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Effect of Crosslinking on swelling behaviour of IPN hydrogels of Guar Gum & Polyacrylamide

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ABSTRACT

An IPN system comprising of guar gum and polyacrylamide has been made in aqueous medium. Polymerization of acrylamide has been achieved in the presence of guar gum using potassium persulphate as initiator. One set of gels has been made with *N,N'*-methylene-bis-acrylamide (MBA) as the crosslinking agent and another with MBA and Gluteraldehyde(GA) as crosslinking agents. The effect of using single and two crosslinking agents on the gel structure has been evaluated by studying the swelling behaviour of gels made with different amounts of crosslinking agents. The gels crosslinked with MBA alone exhibited 3-5 times higher swelling when compared to the gels with 2 crosslinkers. The kinetics of swelling has been studied and the swelling parameters have been evaluated.

Key words: Guar Gum, polyacrylamide, Gluteraldehyde, *N,N'*-methylene-bis-acrylamide , IPN, swelling.

INTRODUCTION

Hydrogels that exhibit swelling changes in response to environmental changes such as temperature, pH, electrical field, radiation etc. are promising as intelligent materials. They attract increasing interest in various biomedical, industrial and agricultural applications [1-12]. The swelling characteristics of the gel are of utmost importance in most of these applications which can be greatly controlled by the chemical structure of the gels. [13-15].

Guar gum is a high molecular weight hydrocolloidal hetero-polysaccharide composed of galactan and mannan units. Guar gum has been modified by derivatization, grafting and network formation to improve its property profile for a wide spectrum of end-uses[16]. Using different initiating systems grafting of methacrylamide[17], acrylonitrile[18], acrylic acid [19, 20] and acrylamide [21] onto guar gum has been reported. Grafting of acrylamide onto guar gum has been achieved using high-energy Co ⁶⁰ γ -radiation. Grafting is observed to enhance the flocculating properties of guar gum for treatment of industrial effluents [22, 23].

Polyacrylamide is a water-soluble polymer with a hydrophobic main chain and a hydrophilic side group. Polyacrylamide is a well known hydrogel, whose swelling nature is not very sensitive to pH or to the presence of electrolytes. The advantage of amide functional groups is that, it can be used to introduce the required ionic functionalities in the gel [24]. In the present work we have attempted to make a network polymer consisting of guar gum and polyacrylamide, by carrying out polymerization of acrylamide in the presence of guar gum in aqueous medium using KPS as initiator and two different crosslinking agents, MBA and GA. The effect of the nature and concentration of the crosslinking agents on swelling behaviour of the gels has been evaluated.

MATERIALS AND METHODS

2.1. Materials and methods

Acrylamide(AAm) and N,N'-methylene-bis-acrylamide(MBA) were obtained from s.d.fine chemicals, Mumbai, India. Guar gum(GG) and potassium persulfate(KPS) were obtained from Merck, Mumbai, India. Gluteraldehyde(GA) (25% w/v) was obtained from Lobo chemicals, Mumbai, India. Acrylamide was purified by recrystallisation from chloroform before use. All other reagents were of analytical grade and used as received. Double distilled water was used in the preparation of hydrogels and for swelling studies.

2.2. Preparation of Buffer solutions :

A solution containing 0.05M KCl and 0.085M HCl was made to obtain a buffer solution of pH-1.2 and a 2% solution of disodium hydrogen phosphate was made to obtain buffer solution of pH 9.

2.3. Synthesis of guar gum-poly (acrylamide) network polymer (GG-PAAm-1)using MBA

The gels containing AAm and GG were prepared by free radical polymerization. Briefly, 0.04g of GG was dispersed in 2.5mL water and stirred overnight. 0.2g AAm and 0.008g KPS were dissolved in 1mL water and the mixture was added to the GG solution and stirred well. MBA solutions were made by dissolving different amounts of MBA(0.04-0.13mmol) in 1mL water and was added to above solution and mixed well. Polymerization was carried out at 60⁰C for 3hrs. The gel obtained was purified by washing with boiling water in a soxhlet extractor. The purified gel was dried at 40⁰C under vacuum (60mm Hg) overnight.

2.4. Synthesis of guar gum-poly (acrylamide) network polymer (GG-PAAm-2)using MBA and GA.

Solutions were made by dissolving 0.008g MBA and different amounts of GA (25%)(0.11-0.55 mmol) were dissolved in 1mL water. Each of these mixtures were added in separate set of experiments, to the AAm-GG solutions containing KPS in the same ratio as mentioned in the previous experiment. Polymerization and purification steps were carried out as stated earlier. The conditions of preparation and the designation of the gels have been summarised in Table 1.

2.5. Characterization of GG-PAAm-1 & GG-PAAm-2

FTIR Analysis

The FTIR spectra of GG and the representative samples, AG-2 and AGG-3 were recorded as KBr pellets on a FTIR spectrophotometer (Perkin-Elmer, USA).

Thermal Analysis

DSC thermograms of AG-2 and AGG-3 were recorded on Q20 V24.4 Build 116 Calorimeter(USA) by heating the samples under nitrogen atmosphere from 30 to 500⁰C at a rate of 10⁰C / minute.

Scanning Electron Microscopic (SEM) Analysis

The micrographs of AG-2 & AGG-3 samples were recorded on a JEOL-JSM 5800LV scanning electron microscope. The micrographs were recorded with magnifications of 500 and 1000 under a voltage of 20kV.

2.6. Swelling studies

The swelling behaviour of the hydrogels under different pH conditions was investigated by carrying out swelling measurements in aqueous buffer media of pH-1.2, 6.7 and 9.0 using distilled water and standard buffer solutions, at 30⁰C. The weight measurements were made using an electronic balance (Shimadza AUX120, Japan) with an accuracy of ±0.1mg. Pre-weighed dry hydrogels were immersed in excess of the buffer solution, maintained at 30⁰C. After specific intervals of the time, the gels were removed from the medium, the surface adhered liquid drops were wiped with blotting paper and the increase in weight was measured. The measurements were continued till the weights of the swollen gels attained constant values. The swelling ratio (%SR) and the amount of water gel can hold at equilibrium (percent equilibrium water content) (%EWC) were calculated [24], using the following expressions,

$$\% \text{ SR} = \frac{\text{Weight of the swollen gel} - \text{Weight of the dry gel}}{\text{weight of the dry gel}} \times 100 \quad (1)$$

$$\% \text{ EWC} = \frac{\text{Weight of the gel at equilibrium} - \text{Weight of the dry gel}}{\text{Weight of the gel at equilibrium}} \times 100 \quad (2)$$

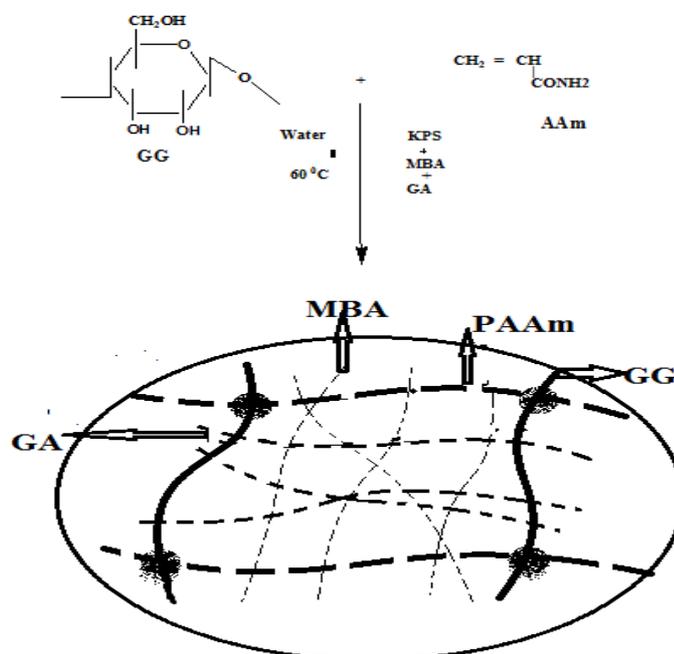
Table 1. Details of preparation and designation of GG-PAAm IPN gels

Formulation code	GG (g)	AAm (g)	MBA (g)	KPS (g)	GA (g)	Reaction Time(hrs)	
GG-PAAm-1	AG-1	0.04	0.2	0.006	0.008	--	3
	AG-2	0.04	0.2	0.008	0.008	--	3
	AG-3	0.04	0.2	0.013	0.008	--	3
	AG-4	0.04	0.2	0.020	0.008	--	3
GG-PAAm-2	AGG-1	0.04	0.2	0.008	0.008	0.04	3
	AGG-2	0.04	0.2	0.008	0.008	0.10	3
	AGG-3	0.04	0.2	0.008	0.008	0.15	3
	AGG-4	0.04	0.2	0.008	0.008	0.20	3

RESULTS AND DISCUSSION

Eight gel samples have been made in the present study by maintaining a fixed concentration of GG, AAm and $\text{K}_2\text{S}_2\text{O}_8$ in the reaction mixture and varying the concentrations MBA and GA. When MBA is the sole crosslinking agent, semi IPN networks are expected to be formed. The Polyacrylamide chains entangled between the GG chains are linked by MBA units. These gels possess appreciable hydrophilic character due to the presence of long PAAm chains and the MBA units. On the other hand, when GA is used along with MBA, a fully interpenetrating network is formed, in which the GG units of different chains are linked by glutaraldehyde and the acrylamide units by MBA. The doubly crosslinked IPN is expected to show more rigidity when compared to the semi IPN system as the chains are held more tightly. The hydrophobic nature of these gels may get enhanced due to the involvement of free -OH groups in crosslinking reaction with glutaraldehyde and that represented in scheme 1.

Scheme 1 : The schematics of the synthesis of Guar gum IPN hydrogels of Guar Gum & Polyacrylamide.



3.1. FTIR characterization of GG-PAAm-1 and GG-PAAm-2

The peaks in the FTIR spectrum of AG-2 & AGG-3 networks have been compared with that of GG (Fig 1a). In the spectra of AGG-3 network (Fig 1b), the broad peak observed at 3217.2 cm^{-1} is due to O-H stretching and other important peaks observed at 1156.5 , 1093.9 , 1020.2 cm^{-1} are attributed to C-O-C stretching from glycosidic linkages and O-H bending of GG component. In addition, the FTIR spectrum of AGG-3 shows peaks corresponding to amide groups. The N-H stretching appears as a shoulder band around 3400 cm^{-1} and has overlapped with a broad peak between 3500 to 3200 cm^{-1} of the hydroxyl group. The sharp peak at 2964.4 cm^{-1} is due to C-H stretching. In AG-2 network (Fig.1c) peak due to O-H groups has been reduced in height, in comparison

with the GG sample, on account of their involvement in crosslinking reactions. The peaks which appear at 2854 and 1461.5 cm^{-1} are attributed to amide C-H stretching and bending respectively.

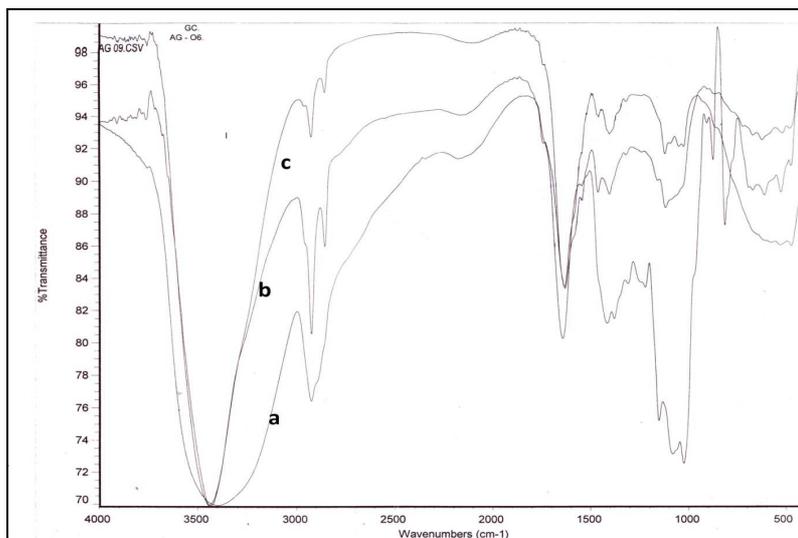


Fig 1. FTIR of (a) GG (b) GG-PAAm-2 and (c) GG-PAAm-1 network

3.2. Thermal analysis

DSC thermograms of GG-PAAm-1 and GG-PAAm-2 are shown in Fig 2. GG-PAAm-1 exhibited two endothermic peaks in the region 250–290 $^{\circ}\text{C}$ and 370–450 $^{\circ}\text{C}$. In GG-PAAm-2 only one sharp endotherm is observed around 100 $^{\circ}\text{C}$ which could be due to loss of water and the network appears to decompose and lose its structure around 300 $^{\circ}\text{C}$. No additional information could be drawn regarding network structures from DSC thermograms.

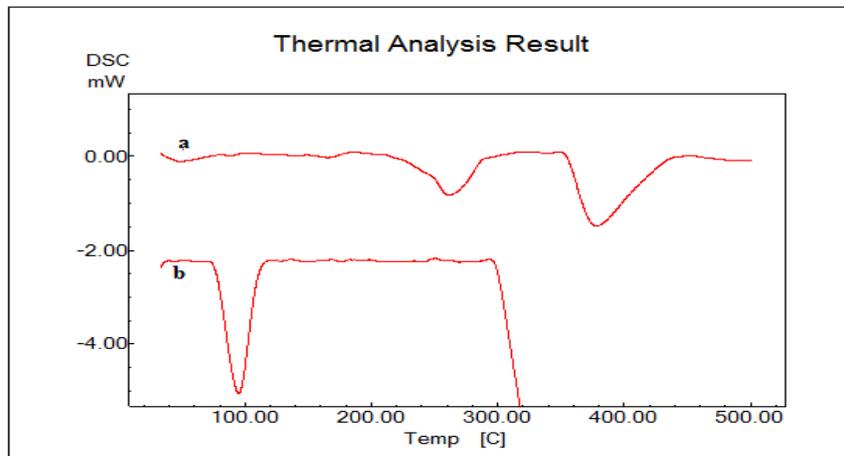


Fig 2. DSC of (a)AG-2 and (b)AGG-3 samples

3.3. Scanning Electron Microscopic (SEM) analysis

Scanning electron micrographs of crosslinked gels are presented in Fig 3. The crystalline character of GG [35] is retained in AG-2 sample, as evidenced from the micrograph in (Fig. 3a). The surface of AGG-3 smooth & rough structure indicates high bonding between components (inter and intra) –OH of GG and NH_2 of PAAm and crosslinkers (Fig. 3b).

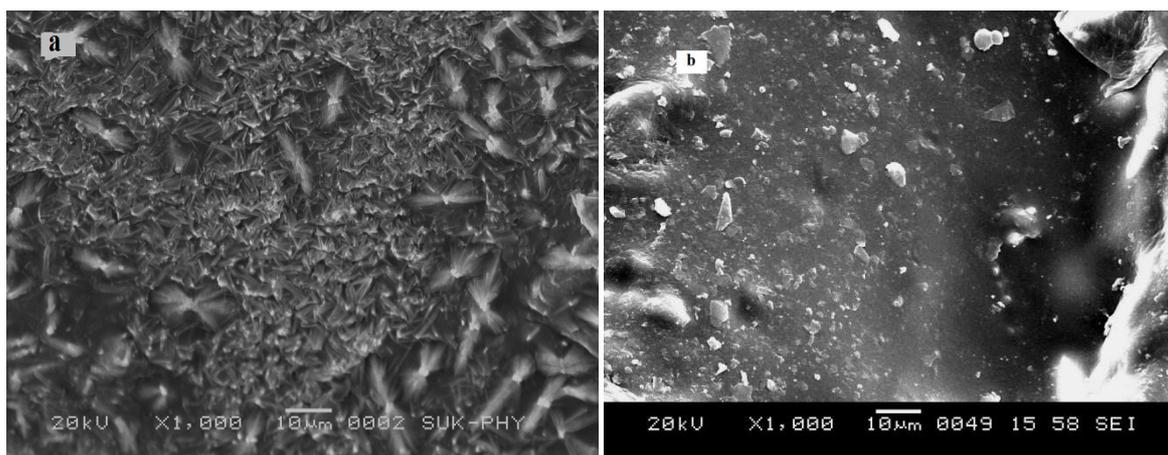


Fig 3. Scanning electron micrographs of (a)AG-2 and (b) AGG-3 samples.

Table 2. Effect of crosslinking and pH on swelling and diffusion characteristics of GG-PAAm-1 gels ; A) pH 1.2 B) pH 9.0

Gel code	AG-1		AG-2		AG-3		AG-4	
	A	B	A	B	A	B	A	B
Equilibrium Swelling ratio (g /g)	14.34	13.23	9.94	10.19	18.59	18.43	13.09	12.86
Equilibrium Water content EWC %	93.0	92.9	91.1	91.0	95.0	95.0	92.7	92.8
The initial swelling rate (Ri) [(g water / g gel)/min]	0.075	0.065	0.089	0.068	0.077	0.079	0.063	0.055
Swelling rate constant (Ks) x 10 ⁻⁴ [(g gel/ g water)/min]	3.0	3.1	7.96	5.5	1.8	1.8	3	2.7
Maximum equilibrium Swelling (S _{max})	15.77	14.50	10.51	11.11	20.78	20.53	14.56	14.3
Swelling Exponent (n)	0.60	0.53	0.50	0.50	0.51	0.52	0.54	0.55
Swelling Constant (K)	0.28	0.37	0.44	0.4	0.55	0.54	0.35	0.32

Table 3. Effect of crosslinking and pH on swelling and diffusion characteristics of GG-PAAm-2 gels ; A) pH 1.2 B) pH 9.0

Gel code	AGG-1		AGG-2		AGG-3		AGG-4	
	A	B	A	B	A	B	A	B
Equilibrium Swelling ratio (g /g)	10.3	8.8	5.3	5.2	5.0	3.0	5.3	4.0
Equilibrium Water content EWC %	91	90	83.9	83.5	82	75	84	80
The initial swelling rate (Ri) [(g water / g gel)/min]	0.11	0.11	0.17	0.18	0.24	0.23	0.18	0.16
Swelling rate constant (Ks) x 10 ⁻⁴ [(g gel/ g water)/min]	13.0	12.5	55.0	62.0	82.0	76.0	70.0	64.0
Maximum equilibrium Swelling (S _{max})	9.3	9.3	5.5	5.4	5.5	5.5	5.0	5.0
Swelling Exponent (n)	0.60	0.55	0.64	0.63	0.67	0.43	0.50	0.36
Swelling Constant (K)	0.28	0.41	0.21	0.21	0.22	0.53	0.38	0.43

3.4. Swelling and Diffusion Analysis

In the present investigation, the influence of crosslinking agent on the gel characteristics was studied by varying concentration of MBA in the range (0.04 to 0.13mmol) and GA in the range (0.11-0.55 mmol). The swelling pattern observed for the GG-PAAm-1 & GG-PAAm-2 in acidic and basic media is shown in Fig 4.

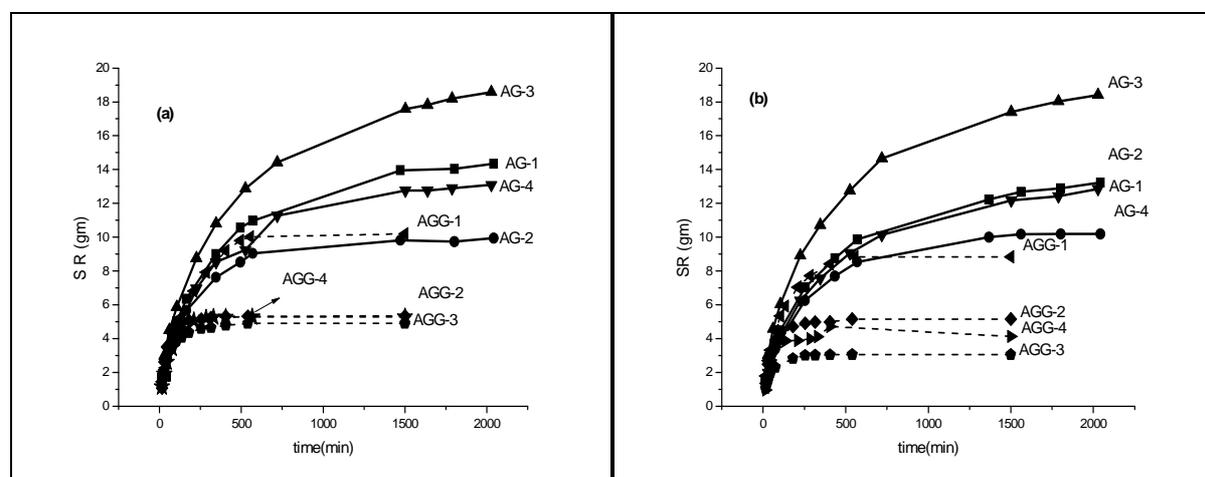


Fig 4.Swelling behaviour of GG-PAAm-1 and GG-PAAm-2 in (a) pH 1.2 & (b)pH 9.0

The gels containing only MBA (GG-PAAm-1) swell to higher extent than the doubly crosslinked GG-PAAm-2 gels under both acidic and basic conditions. The additional crosslinks introduced by GA reduced the Swelling by 50 % in the latter. Also, the singly crosslinked gels took longer time for reaching the equilibrium swelling than the doubly crosslinked gels. It is necessary to know the equilibrium water content of the hydrogels due to their enormous utility in biomedical applications. EWC of GG-PAAm gels calculated using Eq. 2 are reported in Table 2. The maximum water content in GG-PAAm-1 gels is found to be between 91-95% , much higher than the GG-PAAm-2 gels(76-91%) , due to their lightly crosslinked , hydrophilic network structure. The water content of the gel is appreciably reduced by use of two crosslinking agents. The results indicate the tightening of the chains in the IPN system by introducing additional crosslinks using GA. As these gels contain more than 60% water, they may be found suitable for use as biomaterials in medicine and pharmacy.

The effect of pH on the swelling behaviour has been studied for AG-2 and AGG-3 samples and the results are displayed in Figure 5. The swelling of AG-2 gel is in the order pH 9.0>1.2>6.7 whereas AGG-3 gel follows the order pH 1.2> 9.0>6.7 . It is expected that, as the $-NH_2$ groups of the polyacrylamide chains get protonated under acidic pH condition, the chain segments between the crosslinks expand resulting in higher swelling under acidic conditions compared to neutral and basic conditions. Such an effect is seen in the compact AGG-3 sample. The swelling of semi IPN AG-2 network appears to be influenced by factors such as ionic strength of the swelling medium, in addition to protonation effect.

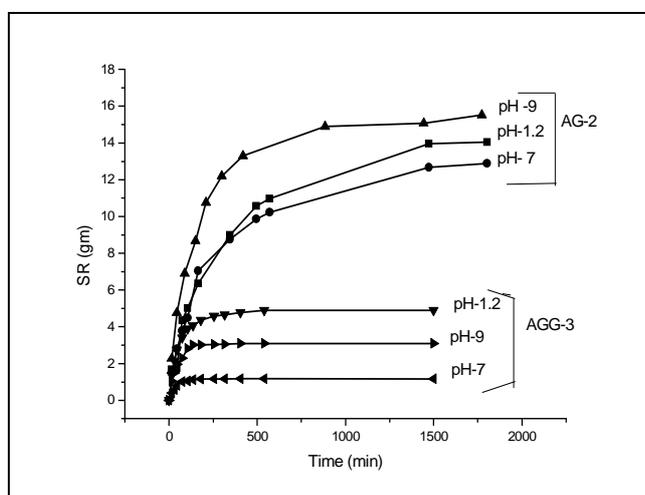


Fig 5. Effect of pH on swelling behaviour of GG-PAAm-1 and GG-PAAm-2 gels.

Swelling and diffusion analysis

Swelling /shrinking and diffusion characteristics of hydrogels are presently being exploited for various applications including control of microfluidic flow, development of muscles-like actuators, filtration/separation and drug delivery. The mechanism of swelling process of hydrogels is determined experimentally by simple kinetic analysis using the following equation for a second order kinetic process[25, 26].

$$\frac{ds}{dt} = R_s (S_{eq} - S)^2 \quad (3)$$

Where S_{eq} & R_s denote the degree of swelling at equilibrium and swelling rate constant, respectively. The integration of Eq. 3 over the limits $S = S_0$ at $t = t_0$ and $S = S$ at $t = t$, gives the following equation:

$$\frac{t}{S} = A + Bt \quad (4)$$

Where $A = 1 / (R_s S_{eq}^2)$ is the reciprocal of the initial swelling rate

$B = 1 / S_{eq}$ is the inverse of the equilibrium swelling and

R_s is the swelling rate constant.

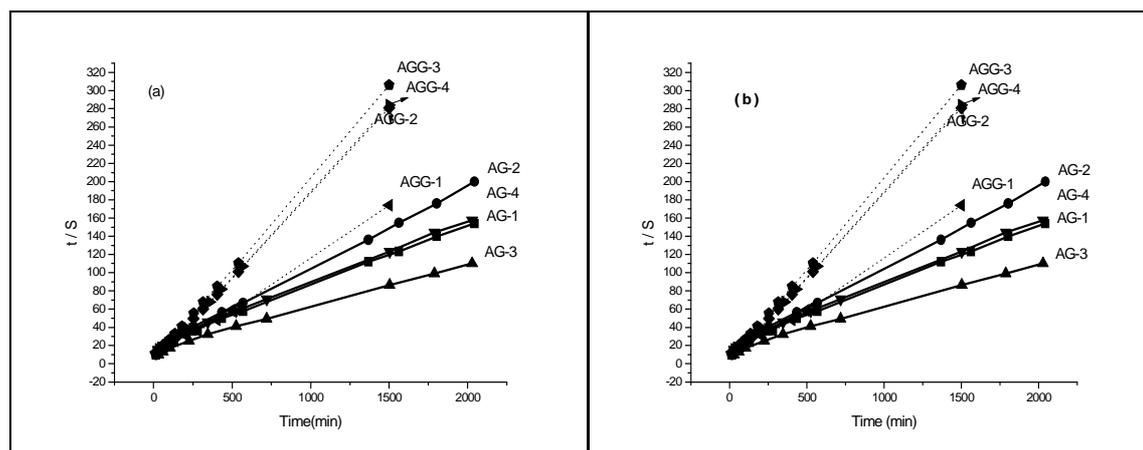


Fig 6. Swelling rate curves of GG-PAAm-1 and GG-PAAm-2 gels for (a) pH 1.2 and (b) pH 9.0

This relation represents swelling as a second order kinetic process. To check the applicability of this equation to the presently studied system, plots of t/S versus t were made for the AG 1-4 and AGG 1-4 samples and are shown in Fig.6. The linearity of the relationship between t/s and t indicate swelling to be a second order kinetic process. The swelling parameters, namely, initial swelling rate (R_i), maximum equilibrium swelling ratio (S_{max}) and swelling rate constant (R_s), were evaluated following methods reported earlier[27-30]. The results are tabulated in Table 2. The slow rate of swelling of the GG-PAAm-1 gels is reflected in the lower values of initial swelling rate (R_i) and Swelling rate constant (K_s) obtained for these gels compared to GG-PAAm-2 gels. The maximum equilibrium swelling ratios calculated theoretically are in good agreement with equilibrium swelling ratios obtained experimentally. The initial swelling rate and the overall swelling rate constants decrease with increasing crosslinking of the gels.

Hydrogels are considered as important materials in agricultural, biomedical, pharmaceutical, and environmental applications. The applicability of these hydrogels may be governed by the mechanism of water diffusion. The absorption process involves the diffusion of water molecules into the free spaces, increasing the segmental mobility leading to expansion of chain segment between crosslinks resulting in swelling. The dynamics of water sorption process was studied by analysing the swelling data obtained for initial 60% of swelling, using the following equation[30-32].

$$\text{Swelling ratio}(S R) = K t^n \quad (5)$$

Where SR is the swelling ratiomass defined in eqn.1, 'k' is a swelling constant related to the structure of the network; and 'n' is the swelling exponent, which indicates the water transport mechanism. 'k' and 'n' were evaluated from the plots of ' $\ln S$ ' versus ' $\ln t$ ' shown in Figure 7.

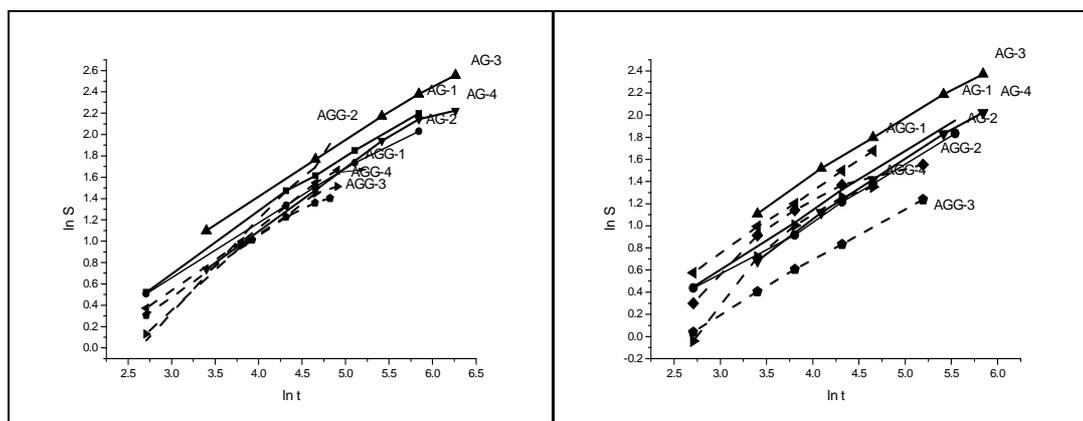


Fig 7. Diffusion rate curves of GG-PAAm-1 and GG-PAAm-2 gels for (a) pH 1.2 and (b) pH 9.0

The swelling exponent was calculated from the slope of the lines of ' $\ln S$ ' versus ' $\ln t$ ' plots. For the gels made with MBA, an n value of 0.5 was obtained indicating fickian diffusion in these gels. The MBA and GA crosslinked gels gave an 'n' value of ~0.6 indicating the possibility of anomalous diffusion in these tightly linked gels. This was

further confirmed by the SR versus $t^{1/2}$ plots (Fig. 8). The curves for GG-PAAm-1 gels exhibited a linear relationship indicating applicability of Ficks diffusion to these gels whereas the curves for GG-PAAm-2 deviated from linearity.

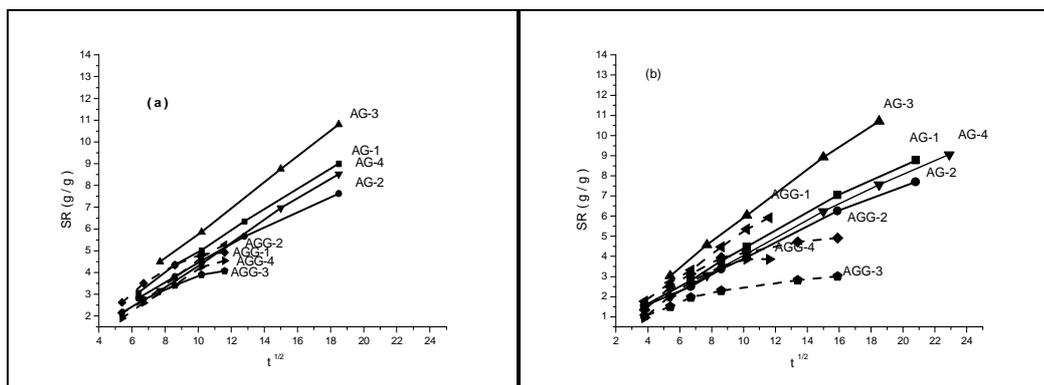


Fig 8. Ficks Diffusion curves of GG-PAAm-1 and GG-PAAm-2 gels for (a) pH 1.2 and (b) pH 9.

3.5. Effect of the Crosslinker on swelling of gels

It has been well proved that the nature and concentration of the crosslinker effects the swelling and mechanical properties of the hydrogels[33,34]. The effect on swelling has been studied in the present case with two crosslinking agents of varying concentration. The results are depicted in Figure 9.

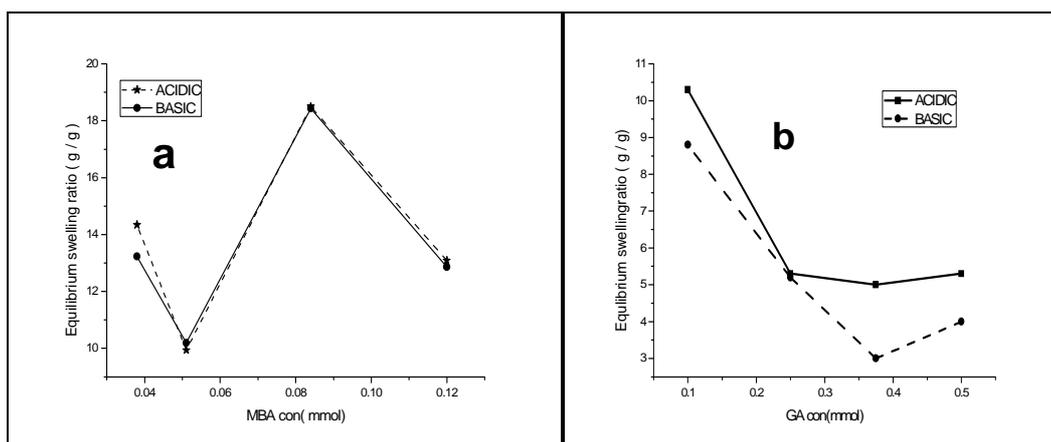


Fig. 9: Effect of crosslinker concentration on swelling of (a) GG-PAAm- 1 and (b) GG-PAAm-2 gels

Generally, the crosslinker concentration is directly related to the density of crosslinks in the gels. At lower crosslinker concentration, the gel may have lower crosslinking density and hence higher swelling capacity. Whereas the gel formed with high crosslinker concentrations will possess higher crosslinking density causing a decrease in the distance between the crosslink points, thereby lowering the swelling capacity. In the case of GG-PAAm-1 gels, decrease in swelling occurred initially with increasing concentration of MBA but further increase in MBA resulted in gels with much higher swelling capacity. Highest swelling was observed in AG-3 sample. The results indicate the intermediate value of MBA as the optimum concentration for obtaining maximum swelling. Similar results were reported earlier in literature for copolymers containing acrylamide[24].

With increase in MBA content the hydrophilicity of the polymer gel and hence the swelling appears to increase counterbalancing the action of crosslinking. Such an effect is not observed in GG-PAAm-2 gels. The GG-PAAm-2 samples showed the expected behaviour of decrease in swelling capacity with increasing concentration of GA indicating that these gels have a compact well controlled structure compared to the former. The swelling capacity of the gels of both types appears to be affected to same extent by acidic and basic conditions of swelling medium indicating the fact that the crosslink density is the deciding factor for controlling the swelling capacity of the presently studied IPN systems.

CONCLUSION

In the present investigation, GG-PAAm IPN systems have been made for the first time with two different crosslinking agents, MBA and GA. The swelling properties of these gels have been compared with semi IPN system made with a single crosslinking agent, MBA. It has been observed that the gels containing only MBA (GG-PAAm-1) swell to higher extent than the doubly crosslinked (GG-PAAm-2) gels under both acidic and basic conditions and hold higher amount of water. Also, the singly crosslinked gels took longer time for reaching the equilibrium swelling than the doubly crosslinked gels. The additional crosslinks introduced by GA reduced the Swelling by about 50%. The swelling of both type of gels is found to be a second order kinetic process. The GG-PAAm-1 gels exhibited slow rate of initial swelling rate (R_i) and Swelling rate constant (K_s) compared to GG-PAAm-2 gels. The initial swelling rate and the overall swelling rate constants were found to decrease with increasing crosslinking of the gels. Swelling exponent 'n' is found to be 0.5 for gels containing only MBA and is higher than 0.5 for gels with MBA and GA. The mechanism of water diffusion is found to be fickian in the first case and anomalous diffusion in the second.

In the case of GG-PAAm-1 gels, swelling studies indicate the intermediate value of MBA as the optimum concentration for obtaining maximum swelling. With increase in MBA content the hydrophilicity of the polymer gel and hence the swelling appears to increase, counterbalancing the action of crosslinking. Such an effect is not observed in GG-PAAm-2 gels. The GG-PAAm-2 samples showed the expected behaviour of decrease in swelling capacity with increasing concentration of GA indicating that these gels have a compact well controlled structure. However, the crosslink density appears to be the deciding factor for controlling the swelling capacity of the presently studied IPN systems.

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