

Polyelectrolyte hydrogels of chitosan and polyacrylamide: A comparison of electroactive characteristics

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Received 31 March 2011; accepted 21 August 2012

In this paper, studies on polyelectrolyte hydrogels of both anionic and cationic type are reported. Partially hydrolysed polyacrylamide-polyvinyl alcohol interpenetrating polymer (IPN) has been synthesized as the anionic hydrogel and chitosan-polyvinyl alcohol interpenetrating polymers have been synthesized as the cationic one, both through a simultaneous IPN method. In both cases, the crosslink densities are varied and investigated for their swelling behaviour and rheological properties. The stimulus sensitivity of the hydrogels is determined by subjecting them to applied electric fields. The responses of the various hydrogels are correlated with the shear moduli, the crosslink densities and the swelling behaviour. An interesting observation of simultaneous bending of multiple gel slabs in different directions upon the application of the electric field is also reported.

Keywords: Chitosan, Hydrogel, Cross-linking, Electroactive, Swelling

In the recent past, a large number of studies have been performed worldwide on polyelectrolyte hydrogels because they find application in the fields of biomedicine, pharmaceuticals, tissue engineering, robotics, microfluidics for sensors, drug delivery systems and actuators¹⁻⁹. Polyelectrolyte hydrogels exhibit unique behaviour of variation in mechanical properties as well as swelling and shrinking in response to physical or chemical stimuli such as temperature, pH, ionic strength, electric field etc.¹⁰⁻¹³ To ensure that the functionality and reliability are achieved in such systems it is important to better understand the behaviour of these materials in response to external stimuli and to model them.

Polyelectrolyte hydrogels are a special class of polymers that are ionizable. When the polymer backbone has negative charge they are grouped as anionic polyelectrolytes, and when the polymer chains accommodate positive charge, they are cationic. Included in the former group are salts of polyacrylic acid and polystyrene sulphonic acid, and in the latter, chitosan and polydimethyldiallyl ammonium chloride. In the present study, both anionic and cationic polyelectrolyte hydrogels have been selected for examining their electroactive characteristics vis-à-vis their physico-chemical properties like swelling and cross-linking. Both the cationic and anionic systems

were modified by incorporating polyvinyl alcohol (PVA) into the polymeric system. PVA extends structural rigidity and enhances the mechanical strength of the hydrogel, apart from introducing biocompatibility and biodegradability¹⁰. The anionic hydrogel selected is a partially hydrolysed PVA-polyacrylamide interpenetrating polymer and the cationic polymer is a naturally occurring biopolymer, chitosan which is used in many industrial and biomedical applications¹⁴⁻¹⁷. These systems were crosslinked to different extents and the detailed investigations of their swelling behaviour, rheology and electroresponsive characteristics are presented.

In addition, an interesting observation of simultaneous bending of multiple gel slabs to different directions, when a voltage is applied is also reported. The cationic and anionic gels behave entirely in opposite directions and it is presumed that this is apparently field dependent. This has multifarious utility in the medical field and for robotic type of applications.

Experimental Procedure

Synthesis

Anionic hydrogel (partially hydrolysed PVA-polyacrylamide IPNs)

Anionic polyelectrolyte is synthesized by partially hydrolyzing a polyacrylamide-PVA IPN system in NaOH solution. The detailed procedure is reported elsewhere¹⁸. 1 wt% or 3 wt% of

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polyethyleneglycoldimethacrylate (PEGDMA) is used for cross-linking polyacrylamide. The gel in which the wt% of PEGDMA is 1, is denoted as PA1 and the one with 3 wt% as PA2.

Cationic hydrogel (PVA-chitosan IPN gel cross-linked with gluteraldehyde (GA))

A homogeneous solution of 2.5 wt% of chitosan in 1:3 acetic acid was prepared by continuous stirring at room temperature. PVA solution was thoroughly mixed with this to get a 1:1 (volume) solution. Required moles of GA are mixed and kept overnight for gel formation by crosslinking of chitosan. Cross-linking of PVA is not expected to take place since cross-linking of hydroxyl by GA takes place at a higher temperature whereas the amine groups of chitosan are easily cross-linked by aldehyde¹⁹. To vary the gel strength, different concentrations of PVA and GA were employed. Four such systems were synthesized and the compositions are given in Table 1. For comparison, a cross-linked chitosan without PVA was also synthesized.

Characterization

Swelling measurements

Accurately weighed dry gel samples of both polyacrylamide and chitosan systems were immersed in different pH environments (2-12) at 25°C until they swelled to equilibrium. The desired pH value of the external swelling medium was maintained by adding HCl or NaOH. The fully swollen samples were weighed after blotting off the surface water. The swelling degree is calculated as the ratio of the swollen weight to dry weight.

Rheological measurements

Rheological studies of the swollen hydrogel systems were performed with a Bohlin CVOR-150 stress rheometer with a parallel plate geometry in the oscillatory shear mode. All measurements were carried out at 25°C. The storage (G') and the loss (G'') moduli, were obtained under dynamic conditions of non-destructive oscillatory tests in the frequency

Table 1—Weight percentages of the components of cationic (chitosan- PVA) gels and their representations

Representation	Chitosan solution (wt%)	PVA solution (wt%)	Amount of GA (mmol)
CH10	2.5	-	2.4
CP11	2.5	2.5	1.2
CP12	2.5	2.5	2.4
CP21	2.5	10	1.2
CP22	2.5	10	

range from 0.1 to 10 Hz. In order to adapt the rheometer for the measurement of hydrogel samples, the top plate of the geometry was pasted with an adhesive tape and thus avoided gel slippage out of the sandwich. The frequency sweep experiments were performed in the linear viscoelastic regime at a maximum strain (γ) of 0.004. This value of γ was determined previously using amplitude sweep experiments in which the storage and loss modulus were measured as a function of γ at a fixed frequency of 1 Hz.

Stimulus sensitivity studies

The electric response behavior was studied in an acrylic cell ($L \times W \times H : 7 \text{ cm} \times 7 \text{ cm} \times 3.5 \text{ cm}$) containing the electrolyte solution. The swollen gels of required size were suspended exactly midway between two carbon electrodes through which the electric field was applied. The deformation was recorded using a CCD camera interfaced with a computer. The response was determined as the bending angle, measured using *Pixel Fly* image analysis software. The responses were driven as a function of electrolyte, applied voltage and size of the gel. In all the experiments, the distance between the electrodes was kept as 20 mm. In the case of multiple gel samples (three nos.) bending simultaneously, the gel samples were suspended exactly 1 cm apart from each other and the linear set of gel samples were placed at 1 cm apart parallel to the line of electrodes.

Results and Discussion

Swelling measurements

Swelling at different pH

The degree of swelling is a significant characteristic of cross-linked hydrogels that determines many of the properties. Polyelectrolyte hydrogels are ionized hydrogels, therefore, their swelling behaviour depends on both the polymer structure and the medium. Figure 1 shows the swelling degrees of polyacrylamide IPNs,

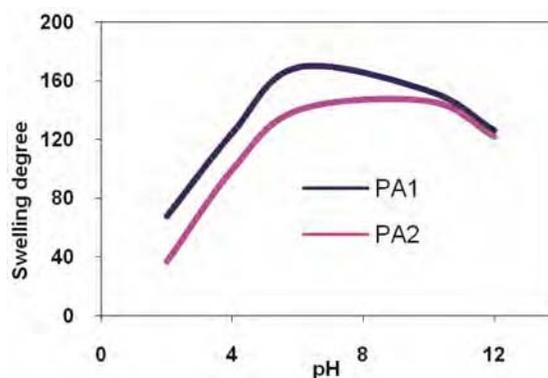


Fig. 1—Swelling data of polyacrylamide IPNs at different pH

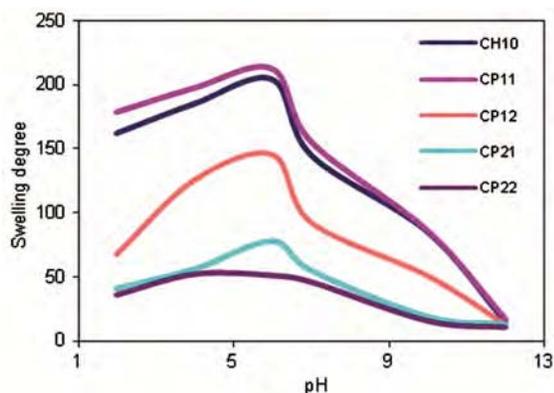
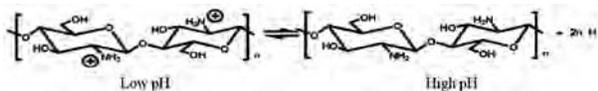


Fig. 2—Swelling data of chitosan IPNs at different pH



Scheme 1— pH responsive switching of chitosan

PA1 and PA2. These gels in the acidic pH, remain in the shrunken state. As the pH is increased, the swelling is increased, reaches a maximum and then decreased. Low pH leads to the change of polyion, $-\text{COONa}^+$ to $-\text{COOH}$ and thus the strong polyelectrolyte nature of the gel is transformed into a weak polyelectrolyte nature^{20,21}. The electrostatic repulsion is very much reduced and the polymer-polymer affinity is maximum at low pH. The flexibility of the polymer chain is rather low and the gel remains in the shrunken stage. However, as the pH is increased, ionization of the acid group takes place. The pKa of acrylic acid is 4.25 and hence it will ionize as the pH increases from 3 to 5. Polyacrylic acid differs in its ionization behaviour slightly since there are ionic interactions along the chain which leads to the broadening of the curve. Thus, the maximum swelling is observed in the pH range 5-6. However, as the pH increases further, the ionic strength also increases. The osmotic pressure difference of free ions between internal and external solution decreases and the gel tends to deswell. Additionally the free cations at higher concentration cause shielding on polycarboxylate groups²². These effects cause the gel to deswell above pH 6. Thus at a pH up to 6, when the polycarboxylic groups are fully ionized, the electrostatic repulsion surpasses the effect of ionic strength and plays the major role to cause swelling of the gel. At higher pH the effect of ionic strength surpasses the effect of electrostatic repulsion and plays the dominant role and causes the deswelling of the gels. PA2 is a higher crosslinked system. This

also shows similar trend, but the magnitude of the swelling degree is lesser. When the amount of cross-linking agent taken was low, the extent of cross-linking of the hydrogel was also low, which in turn results in the decrease of the strength of the hydrogel and the network volume for water preservation ability will be higher.

Figure 2 gives the swelling behaviour of chitosan-PVA gels. Many interesting properties are imparted to chitosan through its primary amino group²³. At low pH, the amino groups remain protonated and make chitosan a cationic polyelectrolyte. The apparent pKa of chitosan is in the pH range 6-7^{24,25}. The pH induced change of chitosan is shown in Scheme 1. Maximum swelling is observed in the region near and just below the pKa. In this pH range the primary amino groups of chitosan get ionised and the positively charged $-\text{NH}_3^+$ groups are distributed in the hydrogel network. The increase in net osmotic pressure difference between inside and outside the gel thus leads to a higher degree of swelling of the gel¹⁰. Also, the electrostatic repulsion between the chains adds the degree of swelling. Thus, maximum swelling of the gel is observed in the pH region 6-7. As the pH further reduces, the ionic strength of the medium plays a dominant role due to the increase in the H^+ ion concentration in the medium. This leads to a reduction in the osmotic pressure difference and therefore reduces the swelling capacity. The shielding effect caused by the excess Cl^- ions in the medium also contributes to the deswelling in this pH region. At high pH, greater than 7, the originally ionized groups in the gel matrix gradually lose their charges by deprotonation of the amino groups and eliminate the osmotic pressure difference. Consequently, to balance the osmotic pressure inside and outside of the hydrogel, the gel matrix contracts and chitosan undergoes a transition from a highly swollen cationic polyelectrolyte to a shrunken polymer, which leads to a very low swelling degree in the alkaline region. Thus, for all the chitosan systems under investigation, the maximum swelling is observed near neutrality, to be precise at pH 6.

When the amount of GA is increased from 1.2 to 2.4 mmol, the effect is reflected in the swelling. CP11, where the amount of GA is lower, has a swelling degree much higher at all pHs compared to CP12, where the amount of GA is higher. Similar is the case for CP21 and CP22. The hydrophilicity of chitosan is reduced by the cross-linking of the

networks by glutaraldehyde. The presence of PVA also has a significant influence. For all the systems containing PVA (except CP11), the swelling is lower than CH10 where PVA is absent. When the PVA content is increased from 2.5 wt% to 10 wt%, the swelling degree is extremely reduced, though PVA is highly hydrophilic. This may be due to highly dense polymeric entanglements introduced when the PVA content is more, which may reduce the effective network volume for preserving the water content.

Rheological Measurements

As can be seen in Figs 3 and 4, in the frequency window explored, storage modulus (G') of all the gels remains almost constant. As the percentage of cross-linking increases, the modulus of the gel increases as evident from the figures. From the increase in the storage moduli values it can be understood that the rigidity of the entire polymer network is increased by increasing the concentration of PEGDMA.

For chitosan based IPN gels, the amount of PVA as well as GA has significant influence in the G' values. As the PVA content as well as GA content increases, the G' value increases. Maximum value of 12 kPa was observed for CP22 which has maximum PVA content and GA content. The equilibrium water content (α swelling degree) for the swollen gel is minimum for this system when compared to the other systems. As the amount of GA is lower in CP11 G' of CP11 is lower than CP12. Similar is the case with CP21 and CP22. The increase in cross-linking densifies the network and thus the mechanical stiffness increases. The increase in crosslinker/monomer ratio leads to an increase in the gel's modulus through the relation, $G'_R = \rho RT/M_c$, where G'_R is the relaxed rubbery modulus, ρ is the density, R is the universal gas constant, T is the temperature, and M_c is the molecular weight between crosslinks²⁶. An alternative form of this equation is $G'_R = \gamma RT$, where γ is the number of crosslink sites per unit volume. This simple relationship can be used to estimate the experimental ratio of crosslink densities, $\gamma H/\gamma L$, where H and L corresponds to higher and lower crosslink densities, which can be compared to the theoretical ratio which is the ratio of amount of GA added during synthesis time. For CP21 and CP22 this ratio was found to be 1.6, close to 2, the theoretical ratio. However, for CP 11 and CP12 the deviation from theoretical value is comparatively high. For PA 1 and PA2, the theoretical $\gamma H/\gamma L$ is 3 and the value calculated from rheological data is

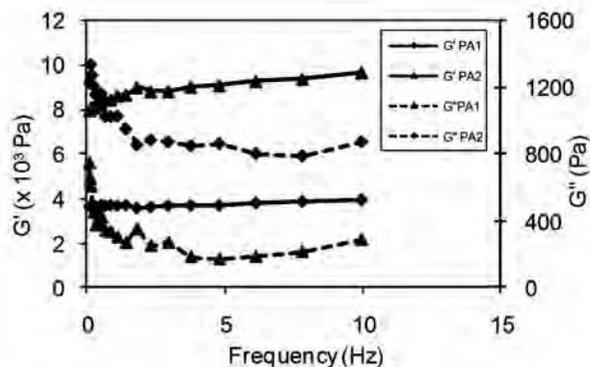


Fig. 3—Frequency sweep experimental data of polyacrylamide hydrogels

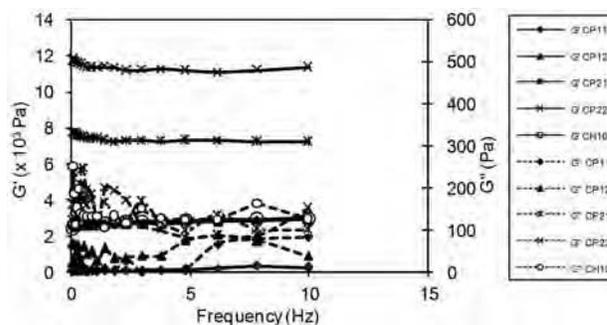


Fig. 4—Frequency sweep experimental data of chitosan hydrogels

around 2.7, very close to the theoretical value. Nevertheless, it is very clear from the graph that the storage modulus and thereby the water retention capacity can be easily controlled by the extend of crosslinking. A comparison of the swelling behaviour with the moduli values confirms this (Figs 1 and 3 or Figs 2 and 4).

Stimulus sensitivity studies: Response to electric field

In order to explore the responsive behaviour of the gels to electric field, the bending deformation experienced by the gels when an electric field is applied has been investigated. The deformation in NaOH as the electrolyte with a single polyacrylamide gel slab placed in the middle of the electrodes has already been presented in elsewhere^{18,27}. When three different gels are placed in the cell as described in the experimental section, and a voltage is applied simultaneously to all these gels, an interesting phenomenon is observed. The three gel slabs bent in entirely different directions. This is apparently field dependent. To understand the phenomenon further, both types of polyelectrolytes, namely cationic and anionic have been selected and the bending deformation of both type in a neutral medium (NaCl)

was explored for comparison. Figure 5 gives sequential photographs of deformation of PA1 at time intervals.

Electroactive characteristics of anionic hydrogel: Polyacrylamide-PVA IPNs

Taking PA1 as a representative, the influence of size and voltage were studied. Experiments conducted on single gel slabs of PA1 or PA2 in NaCl, exhibited bending of the gel towards the cathode. It is observed that the side of the gel facing the positive electrode gains weight and swells and this leads to the bending of the gel towards the negative electrode. The swelling of a polyelectrolyte gel has been explained by osmotic pressure variation theory by Flory²⁸ which is related to the drift of mobile ions in the gel when subjected to a dc electric field. Figure 6 explains the dependence of size and voltage on stimulus sensitivity. Gel slabs of length 30 mm with cross-sections, $0.5 \times 0.5 \text{ mm}^2$, $1.0 \times 1.0 \text{ mm}^2$ and 2.0×2.0

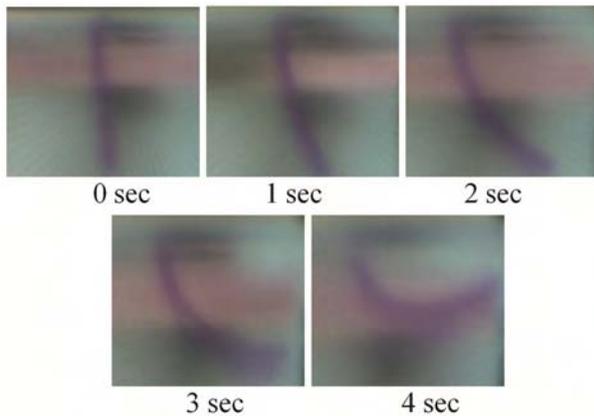


Fig. 5—Bending of PA1 at different time intervals at 20 V in 0.01 M NaCl solution

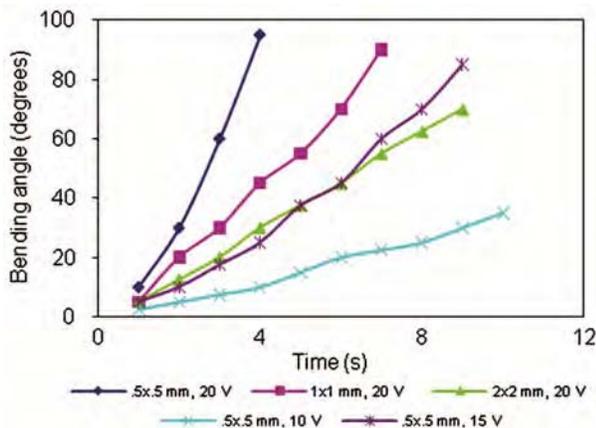


Fig. 6—Effect of size and voltage on electro active characteristics of PA1 in 0.01 M NaCl

mm^2 were studied for their electroactivity at 20 V in 0.01 M NaCl solution. To study the influence of electric field, gel slabs of cross-section $0.5 \times 0.5 \text{ mm}^2$ were subjected to three different electric fields viz., 10 V, 15 V and 20 V. As is evident from Fig. 6, when the size of the gel is reduced, the response becomes faster and larger. The stimulus sensitivity is diffusion controlled and is inversely proportional to the square of the cross-sectional area of the gel under a uniform field²¹. Thus, if the size is reduced to micron scale, the response could be achieved in microseconds. It is clear from Fig. 6 that a gel of cross-section $0.5 \times 0.5 \text{ mm}^2$ bends much faster than a gel of cross-section $1 \times 1 \text{ mm}^2$ or $2 \times 2 \text{ mm}^2$. The applied voltage also plays an important role in bending. The deformation is due to the voltage induced motion of the ions and is enhanced when the applied voltage is higher.

The influence of cross-linking and swelling is shown in Fig. 7. PA2 exhibits a sluggish response compared to PA1. This is clearly in consonance with the swelling degree and storage modulus of the two. Cross-linking increases the stiffness of the material and reduces the swelling and hence the diffusion process under a subsequent application of electric field.

Electroactive characteristics of cationic hydrogel: Chitosan-PVA IPNs

The bending studies of PVA containing gels namely CP12, CP21 and CP22 were carried out and the results are shown in Fig. 8. Unlike PA1 and PA2, these gels bend towards the anode when an electric field is applied. Here, the network possesses negative charges and the bending can again be explained on the basis of difference of osmotic pressure. However,

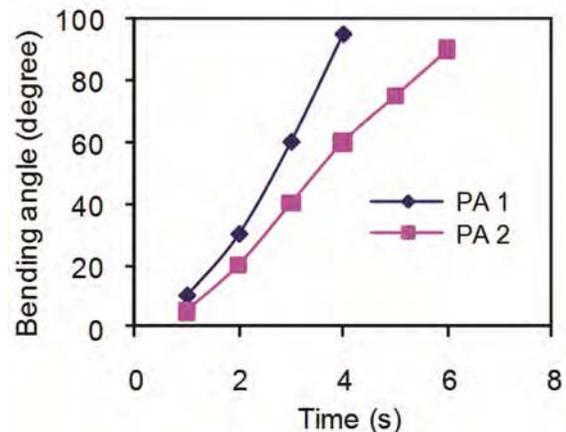


Fig. 7—Bending angles of PA1 and PA2 ($0.5 \text{ mm} \times 0.5 \text{ mm}$) in 0.01 M NaCl

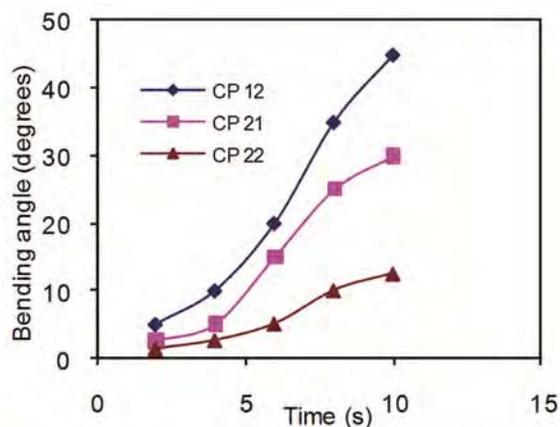


Fig. 8—Bending angles of crosslinked chitosan IPNs (0.5 × 0.5 mm) in NaCl at 20 V

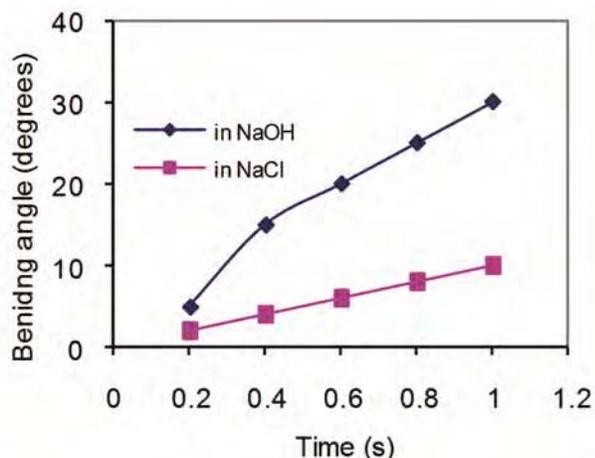
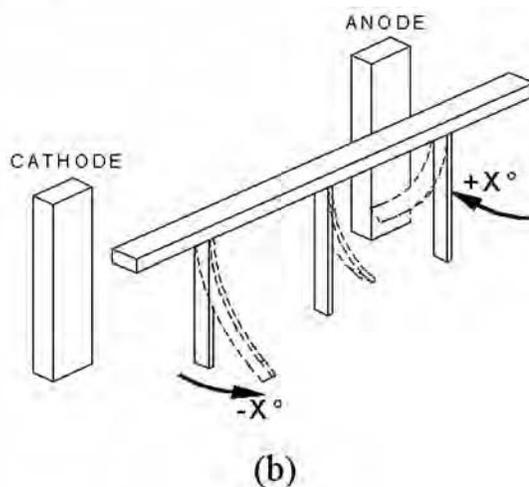
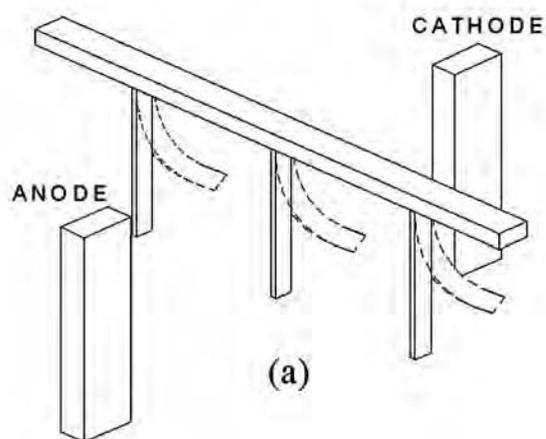


Fig. 9—Ultra fast response of PA1(0.5 × 0.5 mm) in NaOH and NaCl

compared to the acrylamide systems, the responses of the chitosan gels were too slow and low in magnitude. This may be partly due to the fact that acrylamide systems are crosslinked by a relatively larger molecule, PEGDMA whereas chitosan by a small unit GA. Among CP12, CP21 and CP22, the least response was shown by CP22 and the highest by CP12. This is also in agreement with the moduli values and swelling degrees (Figs 3 and 4). Even though the extend of cross-linking is high for CP12 than CP21 (2.4 mmol of GA for CP12 and 1.2 mmol of GA for CP12), probably due to a dense network of PVA in CP 21, the response of CP 21 is less than that of CP12.

Ultra fast response of polyacrylamide gels

In order to demonstrate the ultra fast response of PA systems, the bending studies of these alone were done in a 0.01 M NaOH. The results are shown in Fig. 9.



Scheme 2—Simultaneous bending of multiple gels (a) when the rod suspended with PA1 gels is perpendicular to the line of electrodes and (b) parallel to the line of electrodes and 1 cm away

It is clear that the hydrogels are suitable for microfluidic and other MEMS devices, since the response time could be brought down to milliseconds.

Simultaneous bending of multiple gel slabs

The striking observation of voltage induced simultaneous bending of multiple gel slabs in apparently field dependent directions is described in Scheme 2. Initially, the three gels suspended from a rod at 1 cm apart are placed exactly in the middle of the electrodes perpendicular to the line of electrodes (Scheme 2a). It was observed that all gel slabs bent towards the same electrode, to the same extent at a given interval of time. However, when the position of the rod with the suspended gel slabs is slightly changed, an entirely different behaviour is observed. For example, in the case of PA1, when the rod is placed parallel to the line of electrodes at a distance of

Table 2—Responses during simultaneous bending of multiple gel slabs of PA1

Time	Bending angle for middle gel	Bending angle for gel near cathode	Bending angle for gel near anode
5 s	20°	- 15°	+ 15°
10 s	50°	-40°	+ 40°

1 cm the gel slab near the anode bends towards it, the slab close to cathode bends away from it and the one at the center bends perpendicular to these two, and towards the anode (Scheme 2b). When the experiment is repeated with CP12, the gel slab near the anode bent away from the electrode, that near the cathode bent towards the electrode and the one at the center, perpendicular to these two and towards the cathode. The deformation at intervals of 5 s and 10 s for PA1 ($2 \times 2 \text{ mm}^2$) at a voltage of 15 V is shown in Table 2. Bending of the middle gel is not given any sign, but to differentiate, the bending away from electrode is given a negative sign and that towards the electrode, a positive sign.

The deformation of the gel slabs is apparently field dependent. More extensive electric field mapping experiments are required to fully understand the phenomenon of simultaneous and directional bending of gel slabs.

Conclusions

Both types of hydrogels, i.e., anionic and cationic, showed a pH dependent swelling behaviour. The swelling degrees depend on the extend of cross-linking as well as the PVA content. This was further established by the cross-linking difference investigated through modulli values. The shear modulus was maximum and swelling was minimum for the highly crosslinked chitosan-PVA IPN with higher content of PVA, even though PVA is highly hydrophilic. Between acrylamide systems also, one with higher crosslink density exhibited higher modulus and lower water retention capacity. These properties determined the response of the systems to an electric field. When the swelling ability is higher which is dependent on crosslink density of the system, diffusion process is slower and response will be slower. The bending is field dependent and the anionic gels bent towards the cathode whereas the cationic ones to the anode, in a

NaCl medium. The field dependent phenomenon is further confirmed by the simultaneous bending of the cationic and anionic gels to exactly opposite directions, when multiple gel slabs of each type are subjected to electric field separately.

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