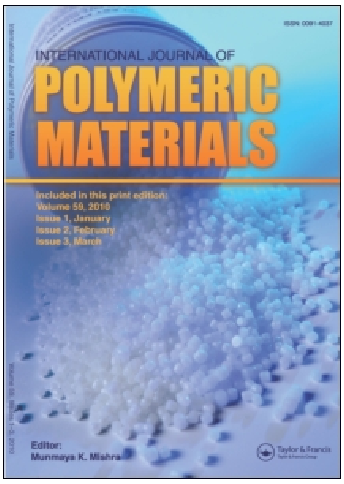

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Swelling and Diffusion Characteristics of Interpenetrating Network Films Composed of Sodium Alginate and Gelatin: Transport of Azure B

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Swelling and Diffusion Characteristics of Interpenetrating Network Films Composed of Sodium Alginate and Gelatin: Transport of Azure B

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Interpenetrating polymer network (IPN) films have been made from two hydrophilic natural polymers, namely, sodium alginate (NaAlg) and gelatin (Gltn) in the presence of glycerol (Glrl) using Ca^{2+} *as crosslinkers. Films have been prepared with varying amounts of crosslinking agent, plasticizer and the component polymers. The effect of these parameters, the preparation conditions and the pH of the medium on the swelling behavior of these gel films has been investigated. Dynamic swelling studies have been carried out and the kinetic parameters for the swelling process have been evaluated. The influence of film characteristics and pH of the medium on the permeability behavior of the films has been studied for a cationic dye, Azure B (AzrB). The results revealed pH sensitivity of the films towards swelling and solute transport. Based on the results, possible mechanisms of water and dye transport through the films have been proposed.*

Keywords: dye-diffusion, IPN polymers, kinetics, pH sensitivity, swelling

INTRODUCTION

The rate of permeation of solute molecules through polymer network structure depends predominantly on the swelling ability of the network in the medium of transport. Several parameters affect the swelling of the network system and permeability of solute, such as the chemical structure of the polymers composing the network system, hydrophilicity of the substituent groups in the polymers, morphology

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of the membrane and the chemical environment of the medium of transport. Thus selective and controlled transport of solute molecules across polymer films can be achieved by a delicate control of the network structure and chemical nature of the medium [1–3].

Carbohydrate polymers find extensive use in biomedical and pharmaceutical fields due to their biocompatible and biodegradable nature. IPN systems of biopolymers, such as sodium alginate, chitosan, carboxymethyl cellulose, gelatin, and others, have been investigated by several researchers as potential biodegradable implants, such as systems for the controlled release of pharmaceuticals and insecticides [4–9]. The presence of weakly ionizable functional groups such as carboxylic acid or amine groups impart pH sensitivity to these materials, which has made them attractive materials in the design of intelligent controlled-release devices [10], that act in response to the external stimuli.

Sodium alginate (NaAlg) and gelatin (Gltn) have been selected as network component polymers in the present investigation. NaAlg is a bioerodible natural polymer [4] that has been widely used in controlled-release applications of drugs and pesticides, because it forms strong gels in aqueous media. It is composed of a linear block copolymer of 1–4 linked β-D-mannuronic acid and α-L-guluronic acid. An aqueous solution of alginate is readily transformed into a hydrogel on addition of metallic divalent cations like Ca^{2+}. Gelatin is derived from collagen, a natural protein. It is a heterogeneous product which consists of α, β and γ peptides. It is a nontoxic, biocompatible and biodegradable material soluble at body temperature, which makes it an ideal material for pharmaceutical applications [5]. NaAlg and Gltn are observed to form compatible homogeneous blends with improved mechanical properties and water absorptivity [6]. The blend films can be further crosslinked with Ca^{2+} to give a three-dimensional network structure, producing free volume for easy encapsulation and the transport of drugs or pesticides.

The aim of the present investigation was to optimize the conditions for obtaining mechanically stable IPN films of NaAlg and Gltn and to study the influence of preparation method and film characteristics on the swelling and diffusion behavior of the films. The films have been made in the presence of glycerol (Glrl). Dynamic swelling studies have been performed in media of different pH and the swelling parameters have been determined. Further, the transport characteristics of the films for low molecular weight solute molecules have been determined using Azure B (AzrB), a cationic dye. The results have been analyzed to understand the mechanism of transport of water and solute molecules through the films.

EXPERIMENTAL

Materials

Gelatin was obtained from Merck (Mumbai, India). Sodium alginate, calcium chloride, glycerol, potassium hydrogen phthalate, potassium dihydrogen orthophosphate, disodium hydrogen orthophosphate dihydrate and hydrochloric acid were obtained from S.D. Fine Chemicals (Mumbai, India). The dye, Azure B, was purchased from Spectrochem (Mumbai, India). Doubly distilled water was used in the preparation of the films and in swelling and diffusion studies.

Preparation of IPN Films

The following method was employed in the preparation of the films used in the present study. A separate 1% (w/v) aqueous solutions of each polymers was prepared separately by stirring at room temperature. Then the two 1% (w/v) aqueous solutions of the component polymers, NaAlg and Gltn, were mixed in different proportions, keeping the total volume constant so as to obtain the following compositions: NaAlg/Gltn(v/v): 1.0, 2.0, 3.0 and 4.0. To the resulting solution, varying amounts of Glrl (0–0.4% w/v) were added and stirred for 4 h to get a homogeneous solution. The optimum amount of each solution was poured on a glass plate and cast into films of thickness ~0.2 mm by solvent evaporation at 60°C. The dried films were removed and immersed in $CaCl_2$ solutions of different concentrations. After specific time intervals, the crosslinked films were taken out and washed with distilled water to remove the adhering $CaCl_2$ solution. The films thus obtained were dried at 40°C under vacuum and stored. The details of the preparation conditions and the codes used for the designation of the films are compiled in Table 1.

FTIR Analysis

FTIR spectra of NaAlg, Gltn and NaAlg/Gltn hydrogels were recorded on a Nicolet Avatar 330 FTIR spectrophotometer using silicon carbide disc.

Thermal Analysis

The DSC measurements were carried out with a Mettler Toledo DSC 822 thermal analyzer. The samples were heated from 0 to 500°C and the heating rate was maintained at 10°C/min.

TABLE 1 Preparation Conditions and Designation of IPN Films

NaAlg:Gltn (wt/wt)	Glrl (wt %)	$CaCl_2$ (M)	Crosslinking time (min)	Film Code
1.0	0.3	0.5	10.0	NG1
1.0	0.3	0.5	30.0	NG2
1.0	0.3	0.5	60.0	NG3
1.0	0.3	0.1	10.0	NG4
1.0	0.3	1.0	10.0	NG5
2.0	0.3	0.5	10.0	NG6
3.0	0.3	0.5	10.0	NG7
4.0	0.3	0.5	10.0	NG8
1.0	0.0	0.5	10.0	NG9
1.0	0.2	0.5	10.0	NG10
1.0	0.4	0.5	10.0	NG11

Scanning Electron Microscopic (SEM) Analysis

The SEM analysis of the NaAlg and NaAlg/Gltn IPN films was carried out with a JEOL-JSM 5800 LV scanning electron microscope at room temperature. The micrographs were recorded at a magnitude of 500 under a voltage of 20 kV.

Swelling Measurements

The swelling behavior of the IPN films was investigated by swelling measurements carried out in buffered medium of pH 1.2, 4.0, 7.0 and 9.0. Pre-weighed dry films were immersed in excess of the chosen buffered medium at room temperature. After specific intervals of time, the films were removed from the medium, the surface-adhered liquid drops were wiped by blotting and the increase in weight of the films was measured using an electronic balance with an accuracy of ±0.1 mg (Shimadzu AUX120, Japan). The measurements were continued until the weight of the swollen films attained a constant value. The degree of swelling (S) was calculated [11–13] using the following expression

$$\text{Swelling (S)}\,\% = \left[\frac{(W_t - W_o)}{W_o}\right] \times 100 \tag{1}$$

where W_o and W_t are the weights of the dry and swollen gels, respectively. The amount of water a swollen gel can hold at equilibrium was expressed as % equilibrium water content (%EWC) which was calculated [11–13] using the following expression

$$\mathrm{EWC}\ (\%) = \left[\frac{(W_e - W_o)}{W_e}\right] \times 100 \tag{2}$$

where W_e is the weight of the gel at equilibrium. All experiments were performed in triplicate.

Dye-Diffusion Measurements

The rate of diffusion of the dye AzrB through the IPN films (NG1-NG11) was measured using an open glass tube diffusion cell, depicted in Figure 1. A specimen film was tied to the end of an open glass tube with an inner diameter of 2 cm. The glass tube was filled with the dye solution (2.0×10^{-6} M) and immersed in a beaker containing an aqueous buffered solution of chosen pH. The whole assembly was placed on a magnetic stirrer and the solution in the receptor compartment was stirred at a constant rate. The temperature was maintained at 30.0 ± 0.1°C. At regular intervals of time, aliquots of the samples were withdrawn from the receptor compartment and analyzed [14] by measurement of absorption at 645 nm ($\lambda_{\max}$ of AzrB), using a UV-vis spectrophotometer (Shimadzu UV-1601, Japan). The volume of solution in the beaker was maintained constant by the addition of an equal amount of fresh solution of corresponding pH. The amount of dye diffused at the given time was calculated from the calibration curve. The measurements were continued until the amount of dye diffused reached a constant value.

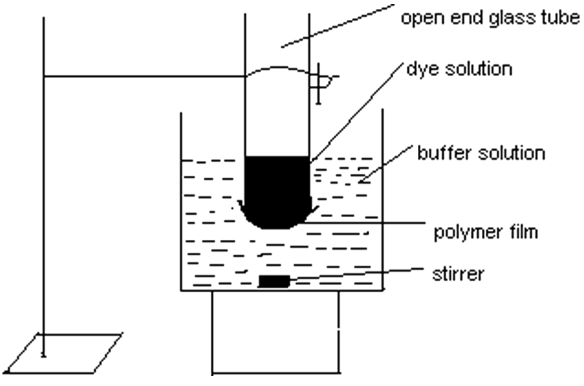


FIGURE 1 Schematic diagram of diffusion experiments using open diffusion cell.

The % cumulative dye diffused was calculated [5,7,9] using the following expression,

$$\%\ \text{cumulative dye diffused} = \mathrm{W_t}/\mathrm{W_\infty} \times 100 \tag{3}$$

where $\mathrm{W_t}$ and $\mathrm{W_\infty}$ denote the amount of the dye diffused at time 't' and at equilibrium, respectively.

RESULTS AND DISCUSSION

Structure and Morphology

The effect of presence of Gltn on the surface structure and morphology of the NaAlg-based gels was investigated using SEM techniques. SEM photographs of pure NaAlg and NaAlg-Gltn IPN films showed that, although the NaAlg surface has a smooth and relatively homogeneous appearance, the NaAlg-Gltn IPN film surface has a heterogeneous appearance. The higher swelling capacity of these films may be attributed to the available pore volume, because of which a larger amount of water can be accommodated within the hydrogel networks.

FTIR Studies

Transparent, free-standing films were obtained by the method employed here for the preparation. The FTIR spectra of NaAlg, Gltn and a representative sample of NaAlg/Gltn are shown in Figure 2. The overlapping of the peaks due to O-H stretching vibration of NaAlg and the N$-$H stretching vibration of Gltn accounts for the appearance of the broad band in the region 3100–3600 $\mathrm{cm^{-1}}$. The peak at 2935 $\mathrm{cm^{-1}}$ is attributed to aliphatic C$-$H stretching of both NaAlg and Gltn. The peaks appearing at 1606 and 1419 $\mathrm{cm^{-1}}$ are the asymmetric and symmetric stretching vibrations of the carboxylate group of NaAlg. The amide I band of Gltn which appears at 1646 $\mathrm{cm^{-1}}$, overlapped with the 1606 $\mathrm{cm^{-1}}$ band of NaAlg and hence appears as a broad band in the region 1590–1650 $\mathrm{cm^{-1}}$. The peak at 1302 $\mathrm{cm^{-1}}$ can be assigned to the C$-$N stretching of Gltn and those appearing at 1103 and 1030 $\mathrm{cm^{-1}}$ indicate C$-$O$-$C stretching of NaAlg. The FTIR spectra thus provides a conclusive evidence for the presence of NaAlg and Gltn in the IPN films.

Differential Scanning Calorimetry

The DSC thermograms of NaAlg, Gltn and NaAlg-Gltn IPN films were recorded in the temperature range 0 to 500°C at a heating rate of 10°C/min under N_2 atmosphere and are presented in Figure 3. The

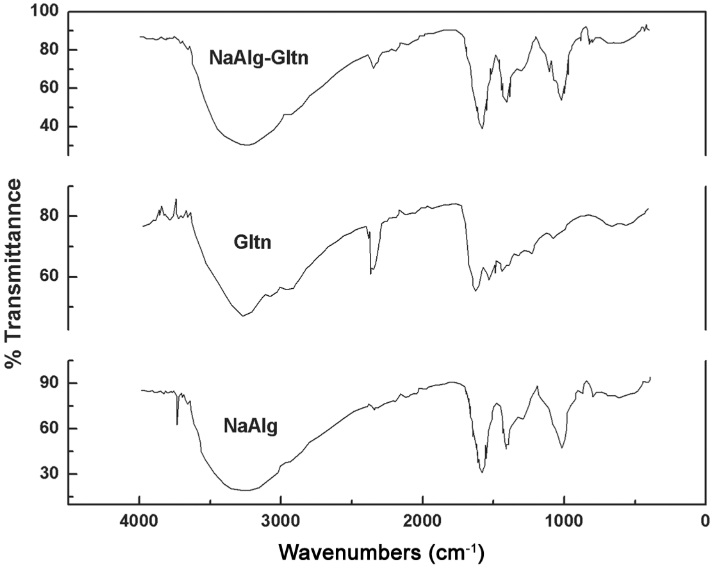


FIGURE 2 FTIR spectrum of NaAlg, Gltn and NaAlg-Gltn IPN films.

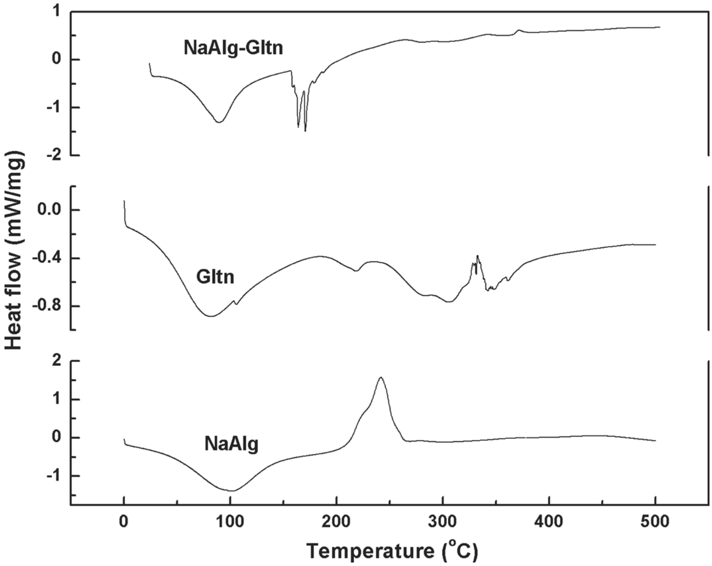
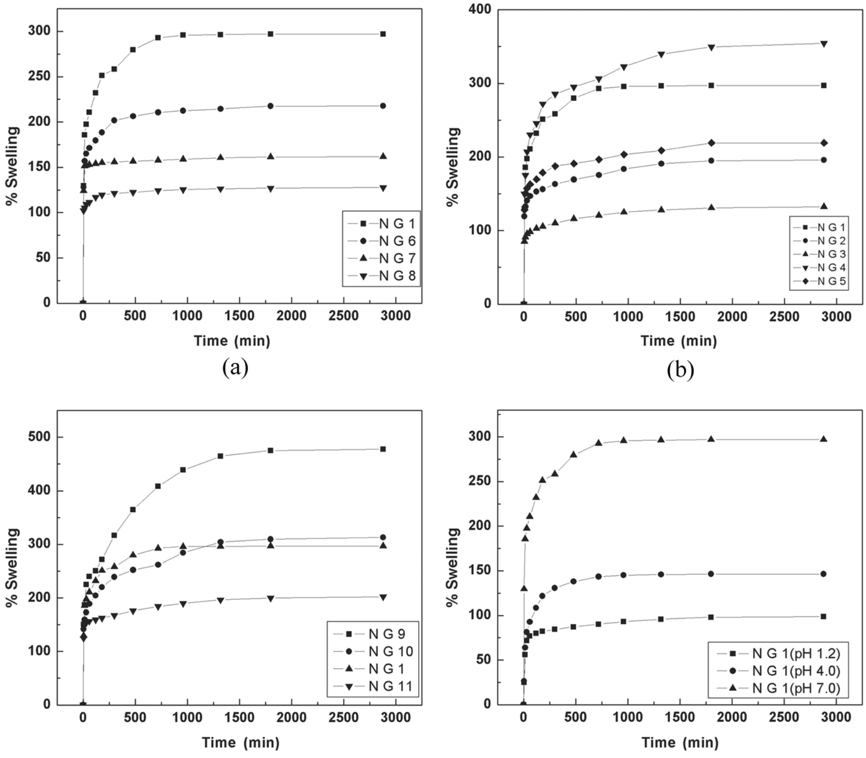


FIGURE 3 DSC thermograms of NaAlg, Gltn and NaAlg-Gltn IPN films.

dehydration of NaAlg is evidenced by an endothermic peak close to 100°C. The decomposition of this polymer is represented by exothermic peaks in the range 240–260°C, supported by literature reports. The dehydration of Gltn is evidenced by an endothermic peak close to 100°C. A peak corresponding to the T_g of Gltn appears around 225°C, whereas the exotherm above 300°C is indicative of the beginning of decomposition. The dehydration of the NaAlg-Gltn IPN systems occurs around 100°C and the Tg of gelatin gets shifted from 225 to 303°C on IPN formation.

Swelling Studies

The % swelling data collected as a function of time in the medium of pH 7.0 are displayed in Figure 4. The data clearly indicate the influence of



(a) (b)

(c) (d)

FIGURE 4 Effect of (a) polymer composition (b) crosslink density, (c) glycerol and (d) pH on swelling of IPN films.

network composition, number of crosslinks, presence of Glrl and the extent of ionization of the functional groups of the polymers on the swelling behavior of the IPN films. The nature of the % S vs. time plot indicates that the amount of water absorbed into the gel increases with time at a faster rate in the beginning and after a certain period, the rate slows down and the gels gradually reach their equilibrium swelling level. From Figures 4a–c, it is observed that the initial rate of swelling and the equilibrium water content of the gels are influenced by the network structure.

Effect of Polymer Composition on Swelling

From Figure 4a, on comparison of the swelling behavior of the films NG1, NG6, NG7 and NG8, it is clear that as the NaAlg content in the films increases (indicated by the ratio NaAlg: Gltn = 1.0, 2.0, 3.0 and 4.0, respectively), the % S decreases and the gels with higher NaAlg content hold lower amounts of water at equilibrium when compared to those with a lower NaAlg/Gltn ratio. As the swelling medium was maintained at pH 7.0, the functional groups on the polymers are in the ionized state and with increased alginate content, increased electrostatic interaction between the carboxylic and amine groups make the network more and more compact, thereby reducing the swelling [6].

Effect of Crosslink Density on Swelling

The number of crosslinks in the network increase both with the increase in the concentration of the $CaCl_2$ and the time period of contact of the films with the crosslinking medium. In Figure 4b, the films crosslinked with 0.1 M $CaCl_2$ solution (NG4) showed the equilibrium swelling ratio of $\sim$300, whereas those made with 0.5 (NG1) and 1.0 M (NG5) solutions showed the value of 275 and 200, respectively. The influence of time of contact of the films with the crosslinking medium was determined by crosslinking the films with 0.5 M $CaCl_2$ for 10, 30 and 60 min (NG1, NG2 and NG 3, respectively). The swelling behavior of these films was in the expected order. The higher the time of contact the lower is swelling, i.e., NG1 > NG2 > NG3.

Effect of Glycerol on Swelling

The effect of the addition of Glrl to the polymer feed mixture during the preparation of the films is reflected on the swelling behavior of the films, as indicated in Figure 4c. The film NG 9 made without Glrl exhibited the highest swelling capacity when compared to those made with an increasing amount of Glrl (NG10 > NG1 > NG11). The glycerol, when added to the polymer mixture, binds to the gelatin chains through H bonding and acts as an additional crosslinker. This enhances the compactness of the chains, effecting a reduction in swelling. Hence, Glrl has no plasticizing effect on the present IPN system but helps in enhancing the compatibility between NaAlg and Gltn in the IPN network.

Effect of pH on Swelling

The effect of pH of the medium on the swelling behavior of the films was studied by maintaining the pH at 1.2, 4.0 and 9.0, in addition to the above studies carried out at pH 7.0. It was observed that at pH 9.0, the films disintegrated and hence the swelling data could not be collected. The swelling behavior exhibited by the films at pH 1.2, 4.0 and 7.0 is shown in Figure 4d. The % S value of the films followed the order pH $1.2 < 4.0 < 7.0$ at all 't' values, and the equilibrium water content of the gels was also affected drastically by the pH of the medium. The observed pH sensitivity of the films can be attributed to the higher degree of dissociation of carboxylic acid groups of alginate at neutral pH compared to that at acidic pH . As the repulsion between the ionized carboxylate groups increases, the network expands, increasing the water uptake capacity of the films.

Kinetics of Swelling

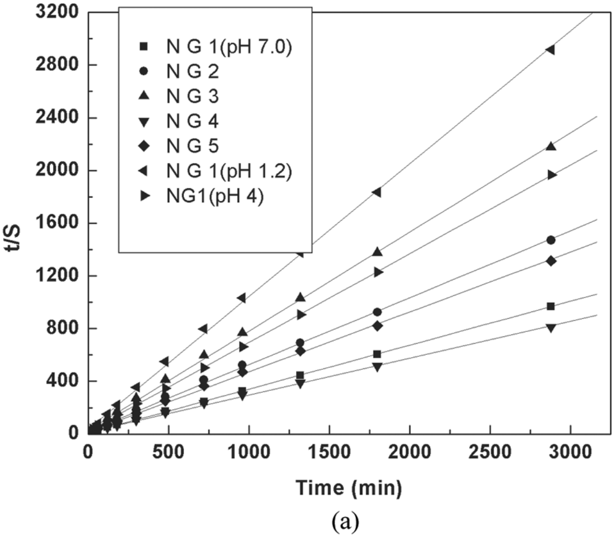
As the matrix consists of hydrophilic polymers with ionizable groups, it is expected that during the swelling process water molecules would interact with the matrix components through ionic, dipolar and hydrogen bonding interactions. A kinetic analysis of the swelling process was made [11,12] using the following equation,

$$dS/dt = k_s(S_e - S)^2 \tag{4}$$

where S_e and k_s denote the degree of swelling at equilibrium and the rate constant of swelling, respectively. Eq. (4) on integration over the limits, $S = S_o$ at $t = 0$ and $S = S$ at $t = t$, takes the form

$$t/S = A + Bt \tag{5}$$

where B is the inverse of maximum equilibrium swelling ($B = 1/S_e$) and $A = 1/(k_s S_e^2)$ is the reciprocal of the initial swelling rate (R_i) and k_s is the swelling rate constant. The plots of t/S vs. t for the various films are shown in Figures 5a and 5b. The linearity of the plot indicates that the swelling process follows second-order kinetics. R_i and k_s for the films were calculated from the intercept of the respective curves on the ordinate axis and theoretical equilibrium swelling (S_e) from the corresponding slopes. The values of these parameters



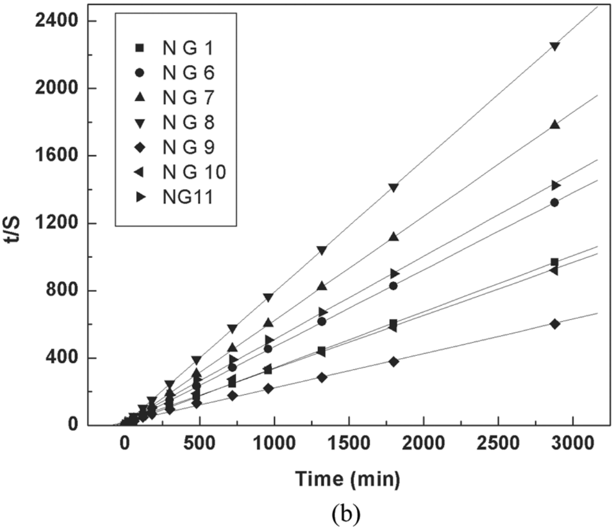


FIGURE 5 Swelling rate curves of NaAlg-Gltn IPN films indicating the effect of (a) pH of the medium and extent of crosslinking and (b) glycerol and polymer composition.

TABLE 2 Swelling Parameters of IPN Films NG1-NG11 at pH 7.0 and of NG1 at pH 4.0

Film code	NG1	NG2	NG3	NG4	NG5	NG6	NG7	NG8	NG9	NG10	NG11	NG 1 (pH 4.0)
Equilibrium Degree of Swelling S%	297	196	132	354	219	218	162	128	478	313	202	146
Equilibrium Water Content EWC%	74.81	66.21	56.96	77.99	68.66	68.53	61.79	56.07	82.69	75.79	66.91	59.41
The Initial Swelling Rate, R_r	0.144	0.06	0.04	0.07	0.07	0.12	0.23	0.11	0.06	0.054	0.06	0.05
Steady-State Swelling Ratio, q	2.31	1.77	1.47	3.25	1.66	–	–	–	–	–	–	–
Swelling Rate Constant, $k_s \times 10^{-3}$, min^{-1}	20	10	24	5.86	14	30	87	69	2.53	5.6	15	25
Maximum Equilibrium Swelling, S_{max}	2.99	1.96	1.32	3.57	2.17	2.17	1.61	1.28	4.88	3.13	2.02	1.47
Swelling Exponent, n	0.14	0.08	0.07	0.15	0.09	0.09	0.05	0.04	0.20	0.14	0.08	0.09
Swelling Constant, k	1.14	1.03	0.74	1.15	1.10	1.13	1.18	1.02	1.05	1.06	1.10	0.76

obtained for the films are presented in Table 2. The theoretical equilibrium swelling values calculated from the plots (expressed as a fraction) are in close agreement with the experimentally determined values (expressed in percentage). The R_i and k_s values are observed to depend on the composition of the films and the compactness of the network chains influenced by the extent of crosslinking.

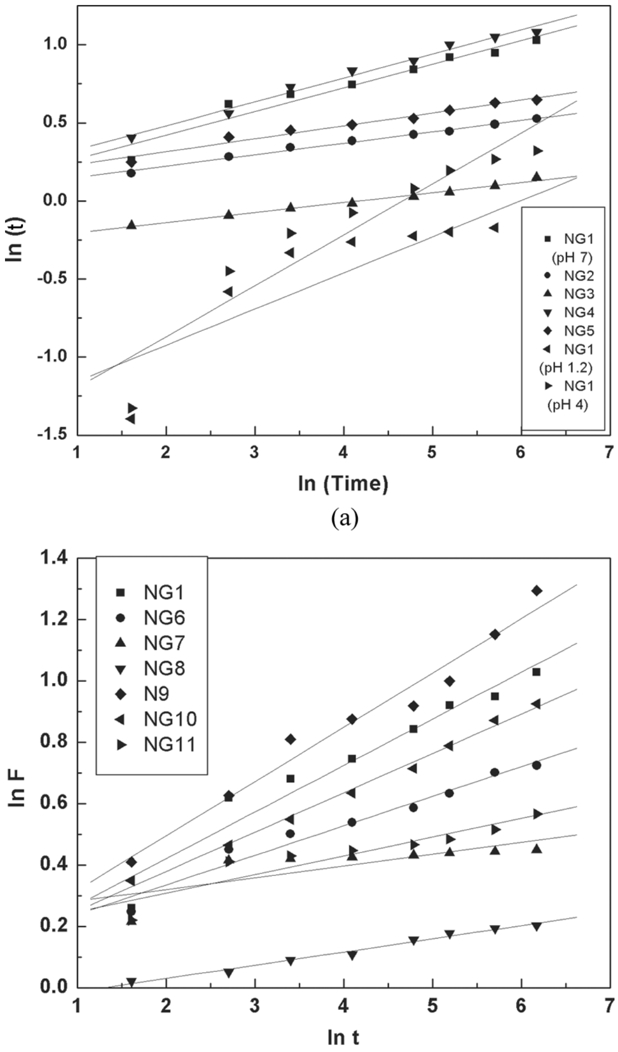
Mechanism of Swelling

The swelling behavior of hydrogels is related to the sorption mechanism of solvent molecules into the polymer matrix. When the dry film is brought in contact with the solvent, the solvent molecules diffuse into the polymer and result in swelling of the films. Both concentration gradient-controlled and relaxation-controlled swelling [13] contribute to the rate and extent of swelling. To understand the diffusion mechanism in the present study, diffusion parameters were calculated from the swelling measurements [7,14,15], using the following expression

$$F_{swp} = (M_t - M_0)/M_0 = kt^n \tag{6}$$

where F_{swp} denotes the swelling power of the film defined as the amount of water contained in the film/ unit weight of the material; $M_t - M_0$ represents the amount of water uptake at time 't'; k is the swelling constant characteristic of the polymer network and n is the swelling exponent which characterizes the mechanism of diffusion of solvent into the network. To determine 'n', ln F_{swp} were plotted vs. ln t. The curves for films with varying crosslink density and polymer composition are shown in Figures 6a and b, respectively. The values of 'n' and 'k' were calculated from the slopes and intercepts of the lines and are listed in Table 2.

Significant decrease in the 'n' values were observed for the films NG1-NG3, with increase in crosslinks in the network. The similar result of decrease in 'n' value with increasing addition of glycerol was observed in films, NG9, NG10, NG1, and NG11. The change in the chemical characteristics of the network structure induced by the changes in the pH of the medium was clearly reflected on the k values exhibited by the film NG1 at two different pH values. Accordingly, the swelling exponent 'n' has decreased from 0.14 to 0.09 for the swelling of NG1 at pH 7.0 and 4.0, respectively. The values of 'n' exhibited by the IPN films studied here ranged from 0.04 to 0.2 and do not provide significant information about the mode of diffusion of water molecules into the network. From the swelling exponent values, it could only be said that the diffusion of water into the IPN system is non-Fickian.

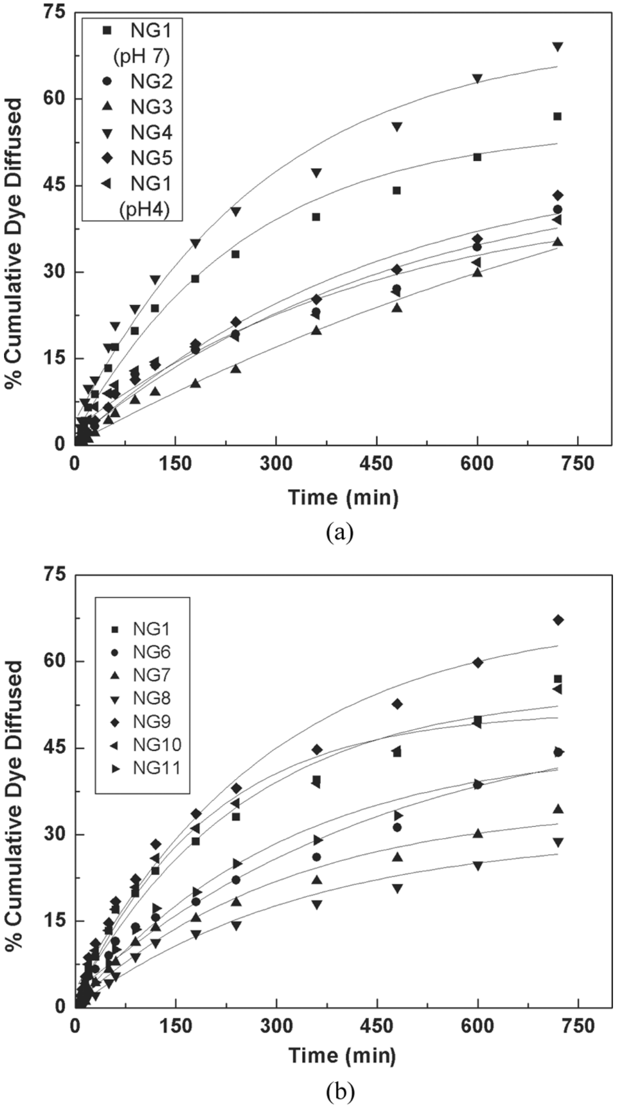

(a)

(b)

FIGURE 6 Swelling rate curves of NaAlg-Gltn IPN films indicating the effect of (a) pH of the medium and extent of crosslinking and (b) glycerol and polymer composition.

Study of Permeability Behavior of IPN Films

The permeability of a solute molecule through the network films was studied to investigate the influence of film characteristics and the nature of solute on the diffusion characteristics. The IPN films were used



(a)

(b)

FIGURE 7 Cumulative dye diffusion curves of NaAlg-Gltn IPN films indicating the effect of (a) pH of the medium and extent of crosslinking and (b) glycerol and polymer composition.

as a membrane barrier in a vertical diffusion cell separating the dye solution from aqueous medium buffered to pH 7.0 and 4.0. Azure B, a basic, cationic dye was chosen as the solute. The amount of dye diffused into the lower aqueous medium was monitored as a function of time at the λ_{max} of the dye. The measurements were continued until the amount of dye permeated reached a maximum value. The permeability data were analyzed applying the equation,

$$W_t/W_\infty = k_d t^n \tag{7}$$

where W_t is the amount of the dye diffused at time t and W_∞ is the dye released at equilibrium; k_d is a constant, characteristic of dye-network system and n is the diffusional exponent which has the same significance as the swelling exponent and is characteristic of the mode of transport of the dye through the membrane. The plots of the % cumulative dye diffused with time through the films with varying crosslink density and polymer composition are shown in Figures 7a and b, respectively.

A calculation of the exponent n was achieved by plotting ln (W_t/W_∞) against ln(t), and the values of n and k_d obtained are listed in Table 3. It was observed that the value of 'n' lies between 0.7 and 1.35.The variation of diffusional exponent 'n'with the structural parameters of the IPN films followed the same trend as that of the swelling exponent. It can be understood from these results that the dye solution is absorbed into the films in the same manner as sorption of pure water, influenced by the network structure. Since the n values for all the films were >0.5, the transport of dye is thought to be controlled by both diffusion and swelling of the network, which indicates

TABLE 3 Diffusion Parameters of IPN Films for Transport of Azure B

	Correlation coefficient (r^2) value					
Gel Type	Zero order	First order	Higuchi's square root	Korsmeyer	(n) value Korsmeyer	Dye diffusion coefficient D × 10^{-6} cm^2 min^{-1}
NG1 (pH 7.0)	0.9112	0.9616	0.9919	0.9332	0.80	7.95
NG2	0.9519	0.9709	0.9872	0.9629	0.83	5.37
NG3	0.9856	0.9922	0.979	0.9654	0.81	4.27
NG4	0.9255	0.9820	0.9958	0.9277	0.72	9.04
NG5	0.9589	0.9789	0.9936	0.9662	0.84	5.37
NG6	0.9521	0.9748	0.9905	0.9534	0.73	5.09
NG7	0.9329	0.9574	0.9945	0.9551	0.79	1.90
NG8	0.9392	0.9577	0.9923	0.9692	0.77	3.08
NG9	0.9264	0.9792	0.9953	0.9417	0.76	0.88
NG10	0.8814	0.9390	0.9819	0.9202	0.79	0.88
NG11	0.9347	0.9657	0.9952	0.9705	0.84	1.42
NG1 (pH 4.0)	0.9415	0.9612	0.9846	0.9441	0.71	4.81

anomalous transport behavior. A completely non-Fickian, or case II, transport is operative in films NG1, NG 4, NG 9, NG 10 and NG11 which exhibited high equilibrium swelling capacity. The pH sensitive behavior of the films towards swelling is also exhibited towards dye

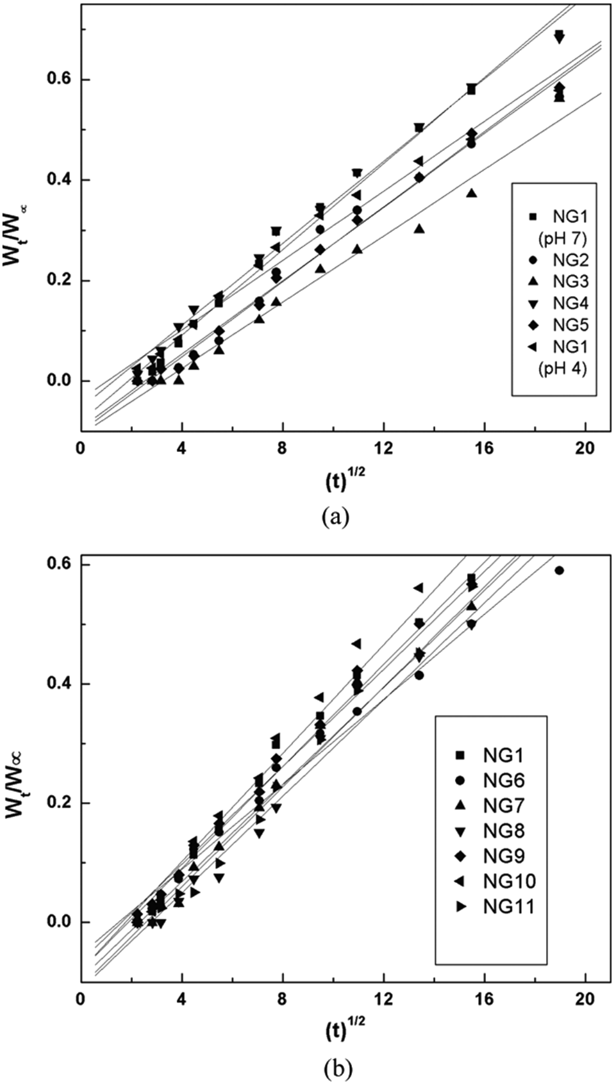


FIGURE 8 Dye diffusion curves of NaAlg-Glth IPN films, indicating the effect of (a) pH of the medium and extent of crosslinking and (b) glycerol and polymer composition.

diffusion as indicated by the low value of n for the film NG1 at pH 4.0, compared to that at pH 7.0.

The diffusion coefficient 'D' of dye in the IPN films was calculated [16] using the equation,

$$W_t/W_\infty = (4/d)((Dt)/\pi^{1/2} \tag{8}$$

where 'd' is the thickness of the films in cm. Eq. (8) was found to be valid for initial process of diffusion only; i.e., for $W_t/W_\infty < 0.4$, where the plot of W_t/W_∞ against $(t)^{1/2}$ was observed to be linear as shown in Figures 8a and b. The 'D' values obtained for the various films are presented in Table 3. Significant difference in the dye-polymer interaction parameter, k_d is observed for the film NG1 at two different

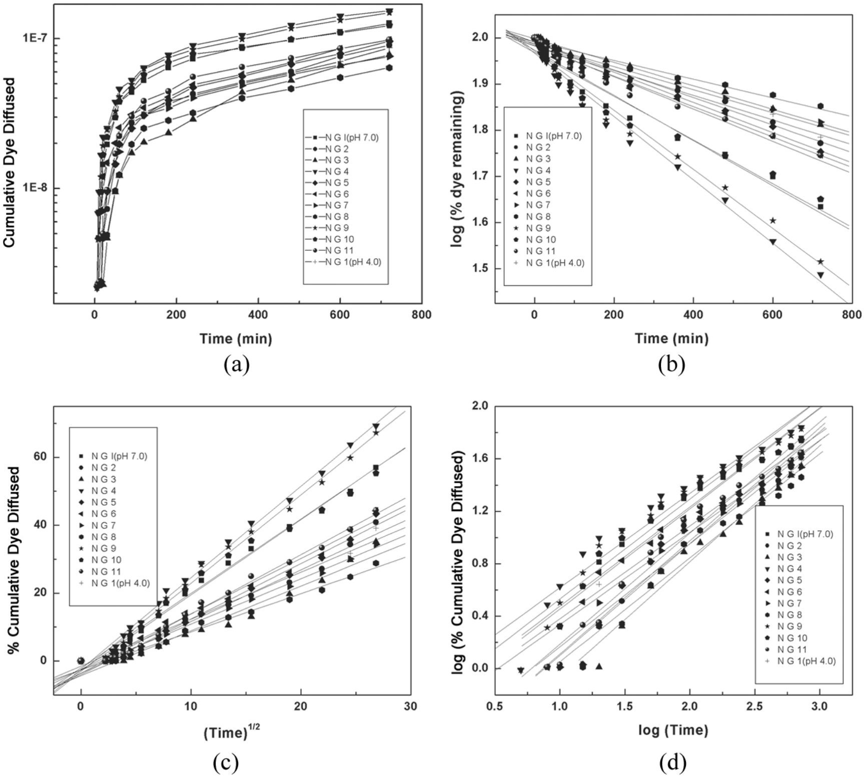


FIGURE 9 Dye release data plotted in accordance with (a) zero order equation, (b) first order equation, (c) Higuchi square root relation and (d) Korsmeyer relation.

pH conditions. The dye is found to strongly interact with the film material under the low swelling conditions that prevail at pH 4.0, which is also reflected in the diffusion coefficient value, indicating slow diffusion through these films.

Kinetics of Diffusion of Azure B through the IPN Films

To analyze the mechanism of dye diffusion through the films, the release data were fitted into zero order, first order, Higuchi's square root equations and the Korsemeyer and Peppas model [17] and are displayed in Figure 9. The model that best fits the release data was selected based on the correlation coefficient (r^2) value of fit. The r^2 values obtained are given in Table 3. It is observed that for all the films, 'r^2' value was higher for first order fit as compared to zero order, indicating that these systems show a first order diffusion. Further, correlation coefficient values obtained for Higuchi equation (corresponding to diffusion-controlled mechanism) were in the range $0.9790 - 0.9958$. When the diffusion data were analyzed as per the Korsemeyer and Peppas equation, the diffusion exponent 'n' was >0.5 for all the formulations, indicating an anomalous diffusion mechanism.

CONCLUSIONS

NaAlg and Gltn-based IPN films have been made in the presence of Glrl using Ca^{2+} as crosslinkers. The films exhibited an equilibrium swelling ratio of 130–480% in neutral medium at 27°C. The swelling capacity of the films and the rate of swelling were observed to be influenced by film composition and the preparation conditions. The swelling of the films was least in a medium of pH 1.2 and highest around pH 7.0. Thus the films exhibited a pH-dependent swelling behavior. The structural parameters of the network and the pH of the medium were also found to influence the permeability property of the films. The extent of absorption of the dye and the diffusion through the films were observed to be directly influenced by network swelling process controlled by the relaxation of polymer segments. As the films are made from biocompatible materials, they may prove good candidates for biomedical and pharmaceutical applications, especially as stimuli-responsive polymer materials for the controlled release of drugs.

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