

A Study on Mechano-Electro-Chemical Behavior of Chitosan/Poly(propylene glycol) Composite Fibers

SHAN SUN,¹ Y. W. WONG,² KANGDE YAO,³ ARTHUR F. T. MAK¹

¹ Jockey Club Rehabilitation Engineering Center, The Hong Kong Polytechnic University, Hong Kong, China

² Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, China

³ Research Institute of Polymeric Materials, Tianjin University, Tianjin 300072, China

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ABSTRACT: Chitosan (CS) and poly(ethylene glycol) (PEG) composite fibers were prepared via solution spinning. The fibers were then crosslinked with epichlorohydrin (ECH) and glutaraldehyde (GA). Data indicated that the swelling behavior of CS-PEG fibers exhibited pH sensitivity, and crosslinking could change the mechanical properties of fibers. Moreover, the mechano-electro-chemical (MEC) performance showed that the bending direction of fiber specimen would invert at a critical concentration of both of the crosslinking agents. i.e., in a 0.1% HCl aqueous solution under a dc electric field, as the ECH concentration was more than $9.0 \times 10^{-3} M$ or GA concentration was more than $5.64 \times 10^{-4} M$, the CS-PEG fibers bent to the cathode, while they bent to the anode if ECH or GA concentration was less than the above values respectively. The mechanisms involve variation in the fixed charge density on the macromolecular network as well as difference in the mechanical properties of the fibers. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 542–551, 2000

Key words: chitosan/poly(ethylene glycol) composite fibers; epichlorohydrin; glutaraldehyde; mechano-electro-chemical behavior; XPS

INTRODUCTION

Chitosan (CS) is a deacetylated derivative of chitin that is poly((1,4)-2-acetamido-2-deoxy- β -D-glucose). It has been widely studied and applied in the biomedical field because of its good biocompatibility, biodegradability, nontoxicity, and easy availability. As a cationic flexible polyelectrolyte, water-swollen chitosan is tough elastic material,¹ but its mechano-electro-chemical (MEC) behaviors have not yet been reported.

Many biomaterials, especially smart hydrogels display the MEC behaviors.^{2–4} They can respond to an electrical pulse, which triggers chemical reaction in the hydrogels, promoting a change of volume or shape and producing concomitant force or motion. Bending in the electric field is one performance of the MEC behaviors. In the past, fixed charged groups on the macromolecular chain and mobile ions inside and outside the network were thought to be the main elements to influence bending direction. Seldom did the researchers consider that the crosslinking and related mechanical properties of the materials could also play key roles in the MEC process.

In this paper, we focused on the influence of crosslinking reagents on the mechanical properties and MEC behaviors of CS/PEG fibers. Chi-

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tosan (CS) was blended with poly(ethylene glycol) (PEG). The composite obtained was spun into fibers and then crosslinked with epichlorohydrin (ECH) and with glutaraldehyde (GA). The mechano-electrochemical (MEC) phenomenon and related performance of the CS/PEG fibers were examined in this paper.

EXPERIMENTAL

Materials

Chitosan ($\bar{M}_n = 9.13 \times 10^5$, degree of N-deacetylation = 76.8%) and poly(ethylene glycol) ($\bar{M}_n = 2500$) were obtained from Acros Organic (Belgium) and Aldrich Company (England), respectively. Epichlorohydrin, glutaraldehyde, and other reagents were chemical grade.

CS-PEG Wet-Spinning Procedure

A spinning bath was prepared by dissolving 5 g chitosan and 2.5 g PEG in 50 mL 2% (v/v) aqueous acetic acid solution. The solution was then poured into a syringe, which was allowed to stand stationary over night to eliminate air bubbles. The degassed solution within the syringe was extruded into a 2% NaOH bath under a suitable nitrogen pressure. The diameter of the needle hole was 1.0 mm, and the filament immersion length was approximate 12 cm. The distance between the end of needle and the surface of the coagulation bath was 15 cm. Drawing was carried out in room temperature, which was 20°C. After being immersed in 2% NaOH for 4 h, the filaments were washed repeatedly by distilled water and then were kept in water, pH 7, for the following tests.

Crosslinked Fibers

According to Y. C. Weis's report,⁵ the fibers were crosslinked in a wet state. A fiber of 15 cm in length and 0.3 g in weight was placed into a vessel containing ECH with different concentrations ranging from 0 to 0.02 M in 0.067 M NaOH (pH 12) aqueous solution. The mixture was allowed to react at 40°C for 4 h. The crosslinking process with GA was similar to that of ECH. The applied concentrations of GA were varied from 0 to 0.0014 M. Crosslinked fibers were then washed with distilled water.

Characterization

Each specimen was thoroughly washed with distilled water and then dried in a vacuum oven at 20°C overnight. The X-ray photoelectron spectroscopy (XPS) spectra were recorded with a Model PHI 5600 spectrometer. The residual gas pressure was 5.0×10^{-8} Torr. An Mg anode, with a standard power of 350.0 W, was used as the X-ray source. Each XPS spectrum was calibrated by C1s binding energy, with peak set at 285.0 eV. The atomic concentrations of C, N, and O in each sample were obtained through peak area measurement.

Three specimen of chitosan/PEG compounds were tested after different treatments. The group with no crosslinking agent was used as the control. The other two samples were crosslinked by 0.01 M ECH and by 0.001 M GA.

Swelling Behavior

The swelling degree of fiber specimen S_v was evaluated from the expression:

$$S_v = \frac{V_t - V_0}{V_0}$$

where V_0 is the average volume of three samples in the beginning of swelling, and V_t is the average value when the specimen reach an equilibrium swelling state in the desired pH solution. The volume was calculated by measuring the length and radius of each fibrous specimen at various times.

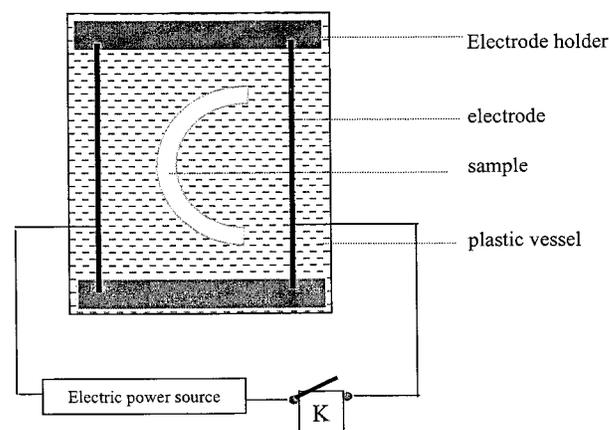


Figure 1 Schematic drawing of specimen deformation under an applied electric field.

Tensile Testing

For the mechanical properties, a 4-cm-long specimen of the CS/PEG fibers was subjected to a tensile test using the Hounsfield Test Equipment H10KM with a 100 N load cell. The measurements proceeded at ambient temperature, with a tensile speed of 10 mm/min, and values of Young's modulus, tensile strength, and elongation at break were calculated.

MEC Behavior

A 0.1% HCl aqueous solution was poured into a plastic case equipped with two parallel platinum electrodes (cf. Fig. 1). The separation between them was 2.5 cm. A fibrous specimen 2.5 cm in length was placed in the center of the case, and voltage up to 25 V dc was applied across the solution between the electrodes. The deformation was recorded and measured by a Video Dimension Analyzer (Model 303). The de-

flection was expressed in terms of the distance between the ends of a gel fiber at various times. The degree of deformation was estimated as follows:

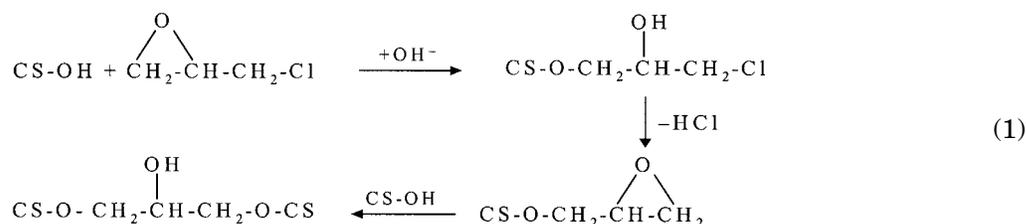
$$\text{Degree of deformation} = \frac{L_t - L_0}{L_0}$$

where L_0 is the specimen's length before applying the electric field, and L_t is the straight-line distance between the ends of a curved gel fiber at various times after applying voltage.

RESULTS AND DISCUSSION

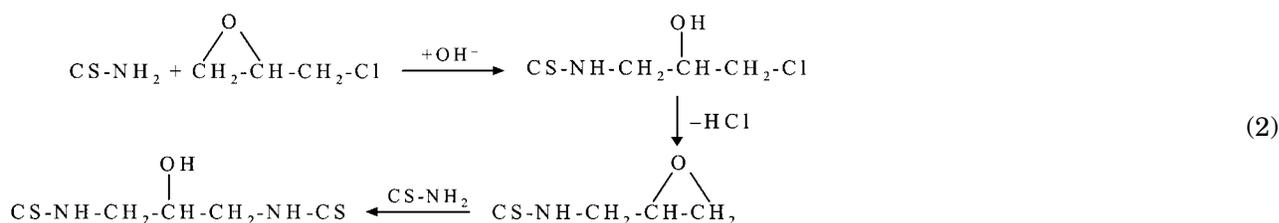
Crosslinking Reaction

The chemical process underlying the crosslinking of CS/PEG composite by epichlorohydrin is as follows:^{6,7}

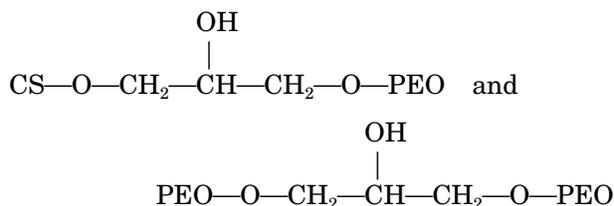


Since there are $-\text{NH}_2$ groups on the chains of chitosan, $-\text{NH}_2$ can also react with ECH in the

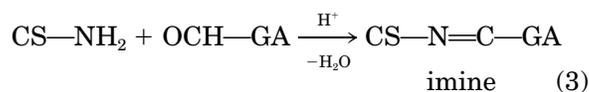
following ways:



Additionally, PEG has a terminate group $-\text{OH}$, which can also be crosslinked by ECH, yielding possibly the following secondary products:



With regard to GA, the mechanism of this crosslinking reaction is not clear. According to a widely held view,⁸ the crosslinking process may be described as below, which has yet to be proven:



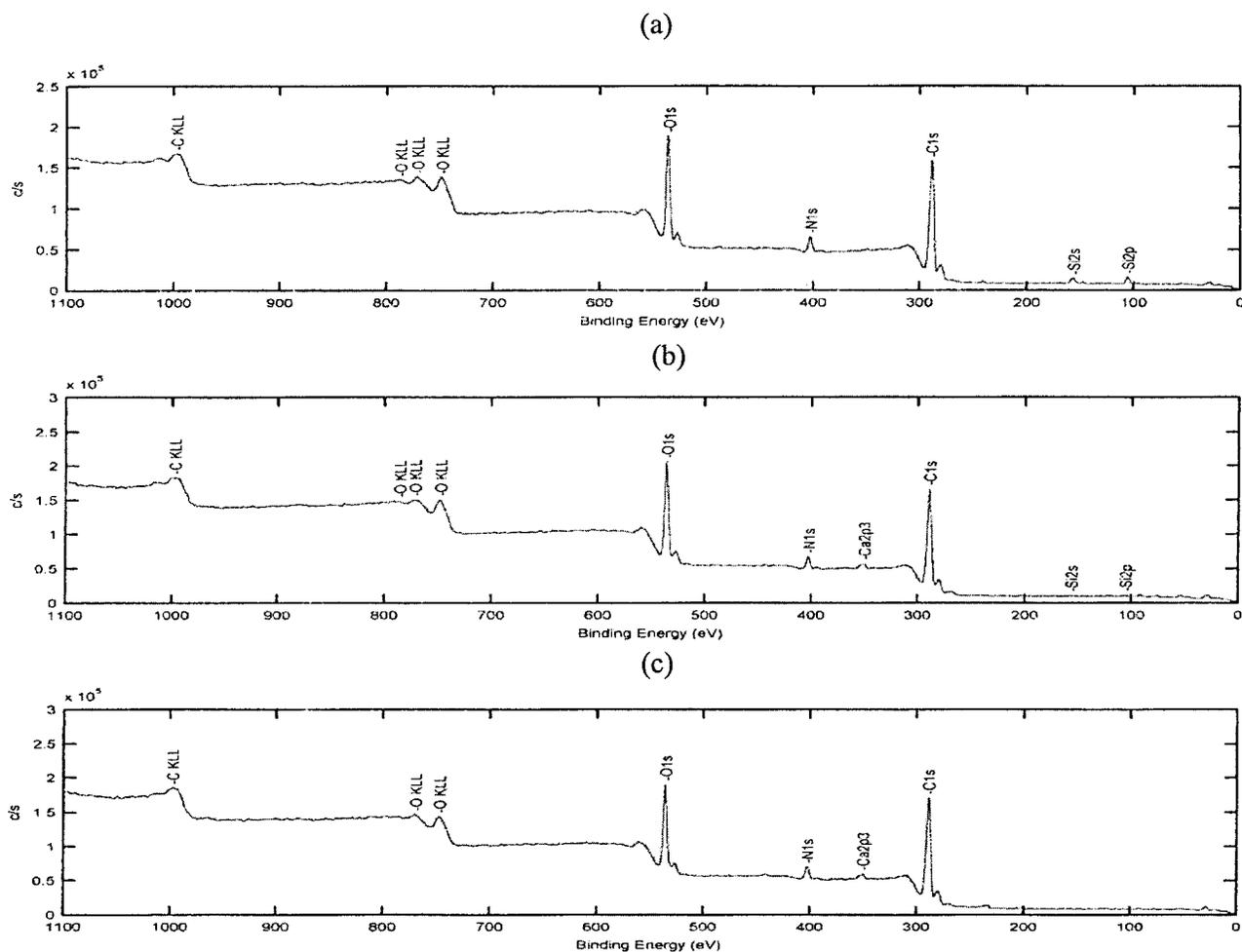
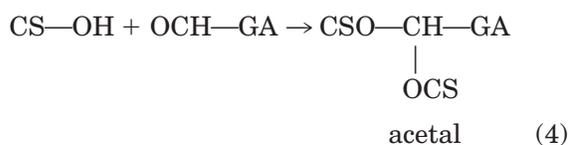


Figure 2 General survey of XPS of the samples crosslinked (a) by none (b) by ECH (c) by GA.



A convenient indication of crosslinking is the swelling behavior of the crosslinked fiber in pH 2 HCl solution. Simple swelling measurements were used to prove the existence of crosslinkage. The obvious decrease in degree of swelling after ECH or GA treatment may be attributed to the crosslinkage among the CS and PEG chains. When CS/PEG fibers were immersed in pH 2 HCl aqueous solution without any crosslinking reagents, they would dissolve into the acidic solution a few hours later, whereas after crosslinked by ECH or GA, they could keep their shapes in the same medium. This is a clear indication of partial crosslinking in the polymeric network. The fol-

lowing experimental results of XPS provides some proof of the above reactions.

XPS Analysis

The general survey of the three specimens after different treatments are shown in Figure 2. As the peaks of O1s, N1s, and C1s could be easily found. The concentrations of various crosslinking reagents were very low, the peak shifts were not expected to be large as shown in this figure. However, the subtle differences among the spectra could be seen in the following spectra of single element. There were two possible reasons that there was no C1 peak in Figure 2(b): one was that the ECH concentration was very low, and most small molecular HCl could be removed in the process of vacuum. The other reason was probably because the crosslinking reaction was per-

Table I Atomic Concentration Table

	Atom Concentration (%)		
	C1s	N1s	O1s
Sample 1 (none crosslink)	70.19	4.87	24.93
Sample 2 (ECH treatment)	67.67	4.75	27.58
Sample 3 (GA treatment)	70.78	4.91	24.31

formed so thoroughly that almost no intermediate product was left in the specimen.

The atomic concentrations are listed in Table I. After the treatment of ECH, the slight increase in the O concentration suggested that both reactions (1) and (2) might happen, resulting in the concentration of O being slightly increased by the adding of O in ECH.

C1s

Comparing the C1s XPS of the sample with no crosslinking treatment with those treated with ECH and with GA (cf. Fig. 3), we could observe that the peak at 286.6 eV before crosslinking became somewhat smooth after treatment with ECH and GA. This might be attributed to (C*—OH) in chitosan being changed to (C*—O—C), with a mean binding energy⁹ of 286.45 eV, as indicated in the reactions shown in eqs. (1) and (4). Additionally, the C in the unsaturated production (C*—N), as shown in eq. (3) might also contribute to this small shift, but there were no standard spectra to prove it.

N1s

The N1s spectra are shown in Figure 4. It would be easy to see that both N1s spectra shifted obviously to a lower binding energy after crosslinking treatment. Though very small, the shift at least showed that groups —NH₂ were changed after crosslinking reactions. The N1s core-level spectrum of chitosan gave the peak of component (CS—N*H₂) with binding energy⁹ at 399.4 eV [cf. Fig. 4(a)]. The peak at 399.2 eV in the Figure 4(b) could be attributed to the nitrogen in the group⁹ (C—N*H—C), which was the product of reaction (2). The variation shown in Figure 4(c) might attribute to the reaction shown in eq. (3); since the standard N1s spectra are somewhat limited, this needs to be proven by the further analyses in the future.

O1s

The O1s XPS spectra were shown in Figure 5. The spectra of the three samples were obviously different from each other. In the case of ECH treatment, O1s shifted more than those of the GA treatment, say from (C—O*H) 532.6 eV to (C—O*—C) 532.3 eV⁹, which result from reaction (1).

A similar reaction could happen in the course of treatment with GA, as shown in eq. (4). In this case, (C—O*H) 532.6 eV in chitosan became (C—O*—C) in the acetal production. However, this reaction might not be prominent, because the samples were almost same as those before treatment. The shift for the sample crosslinked by GA was not as great as that of the ECH-treated sample.

Experimental results showed that XPS was an effective technique in detecting the subtle varia-

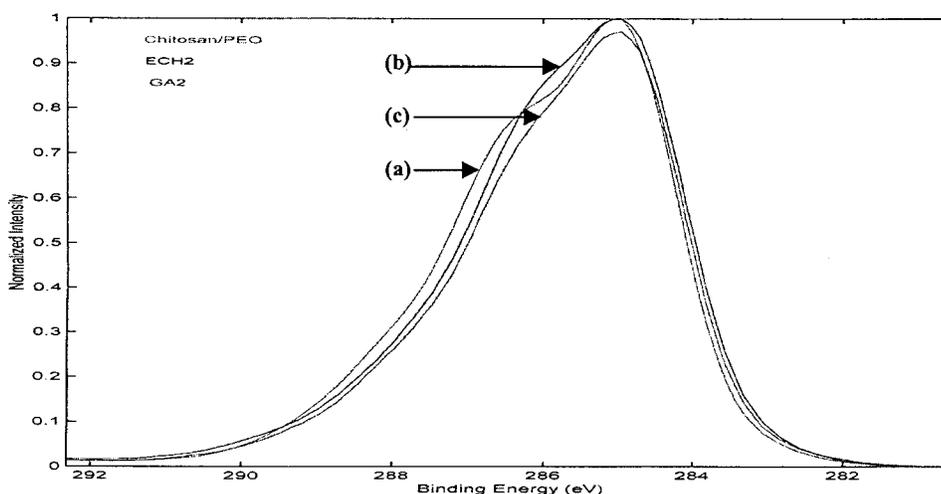


Figure 3 C1s XPS spectra of the samples crosslinked (a) by none (b) by ECH (c) by GA.

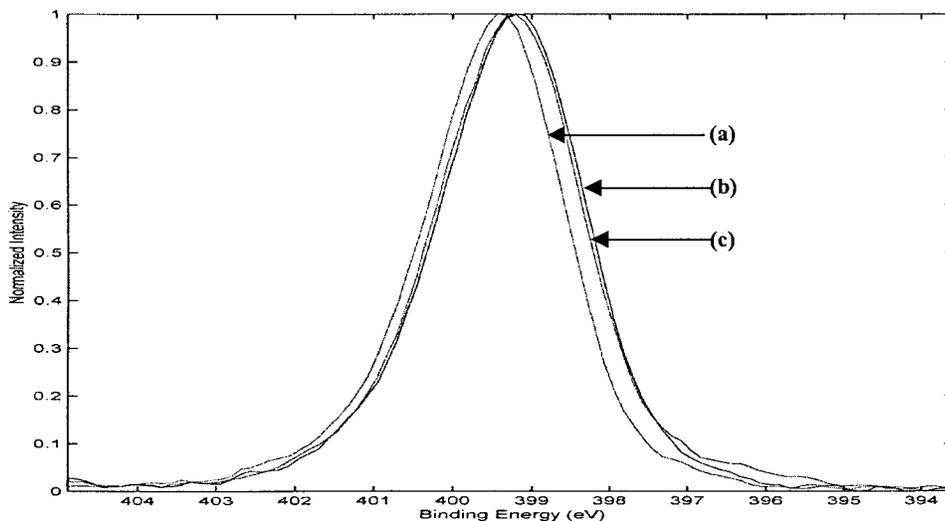


Figure 4 N1s XPS spectra of the samples crosslinked (a) by none (b) by ECH (c) by GA.

tion in atomic binding energy before and after crosslinking. In Figures 2 through 5, we observe that some —NH_2 groups changed after crosslinking by ECH or GA, which means that the fixed charge density might be reduced because of the

crosslinking reaction. Additionally, according to the C1s and O1s XPS spectra, all the reactions shown in eqs. (1) through (4) could probably happen. Hence, CS-PEG could indeed be crosslinked either by ECH or by GA.

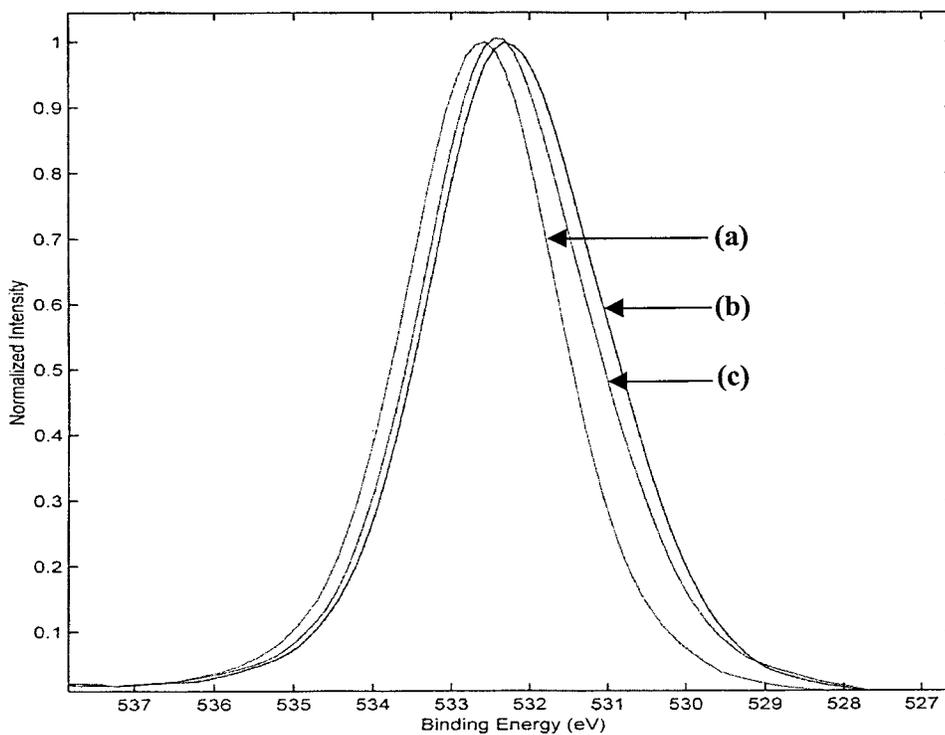


Figure 5 O1s XPS spectra of the samples crosslinked (a) by none (b) by ECH (c) by GA.

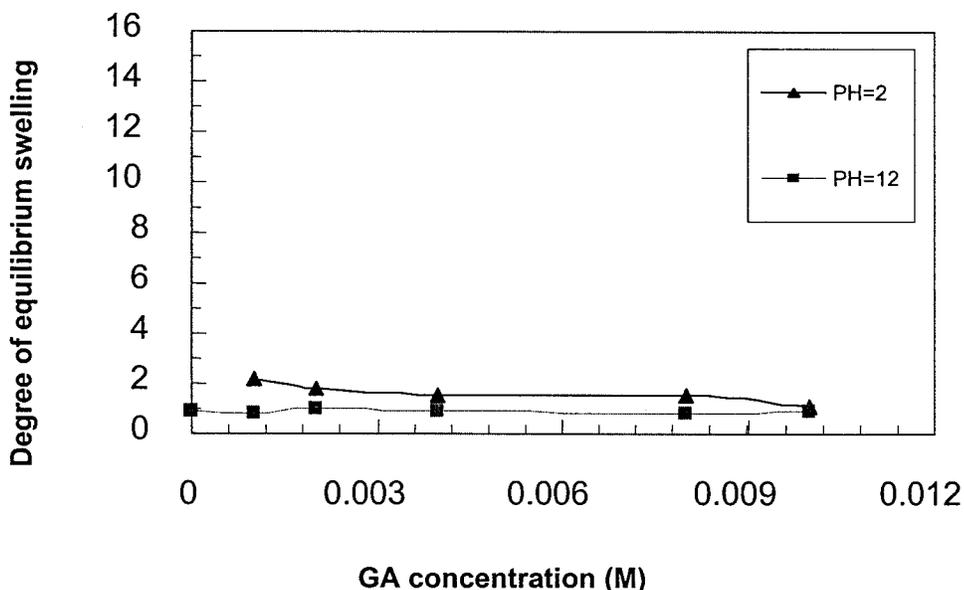
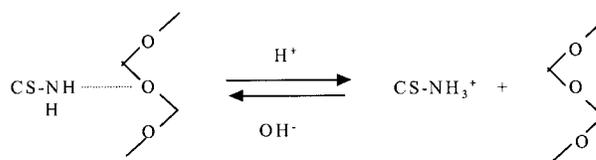


Figure 6 Equilibrium swelling of CS/PEG crosslinked by GA, pH 2 and pH 12.

Swelling Behavior

The equilibrium degrees of swelling at pH 2 and pH 12 for different concentrations of ECH and GA are shown in Figure 6 and Figure 7, respectively.

The CS/PEG hydrogel fibers swelled significantly in a pH 2 solution but swelled only slightly in pH 12 environment. Because there is hydrogen bonding between amino hydrogen of CS and oxygen from PEO, the hydrogen bonds would change as follows¹⁰:



In the acidic medium hydrogen bonds tend to dissociate, which results in a decrease of interaction among chains and an increase in equilibrium

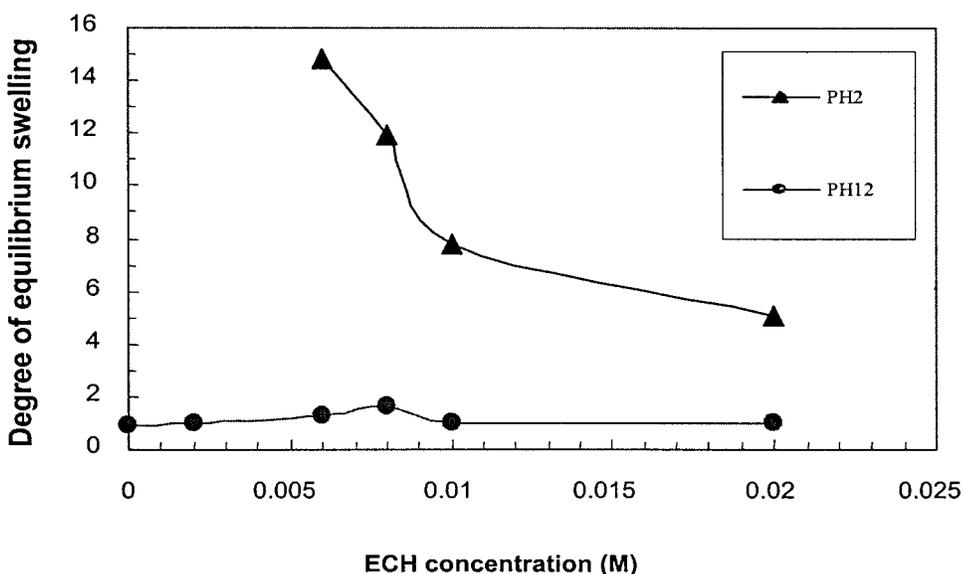


Figure 7 Equilibrium swelling of CS/PEG crosslinked by ECH in pH 2 and pH 12.

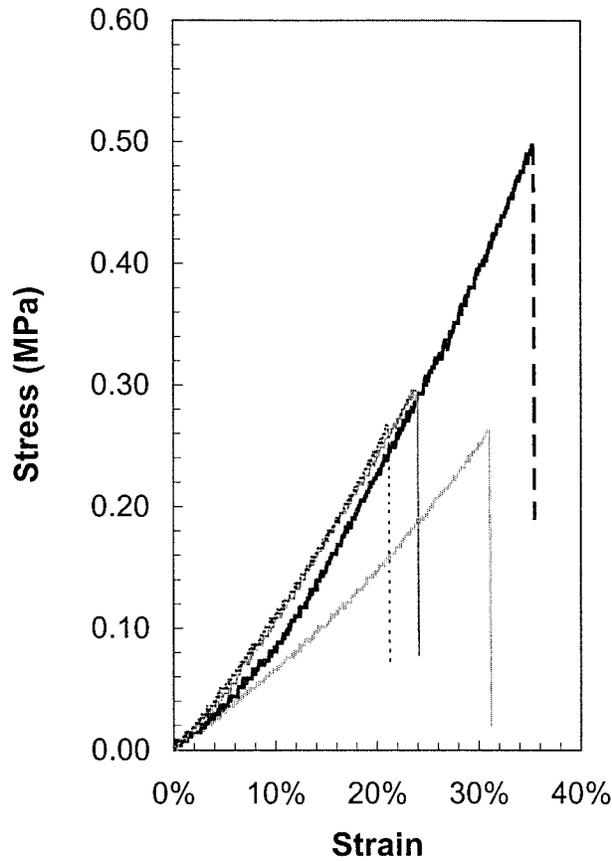


Figure 8 The effect of ECH at different concentrations on the mechanical properties of CS/PEG fibers. (stippled line), ECH = 0; (dashed line), ECH = 0.04; (black line), ECH = 0.08; (dotted line), ECH = 0.02.

volume. On the other hand, in the alkaline medium, the hydrogen bonds limit network swelling no matter how the ECH or GA concentrations change.

By comparing Figure 6 with Figure 7, it can be seen that the difference between swelling in the two mediums for CS/PEG fibers with ECH crosslinking is more significant than that with GA crosslinking. This result indicates that in response to pH stimulation, CS/PEG crosslinked by ECH is more sensitive than that by GA. The significant difference of CS-PEG swelling behaviors between acidic and alkaline environments made this composite hydrogel fiber an interesting candidate for artificial muscles.

Mechanical Properties

The tensile properties of the wet, crosslinked fiber at the ECH and GA concentration are shown in Figure 8 and Figure 9, respectively, and ultimate

tensile strength, elongation, and Young's modulus are listed in Table II. The Young's modulus was calculated from the ratio of tensile stress and strain. Because in the case in which concentration of GA was equal to $5.64 \times 10^{-4} M$, the ultimate elongation was too small to be observed, the relationship of stress against strain was not given in Figure 9. The corresponding Young's modulus of the specimen was calculated, based on the experimental data.

It is known that the mechanical properties of polymers result from the chain structure of the materials.¹¹ Experimental results here showed that the Young's modulus of the fibers was improved by increasing the concentrations of either ECH or GA, meaning that stiffness of the fibers was enhanced by the additional crosslinking bonds. Meanwhile, the ultimate elongation of the samples decreased, except for the case in which ECH concentration was $0.004 M$, which also could

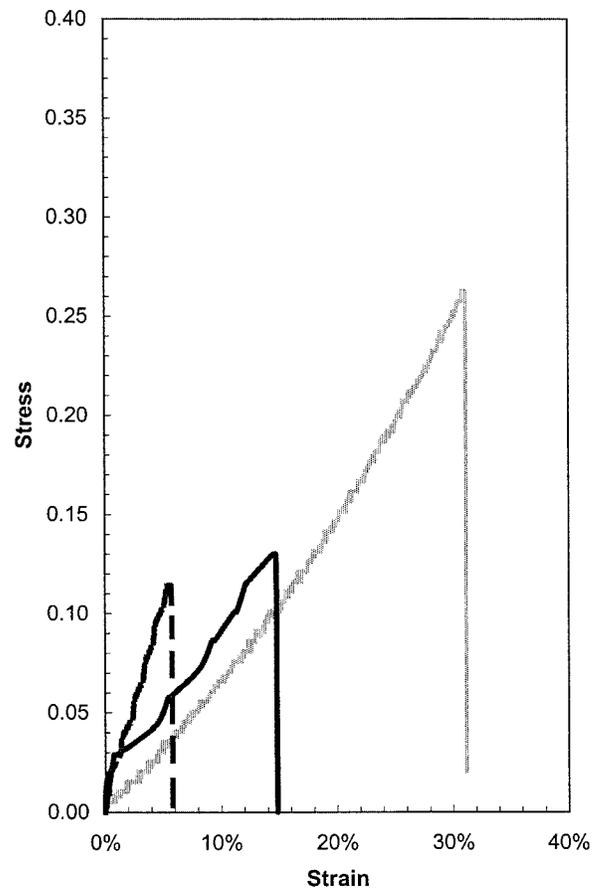


Figure 9 The effect of GA at different concentrations on the mechanical properties of CS/PEG fibers. (stippled line), C = 0; (black line), C = 0.00014; (dashed line), C = 0.00028.

Table II Effects of Crosslinking Agents on the Mechanical Properties of CS/PEG Fibers

Crosslinking Agent	Concentration (M)	Ultimate Tensile Strength (MPa)	Ultimate Elongation (%)	Young's Modulus (MPa)
Control	0	0.282	31.0	0.661
	0.004	0.523	35.4	0.781
ECH	0.008	0.327	24.0	1.063
	0.020	0.295	21.2	1.394
	1.396×10^{-4}	0.130	14.7	0.722
GA	2.792×10^{-4}	0.114	5.70	4.915
	5.584×10^{-4}	0.044	0.43	6.264

be attributed to the crosslinking function of limiting the relative motion among the polymer chains. A reduction of ultimate tensile strength also was noted due to crosslinking.

At the ECH concentration of 0.004 M, all the mechanical factors listed in Table I were higher than those of the control group without the crosslinking agent. A similar phenomenon was not observed for the specimens crosslinked by GA, although their crosslinking concentration was much less than that of ECH. It may be because the crosslinking bonds of ECH were mainly ether bonds, whereas those of GA were imine bonds and additional hydrogen bonds, which could hold the chains more tightly than the more flexible ether bonds. This result showed that light crosslinking with ECH could improve the tenacity properties of CS/PEG hydrogel fibers.

Bending in the Electric Field

A CS/PEG gel specimen immersed in 0.1% HCl aqueous solution was bent into a circular arc un-

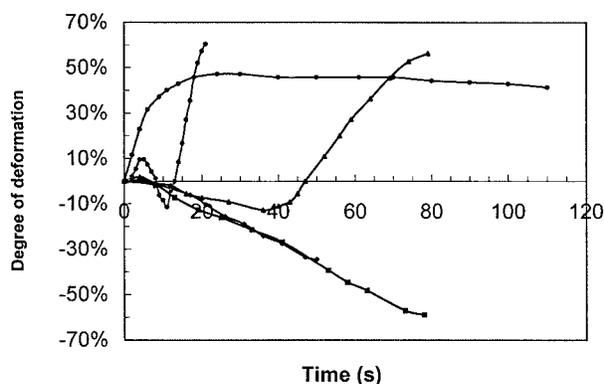


Figure 10 MEC behavior of CS/PEG crosslinked with different concentrations of ECH. (○), C = 0; (●), C = 0.001; (▲), C = 0.006; (■), C = 0.009; (◆), C = 0.01.

der a dc electric field. Figure 10 and Figure 11 showed the time dependent deformation of the samples in different concentrations of ECH or GA, respectively. For low crosslinkage, both ends of the gel fibers moved toward the anode. The higher the crosslinking reagent concentration, the slower the specimen bent, and when the ECH concentration was more than 0.009 M or the GA concentration was more than 0.00056 M, both ends of the gel fiber moved toward the cathode.

According to De Rossi and Tanaka,^{12,13} the effects of an electric field on the polyelectrolyte hydrogels were related to the dissociation of the acidic or basic moiety, motion, and the redistribution of mobile charged species. Shahinpoor¹⁴ thought that there were generally three competing forces acting on the ionic gel polymer network: the rubber elasticity, the polymer-polymer affinity, and the ion pressure. Most previous work emphasized the latter two effects on the bending direction^{15,16} and proposed that the elastic prop-

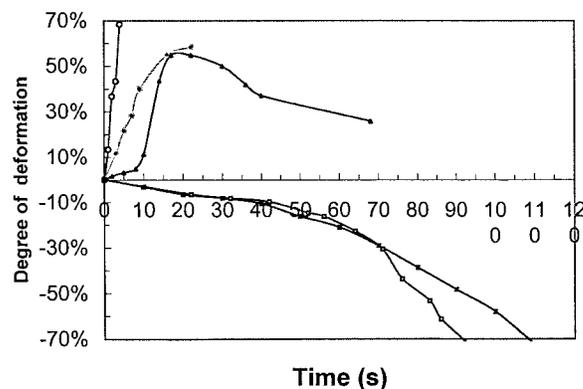


Figure 11 MEC behavior of CS/PEG crosslinked with different concentrations of GA. (●), C = 0; (○) C = 0.00140; (▲), C = 0.00028; (□), C = 0.00056; (×), C = 0.0011.

erties of the polymeric network was a kind of passive function. According to this view, the last two types of force, say the charged groups on the network and the mobile ions both inside and outside the gel fiber, may be the main contributors to the change in the bending direction.

According to the XPS analyses, N1s XPS spectra shifted toward the direction of lower binding energy after crosslinking either by ECH or GA. This showed that some charged groups $-\text{NH}_2$, which were the prominent contributors in hydrogel fibers, could be changed after crosslinking treatments, resulting in the decreasing of the fixed charge density on the polymeric chains. The variation in the fixed charge density would then change the difference of ionic concentrations inside and outside the hydrogel network. This difference might be the main promoting force of the motion of water and ions. At a lower crosslinkage, the fixed charge density would be much higher than the ionic concentration in the extra solution. With a greater increase of crosslinking concentration, more fixed charges on the polymer chains would be lost, under certain condition, the ionic lever might be reversed, so the MEC behavior, such as bending in the electric field, would be changed completely.

As ECH concentration became higher than 0.009 *M* (Fig. 10) or GA concentration higher than 0.00056 *M* (Fig. 11), the fiber began to bend toward the opposite direction. This difference in the concentration of crosslinking agents might reflect that some reactions might become prominent when there was more than one reaction mechanism in the system. From the analyses of the XPS spectra of C1s and O1s, the first reaction might be prominent in the ECH treatment, whereas the third reaction might mainly happen in the GA treatment.

However, it seems that the elastic force might be an important factor in determining the bending direction. With the other two factors, this may determine the conditions for the change in the bending direction. Further experiments need to be performed to confirm the above speculations.

CONCLUSIONS

Both GA and ECH are effective crosslinking reagents for the CS-PEG fiber, as reflected in the

XPS spectra, the swelling behavior, the mechanical strength, and the bending behavior under a noncontacting electric field. ECH of a low concentration can improve the mechanical properties of the fibers for biomedical applications. The direction and the speed of bending can be modulated via pH, ionic strength, the applied electric field, as well as ECH and GA concentration. From our point of view, the fixed charge density on the chitosan chains may play an active role in the MEC process. In addition, the mechanical properties such as the network elasticity may provide some contribution to the reversal of the bending direction.

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