial acrylic fibers, was obtained from Jinshan Petrochemical Co. (Shanghai, China). Soy protein powder (SP) was purchased from Shenyuan Food (Group) Co. (Shanghai, China). Glutaraldehyde 25% (w/v) was purchased from Shanghai Chemical Reagent Company. Sodium hydroxide (NaOH), sodium sulfate (Na_2SO_4), and 98% (w/v) sulfuric acid were of analytical grade and purchased from Shanghai Chemical Reagent Company. Distilled water was used in all experiments.

Preparation of H-PAN/SP spinning dope

Given amounts of PAN and NaOH ($W_{\text{PAN}} : W_{\text{NaOH}} = 1 : 0.6$, total weight = 48 g) were mixed in distilled water (120 mL). The mixture was continuously stirred and heated to 90°C. After it reached 90°C, the temperature was maintained for 1 h.²⁸ The obtained viscous H-PAN solution was allowed to cool to room temperature and pH was adjusted to 11. The H-PAN solution was then flocculated by ethanol. The obtained flocculating colloid H-PAN was dried and cut into small pieces.

SP powder was preswelled in distilled water at 30°C for 2 h. Then, the controlled amounts of prepared H-PAN and SP ($W_{\text{H-PAN}} : W_{\text{SP}}$ varied from 4 : 6 to 7 : 3, total weight = 5 g) were mixed and the pH was adjusted to 12 by addition of 2.5M NaOH solution to have SP denatured. The mixture was continuously stirred while the temperature of the solution was increased from 30 to 70°C at a heating rate of 1°C/min, and after every 10°C increment the temperature was maintained for 10 min. After it reached 70°C, the temperature was maintained for 30 min.^{29,30} In this way, the interactions (such as hydrogen bonding, electrostatic interaction, and hydrophobic interaction) among the SP molecules can be partially broken, and the degradation of the protein molecules induced by alkali and heat will be reduced to a lower level. Finally, a viscous mixture of H-PAN/SP was formed and allowed to cool to room temperature and to remove air bubbles. Table I shows the composition of H-PAN/SP spinning dope in detail.

Preparation of H-PAN/SP hydrogel fibers

The H-PAN/SP hydrogel fiber was produced in a laboratory scale wet spinning device. The spinning dope was added into a syringe and extruded into the coagulating bath under a constant force. The coagulating bath contained saturated sodium sulfate, 1% (v/v) glutaraldehyde as a crosslinking agent, and 0.5M sulfuric acid. The temperature of the coagulating bath was maintained at 25°C. The spinning nozzle was immersed in the coagulating bath, and the diameter of pin hole in the nozzle was 0.4 mm. The

TABLE I
Composition of H-PAN/SP Spinning Dope

$W_{\text{H-PAN}} : W_{\text{SP}}$	4 : 6	5 : 5	6 : 4	7 : 3	10 : 0
H-PAN (g)	2	2.5	3	3.5	5
SP (g)	3	2.5	2	1.5	0
2.5M NaOH solution (mL)	2	1.5	1	0.5	0
H ₂ O (mL)	28	28.5	29	29.5	30

extruded fiber was crosslinked in the coagulating bath for 14 h by reacting with glutaraldehyde. Then, the raw fiber was drawn with a drawing ratio of 4 and washed in distilled water and dried in air. The formed H-PAN/SP hydrogel fibers were $\sim 90 \mu\text{m}$ in diameter.

Infrared Analysis

The change in chemical structure from PAN to H-PAN was studied by FTIR (ABB Momem MB-100 FTIR spectrophotometer). The PAN and H-PAN samples were crushed with KBr to make pellets. The measuring resolution was 4 cm^{-1} , and iterations were performed for 32 times.

Measurement of the degree of hydrolysis of H-PAN

To estimate the hydrolysis degree of H-PAN, the relative contents of carbon and nitrogen in H-PAN were examined by Vario ELIII Element Analyzer (Elementar Co., German), and according to the mechanism of this hydrolysis reaction, the degree of hydrolysis was calculated using the following equation:

$$\text{Degree of hydrolysis of H-PAN} = [1 - (32\text{N}\%)/(14\text{C}\%)](\%) \quad (1)$$

where N% and C% are the relative contents of Carbon and Nitrogen, respectively.

Scanning electron microscopy

The H-PAN/SP hydrogel fiber samples washed by distilled water several times were frozen in liquid nitrogen, and then lyophilized. The surface morphology of the samples was investigated using DI-NSIV scanning electron microscope with a magnification of 500, and the accelerating voltage was 10 kV.

Polarizing optical microscope

The H-PAN and H-PAN/SP hydrogel fiber samples were immersed alternately in acidic solution (pH = 1) and alkaline solution (pH = 13) for several times and then observed both at their swollen state and shrunken state by polarizing optical microscope (POM) with a magnification of 20.

Measurement of elongation/contraction behaviors

Dynamic and static elongation/contraction behaviors of the hydrogel fibers, stimulated by different environmental solutions were studied as a function of the fiber length. The change in length at a constant load was investigated by using an apparatus shown in Scheme 1. The dynamic elongation/contraction behavior of the hydrogel fibers against time was measured when the fibers were changed to 0.1M NaOH solution from 0.1M HCl solution (elongation) or *vice versa* (contraction) at a load of 210 kPa. The static elongation/contraction behavior of the fibers was measured when the changes in length reached equilibrium after immersion in a given pH solution at a load of 60 kPa. All the solutions were kept at a temperature of 25°C.

The swelling elongation degree and equilibrium swelling elongation degree of the hydrogel fibers were calculated using the following equations, respectively:

$$\text{Swelling elongation degree} = \Delta L/L_0(\%) \quad (2)$$

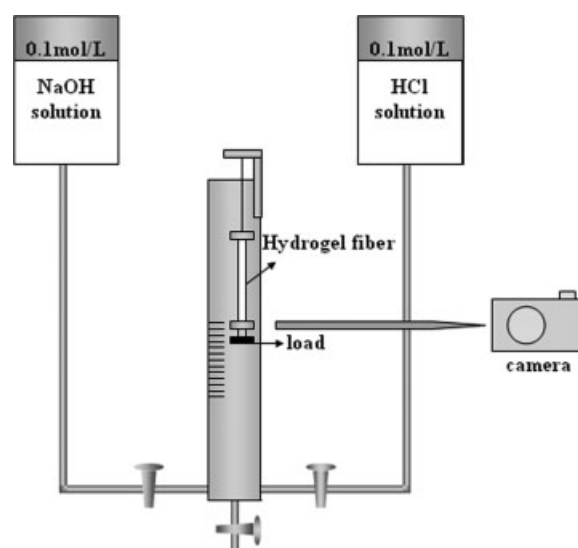
$$\text{Equilibrium swelling elongation degree} = \Delta L_\infty/L_0(\%) \quad (3)$$

where $\Delta L = L - L_0$, $\Delta L_\infty = L_\infty - L_0$, L is the length on the measurement, L_∞ is that at equilibrium, L_0 is that at the initial state (equilibrated in 0.1M HCl solution). The pH of the solutions was monitored with a pH meter (PHS-3C meter, Shanghai, China).

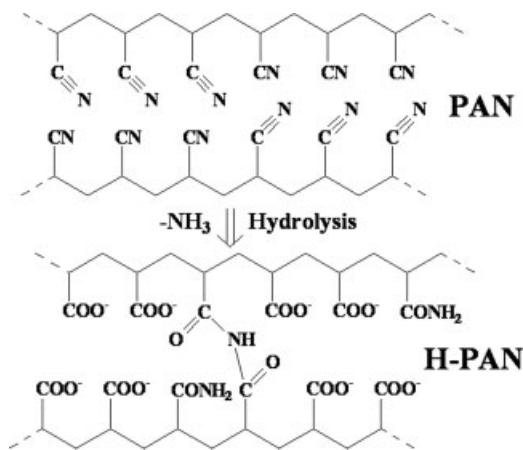
RESULTS AND DISCUSSION

Mechanism of formation of H-PAN/SP hydrogel

The PAN was hydrolyzed with NaOH solution under heating to form H-PAN. During the hydro-



Scheme 1 Measurement of elongation/contraction behaviors.



Scheme 2 Mechanism of crosslinking during the preparation of H-PAN.

lytic process, most of the nitrile groups ($-\text{CN}$ groups) were hydrolyzed into carboxylate groups ($-\text{COO}^-$ groups) or into amide groups and some crosslinked domains formed (see Scheme 2).²⁸ Infrared absorption analysis of H-PAN shows no nitrile functionality (the peak at 2225 cm^{-1} disappeared) when compared to the initial PAN [Fig. 1(A) compared with Fig. 1(B)]. Therefore, according to the mechanism of this reaction and element analysis of the relative contents of Carbon and Nitrogen in H-PAN, the degree of hydrolysis of H-PAN was calculated by equation 1. N% and C% obtained from measurement were 5.53% and 47.96%, respectively, so the degree of hydrolysis was 70%, which illuminated that there were 70% of $-\text{CN}$ groups converted into $-\text{COO}^-$ groups and the remaining 30% of $-\text{CN}$ groups were all converted into amide groups.

The resulting H-PAN was mixed with the denatured SP, and then the hybrid was injected into the coagulating bath, where the SP was crosslinked by

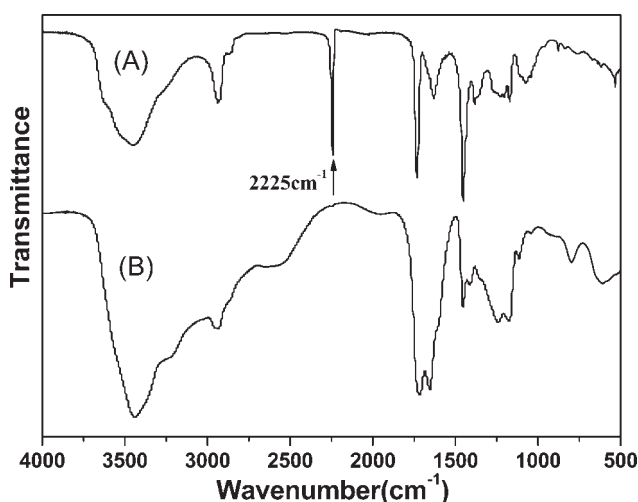
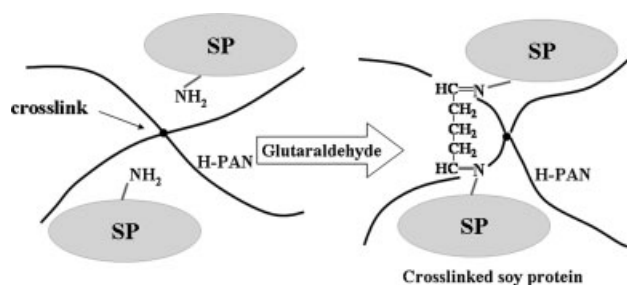


Figure 1 Infrared Spectra of PAN (A) and H-PAN (B).



Scheme 3 Formation of crosslinked H-PAN/SP hydrogel.

glutaraldehyde. Accordingly, we can imagine the formation of H-PAN/SP hydrogel (see Scheme 3).

Morphological Studies of H-PAN/SP hydrogel fibers

SEM can be used directly in the observation of the surface morphology of hydrogel. Because of the volume change after drying, the common method of vacuum drying would lead to destroy of the structure of hydrogel. Here, we treat the hydrogel fiber samples with liquid nitrogen first. In this way, the change in morphology of hydrogel can be minimized. Figure 2 depicts the SEM images of the surface morphology of H-PAN/SP hydrogel fibers and H-PAN hydrogel fibers all equilibrated in neutral solution. It was easy to find that H-PAN/SP hydrogel fibers showed multiporous morphology and with an increase in the content of SP, more and more pores were formed. However, there was hardly a pore in H-PAN hydrogel fiber, which exhibited a little compact and even-textured morphology.

To characterize the hydrogel fibers deeply, POM was used to observe their morphology both at swollen state and shrunken state. Figure 3(A,B) show the transmission optical micrographs of the H-PAN/SP hydrogel fiber kept in acidic solution and alkaline solution, respectively. It was obvious that inhomogeneous morphology existed both at their swollen state and shrunken state. However, in the case of H-PAN hydrogel fiber, it was nearly homogeneous [see Fig. 3(C)].

These phenomena above indicate that the presence of SP greatly alters the microstructures of the H-PAN/SP hydrogel fibers, which may be caused by the difference between SP and H-PAN on coagulation rates.

Dynamic elongation/contraction behavior of H-PAN/SP hydrogel fibers

Figure 4 reveals a typical dynamic elongation/contraction behavior of the H-PAN/SP hydrogel fibers made from various weight ratios of H-PAN and SP, subjected to different pH conditions at a load of 210

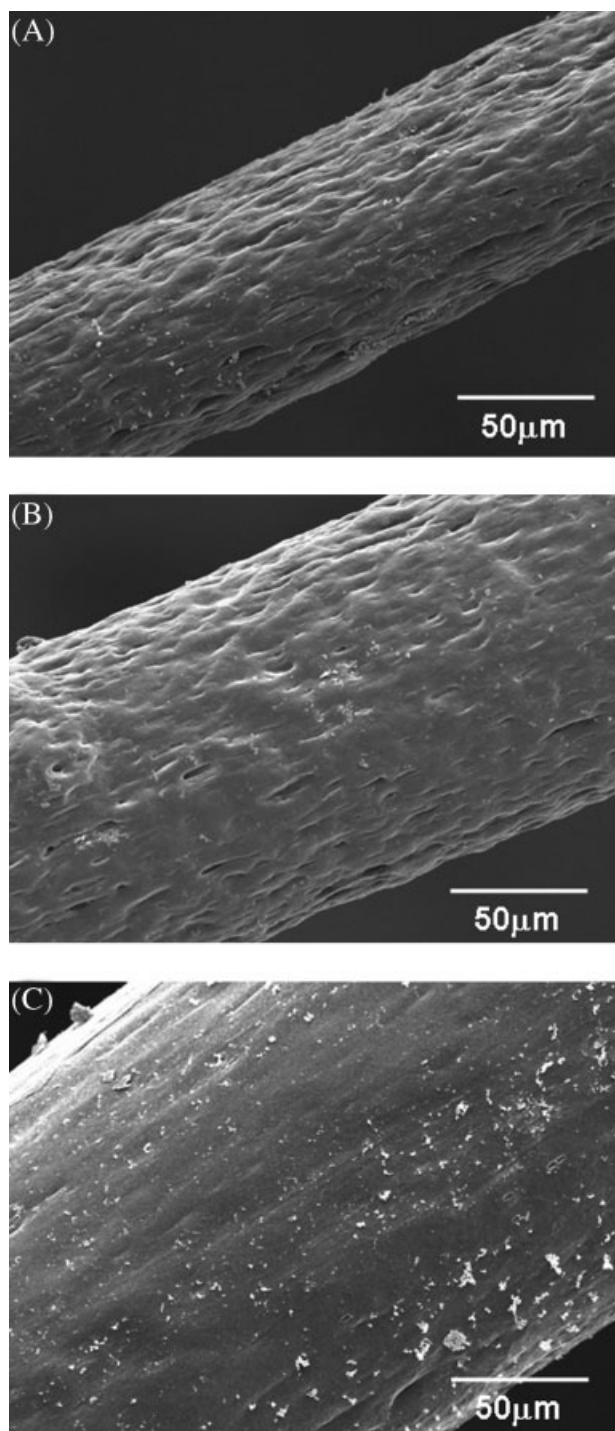


Figure 2 SEM images showing structures of H-PAN/SP hydrogel fibers in neutral solution, (A) $W_{\text{H-PAN}}, W_{\text{SP}} = 5, 5$; (B) $W_{\text{H-PAN}}, W_{\text{SP}} = 7, 3$; (C) $W_{\text{H-PAN}}, W_{\text{SP}} = 10, 0$. The size of the bar is $50 \mu\text{m}$.

kPa. The marked features observed are as follows: (i) The prepared H-PAN/SP hydrogel fibers demonstrated excellent reverse pH-sensitivity, i.e., swelling in an alkaline solution and shrinking in an acidic solution. (ii) The equilibrium swelling elongation degree ($\Delta L_{\infty}/L_0$) of H-PAN/SP hydrogel fibers was

between 30 and 50%, and the variations in the first few seconds of dynamic elongation and contraction took up about 60% of the equilibrium swelling elongation. (iii) The dynamic elongation/contraction behavior was repetitive. (iv) The H-PAN hydrogel fiber showed a slow response rate.

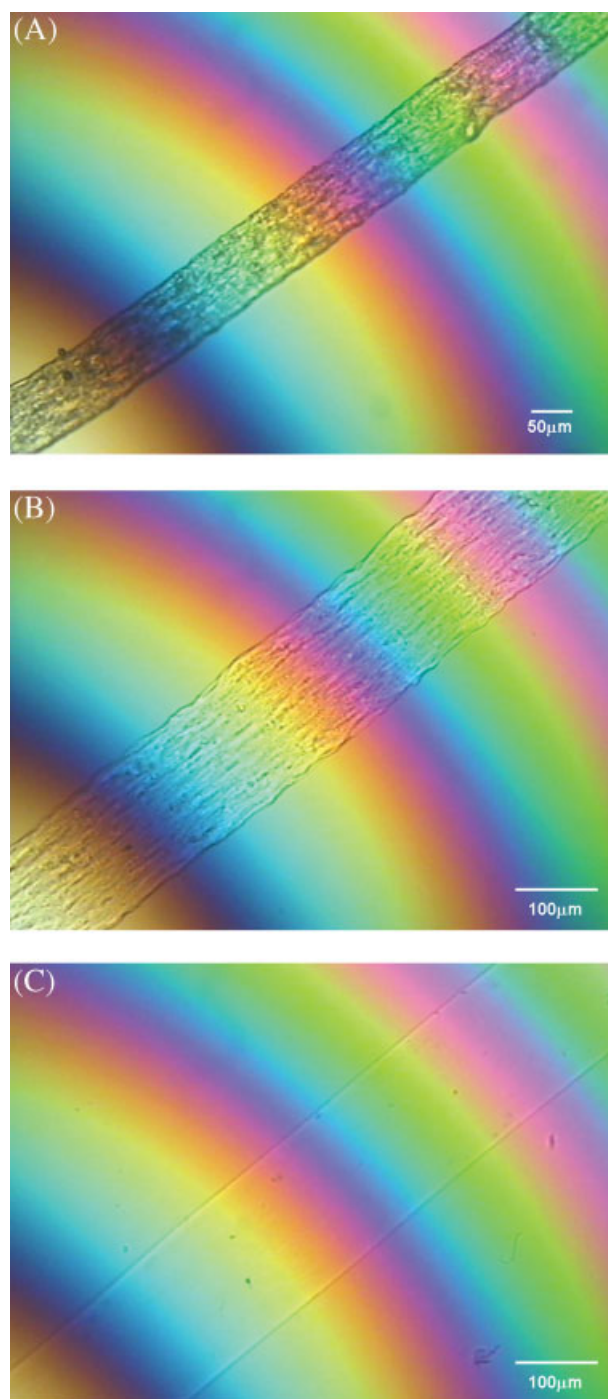


Figure 3 Polarizing optical micrographs of H-PAN/SP hydrogel fiber ($W_{\text{H-PAN}}, W_{\text{SP}} = 4, 6$) in swollen state (A) and shrunken state (B) and H-PAN hydrogel fiber in swollen state (C). The size of the bar in A is $50 \mu\text{m}$, and in B and C is $100 \mu\text{m}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

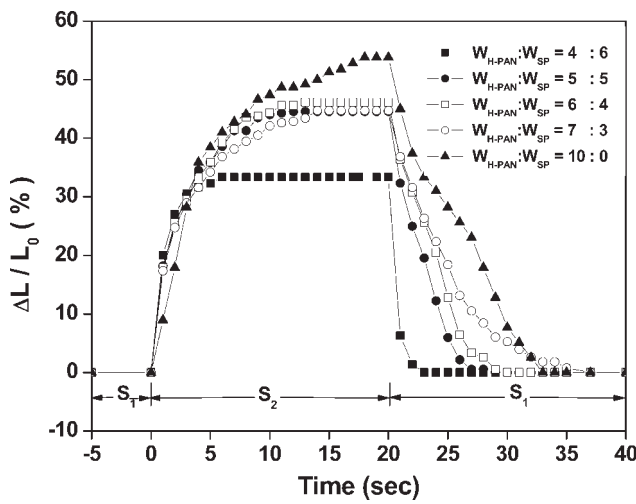


Figure 4 Dynamic changes in length of H-PAN/SP hydrogel fibers at 25°C. Solution S₁ was 0.1M HCl, and solution S₂ was 0.1M NaOH. Change from S₁ to S₂ was elongation and from S₂ to S₁ was contraction.

Elongation and contraction kinetics

The kinetic study of the swelling and shrinking in response to a sudden change of pH is very important in understanding the pH-sensitivity of a gel. With respect to the swelling–shrinking kinetics of gels, Tanaka et al.^{3,31} have shown that the response time (τ) taken for a gel to swell or shrink is given by

$$\tau = l^2/\pi^2 D \tag{4}$$

where l denotes the characteristic linear dimension of the gel and D is the collective diffusion coefficient of the networks. For a gel spherical in shape and when its volume change is small, τ is related to the swelling ratio (Q_t) and time (t) by

$$Q_t \sim \frac{6}{\pi^2} \exp\left(-\frac{t}{\tau}\right) \tag{5}$$

In our experiment, samples were hydrogel fibers so that equation 5 may not be directly applied to our data in the swelling and shrinking processes. As shown in Figure 5, the kinetic of the hydrogel fiber elongation and contraction was analyzed by fitting the length–time data to eq. (6) based on Voigt model.^{32–34}

$$\frac{L_\infty - L}{L_\infty - L_0} = \exp\left(-\frac{t}{\tau}\right) \tag{6}$$

where L_∞ is fiber length at equilibrium, L is fiber length at time t , L_0 is fiber length at the initial state (equilibrated in 0.1M HCl solution). And for convenience, we make that

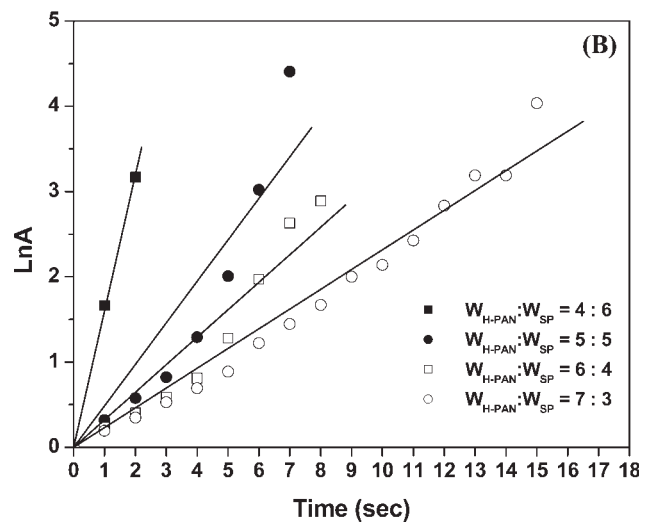
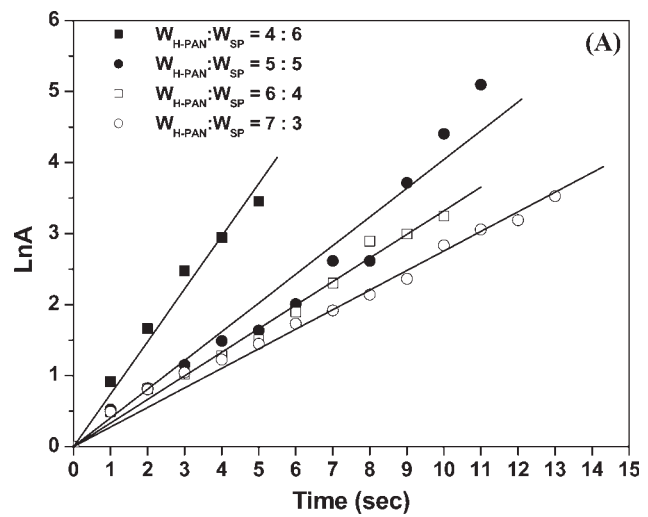


Figure 5 LnA of H-PAN/SP hydrogel fibers versus time at 25°C, (A) elongation process and (B) contraction process.

$$A = \frac{L_\infty - L_0}{L_\infty - L} \tag{7}$$

As a result, the elongation/contraction response times (τ_e , τ_c) were estimated from the slope of LnA versus t plots and are shown in Table II.

Effect of SP content on pH-sensitive behavior

Impacts of SP weight ratio on elongation and contraction times (τ_e , τ_c) are shown in Figure 6. With an

TABLE II
Elongation/Contraction Response Times (τ , s) of H-PAN/SP Hydrogel Fibers

Hydrogel fibers ($W_{H-PAN} : W_{SP}$)				
Process	4 : 6	5 : 5	6 : 4	7 : 3
Elongation	$\tau_e = 1.35$	$\tau_e = 2.47$	$\tau_e = 3.01$	$\tau_e = 3.63$
Contraction	$\tau_c = 0.63$	$\tau_c = 2.05$	$\tau_c = 3.10$	$\tau_c = 4.32$

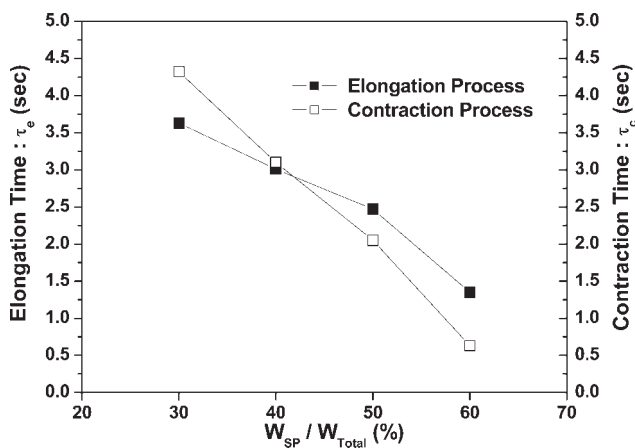


Figure 6 Impacts of SP weight ratio on elongation and contraction times (τ_e , τ_c).

increase in the content of SP, both response times were shortened. To explain this phenomenon, it would be required to learn the morphology of the H-PAN/SP hydrogel fibers. As hydrogel's swelling and shrinking kinetics are typically governed by diffusion-limited polymer network transport in solvent, then hydrogel size and the contact surface area of polymer and solvent become two important factors.³⁵ So when the diameters of hydrogel fibers were unified, the contact surface area of hydrogel fiber, which correlates with the multiporous structure of hydrogel, would exhibit the main effect on the response times. It is just that this kind of structure increases the surface area and allows the solvent to diffuse rapidly into the hydrogel fibers, resulting in fast length changes.

We also found that the contraction time was reduced more rapidly than the elongation time. At $W_{H-PAN} : W_{SP} = 7 : 3$, the contraction time ($\tau_c > 4$ s) was longer than the elongation time ($\tau_e = 3.63$ s), while at $W_{H-PAN} : W_{SP} = 4 : 6$, the response times of the contraction and the elongation (τ_c and τ_e) were about 0.63 and 1.35 s, respectively, which shows a dramatic change (great improvement in contrast with the PAN series hydrogel fiber, whose response times were about 2 and 4 s). The presence of SP, which is an amphoteric material containing both ionizable amino groups ($-NH_2$ groups) and carboxylic acid groups ($-COOH$ groups), contributed to the improvement. During the contraction process, the H^+ ions could quickly diffuse into the swollen multiporous hydrogel and the $-NH_2$ groups were protonated into ammonium cations ($-NH_3^+$ cations) in a short time. However, there were still some COO^- groups remaining in the hydrogel. The $NH_3^+COO^-$ attraction may lead to the improvement in the contraction time and this just explains why there was nearly 60% variation in length in the first few seconds. Overall, the addition of SP contributes to the reduced response times.

Effect of SP content on equilibrium swelling elongation

Equilibrium swelling elongation data obtained in 0.1M NaOH solution are shown in Figure 7. The result indicates that the equilibrium swelling elongation decreased with an increase in the content of SP. This can be explained by the osmotic pressure arising from the network-fixed negative groups (COO^-). It is known that the repulsion of the fixed charges will enhance the hydrogel expansion, while the charged groups are forced to remain in proximity by the chain constraints.³⁶ In the case of H-PAN/SP hydrogel fibers, with an increase in the content of SP, COO^- groups became less and less, and led to a weakening in electrostatic repulsion effect. Therefore, the equilibrium swelling elongation decreased with the addition of SP.

Static elongation/contraction behavior of H-PAN/SP hydrogel fibers under different pH

Figure 8 shows equilibrium swelling degrees of the H-PAN/SP hydrogel fibers made from various weight ratios of H-PAN and SP as a function of pH at a load of 60 kPa. With decrease of pH values in solution gradually from 14 to 0, all hydrogel fibers elongated slightly in the pH range of 14–0.5, and showed a constant length in the pH range of 10.5–3. At about pH 3, the elongated hydrogel fibers abruptly contract. However, in the pH range of 3–0, there was a slight elongation near pH 1, while there was no elongation in the H-PAN hydrogel fiber. On the other hand, when the pH was increased from 0 to 14, there was also a same elongation between pH 0 and 3 in the H-PAN/SP hydrogel fibers, while this phenomenon was not observed in the H-PAN hydrogel fiber. In the pH range from 3 to 10.5, all the

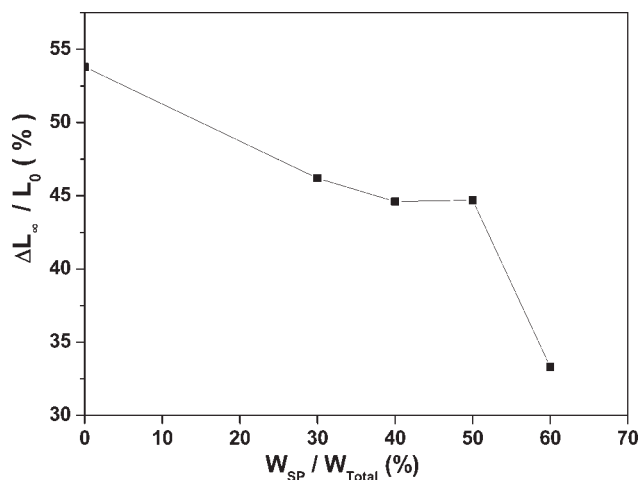


Figure 7 Impacts of SP weight ratio on equilibrium swelling elongation.

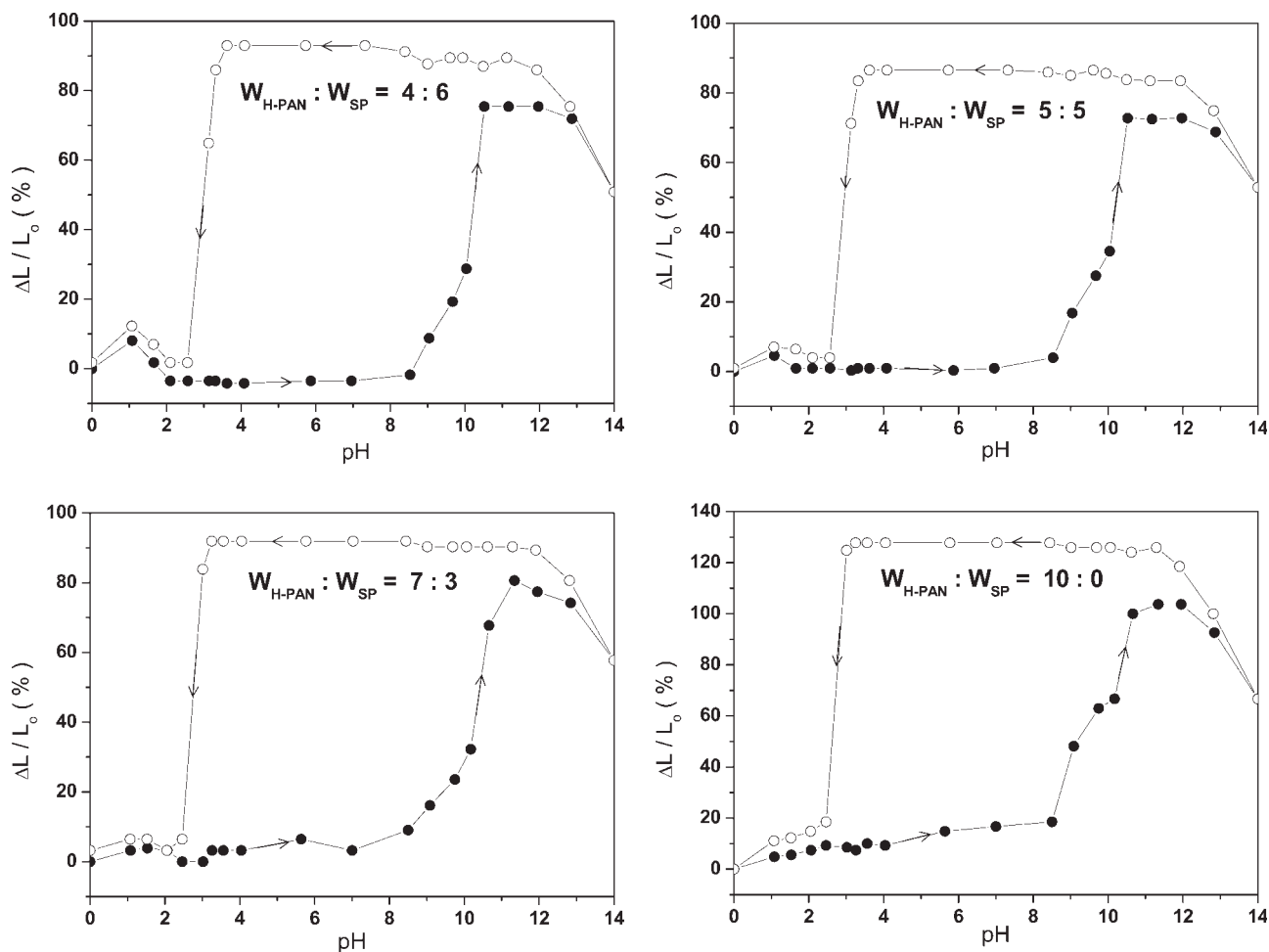


Figure 8 Equilibrium swelling elongation degree in length of H-PAN/SP hydrogel fibers as a function of pH at 25°C. The symbols indicate ●, pH increase; ○, pH decrease. The arrows indicate the direction of the changes.

fibers showed same behavior and abruptly elongated at about pH 10.5. When the pH value was greater than 10.5, the fibers contracted slightly again. Completing the above processes forms a hysteresis loop.

The swelling behaviors of the fibers at pH range from 3 to 0 are plotted in Figure 9, showing that the discontinuous change in swelling degree became obvious as the increase of SP content in this narrow pH range. H-PAN/SP hydrogel fibers is a complicated system, containing three main functional groups, i.e., $-\text{NH}_2$, $-\text{COOH}$ and acrylamide groups ($-\text{CONH}_2$ groups). In contrast to the latter, both $-\text{NH}_2$ and $-\text{COOH}$ groups can be ionized depending on pH conditions. The ionic groups play an important role in swelling variations. Either protonated $-\text{NH}_3^+$ or deprotonated $-\text{COO}^-$ groups can increase charge density on the polymer causing an enhancement of osmotic pressure inside the hydrogel due to the $\text{NH}_3^+-\text{NH}_3^+$ or $\text{COO}^--\text{COO}^-$ electrostatic repulsion. This osmotic pressure difference between the internal and external solution of the network is balanced by the swelling of the

hydrogel. According to Figure 9, the hydrogel fibers containing more SP showed much clearer discontinuous change in swelling. This is due to the $\text{NH}_3^+(\text{NH}_3^+$ electrostatic repulsion. At $\text{pH} < 1$, the screening effect of excess counter ions Cl^- might be involved, which causes a decreasing of swelling. At highly acidic conditions, Cl^- anions may shield the charge of the NH_3^+ cations and prevent an efficient repulsion, leading to decreased swelling.²⁸ Similarly, at $\text{pH} > 10.5$, the excess amount of counter ions Na^+ cations have screening effect on the $-\text{COO}^-$ groups, which leads to decreased swelling. Since the H-PAN/SP hydrogel fibers are comprised of both acidic and basic groups, they exhibit polyampholytic properties.

CONCLUSIONS

H-PAN/SP hydrogel fibers were prepared by using hydrolyzed polyacrylonitrile (H-PAN) and soy protein (SP) as the raw materials and a wet spinning method. The chemical structure of H-PAN, surface

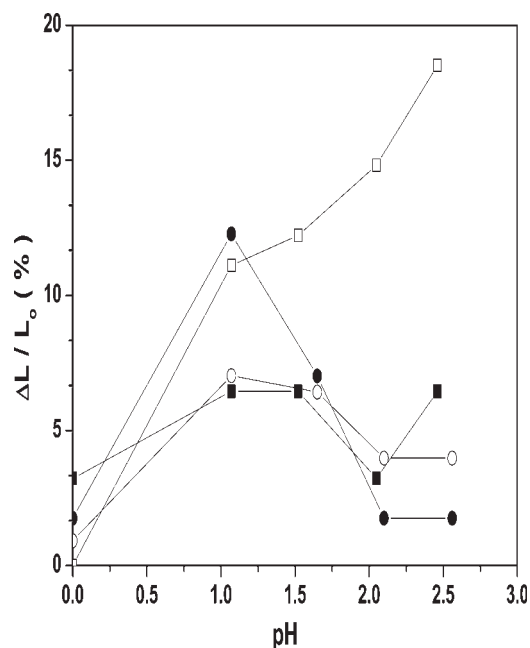


Figure 9 Equilibrium swelling elongation degree in length of H-PAN/SP hydrogel fibers in a pH range of 0–3. The symbols indicate the weight ratio of ●, $W_{\text{H-PAN}}, W_{\text{SP}} = 4, 6$; ○, $W_{\text{H-PAN}}, W_{\text{SP}} = 5, 5$; ■, $W_{\text{H-PAN}}, W_{\text{SP}} = 7, 3$; □, $W_{\text{H-PAN}}, W_{\text{SP}} = 10, 0$.

morphology, dynamic and static elongation/contraction behaviors as well as impacts of SP weight ratio on pH-sensitivity of the hydrogel fibers were studied in detail. The important results obtained are as follows: (i) the chemical structure of H-PAN/SP hydrogel was given, (ii) with the addition of SP, the H-PAN/SP hydrogel fibers showed inhomogeneous and multiporous structure, (iii) with an increase in the content of SP, pores in the hydrogel fibers became more and more, (iv) the hydrogel fibers demonstrated excellent reverse pH-sensitivity, i.e., swelling in an alkaline solution and collapsing in an acidic solution and this behavior was repetitive, (v) the equilibrium swelling elongation, which decreased gradually with the content of SP increasing, was between 30 and 50%, and the variations in the first few seconds of dynamic elongation/contraction accounted for about 60% of the equilibrium swelling elongation, (vi) an increase in the content of SP led to diminishing of elongation/contraction response times, (vii) when $W_{\text{H-PAN}} : W_{\text{SP}} = 4 : 6$, the best elongation/contraction response times were obtained at 0.63 s/1.35 s, respectively, (viii) three pH response regions and hysteresis loops of the H-PAN/SP hydrogel fibers were found.

The hydrogel system reported here is very simple in preparation, but quite complex in the chemical composition. However, the technological application of the present results seems to be of importance,

which would provide some idea about the development of new pH-sensitive hydrogel systems.

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