

# Bending Behavior of Gelatin/Poly(hydroxyethyl methacrylate) IPN Hydrogel under Electric Stimulus

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## SYNOPSIS

This article deals with an interpenetrating polymer network composed of crosslinked gelatin (Gel) with glutaraldehyde (GA) and poly(hydroxyethyl methacrylate) (PHEMA) crosslinked with *N,N'*-methylene bisacrylamide (BisAm). The hydrogel network is able to bend under an electric field stimulus. The composition of the interpenetrating polymer network (PN), pH, ionic strength, and voltage can influence the degree of bending. The mechanism of the electromechanochemical (EMC) effect is discussed as well. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

"Smart" materials have recently attracted more and more attention. Polyelectrolyte hydrogels have been claimed to be smart materials because they can respond to changes in their environment, such as pH, ionic strength, and electric field,<sup>1-3</sup> by changing their shape. Literature on research activities in this area focuses on synthetic hydrogels. Considering that the synthetic and natural macromolecules complement each other in most of their properties, an interpenetrating hydrogel network, based on gelatin (Gel) crosslinked with glutaraldehyde (GA) and (PHEMA) crosslinked with *N,N'*-methylene bisacrylamide (BisAm), was prepared, while bending behavior of the hydrogel network, Gel/PHEMA, was studied. The effects of composition on the network, pH, ionic strength, and voltage are discussed in this article.

## EXPERIMENTAL

### Materials

Gelatin (biologic reagent),  $[\eta] = 49.3$  mL/g in 1.0M NaCl at 40°C, glutaraldehyde (chemical grade 50%), and hydroxyethyl methacrylate (HEMA), *N,N'*-

methylene bisacrylamide, potassium persulfate, sodium sulfate, sodium chloride (all analytic grade) were used without further purification.

### Synthesis of Gelatin/Poly(hydroxyethyl methacrylate) Interpenetrating Hydrogel Network

Gelatin was dissolved in distilled water and then calculated amounts of HEMA, BisAm, and potassium persulfate were added to the gelatin solution under agitation. After dissolving completely, a 1% GA solution was incorporated, and then the mixture was poured into a mold of poly(methyl methacrylate) for hydrogel formation. The composition of the mixture used for synthesizing the interpenetrating polymer network (IPN) is listed in Table I.

### IR Spectra

The ATR-IR spectra of gelatin and its IPN with PHEMA were obtained with a Nicolet 170SX FTIR spectrometer.

### Bending Behavior

A rectangular sample ( $13 \times 10 \times 1$  mm) of the Gel/PHEMA IPN hydrogel was placed between two non-contact titanium electrodes, and one end of the specimen was fixed. All were in a  $\text{Na}_2\text{SO}_4$  solution contained in a glass vessel (cf. Fig. 1). A direct current (dc) potential was applied across the flat elec-

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**Table I** Details of Synthesis of Gelatin PHEMA IPN

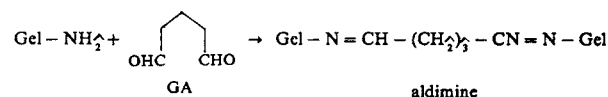
Specimen	Concentration by wt %				Gelatin/PHEMA by Weight
	Gel	G A	PHEMA	Bis Am	
A	7.89	0.131	0	0	1/0
B	7.83	0.130	0.783	0.0235	1/0.1
C	7.58	0.127	3.79	0.114	1/0.5
D	5.86	0.098	5.86	0.176	1/1

trodes, which were 6 cm apart. When the switch was on, it was observed that the sample bent with deflection  $Y$  of the free end of the sample. The value of  $Y$  was monitored with a height finder.

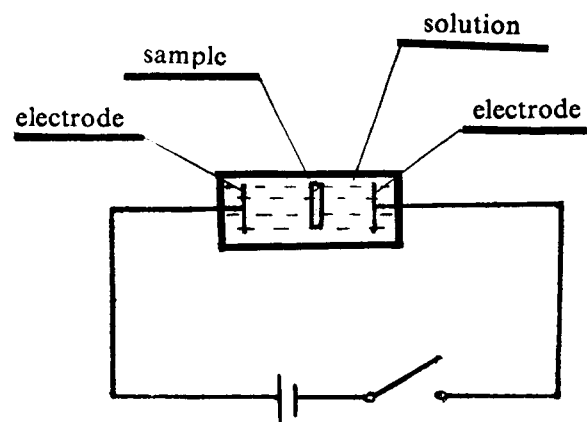
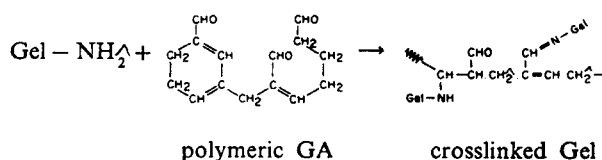
## RESULTS AND DISCUSSION

### Gelatin/PHEMA IPN

The GA crosslink of gelatin (Gel) includes aldimine linkages.



and Michael adducts<sup>4</sup>:

**Figure 1** Schematic drawing of electromechanochemical experiment.

The IR spectrum of the crosslinked gelatin is shown in Figure 2(a). In addition to the characteristic peak of carbonyl stretching vibration at  $1628 \text{ cm}^{-1}$ , there is a band assigned to the  $-\text{N}=\text{C}-$  crosslinking bond at  $1538 \text{ cm}^{-1}$ ,<sup>5</sup> while Figure 2(b) displays the IR spectrum of Gel/PHEMA (sample C). The characteristic bands at  $1199 \text{ cm}^{-1}$  ( $=\text{C}-\text{O}$ ) and  $1082 \text{ cm}^{-1}$  ( $\text{C}-\text{O}$ ), which are attributed to PHEMA, are obvious.

### EMC Behavior of Gel/PHEMA IPN

As is known, gelatin is a polymeric ampholyte. According to De Rossi, relevant effects are caused by an electric field on the swollen polyelectrolytic gelatin, e.g., influence on the degree of dissociation of the acidic or basic moiety, motion, and redistribution of mobile charged species, etc.<sup>3</sup>

The bending deformation is associated with ionic mobilization between the ampholytic Gel/PHEMA network and the surrounding  $\text{Na}_2\text{SO}_4$  solution. The bending force comes from the osmotic pressure differential  $\Delta\pi$ , which is related to a concentration differential of the ionic species. Based on Donnan equilibrium, the bending degree  $\delta$  of a specimen with thickness  $D$ , and original length  $L$ , under a dc electric field, can be expressed as<sup>6</sup>:

$$\delta = Y \cdot D/L^2 = \frac{RTC_p V_2 h t (1 - h t)}{3EV_1} \quad (1)$$

where  $Y$  is the deflection of the free end of the specimen;  $R$  is the gas constant;  $T$  is temperature;  $C_p$  is the concentration of the counterion;  $V_2$  and  $V_1$  are the volumes of gel and surrounding solution, respectively;  $h$  is the transfer rate of the counterion of the polyion from gel to solution and vice versa;  $t$  is the duration of the applied electric field; and  $E$  is Young's modulus.

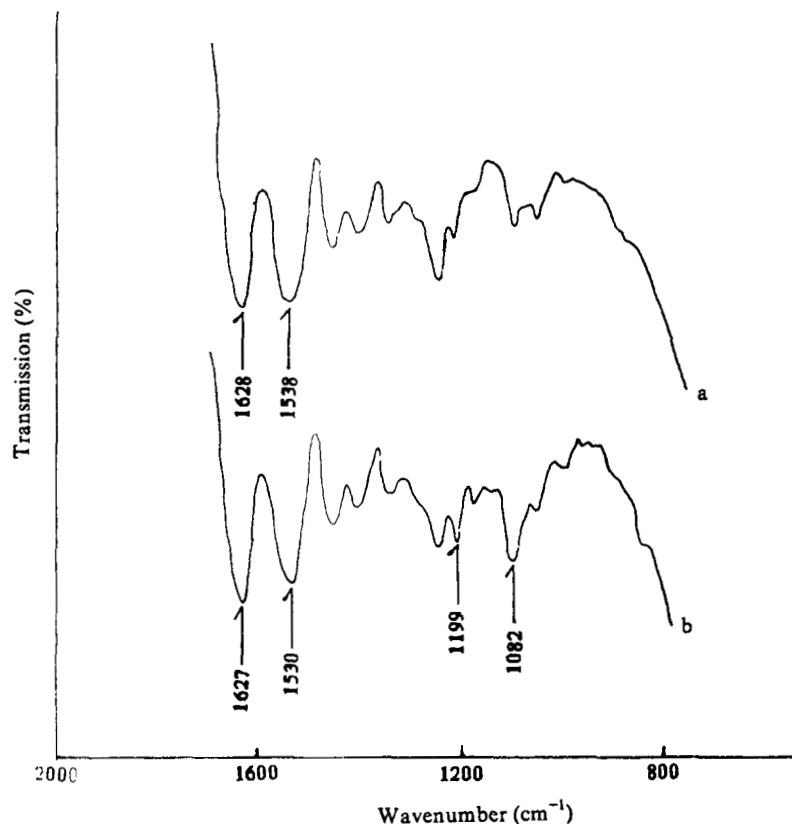


Figure 2 ATR-IR spectra of crosslinked gelatin (a) and Gel/PHEMA (b).

Therefore the value of  $\delta$  is a function of the concentration of the polyion, the mobilizing rate of the counterion, elastic modulus and geometry of the sample, and conditions of electric stimulation.

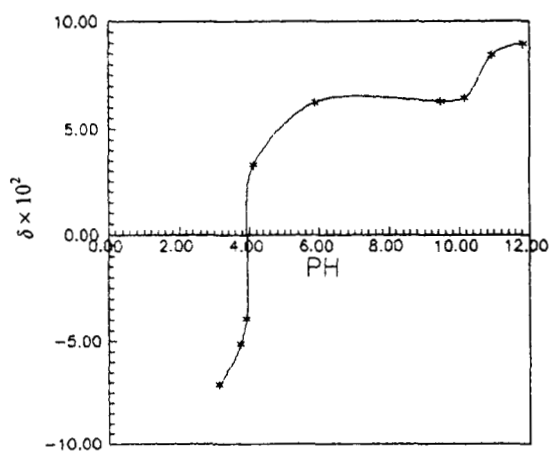
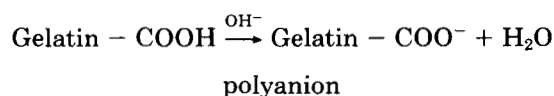
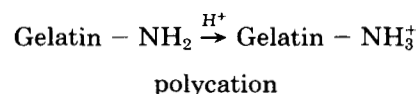


Figure 3 Electromechanochemical behavior of gelatin at 25°C with ionic strength  $I$  of 0.03 under an electric field of 27 V.

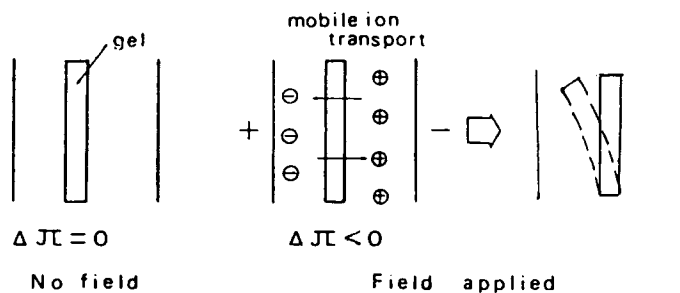
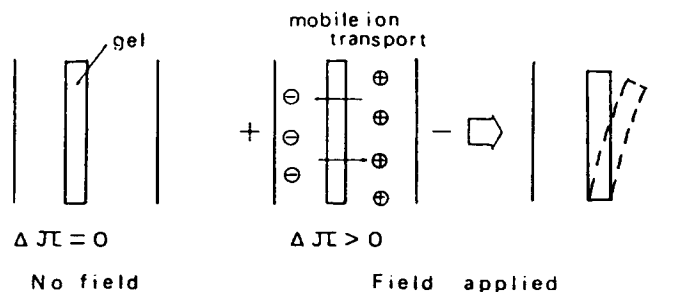
The EMC behavior of the crosslinked gelatin sample is shown in Figure 3. Data reveals that such a gelatin can bend reversibly under a noncontact dc electric field. While the sample bends to the cathode when  $\text{pH} > 4$ , it flexes toward the anode at  $\text{pH} < 4$ . Because the isoelectric point of the ampholytic gelatin is ca.  $\text{pH} 4$ , the gelatin becomes polyanionic above the isoelectric point,



The gelatin specimen bends toward the cathode due to the mobilization of the counterion (cf. Fig. 4[a]), while gelatin is protonized at  $\text{pH}$  values lower than the isoelectric point and turns polycationic:



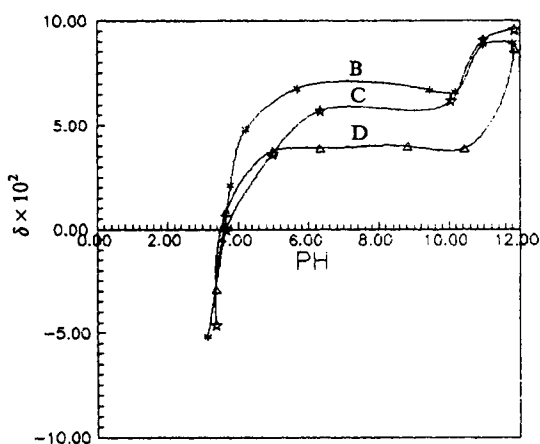
and the corresponding specimen flexes toward the anode (cf. Fig. 4[b]).



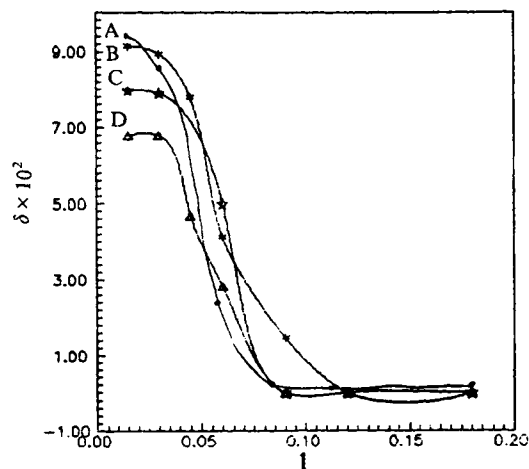
**Figure 4** Bending of gelatin specimen under electric stimulus at pH > 4 (a) and pH < 4 (b).

Figure 5 indicates the EMC phenomenon of Gel/PHEMA specimens. The tendency is similar to that in Figure 3, but the level of bending corresponding to a change in pH declines with an increase in the

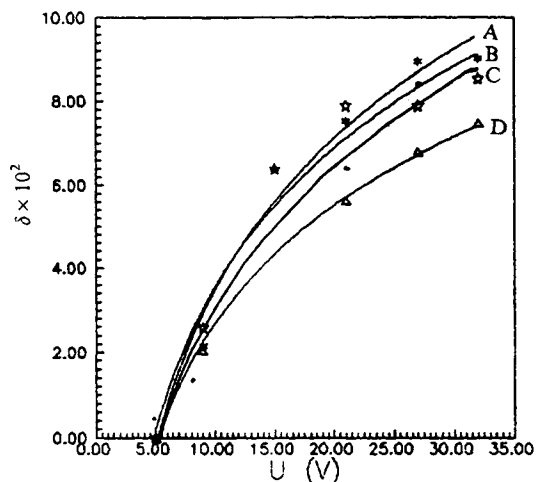
composition of PHEMA in the IPN. This is due to a reduction in  $C_p$ , while an increase in  $E$  (cf. eq. [1]) results in a decrease in the bending degree,  $\delta$ .



**Figure 5** Electromechanochemical phenomenon of gelatin/PHEMA interpenetrating network specimen at 25°C and  $I = 0.03$  under an electric field of 27 V (compositions of materials are in Table I).



**Figure 6** Bending degree of gelatin and Gel/PHEMA specimen versus ionic strength at pH = 10.8 and 25°C under an electric field of 27 V (compositions of materials are in Table I).



**Figure 7** Bending degree of gelatin and Gel/PHEMA samples as a function of voltage in 0.01 M/L  $\text{Na}_2\text{CO}_3$  at pH = 10.8 and 25°C (compositions of materials are in Table I).

### Factors Influencing the Degree of Bending in Electric Fields

#### Ionic Strength

There is a critical ionic strength,  $I_c$ , for the bending of crosslinked gelatin, e.g., the value of  $I_c$  is ca. 0.03 at pH = 10.80 (cf. Fig. 6). The bending degree obviously increases when  $I < I_c$ . This is attributed to the shielding effect of polyions by the ions of the electrolytic solute, which leads to a reduction in the electrostatic repulsion of polyions and a decrease in the degree of bending.

#### Voltage

The degrees of bending of IPNs of crosslinked gelatin and gel/PHEMA specimens vary with increases in the voltage of the applied electric field (cf. Fig. 7). This is attributed to the enhancement in transfer rate of counterions of the polyion from gel to solution

and vice versa, as an increase in electric potential gradient. There is a low critical voltage (LCV) of 5 V, below which bending of the sample may not be observed. The existence of the LCV relates to the decomposition voltage of an electrolyte solution; the ion immobilization occurs only at voltages > 5 V. Moreover, data in Figure 7 indicate that LCV values for Gel/PHEMA specimens B, C, and D are all around the same value of 5 V. The results reveal that the bending deformation of polyionic hydrogels under a non-contact electric field is caused by the mobility of ions in solution.

### CONCLUSION

Gelatin/PHEMA interpenetrating hydrogel networks show electromechanochemical phenomena under a non-contact electric field. The bending degree of polyampholyte IPN samples can be modulated via pH, ionic strength, and voltage of the applied electric field.

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### REFERENCES

1. K. D. Yao and S. Sun, *Polym. Bull.*, **28**, 677 (1992).
2. K. D. Yao and S. Sun, *Polym. Inter.*, **32**(1), 16 (1993).
3. Y. Osada and J. P. Gong, *Prog. Polym. Sci.*, **13**(1), 187 (1993).
4. H. Kaur and P. R. Chatterji, *Macromolecules*, **23**, 4868 (1990).
5. K. D. Yao, T. Peng, M. F. A. Goosen, J. M. Min, and Y. Y. Me, *J. Appl. Polym. Sci.*, **48**(2), 343 (1993).
6. T. Shiga and T. Kurauchi, *J. Appl. Polym. Sci.*, **39**, 2305 (1990).

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