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A. K. Bajpai[a]; Manish Sharma[a]
[a] Bose Memorial Research Laboratory, Department of Chemistry, Government Autonomous Science College, Jabalpur, M.P., India

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Preparation and Characterization of Binary Grafted Polymeric Blends of Polyvinyl Alcohol and Gelatin and Evaluation of their Water Uptake Potential

A. K. BAJPAI AND MANISH SHARMA

Bose Memorial Research Laboratory, Department of Chemistry, Government Autonomous Science College, Jabalpur (M.P.), India

Binary hydrophilic blends of poly(acrylamide-co-methylene bis acrylamide) grafted polyvinyl alcohol (PVA) and gelatin (GEL) were prepared by redox polymerization method and the end product was characterized by infra red (IR) spectral analysis, differential scanning calorimety (DSC) measurements, and scanning electron micrograph (SEM). Network parameters such as molecular weight between crosslinks (M_c) and crosslink density of the hydrogel were also determined by swelling measurements. In addition, the blend hydrogels were assessed for their water sorption characteristics and influence of various factors such as composition of the blend, pH and temperature of the swelling bath and, the presence of electrolytes were investigated on the water uptake potential of blend hydrogels.

Keywords blend hydrogel, polyvinyl alcohol, gelatin, grafting, swelling

Introduction

Hydrogels, alternatively called as 'hungry networks' are covalently bonded three dimensional macromolecular matrices possessing an extraordinary potential to accommodate water into their structure without undergoing dissolution (1). Hydrogels are very versatile materials and find extensive applications as biomaterials in the biomedical and pharmaceutical fields (2). The exact suitability of hydrogels as biomaterials stems from the similarity of their physical properties to those of living tissues. This resemblance originates mainly due to their high water content, soft and rubbery texture, greater stability in biological fluids, minimum mechanical irritation to surrounding tissues, etc. The high water content of hydrogels allows the extraction of undesirable reaction byproducts prior to implantation and easy penetration of small molecules such as water, electrolytes and metabolites into them *in vivo.* Thus, besides the applications of hydrogels in implantation technology (3–5), they are also used in controlled drug delivery systems (6–8), burn dressings (9), dialysis membranes (10), agrochemistry (11), etc. Moreover, their

Received May 2004, Accepted January 2005.
Address correspondence to A. K. Bajpai, Bose Memorial Research Laboratory, Department of Chemistry, Government Autonomous Science College, Jabalpur (M.P.) 482 001, India. E-mail: akbmrl@yahoo.co.in

swelling response to external stimuli like pH, temperature, electric field, ultraviolet light causes them to be referred to as 'intelligent polymers'. The fundamental property to which all such biomedical applications are greatly dependent is water-uptake capacity of the hydrogel, which mainly arises due to a spontaneous transition of polymer from glassy to rubbery state when the polymer contacts a thermodynamically compatible solvent such as water. Furthermore, variation in chemical composition of the hydrogel provides an opportunity to desirably modulate the swelling characteristics of the hydrogel. Thus, the study of swelling characteristics of a network is a subject of vital significance.

Being motivated by the biomedical significance of hydrogels, the present study aims at preparing and characterizing a binary polymeric blend of polyacrylamide grafted polymers of polyvinyl alcohol and gelatin and investigating its water sorption capacity. The selection of polyvinyl alcohol (PVA) as one of the components of the present hydrogel lies in its popularity in the biomedical community (12–14). Polyvinyl alcohol is used as a basic material for a variety of biomedical applications such as contact lenses (15), artificial meniscus (16), reconstruction of vocal cords (17), etc. because of their inherent non-toxicity, non-carcinogenicity, good biocompatibility and desirable physical properties such as elastic nature, high degree of swelling in aqueous solution and good film forming property. However, its weak mechanical strength restricts its use in those applications where the material has to withstand prolonged stress. Thus, the introduction of other polymeric components into the PVA matrix could improve its mechanical properties.

The other polymer chosen for the hydrogel preparation is gelatin, which is known for its biodegradability, non-carcinogenicity and hydrophilicity (18). Moreover, incorporation of this biopolymer into the PVA matrix could improve its properties because of the presence of multi functional groups in the gelatin molecule. As far as polyacrylamide is concerned, its hydrophilic nature and biomedical applications are well recognized (19).

Experimental

Gelatin was obtained from Merck (India) Limited (Mumbai) and used as received. Polyvinyl alcohol (PVA) (hot process, mol. wt. 40,000, degree of hydrolysis 98.6%) was obtained from Loba Chemie India and used without pretreatment. Acrylamide (AM) (Research Lab, Poona, India) was crystallized twice in methanol and dried in vacuum over anhydrous silica for a week. *N,N′*-methylene bis acrylamide (MBA) (Central Drug House, Lucknow, India) and potassium persulphate (KP) (Loba Chemie, India) employed as crosslinking agent and initiator, respectively, were used as received. Potassium metabisulphite (MBS) (Loba Chemie, India) was used as an activator in the redox system. Other required chemicals used were of analytical reagent grade and double distilled water was used throughout the study.

Method

Preparation of Ternary Hydrogels

The hydrogels were prepared by a redox polymerization method (20). Gelatin (1 gm) and PVA (2 g) were dissolved in 20 mL distilled water under hot conditions (60°C) and into this solution were added acrylamide (1.5 g), crosslinker methylene bis acrylamide (MBA) (0.02 g) and redox initiator comprising of potassium metabisulphite (KMBS) and potassium persulphate. After proper mixing, the entire viscous material was

transferred to a petri dish (2 inch diameter, Corning) which was then kept at 27°C for 6–7 days so that it changed into a thin circular film. The hydrogel film so prepared was freed from unreacted chemicals by equilibrating it in distilled water for 4 days. Then the gel was dried at room temperature. The dry gel film was cut into nearly identical sized thin circular pieces (diameter 0.7 cm, thickness 0.12 cm) and stored in airtight polyethylene bags. A photograph of dry and swollen gel is shown in Figure 1.

IR Spectroscopy

The structural characterization of the hydrogel was perfomed by recording IR spectra of the gel of definite composition (Gel 1 g, AM 1.5 g, PVA 2 g, MBA 0.02 g) on a FTIR spectrophotometer (Perkins-Elmer, Model Paragon 1000).

DSC Measurement

A differential scanning calorimetry measurement of prepared hydrogels was recorded on a DSC instrument (2100, DuPont) in the temperature range 30 to 400°C under N_2 atmosphere and at a heating rate of 10°C/min.

Scanning Electron Microscopy

The SEM analysis of the prepared blend was performed on a scanning electron micrograph (STEREO SCAN, 430, Leica SEM, USA).

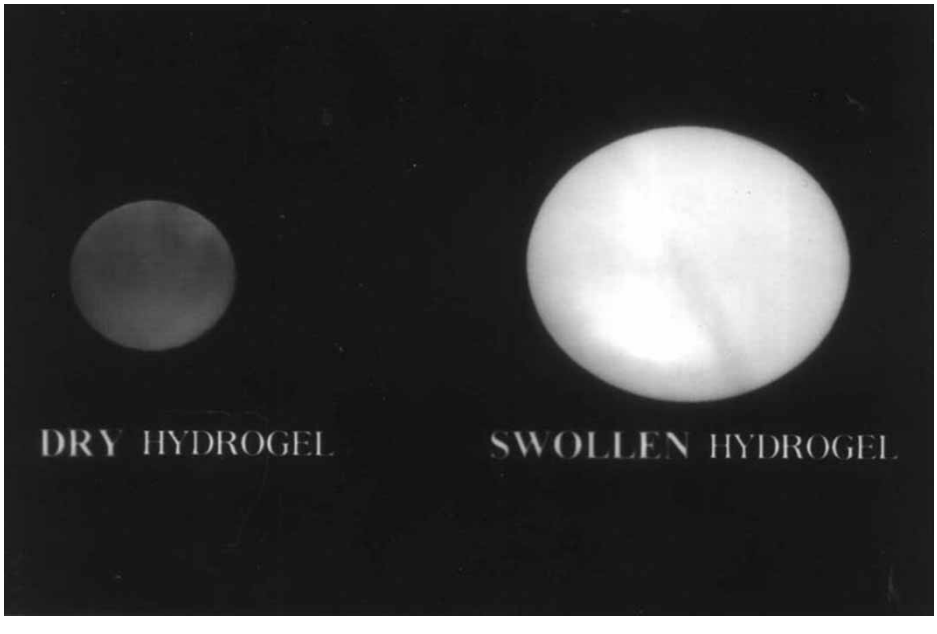

Figure 1. A photograph depicting (a) dry and (b) swollen blend hydrogels.

Swelling Studies

Swelling of the hydrogel in double distilled water was monitored gravimetrically as described in literature (21). In a typical swelling measurement, a pre-weighed piece of hydrogel (0.1 g) was immersed in an aqueous reservoir and allowed to swell for a definite time period. The swollen gel was weighed after pre-determined time intervals. Before weighing, each time the gels were carefully pressed in between the two filter papers to remove excess water.

The following parameter was determined for the swollen hydrogel samples.

$$\text{Swelling ratio} = \frac{\text{Weight of swollen gel}}{\text{Weight of dry gel}} \tag{1}$$

Kinetics of Swelling

Most often, the kinetics of water sorption dynamics has been studied either by monitoring the change in physical dimensions of swollen hydrogel or by knowing the amount of water imbibed by the hydrogel at various time periods (22–24).

Furthermore, in the present work, the later procedure was followed. The swollen hydrogel was taken out at different time intervals and its weights were recorded. The following equation was used to determine the kinetic parameters of the swelling process:

$$\frac{W_t}{W_\infty} = kt^n \tag{2}$$

where k is the swelling rate front factor, n is swelling exponent, W_t and W_∞ are the water intakes at time t and equilibrium time, respectively. The above equation is a phenomenological rate law where the swelling exponent n provides insights into the water transport mechanism that is in operation.

For instance, for a Fickian kinetics in which the rate of diffusion is rate limiting ($n = 0.5$), (Case 1), whereas the value of n between 0.5 to 1.0 indicates a non-Fickian process. In a non-Fickian mechanism, the relaxation of polymeric chains of the hydrogel determines the rate of water sorption. The value of n can usually be determined by the double logarithmic plot of W_t/W_∞ and time t.

The following equation was used to calculate diffusion constant D of water into the hydrogel.

$$\frac{W_t}{W_\infty} = 4\left[\frac{Dt}{\pi l^2}\right]^{1/2} \tag{3}$$

where D is the diffusion constant of water ($cm^2\,sec^{-1}$) and l is the thickness (cm) of dry hydrogel.

The above equation clearly implies that a plot between W_t/W_∞ and $\sqrt{t}$ will yield a straight line and with the slope of graph, the value of diffusion constant D can be calculated.

Results and Discussion

Scheme of Polymerization

The preparation of polymeric blend of poly(acrylamide-g-PVA) and poly(acrylamide-g-gelatin) may be modeled via the following scheme of polymerization reactions.

(a) $\text{Redox} \longrightarrow \text{R}^{\bullet}$

(b)
$$\begin{array}{ll} \text{R}^{\bullet} + \text{nAm} & \text{R} - (\text{AM})^{\bullet}_{\text{n}-\text{i}-} \\ \quad +\text{mMBA} & \qquad\quad | \\ & \qquad (\text{MBA})_{\text{m}} \\ & \qquad\quad | \\ & \qquad -(\text{AM})_{\text{i}-} \\ & \qquad\quad (\mathbf{I}) \end{array}$$

(c) $\text{R}^{\bullet} + \text{PVA} \longrightarrow \text{PVA}^{\bullet} + \text{RH}$

(d) $\text{R}^{\bullet} + \text{Gel} \longrightarrow \text{Gel}^{\bullet} + \text{RH}$

(e)
$$\begin{array}{lll} \text{PVA}^{\bullet} + \mathbf{I} & \longrightarrow & \text{PVA} \\ & & \quad | \\ & & \quad \mathbf{I} \end{array}$$

(f)
$$\begin{array}{lll} \text{Gel}^{\bullet} + \mathbf{I} & \longrightarrow & \text{Gel} \\ & & \quad | \\ & & \quad \mathbf{I} \end{array}$$

(g)
$$\begin{array}{lll} \text{PVA} + \text{Gel} & \longrightarrow & \text{(Blend Hydrogel)} \\ \quad | \quad | & & \\ \mathbf{I} \quad \mathbf{I} & & \end{array}$$

IR Spectral Analysis

The infrared spectra of an uncured reaction mixture of hydrogel and cured hydrogel film clearly depicts a significant difference between the two spectra. Whereas, in uncured hydrogel spectra, the peaks obtained are quite broad because of the presence of water molecules in the feed mixture, the bands, which appeared in the cured hydrogel spectra, are quite sharp. Moreover, some new absorption peaks are also visible in the later spectra.

The spectra of hydrogel clearly marks the presence of both PVA and gelatin as evident from the observed peak at 3448 cm^{-1} which could be assigned jointly to O–H stretching of hydroxyl of PVA and N–H stretching of gelatin. It is notable here that because of the simultaneous occurrence of N–H and O–H stretchings, separate appearance of respective peaks is rather not visible in the spectra. The spectra also shows characteristic absorption peak at 1630 cm^{-1} indicative of C═O stretching of gelatin and polyacrylamide. Other significant peaks shown in the spectra are at 2929 cm^{-1} (C–H stretching of PAM and PVA), 1399 cm^{-1} (CH_2 twisting of PVA and PAM), and 600–700 cm^{-1} (broad N–H out of plane bending of amide). It is also observed in the spectra of cured hydrogel that there is a

disappearance of vinyl group peak which does appear in the spectra of uncured hydrogel at $1434\,cm^{-1}$.

In the present study it has also been attempted to visualize the progress of the hydrogel formation by a continuous recording of IR spectra, which clearly reveal that as the hydrogel formation progresses, the spectral peaks become increasingly sharp and ultimately a well-defined spectra is obtained.

DSC Analysis

The thermal behavior of the prepared hydrogel was monitored by constructing DSC thermograms of pure gelatin and hydrogel as shown in Figure 2(a) and (b), respectively. The thermogram of pure (uncrosslinked) gelatin shows three prominent endotherms at 66°, 176° and 193°C, which is an unusual observation. The first endotherm at 66°C may be attributed to the loss of moisture, while the other two sharp endotherms observed at 176° and 195°C may be attributed to the block copolymer model for the amino acid content of gelatin (25). These two glass transition temperatures represent the block of amino acids, proline, hydroxyproline and glycine.

However, the DSC thermogram of hydrogel shown in curve (b) differs greatly with that of the pure gelatin. The broad endotherm of hydrogel suggests a hydrophilic and amorphous nature of the end polymer. A close examination of the curve depicts weak endotherms around 60–70°C due to first glass transition temperature (Tg) of gelatin and 70–80°C because of glass transition of PVA. It is important to note here that the endotherms at 203 and 223°C are actually the enhanced Tg's of gelatin (see curve (a)) which, because the interpenetrating nature of the hydrogel chains appear at higher temperatures. It is interesting to note here that both the Tg's of pure gelatin (176° and 195°C) were increased by 28°C in the hydrogel thermogram (203° and 223°C, respectively). The thermogram also indicates a broad melting endotherm around 250°C, which may be attributed to the melting of PVA. The thermograms, however, shows a sharp melting endotherm at 280°C which may be assigned to melting of polyacrylamide. It is, therefore, clear that a significant change in thermal behavior is brought about due to hydrogel preparation.

SEM Analysis

The morphological features of the hydrogel have been investigated by examining scanning electron micrographs of the hydrogel as shown in Figure 3. It is clearly revealed by the photograph that the graft hydrogel has a porous surface with pore sizes varying approximately between 1 μm to 4 μm. A large sized porous network is also expected that because of grafting of crosslinked polyacrylamide chains onto PVA and gelatin, a wider mesh sized network will be formed. The SEM observation obviously supports the graft nature of the hydrogel.

Network Parameters

One important structural parameter characterizing crosslinked polymer is M_c the average molar mass between crosslinks directly related to the crosslink density. The magnitude of M_c significantly affects the physical and mechanical properties of crosslinked polymer and its determination has great practical significance. Equilibrium swelling is widely used to determine M_c. Flory and Rehner's early research laid the foundation for analysis of equilibrium swelling.

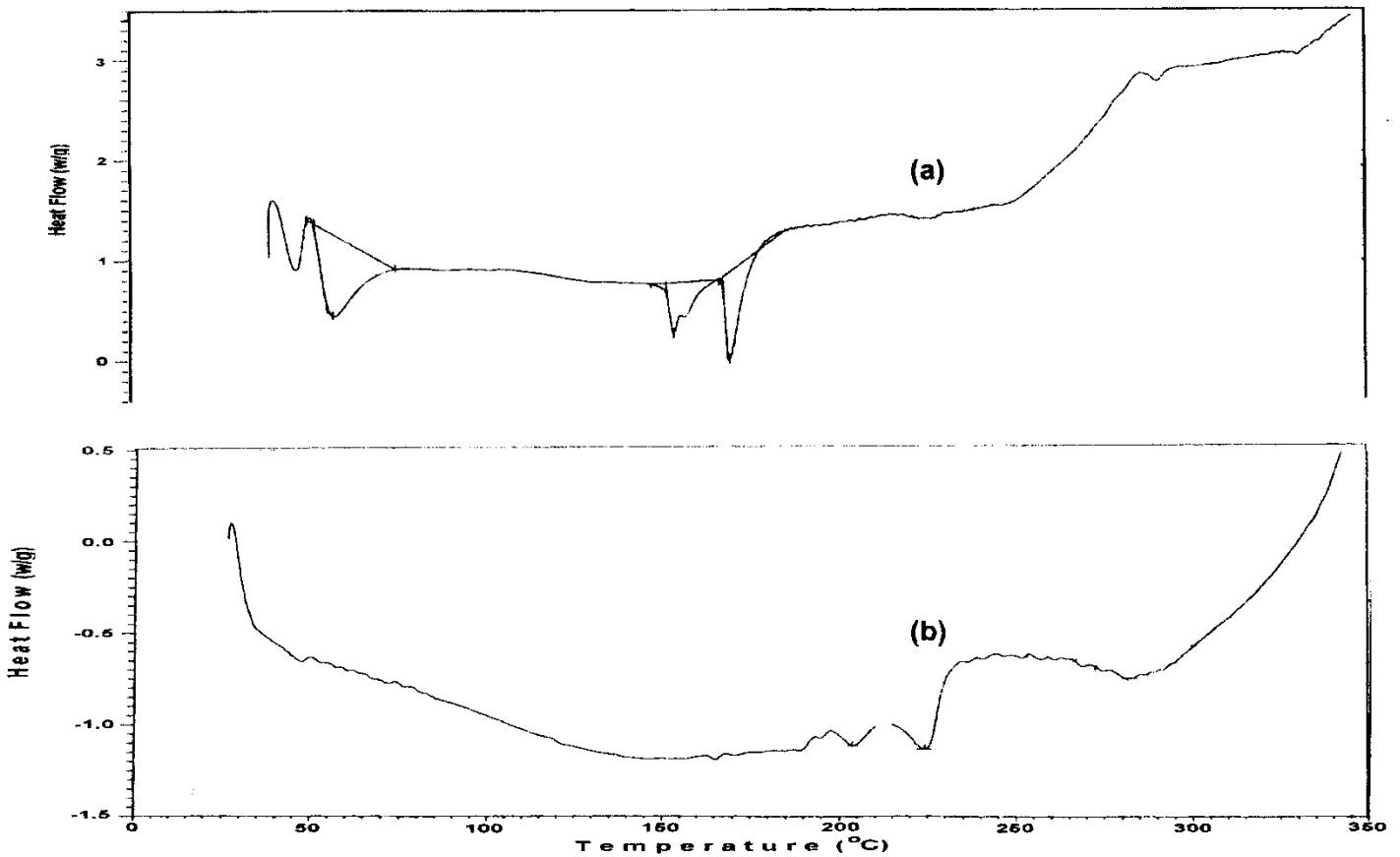

Figure 2. DSC thermogram of (a) pure gelatin and (b) cured hydrogel.

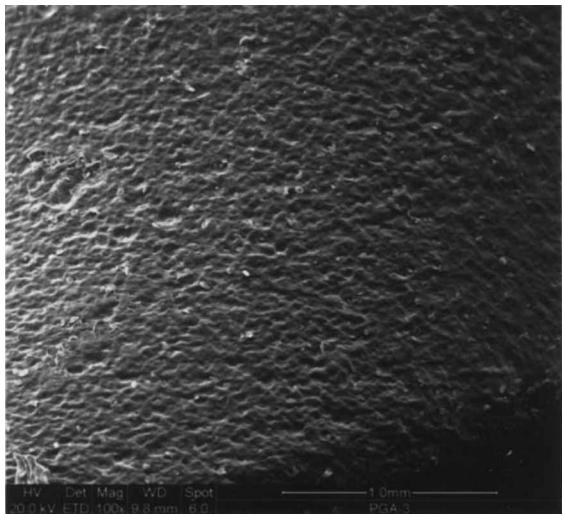

Figure 3. Scanning electron micrograph of dry hydrogel.

According to the theory of Flory and Rehner, for the perfect network:

$$M_c = \frac{-V_1 d_p (V_s^{1/3} - V_{s/2})}{\ln(1 - V_s) + V_s + \chi V_s^2} \tag{4}$$

where M_c is the number average molar mass of the chain between crosslinks. V_1 is the molar volume of water (ml mol^{-1}), d_p is the polymer density (g ml^{-1}), V_s is the volume fraction of the polymer in the swollen gel, χ is the Flory-Huggin's interaction parameter between solvent and polymer (26).

The swelling ratio is approximately equal to $1/V_s$. Here, the crosslink density q is defined as the mole fraction of crosslinked units.

$$q = M_o/M_c \tag{5}$$

where M_o is the molar mass of repeating unit.

Other authors defined a crosslink density, V_e, as the number of elastically effective chains, totally included in a perfect network per unit volume. V_e is simply related to q since:

$$V_e = d_p \frac{N_A}{M_c} \tag{6}$$

The values of V_1 and χ were taken from related literature (27–29), N_A is the Avogadro's number. The density of gel d_p was determined to be 0.83 gm cm^{-3}. The values of M_c, q and V_e of the networks have been calculated and summarized in Table 1 for varying composition of the hydrogel.

Mechanism of Water Uptake

The hydrogel prepared in the present study are the intimate mixture of crosslinked polyacrylamide grafted PVA (Polyvinyl alcohol) and gelatin chains bonded to one another through H-bonding and electrostatic type of forces as shown in Figure 4.

Table 1
Network parameters of the hydrogels of different compositions

S. no.	Composition				Average mol. wt between crosslinks $M_c \times 10^{-3}$	Crosslink density $q \times 10^3$	No. of elastically effective chains $V_e \times 10^{-20}$
	AM (mM)	Gelatin (g)	PVA (g)	MBA (mM)			
1.	14.0	1.0	2.0	0.12	2.84	24.91	200.3
2.	21.1	1.0	2.0	0.12	5.73	12.39	402.74
3.	28.1	1.0	2.0	0.12	2.63	26.99	184.8
4.	10.5	1.0	2.0	0.12	3.34	21.25	234.8
5.	21.1	0.0	2.0	0.12	4.035	17.596	285.14
6.	21.1	0.5	2.0	0.12	1.297	54.74	91.15
7.	21.1	1.5	2.0	0.12	1.410	50.354	99.10
8.	21.1	1.0	2.0	0.12	5.73	12.39	402.74
9.	21.1	1.0	1.5	0.12	2.896	24.51	203.59
10.	21.1	1.0	2.0	0.12	5.730	12.39	402.74
11.	21.1	1.0	2.5	0.12	2.989	23.75	210.10
12.	21.1	1.0	3.0	0.12	2.238	31.72	157.3
13.	21.1	1.0	2.0	0.06	21.746	32.64	152.87
14.	21.1	1.0	2.0	0.12	5.73	12.39	402.74
15.	21.1	1.0	2.0	0.19	1.357	52.32	95.37
16.	21.1	1.0	2.0	0.25	1.0651	66.66	74.85

The polyacrylamide chains in the present hydrogel, were crosslinked with the crosslinking agent in the solution so that the macromolecules assumed the most probable extended conformations. As a result, in the dehydrated state (xerogel) the end-to-end distances is shorter and the polymer has an overwhelming tendency to become solvated. Thus, the water molecules penetrate the network through the available free volumes as shown in Figure 4. The water so absorbed in such hydrogel systems has been a subject of investigation for the last few years (30). The importance of all such studies has been to explore the possibilities of existence or non-existence of "different states" or different types of water in homogeneous mixtures of water and amorphous polymer network. It has been revealed from differential thermal analysis (DTA) and differential scanning calorimetry (DSC) measurements (31) that two states of water molecules are present in the hydrogel—(a) The water molecules close to the hydrophilic polymer chains and some way 'bound' to the polymer, and (b) free water molecules which are unbound to the network chains. The two states of water are shown in Figure 4.

Effect of Monomer on Swelling

In the present study, the effect of increasing concentration of acrylamide on the swelling behavior of hydrogel has been observed by polymerizing acrylamide in the feed mixture in an increasing concentration range from 10 mM to 28.1 mM.

The results are shown in Figure 5, which clearly show that the swelling ratio of the hydrogel initially increases with increasing AM in the 10.5 mM to 21.1 mM range,

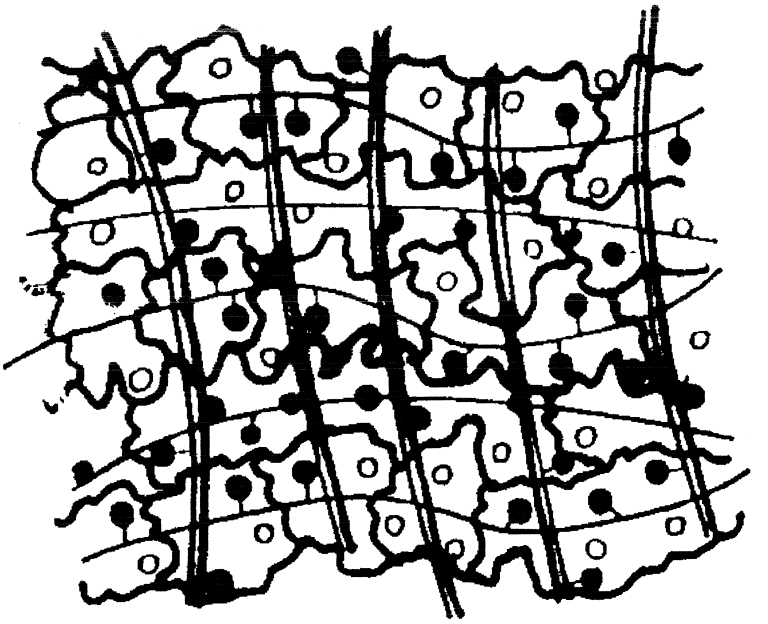

Figure 4. A model depicting the uptake of bond and unbond water molecule by the hydrogel (●) bond water, (○) unbond water, (——) PVA chains, (═══) gelatin chains and (∿∿) crosslinked AM chains.

while a fall is noticed beyond it. The initial increase in degree of water sorption may be attributed to the fact that increasing AM results in an increasing hydrophilicity of the network, which obviously results in a greater swelling ratio. However, beyond a definite concentration of AM (21.1 mM) the decrease noticed in the swelling ratio may be due to the fact that with an increased number of PAM chains in the hydrogel the network become quite compact and thus, the mobility of macromolecular chains become restrained and this obviously brings about a decrease in the swelling ratio.

The fall in swelling ratio can also be interpreted by the fact that with increasing hydrophilic segments in IPN, the polymer volume fraction decreases which reduces the mesh sizes of the free volumes. The mesh size characterizes the space between the macromolecular chains. Obviously, a decrease in mesh size prevents the entrance of water molecules into the polymer network. Similar types of results have been largely published in the literature (32).

Effect of PVA Variation

In the present investigation, the influence of PVA content in the hydrogel on its swelling ratio has been studied by varying the PVA concentration in the 1.5 to 3.0 g range. The results are shown in Figure 6, which clearly depict that the swelling ratio initially increases up to 2.0 g of added PVA, while a fall in a degree of water sorption is noticed beyond it. The observed results may be explained by the fact that an increase in PVA results in increased hydrophilicity of the gel which obviously enhances the degree of water sorption. However, beyond 2.0 g of PVA, the observed decrease in the swelling ratio may be attributed to the reason that the addition of more PVA decreases the mesh

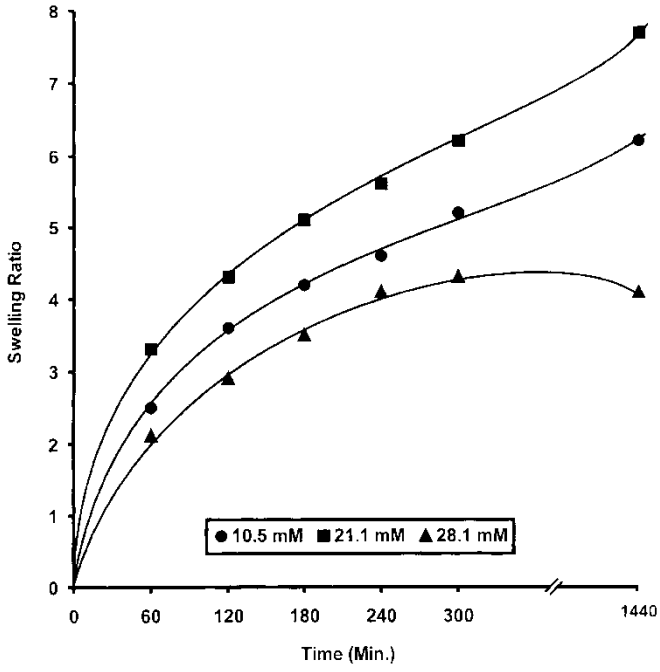

Figure 5. Effect of varying concentrations of monomer (acrylamide) content in the blend hydrogel on the swelling ratio of the hydrogel at fixed composition of [PVA] = 2.0 g, [Gelatin] = 1.0 g, [MBA] = 0.12 mM, [KPS] = 0.36 mM, [MBS] = 4.04 mM, Temp. = 25 ± 0.2°C.

size of the networks available for accommodation of water molecules and, as a consequence, the swelling ratio decreases. Similar types of results have also been reported in the literature (33).

Effect of Gelatin

Gelatin is a hydrophilic and biodegradable component of the hydrogel and has been found to exert an appreciable influence on the water sorption characteristics of the hydrogel. In the present study, the influence of the gel has been examined by adding gelatin in the 0.5 to 1.5 g range. The results are shown in Figure 7, which clearly shows that the swelling ratio initially increases up to 1.0 g of gelatin, while beyond it a decrease in swelling ratio is noticed. The observed increase in the initial concentration range may be attributed to the hydrophilic nature of gelatin molecules along which a large number of functional groups like $-COOH$, $-NH_2$, etc. are present. Water molecules are attached to these functional groups and thus, the swelling ratio increases. It is also worth mentioning here that because of the polyelectrolyte nature of gelatin, the charged centers along the gelatin molecules repel each other thus producing a loose network, which facilitates the entrance of water molecules into the hydrogel. All these reasons reveal an increased swelling of the network. However, the decrease in the swelling ratio observed beyond 1.0 g of gelatin may be attributed to the increased volume fraction of the polymer in the hydrogel, which results in a reduction in accessible free volume available within the hydrogel network. This clearly lowers the swelling ratio of the hydrogel.

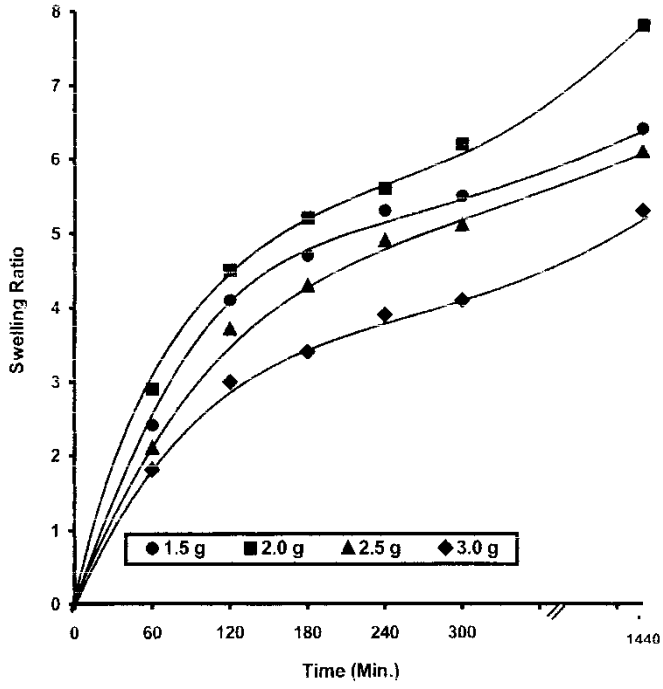

Figure 6. Effect of varying concentrations of PVA on the swelling ratio of the hydrogel at fixed composition of [AM] = 21.1 mM, [Gelatin] = 1.0 g, [MBA] = 0.12 mM, [KPS] = 0.36 mM, [MBS] = 4.0 mM, Temp. = 25 ± 0.2°C.

Effect of Crosslinking Density

N,N′-methylene bis-acrylamide (MBA), employed as a crosslinker in the present study, exerts a greater impact on the swelling characteristics of the hydrogel. In order to investigate the effect of the crosslinking agent on the swelling ratio, varying amounts of MBA ranging from 0.06 mM to 0.25 mM were added while preparing different samples of the gel. The results are depicted in Figure 8, which clearly shows that up to a definite concentration of MBA, i.e. 0.12 mM, the prepared hydrogel exhibits an increased swelling ratio while beyond this amount of MBA hydrogel shows a decreased swelling ratio. The observed initial rise in the swelling ratio may be attributed to the fact that MBA is itself a difunctional but hydrophilic monomer and its incorporation in the hydrogel results in an increase in the swelling ratio. However, at higher MBA concentrations, a fall is noticed.

The reason for the observed decrease in swelling ratio is quite expected as increasing the crosslinker makes the hydrogel more and more compact, and as a consequence, the water permeation becomes increasingly difficult. As shown in Table 1, the increasing amount of MBA decreases the value of M_c, i.e., molecular mass between the crosslinks, which obviously reduces the mesh size of the free volumes accessible to the water molecules and, therefore, the swelling ratio decreases. Similar type of results have also been reported elsewhere (34). Some workers have reported an increase in the glass transition temperature (T_g) of the polymer with increasing crosslinking density and thus glassy

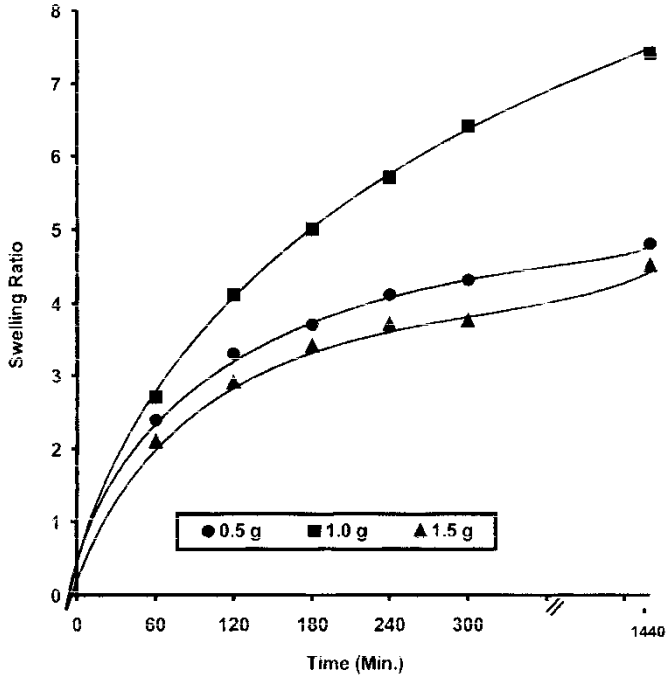

Figure 7. Effect of varying amount of gelatin content in the hydrogels on their swelling ratio at fixed composition of [AM] = 21.1 mM, [PVA] = 2.0 g, [MBA] = 0.12 mM, [KPS] = 0.36 mM, [MBS] = 4.04 mM, Temp. = 25 ± 0.2°C.

nature of the matrix does not permit loosening of the macromolecular chains, which results in lower water sorption (35).

Effect of pH

Swelling characteristics of an IPN can be modulated by changing the pH of the swelling medium. This great significant property facilitates hydrogels to function desirably in various working pH media and helps in targeted drug delivery. In the present investigation, the effect of pH has been investigated on water sorption characteristics of the hydrogel in the pH range 1.8 to 11.6, i.e., strong acidic to strong basic medium. The results are depicted in Figure 9, which clearly indicate that initially as the acidity lowers, the value of equilibrium swelling ratio decreases. It again tends to increase through basic medium and become optimum at pH 10.4 and thereafter, in highly basic medium again the swelling ratio falls. The results may be explained as below:

(i) When pH is very low (1.8), because of an excess of H^+ ions in the solution, the amino groups of gelatin molecule get protonated (NH_3^+) and cause repulsion among gelatin chains. This obviously results in a loosening of the network that creates wide pore sizes in the network and, as a consequence, degree of water sorption is high. However, beyond pH 1.8 as the concentration of H^+ ions goes on decreasing, the extent of repulsion among gelatin network chains also decreases, thus resulting in a decrease in the swelling ratio

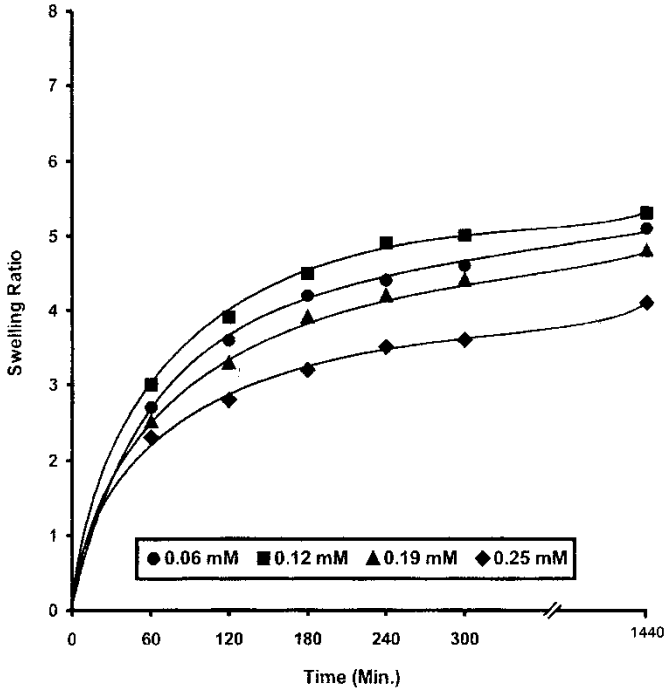

Figure 8. Effect of varying concentration of crosslinker (MBA) on the swelling ratio of the hydrogel at fixed composition of [AM] = 21.1 mM, [PVA] = 2.0 g, [Gelatin] = 1.0 g, [KPS] = 0.36 mM, [MBS] = 4.04 mM, Temp. = 25 ± 0.2°C.

(ii) However, at a pH of 3.4, the swelling ratio becomes minimum, which may be attributed to the reason that at pH 3.4, which is near to the isoelectric point of gelatin, the macromolecular chains of gelatin become neutral charged and acquire a compact configuration. Thus, the swelling becomes minimum

(iii) However, beyond pH 3.4, the gelatin chains become negatively charged due to deprotonation of carboxyl groups, which again produces repulsion among gelatin chains. This results in an increasing swelling which continues up to pH 10.4. Beyond pH 10.4, the hydrogel become so swollen that it tends to erode and, consequently, the swelling ratio decreases.

Effect of Temperature

In order to investigate the effect of temperature of swelling medium on the water uptake potential of hydrogel, experiments were performed at different temperatures ranging from 10 to 50°C. The results shown in Figure 10, which clearly indicate that the swelling ratio increases with increase in temperature of the swelling bath.

The results can be explained on the basis of the fact that at a higher temperature (higher than room temperature 25 ± 0.2°C), the segmental mobility of hydrogel chains increases effectively so the water sorption capacity of hydrogel increases. As depicted in the figure at a considerable high temperature, the equilbrium swelling ratio falls because the hydrogel chain must have acquired complete relaxation so that with a

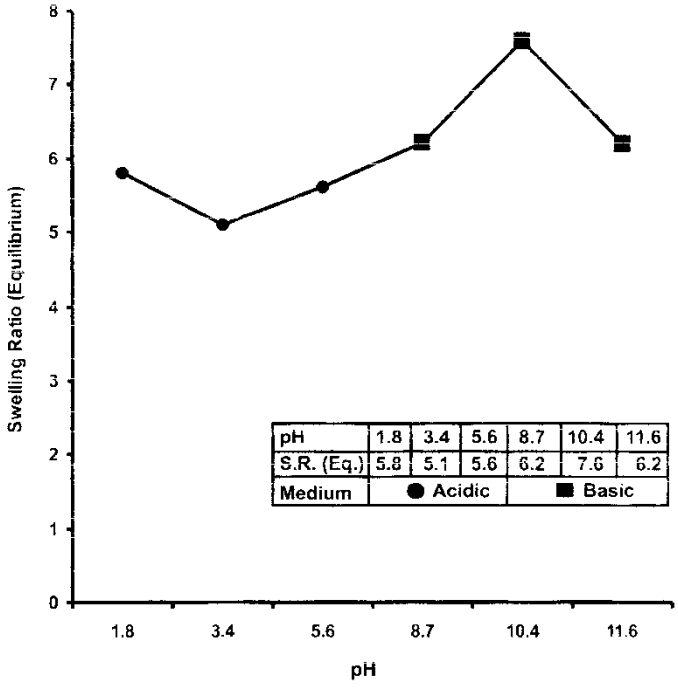

Figure 9. Effect of pH of the swelling both on the swelling ratio of the hydrogel at a definite composition of [AM] = 21.1 mM, [PVA] = 2.0 g [Gelatin] = 1.0 g, [MBA] = 0.12 mM, [KPS] = 0.36 mM, [MBS] = 4.04 mM, Temp. = 25 ± 0.2°C.

further increase in temperature the water molecules bound to hydrogel chains via hydrogen bends get broken and there is a fall in the water uptake capacity of the hydrogel.

Gibbs-Helmholtz equation can also be applied to calculate the value of ΔH_m, i.e., enthalpy of mixing. The Gibbs-Helmholtz equation is:

$$\frac{d \ln(W_\infty)}{d(1/T)} = -\Delta H_m/R \tag{7}$$

where R is the gas constant and ΔH_m is the enthalpy of mixing between the dry polymer and an infinite amount of water. When W_∞ is plotted against the reciprocal of swelling temperature $(1/T)$, a straight line with a negative slope is obtained (not shown here) which implies an endothermic process. The value of ΔH_m was calculated to be $-0.24\,kJ/mol$.

Electrolyte Effect

Theoretical (36) as well as experimental (37) considerations have established that a balance between the osmotic pressure and the polymer elasticity sets the physical dimensions of hydrogels. The osmotic pressure results from a net difference in concentrations of mobile ions between the interior of the gel and the exterior solution. Increasing the ionic concentration in bathing medium reduces the mobile ion concentration difference between the polymer gel and the external solutions (osmotic swelling pressure) and hence, the gel

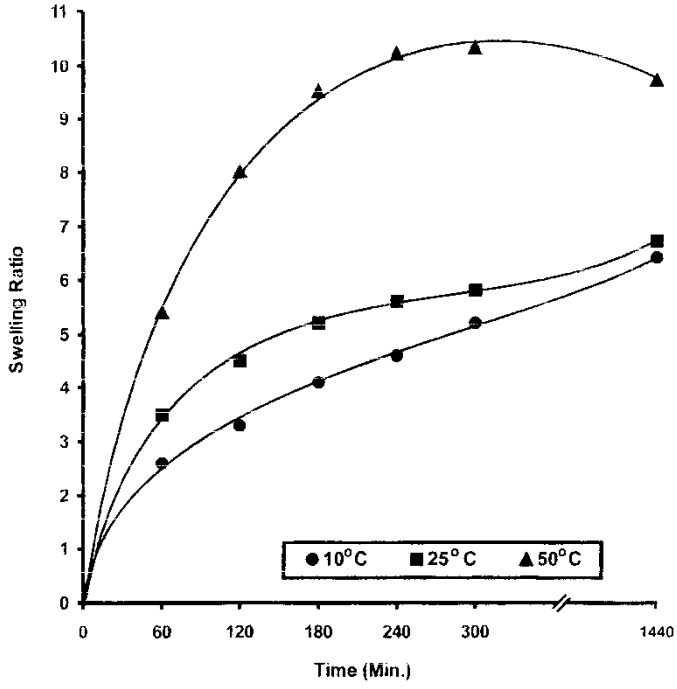

Figure 10. Effect of temperature of the swelling medium on the swelling ratio of the hydrogel for a definite composition of [AM] = 21.1 mM, (PVA) = 2.0 g [Gelatin] = 1.0 g, [MBA] = 0.12 mM, [KPS] = 0.36 mM, [MBS] = 4.04 mM, Temp. = 25 ± 0.2°C.

volume is reduced, i.e., the gel shrinks. Although there are various theories and models which can predict the equilibrium swelling response of hydrogels to change in ionic strength, however, the Donan membrane equilibrium theory can well interpret the results. According to this theory, when a gel is placed in contact of a liquid the solvent chemical potential μ, in both the gel and the solution phase, must be equal at equilibrium.

$$\Delta\mu_{\perp}^{g} = \Delta\mu_{\perp}^{s} \tag{8}$$

where the subscripts g and s represent the gel and the solution phase, respectively.

In terms of osmotic pressure, π, Equation (8) can be written as:

$$\pi = \frac{-(\Delta\mu_1^g - \Delta\mu_1^s)}{V_1} = 0 \tag{9}$$

where V_1 is the molar volume of the solvent. Osmotic pressure π of the gel determines whether the gel will expand or shrink. In the case of an ionic system, the osmotic pressure is mainly contributed by π ions which is caused by the counter ion difference between the gel and the outer solution. Now, avoiding ion-ion, ion-solvent and ion-polymer interaction, we can write the above Equation (9) as:

$$\pi_{ion} = R\ T\ \sum_i (C_i^g - C_j^s) \tag{10}$$

where C_i is the mobile ion concentration of species i and the superscripts 'g' and 's' represent gel and solution phases, respectively. The above equation implies clearly that

the greater the difference between the concentration of mobile ions inside and outside of the gel, the greater would be the osmotic pressure and larger would be the swelling of the hydrogel.

In the present investigation, the relative effects of added anions on the degree of water sorption have been investigated by adding sodium salts of Cl^-, SO_4^{2-} and PO_4^{3-} ions into the release system at equimolar concentration (0.1 M). The results are shown in Figure 11, which indicate that the addition of salts brings about a fall in the swelling ratio which is quite obvious and may be explained with the help of (Equation (10)). The relative order of effectiveness of added anions in suppressing the swelling ratio obey the following sequence

$$Cl^- < SO_4^{2-} < PO_4^{3-}$$

The observed order of effectiveness may be explained on the basis of the fact that due to a smaller size, some of the added Cl^- ions diffuse into the network and enhance the ionic concentration (C_i^g). This obviously tends to increase the swelling ratio. However, at the same time because of a significant increase in ionic concentration the osmotic pressure (π_{ion}) decreases and consequently the swelling ratio will be low. Thus, the combined effect of the above two explanations would result in a slight fall in the swelling ratio of the IPN. On the other hand, in the case of SO_4^{2-} and PO_4^{3-} ions because of comparatively bigger sizes, the diffusion of these two ions into the IPN is less likely and, therefore, the swelling will be low.

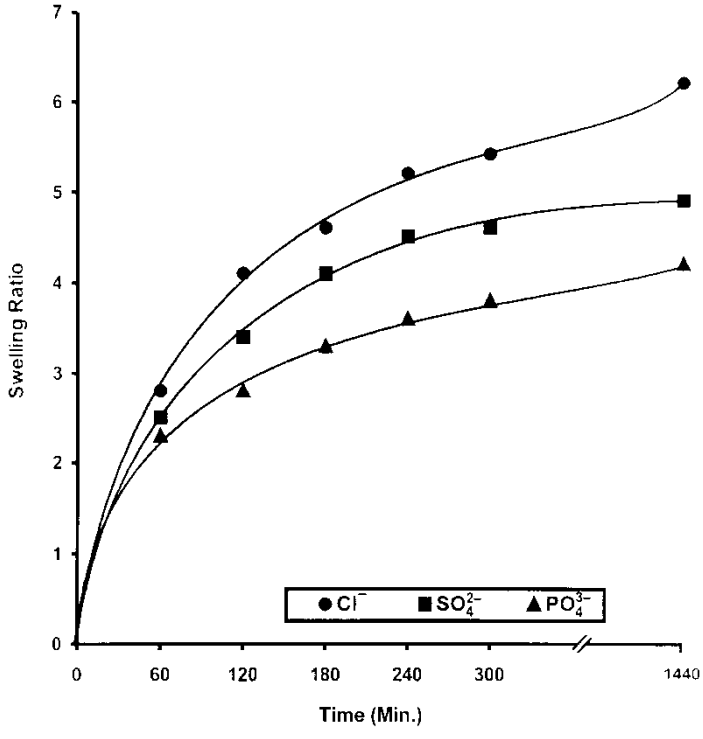

Figure 11. Effect of addition of anions of sodium on the swelling ratio of the hydrogel for a definite composition of [AM] = 21.1 mM, [PVA] = 2.0 g [Gelatin] = 1.0 g, [MBA] = 0.12 mM, [KPS] = 0.36 mM, [MBS] = 4.04 mM, Temp. = 25 ± 0.2°C.

Kinetic Analysis of Sorption Data

The dynamics of the water sorption process is basically a collaborative contribution of several factors like hydrophilicity of the hydrogel, morphology of the network, relative ease of diffusion of penetrant water molecules, and relaxation of polymeric chains, volume fractions of polymers, network's structural parameter, etc. Fick's Equation (2) gives an insight into the transport of water molecules within the hydrogel and determines the type of mechanisms of the swelling process. The values of swelling exponent 'n' for hydrogels of varying compositions are summarized in Table 2. It is very clear from the data that 'n' is almost or near to 0.5 for all composition and, therefore suggests a diffusion controlled (or Fickian) swelling mechanisms. The possible reason for such an unusual tendency may be due to the reason that the crosslink density (q) for almost all the composition is quite greater (Table 1) and this results in a gel with smaller pore sizes. This obviously slows down the diffusion if water molecule into the hydrogel and thus yields a diffusion-controlled swelling process.

Conclusions

Grafted copolymerization of acrylamide (AM) and *N,N′*-methylene bis acrylamide (MBA) on to polyvinyl alcohol (PVA) and gelatin (GEL) together results in a hydrophilic matrix that could be considered as a polymeric blend of PVA and GEL chains each grafted with copolymeric chains of AM and MBA.

The infra red spectral characterization of the blend hydrogel confirms the presence of PVA, GEL and PAM (polyacrylamide) in the blend. The DSC thermogram of the resulting

Table 2
Date showing the swelling exponent 'n' and diffusion constant 'D' at various compositions of hydrogel

S. no.	AM (mM)	PVA (g)	Gel (g)	MBA (nM)	n	DØ10^6 $cm^2\,sec^{-1}$	Mechanism
1.	14.0	1.0	2.0	0.12	0.56	9.6	Fickian
2.	21.1	1.0	2.0	0.12	0.46	12.1	Fickian
3.	28.1	1.0	2.0	0.12	0.50	10.4	Fickian
4.	10.5	1.0	2.0	0.12	0.50	21.9	Fickian
5.	21.1	0.0	2.0	0.12	0.45	11.2	Fickian
6.	21.1	0.5	2.0	0.12	0.43	17.4	Fickian
7.	21.1	1.5	2.0	0.12	0.46	11.6	Fickian
8.	21.1	1.0	2.0	0.12	0.46	12.0	Fickian
9.	21.1	1.0	1.5	0.12	0.26	16.1	Less Fickian
10.	21.1	1.0	2.0	0.12	0.46	12.1	Fickian
11.	21.1	1.0	2.5	0.12	0.37	15.3	Fickian
12.	21.1	1.0	3.0	0.12	0.27	14.8	Less Fickian
13.	21.1	1.0	2.0	0.06	0.40	18.4	Fickian
14.	21.1	1.0	2.0	0.12	0.46	12.1	Fickian
15.	21.1	1.0	2.0	0.19	0.34	15.8	Less Fickian
16.	21.1	1.0	2.0	0.25	0.28	20.4	Less Fickian

blend presents combined features of PVA, GEL and PAM. Moreover, interpenetrating nature of polymeric chains results in an enhanced glass transition temperature of gelatin. The SEM image of the hydrogel confirms a porous morphology of the end polymer.

The water sorption capacity of the blend hydrogel is mainly determined by the chemical architecture of the gel. When the concentrations of PVA, GEL, AM and MBA are varied in the studied range, it is found that up to a certain concentration the swelling ratio increases while beyond it, a fall in degree of water sorption is noticed.

The hydrogel, due to the polyelectrolyte nature of gelatin, shows a modulating water sorption with varying pH of the swelling medium. It is found that in both highly acidic and highly alkaline media, the swelling decreases, while from moderately acidic to a moderately alkaline range, the swelling ratio of the hydrogel constantly increases. The blend hydrogel shows an enhanced water sorption at high temperature while a fall in swelling ratio is noticed when salts such as NaCl, Na_2SO_4 and Na_3PO_4 are present in the aqueous swelling medium.

The kinetic analysis of water sorption data confirms a Fickian, i.e., diffusion controlled water transport mechanism in almost the hydrogel compositions.

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References

1. Tokita, M. and Tanaka, T. (1991) Friction coefficient of polymer network of gels. *J. Chem. Phys.*, 95: 4613.
2. Laporte, R.J. (1997) *Hydrophilic Polymeric Coating for Medical Devices*; Technomic Publishing Company, Inc.: Lancaster, PA.
3. Kaijwara, K. and Rossmurphy, S.B. (1992) Synthetic gels on the move. *Nature*, 355: 208.
4. Jeyanthi, R. and Rao, K.P. (1990) *In vivo* biocompatibility of collagen poly(hydroxy ethyl, methylacrylate) hydrogels. *Biomaterials*, 11: 288.
5. Williams, D.F. *Concise Encyclopedia of Medical and Dental Materials*; Pergamon Press: Oxford, England (1999).
6. Vasir, J.K., Tambwekar, K., and Garg, S. (2003) Bioadhesive microspheres as control drug delivery system. *International Journal of Pharmaceutics*, 255 (1–2): 13.
7. Changez, M., Burugapalli, K., Koul, V., and Chowdary, V. (2003) The effect of composition of poly(acrylic acid)-gelatin hydrogel on gentamicin sulphate release: *in vivo*. *Biomaterials*, 24 (4): 527.
8. Sinha, V.R. and Kumaria, R. (2001) Polysaccharides in colon specific drug delivery. *International Journal of Pharmaceutics*, 224 (1–2): 19.
9. Rosiak, J.M., Ulanski, R., Pajwaski, L.A., Yoshida, F., and Makuuchi, K. (1995) Radiation formation of hydrogels for biomedical purposes, some remarks and comments. *Radiation in Physics, II Chemistry*, 46 (2): 161–168.
10. Paul, W. and Sharma, C.P. (1995) Polyacrylonitrile-reinforced poly(vinyl alcohol) membranes, mechanical and dialysis performance. *J. Appl. Poly. Sci.*, 57 (12): 1447.
11. Bajpai, A.K. and Giri, A. (2002) Swelling Dynamics of a ternary interpenetrating polymer network (IPN) and control release of potassium nitrate as model agrochemical. *J. Macro. Sci.-Pure & Appl. Chem.*, A39: 75.
12. Kim, S.J., Park, S.J., and Kim, S.I. (2003) Swelling behavior of interpenetrating network hydogels composed of poly(vinyl alcohol) and chitosan. *Reac. Funct. Anal.*, 55: 53.

13. Ruiz, J., Mantecon, A., and Cadiz, V. (2003) Investigation of loading and release of PVA-based hydrogels. *J. Appl. Poly. Sci.*, 85 (8): 1644.
14. Ruiz, J., Mantecon, A., and Cadiz, V. (2003) Network characterization and swelling behavior of chemical hydrogel based on acid containing poly(vinyl alcohol). *J. Appl. Poly. Sci.*, 88: 3026.
15. Hyon, S.H., Cha, W.I., Ikada, Y., Kita, M., Ogura, Y., and Honda, Y. (1994) Poly(vinyl alcohol) hydrogels as soft contact lense. *Biomaterials*, 5: 397.
16. Kobayashi, M., Toguchida, J., and Oka, M. (2003) Primary study of polyvinyl alcohol hydrogel (PVA-H) artificial meniscus. *Biomaterials*, 24: 639.
17. Peppas, N.A. and Benner, R.E., Jr. (1980) Proposed method of intracopdal injection and gelatin of poly(vinyl alcohol) solution in vocal chords: consideration. *Biomaterials*, 1: 158.
18. Okino, H., Nakayama, U., Tanaka, M., and Mastuda, M. (2002) *In situ* hydrogelation of photocurable gelatin and drug release. *J. Biomed. Rea.*, 59: 233.
19. Bajpai, A.K. and Giri, A. (2003) Water sorption behavior of highly swelling (carboxy methyl cellulose-g-polyacrylamide) hydrogel and release of potassium nitrate as agrochemical. *Carbohydrate Poly*, 53: 271.
20. Bajpai, A.K. and Shrivastava, M. (2002) Dynamic swelling behavior of polyacrylamide based three component hydrogel. *J. Macromol. Sci., Pure & Appl. Chem.*, 37 (9): 1069.
21. Guddeman, L.F. and Peppas, N.A. (1995) Preparation and characterization of pH sensitive interpenetrating network of poly(vinyl alcohol) and poly(acrylic acid). *J. Appl. Poly. Sci.*, 55: 918–919.
22. Vazquez, A. and Roman, J.S. (1997) Polymeric hydrophilic hydrogels with flexible hydrophobic chains, control of the hydration and interaction with water molecules. *Macromolecules*, 30: 8440.
23. Wang, C., Li, Y., and Hu, Z. (1997) Swelling kinetics of polymer gels. *Macromolecules*, 30: 4727–4732.
24. Bajpai, A.K. and Giri, A. (2002) Swelling dynamics of a macromolecular hydrophilic network and evaluation of its potential for control release of agro chemicals. *Rea. Funct. Analy.*, 53: 129.
25. Fraga, Roberts A.N., and Williams, R.J. (1985) Thermal properties of gelatin film. *Polymer*, 26: 113.
26. Ding, Z.Y., Akinbis, J.J., and Saloger, R. (1991) Model filled polymers VI, determination of crosslinked density of polymeric beads by swelling. *J. Poly. Sc. Poly. Phy. (Part-B)*, 29: 1035.
27. Kabra, B.G., Gehrke, S.H., Hwang, S.T., and Ritschel, W.A. (1991) Modification of the dynamic swelling behavior of poly(2-hydroxy ethyl methacrylate) in water. *J. Appl. Poly. Sci.*, 42: 2409–2416.
28. Rosiak, J., Burczak, K., Czolzyanoka, T., and Pakela, N. (1983) Radiation crosslinked hydrogels from acrylamide water solution. *Radiation in Physics Chemistry*, 22: 917.
29. Hooper, H.H., Baker, J.P., Blanch, H.W., and Prausnitz, J.M. (1990) Swelling equilibria for positively ionized polyacrylamide hydrogels. *Macromolecules*, 23: 1096.
30. Frisch, K.C. and Klempner, D. (1988) Recent development in polyurethane and interpenetrating polymer network. Technomics: Lancaster, PA.
31. Plathe, F.M. (1998) Different states of water in hydrogels. *Macromolecules*, 13: 6721.
32. Firestone, B.A. and Siegel, R.A. (1991) Kinetics and mechanism of water sorption in hydrophobic ionizable copolymeric hydrogels. *J. Appl. Poly. Sci.*, 43: 901.
33. Bajpai, R., Bajpai, A.K., and Shukla, S. (2001) Water sorption through a semi interpenetrating polymer network (IPN) with hydrophilic and hydrophobic chains. *React. and Funct. Polymer*, 50: 16.
34. Shukla, S., Bajpai, A.K., and Bajpai, J. (2003) Swelling control delivery of antibiotics from hydrophilic macromolecular matrix with hydrophobic moieties. *J. Macro. Res.*, 11 (4): 373.
35. Ramraj, A. and Radhakrishnan, G. (1994) Modifications of the dynamic swelling behavior of poly(2-hydroxyl methacrylate) hydrogels in water through interpenetrating network (IPNs). *Polymer*, 35: 2167.
36. Flory, P.J. (1953) *Principles of Polymer Chemistry*. Cornell University Press: Ithaca, N.Y.
37. Flory, P.J. (1996) *Proc. R. Soc. London, Ser*, A1: 391.