

Synthesis and Characterization of Sodium Alginate/Acrylamide Semi-Interpenetrating Polymer Networks

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ABSTRACT: Sodium alginate (NaAlg)/acrylamide (AAm) semi-interpenetrating polymer networks (IPNs) were prepared with three different compositions, in which the NaAlg concentration was 1, 2, or 3% (w/v) in 50% (w/v) AAm solutions. These solutions were irradiated with a ^{60}Co γ source at different doses. The conversion percentage was determined as follows. The NaAlg/AAm IPN hydrogels were immersed to swell in a solution of the desired pH (3–9) at 25°C. The swelling results at pHs 7.0 and 9.0 indicated that the NaAlg/AAm IPN hydrogel containing 3% NaAlg showed the maximum swell-

ing percentage in water. The diffusion of water within the NaAlg/AAm IPN hydrogels was non-Fickian in character. The diffusion coefficients of the NaAlg/AAm IPN hydrogels in water were calculated. The thermal properties of NaAlg, polyacrylamide, and NaAlg/AAm IPNs were determined. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 335–342, 2006

Key words: diffusion; hydrogels; irradiation; networks; swelling

INTRODUCTION

Hydrogels may exhibit swelling behavior dependent on the external environment. Thus, in the last 30 years, there has been major interest in the development and analysis of environmentally or physiologically responsive hydrogels.¹ These hydrogels show drastic changes in their swelling ratio due to changes in the external pH, temperature, ionic strength, nature of the swelling agent, and electromagnetic radiation. Hydrogels that exhibit pH-dependent swelling behavior contain either acidic or basic pendant groups. In aqueous media of the appropriate pH and ionic strength, the pendant groups can ionize, developing fixed charges on the gel. Some advantages of ionic materials, such as pH and ionic strength sensitivity, are relevant to drug-delivery applications. In an exceptional new review in the field, am Ende and Mikos² offered a thorough physicochemical and mathematical interpretation of the conditions of diffusional release of various bioactive agents in hydrogels and other polymeric carriers, with an emphasis on the conditions for stability of peptides and proteins during delivery. Park and Park³ presented a very useful commentary with respect to the biocompatibility of implantable hydrogel-based delivery systems.

Interpenetrating polymer networks are composed of two or more polymer networks synthesized or crosslinked in the immediate presence of each other. Because in interpenetrating polymer networks there is no chemical bonding between the two networks involved in the system, each network should retain its properties. Thus, an interpenetrating polymer network property can be tuned by a simple change in the composition of each component. The molecular interpenetration results in physical entanglements in the interpenetrating polymer networks that increase the apparent crosslinking density and further lead to higher mechanical strength of the material.⁴ Environmentally sensitive biocompatible hydrogels have been used to make interpenetrating polymer networks.

EXPERIMENTAL

Materials

Medium-viscosity sodium alginate (NaAlg; A-2023, Sigma Chemical Co., St Louis, MO), obtained from *Macrocystitis pyrifera*, was used in all studies. The monomer used in this study, acrylamide (AAm), was obtained from BDH (Poole, UK). Sodium phosphate, disodium hydrogen phosphate-2-hydrate, and phosphoric acid, used to prepare phosphate buffer solutions, were obtained from BDH. Nitric acid and sodium hydroxide, used to adjust the pH of the medium, were obtained from Merck (Darmstadt, Germany). All materials were used without any further purification.

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Preparation of the semi-interpenetrating polymer network (IPN) hydrogels

Alginate solutions of three concentrations were prepared: 1, 2, and 3% (w/v) in 50% (w/v) AAm solutions. These solutions were placed in poly(vinyl chloride) straws 3 mm in diameter and irradiated in air at the ambient temperature in a Gammacell 220 γ irradiator (Atomic Energy of Canada Ltd., Ottawa Commercial Products, Canada). Doses of 2.0–20.0 kGy were applied at a fixed dose rate of 0.14 kGy/h. IPN hydrogels obtained in long, cylindrical shapes were cut, washed with distilled water for the removal of unreacted monomers (if any), dried in air and in vacuo, and stored for later evaluations. The conversion percentage was determined gravimetrically; 100% gelation was achieved for all mixtures at a 10.0-kGy dose.

Determination of the gelation percentage

The obtained IPN hydrogels were cut into pieces approximately 2 mm long. The prepared IPN gels were washed in deionized water for a week to remove the uncrosslinked polymer and low-molecular-weight substances. Then, the IPN gels were dried in a vacuum oven until a constant weight was reached for each sample. The conversion percentages of the NaAlg/AAm 1–3 IPN hydrogels as insoluble networks were determined with the weight of this hydrogel according to its initial weight. The gelation percentage of the NaAlg/AAm 1–3 IPN hydrogels obtained from AAm and NaAlg were calculated as follows:

$$\% \text{ Gelation} = \frac{\text{Weight of dry IPN hydrogel}}{\text{Initial weight of IPN hydrogel}} \times 100 \quad (1)$$

Swelling studies

The dried IPN hydrogels were weighed. Then, they were immersed to swell in a solution of the desired pH (3–9) at 25°C. Periodically, the IPN hydrogels were withdrawn from the solution and weighed after the removal of excess surface water. This procedure was continued until the weights of the IPN hydrogels reached a constant value. The swelling percentage of each IPN hydrogel was calculated with the following relation:

$$\text{Swelling (\%)} = \frac{(m_t - m_0)}{m_0} \times 100 \quad (2)$$

where m_t is the mass of swollen IPN at time t and m_0 is the initial mass of dry IPN. Some parameters (diffusion characteristics, equilibrium water content, etc.) were calculated with the swelling data.

Spectroscopic and thermal analysis

Fourier transform infrared (FTIR) spectra of the homopolymers and IPN hydrogels were recorded between 4000 and 400 cm^{-1} on a Nicolet 520 FTIR spectrometer (Madison, WI) as KBr pellets. The IPN hydrogels were characterized by a comparison of the FTIR spectra of the homopolymers and IPN hydrogels. A Dupont 910 model thermogravimetric analyzer (Wilmington, DE) was used for the determination of the thermal stabilities of the homopolymers and IPN hydrogels. Samples weighing 5–10 mg were heated in a dynamic nitrogen atmosphere from 20 to 800°C at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Polysaccharides such as cellulose derivatives, chitin/chitosan, alginate, and carrageenan are widely used in food, medicine, and cosmetics because of their unique structures, distinctive properties, safety, and biodegradability. Modification by the crosslinking, grafting, and degradation of natural polymers is expected to expand their application field. On the other hand, a radiation technique can provide a useful method for the degradation of different natural polymers.⁵ Incorporating NaAlg into a water-insoluble matrix increases the mechanical stability. We prepared NaAlg/AAm IPN hydrogels that were durable and reusable.

NaAlg is the sodium salt of alginic acid and is a water-soluble anionic polymer. Alginic acid is a linear copolymer of D-mannuronic acid and L-guluronic acid units. The proportions of these units in various seaweeds differ, depending on the sources, but D-mannuronic acid is usually 60% polysaccharide. D-Mannuronic acid units are connected by β -(1 \rightarrow 4)-linkages, and L-guluronic acid units are connected by (1 \rightarrow 4)-linkages, presumably in the α configuration. The structural segment of NaAlg along with the conformation of sodium mannuronate and sodium guluronate is shown in Figure 1. The medium-viscosity contains 39% guluronic acid.^{6–8} Modification by the crosslinking, grafting, and degradation of natural polymers is expected to expand their application field. The degradation and crosslinking of polymers are affected by the atmosphere of the irradiation. A possible reaction mechanism of AAm with NaAlg by γ -ray irradiation is shown in Figure 2. When a solution of AAm was irradiated, a bond in the double bond of AAm was broken, and monomer radicals were formed. When the irradiation was continued, a crosslinking reaction started, chains were crosslinked to one another, and gelation occurred in the system.

It has been determined that the gelation of a polyacrylamide (PAAm) hydrogel occurs at 2.0-kGy γ -ray doses at the ambient temperature.⁹ The degradation of NaAlg in an aqueous solution has been observed at the beginning of irradiation.¹⁰ Thus,

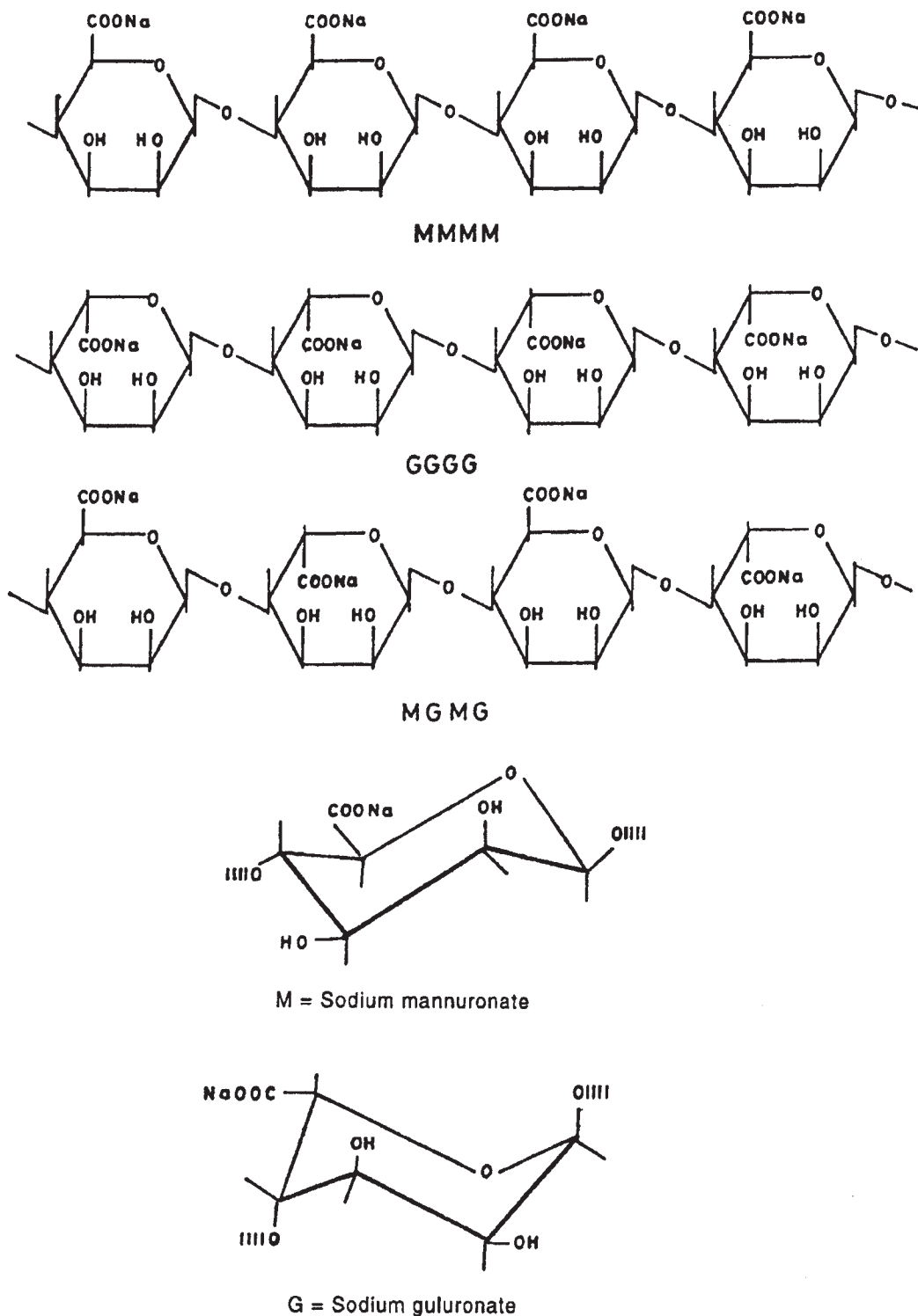


Figure 1 Structural segments of NaAlg.

2.0-kGy and upper γ -ray doses were used for the preparation of the NaAlg/AAm IPN hydrogels. After some experimental observations and results, the suitable conditions for the preparation of the NaAlg/AAm IPN hydrogel systems were determined to be 2.0–20.0-kGy γ -ray doses.

Gelation

The gelation percentages of the NaAlg/AAm IPN hydrogels are presented in Table I. Approximately 100% gelation occurred with 10.0-kGy irradiation. The gelation percentages of the IPN hydrogels decreased with

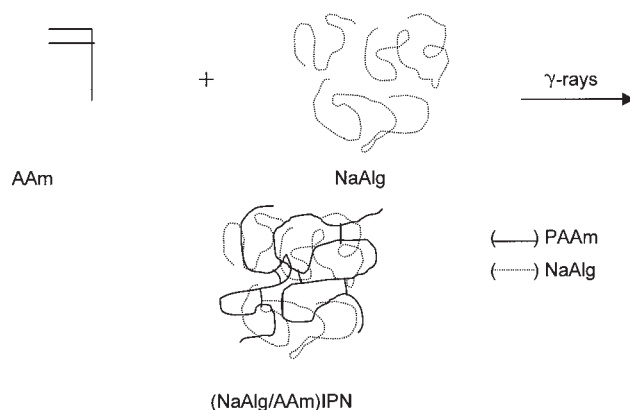


Figure 2 Possible reaction mechanism of AAm with NaAlg by irradiation.

increasing irradiation doses after 10.0-kGy irradiation doses. IPN hydrogels irradiated with a 10.0-kGy irradiation dose was used in this study. The NaAlg/AAm 1 IPN hydrogel, NaAlg/AAm 2 IPN hydrogel, and NaAlg/AAm 3 IPN hydrogel had NaAlg concentrations of 1, 2, or 3% (w/v), respectively.

Spectroscopic characterization

FTIR is important for the study of molecular structures. The width and intensity of spectral bands, as well as the positions of peaks, are all sensitive to environmental changes and the conformations of the macromolecule on a molecular level. In interpenetrating polymer networks, there are intermolecular interactions. Therefore, the FTIR spectra of interpenetrating polymer networks are different from those of pure polymers, and this is advantageous for the study of interpenetrating polymer network formation. Figure 3 shows the IR spectra for NaAlg, NaAlg/AAm IPN, and PAAm in the wavelength range of 4000–400 cm^{-1} . In the IR spectrum, NaAlg shows a broad peak at 3450 cm^{-1} for the —OH group, two peaks at 1618 and 1440 cm^{-1} for the —COO[−] group, and one sharp peak at 1050 cm^{-1} for the C—O group. The characteristic peak of NaAlg appears at 819 cm^{-1} (Na—O). The IR spectrum of PAAm exhibits bands at 3400 and 3200 cm^{-1} , which were assigned to stretching vibrations of N—H, at 1670 cm^{-1} (C=O stretching), and at 1622 cm^{-1} (NH bending). Bands at 2932 (CH stretching) and 1500–1300 cm^{-1} (various CH bendings) were also detected. The spectra of the NaAlg/AAm IPN hydrogel are characterized by the presence of absorption bands typical of the pure components. The characteristic peak of NaAlg appearing at 819 cm^{-1} was not observed in the spectra of the NaAlg/AAm 3 IPN hydrogel. The absorption peaks at 1633 cm^{-1} , assigned to the asymmetrical stretching vibration of —COO[−] groups, coupled with the peaks at 1670 and

1622 cm^{-1} of PAAm and shifted to 1633 cm^{-1} , suggest that new hydrogen bonds formed between the —COO[−] groups of NaAlg and the —CONH₂ groups of PAAm. Furthermore, the bands of PAAm, centered at about 3400 and 3200 cm^{-1} , which are the stretching vibrations of —NH₂ groups involved in both intermolecular and intramolecular hydrogen bonds, are broadened and coupled with the —OH band of NaAlg at 3450 cm^{-1} , which is included by the addition of NaAlg to PAAm, implying the occurrence of hydrogen bonds between —OH groups of NaAlg and —NH₂ groups of PAAm molecules.^{6,11}

The IR spectra of the NaAlg/AAm IPN hydrogels with different NaAlg contents are shown in Figure 4. The most important peaks appear at 1633 and 1440 cm^{-1} . The peaks in this region increase gradually with increasing NaAlg content in the NaAlg/AAm IPN hydrogels. In addition to this change with an increase in the PAAm content in the NaAlg/AAm 1–3 IPN hydrogels, the absorption peaks at 1633 cm^{-1} were assigned to the asymmetrical stretching vibration of —COO[−] groups coupled with the peaks at 1670 and 1622 cm^{-1} of PAAm and shifted to 1633 cm^{-1} .

Thermal analysis of the NaAlg/AAm IPN hydrogels

To investigate the thermal properties of NaAlg, PAAm, and NaAlg/AAm IPN hydrogels, their thermograms were recorded, and they are given in Figure 5. To determine the thermal stability of NaAlg, PAAm, and NaAlg/AAm IPN hydrogels, the temperature for the maximum weight loss (T_{max}) and the temperature for the half-life ($T_{1/2}$) were determined directly from their dynamic thermograms. PAAm gave 25% residue at 600°C. T_{max} of PAAm was 396°C, and $T_{1/2}$ was 418°C. There were three decomposition stages at 60–100, 259, and 396°C; the former was attributed to moisture loss, the weight loss at 259°C could be related to thermal processes involving the degradation

TABLE I
Percentage Gelation of NaAlg/AAm Mixtures Irradiated at Various Doses for NaAlg/AAm IPN Hydrogels

Dose (kGy)	Gelation (%)		
	NaAlg/AAm 1 IPN	NaAlg/AAm 2 IPN	NaAlg/AAm 3 IPN
2.0	64	62	65
5.0	71	72	71
7.5	81	74	63
10.0	100	100	91
12.5	100	92	82
15.0	81	81	81
17.5	72	70	68
20.0	61	65	60

Dose rate = 0.14 kGy/n.

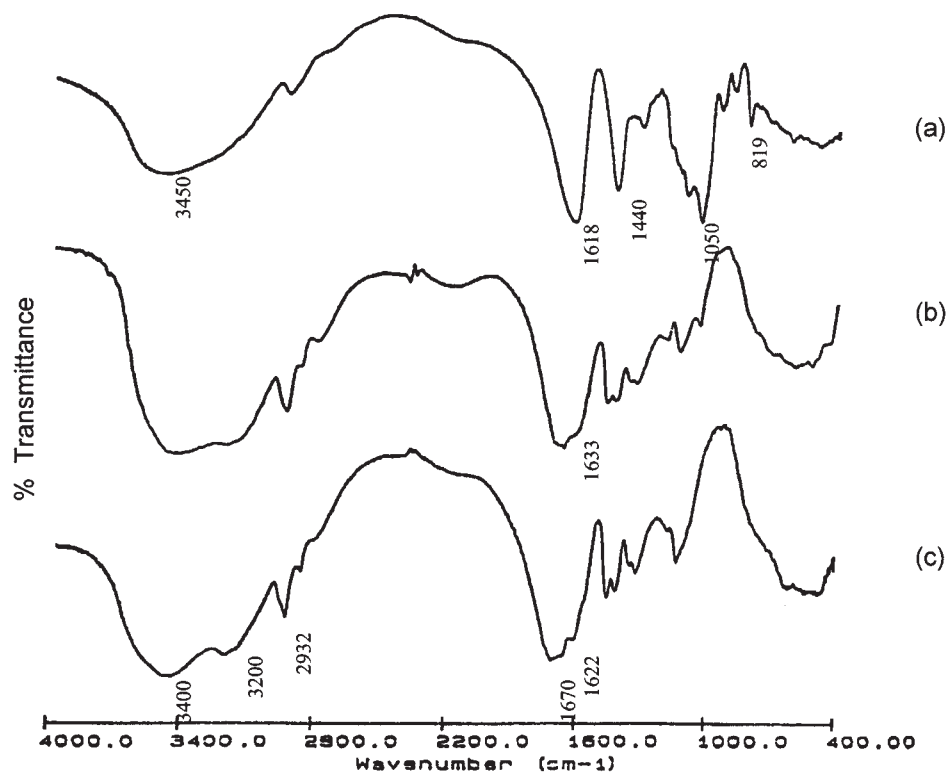


Figure 3 FTIR spectra of (a) NaAlg, (b) NaAlg/AAm 3 IPN, and (c) PAAm.

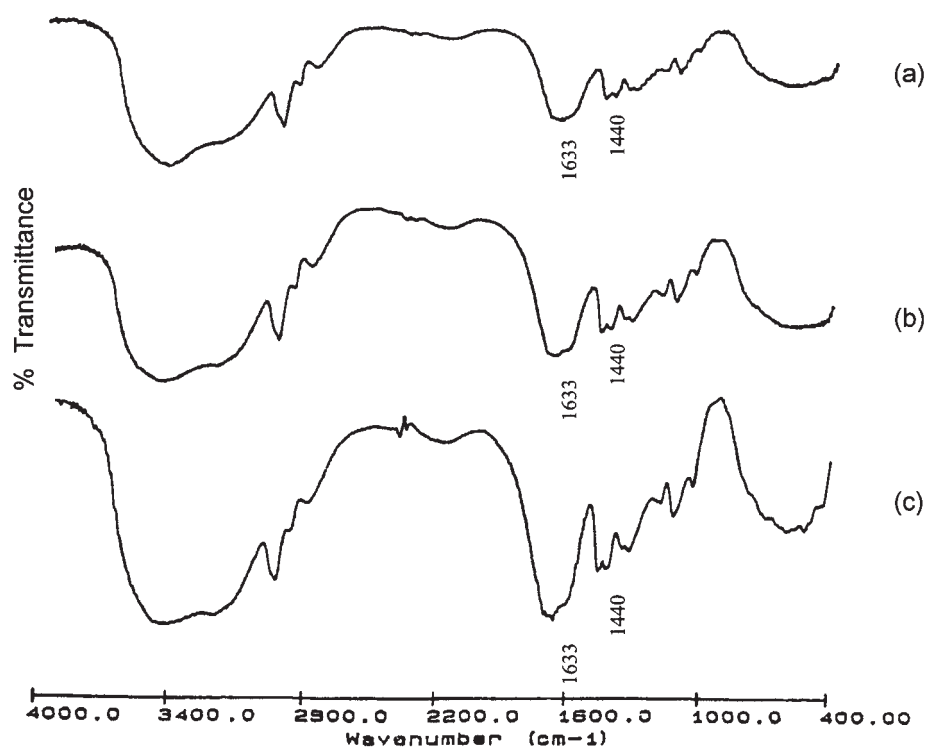


Figure 4 FTIR spectra of (a) NaAlg/AAm 1 IPN, (b) NaAlg/AAm 2 IPN, and (c) NaAlg/AAm 3 IPN.

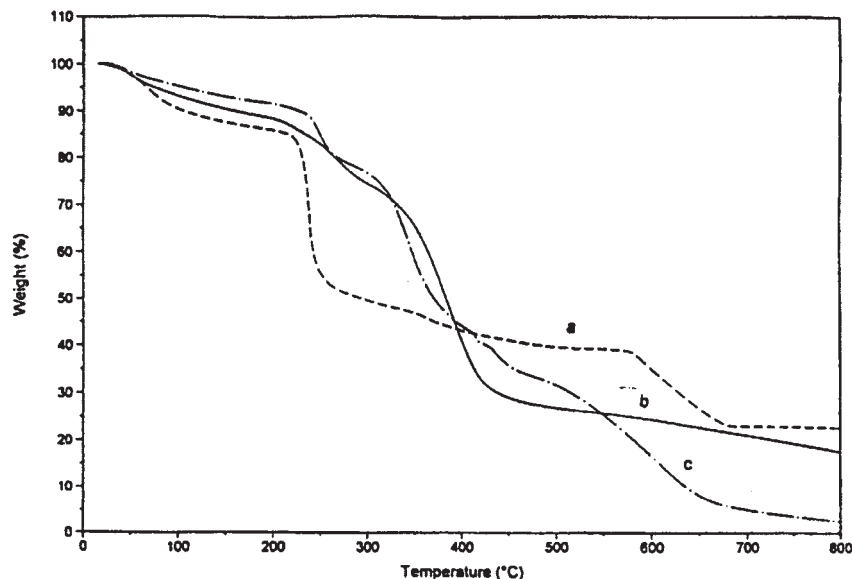


Figure 5 Thermograms of (a) NaAlg, (b) PAAm, and (c) NaAlg/AAM 3 IPN.

of PAAm chains, and the third stage at 396°C was indicative of the occurrence of more extensive thermal degradation processes. For NaAlg, T_{\max} was 238°C, and $T_{1/2}$ was 300°C; NaAlg gave 30% residue at 600°C. NaAlg showed a peak at 95°C attributed to the loss of water absorbed; the peak at 238°C indicated the thermal degradation of the intermolecular side chain. The thermogram of NaAlg shows two stages of weight loss. The first weight loss at approximately 60–120°C was due to the loss of water; the second weight loss started at about 238°C, implying the occurrence of different extents of thermal degradation of NaAlg. The third weight loss at 578°C may have been the occurrence of more extensive thermal degradation. The greatest thermal degradation peak shifted to the higher temperature, resulting from the addition of PAAm to NaAlg. The thermogravimetric analysis curve of the NaAlg/AAM 3 IPN hydrogel shows the greatest weight loss at 346°C. As shown in Figure 5, the thermal stability and T_{\max} of the NaAlg/AAM 3 IPN hydrogel were between those of NaAlg and PAAm. When a less stable species was combined with a species of higher thermal stability, the NaAlg/AAM IPN hydrogels gained new thermal characteristics. T_{\max} for the NaAlg/AAM 3 IPN hydrogel was 346°C, and $T_{1/2}$ was 384°C.

Swelling and diffusion studies

The equilibrium swelling of the NaAlg/AAM 1–3 IPN hydrogels was investigated as a function of the pH and ionic strength (I) (0.05M). Figure 6 shows a typical diagram of the swelling behavior of the NaAlg/AAM 3 IPN hydrogel, which contained 3% NaAlg, at 25°C in water with the pH ranging from 3.0–9.0. The swelling

ratios of the NaAlg/AAM IPN hydrogels increased with the pH. The swelling was fast at the beginning and became slower and slower until the hydrogels reached their maximum swelling ratios. At last, the weights of the hydrogels no longer changed. When the pH was increased, the equilibrium swelling increased significantly. The effect of the NaAlg content in the hydrogels on the equilibrium swellings of the NaAlg/AAM IPN hydrogels was determined at pHs 7.0 and 9.0. The equilibrium swellings of the NaAlg/AAM IPN hydrogels versus the NaAlg content in the hydrogels are plotted in Figure 7. The swelling properties of the NaAlg/AAM IPN hydrogels increased with increasing NaAlg content in the NaAlg/AAM IPN hydrogels. The equilibrium swelling of the NaAlg/AAM

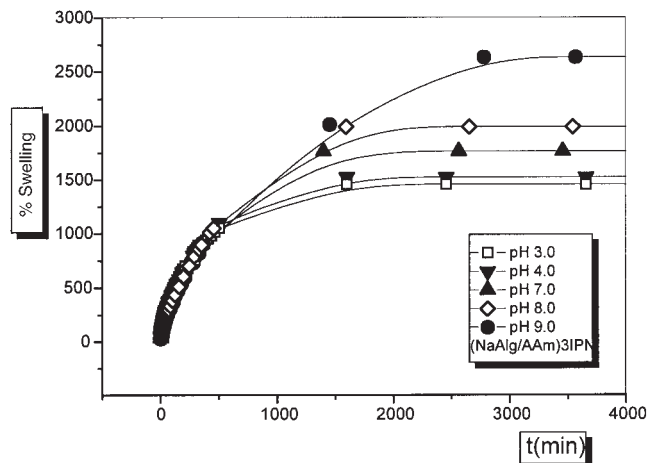


Figure 6 Effect of the pH on the swelling behavior of the NaAlg/AAM 3 IPN hydrogel at 25°C ($I = 0.05$, dose = 10.0 kGy).

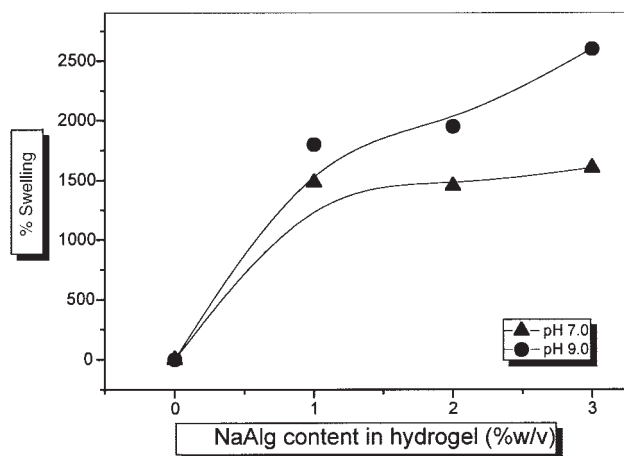


Figure 7 Effect of the NaAlg content in the hydrogel on the swelling behavior of the NaAlg/AAm IPN hydrogels at pHs 7.0 and 9.0 and at 25°C ($I = 0.05$, dose = 10.0 kGy).

3 IPN hydrogel was higher than the equilibrium swelling of the NaAlg/AAm 1 and 2 IPN hydrogels. The reason was the hydrophilic groups on NaAlg. The more hydrophilic groups were on NaAlg, the more swelling the NaAlg/AAm IPN hydrogels had.

An analysis of the mechanisms of diffusion in swellable polymeric systems has received considerable attention in recent years because of the important applications of swellable polymers in biomedical, pharmaceutical, environmental, and agricultural engineering.¹² The following equation is used to determine the nature of diffusion of water into hydrogels:

$$F = M_t/M_\infty = kt^n \quad (3)$$

where M_t and M_∞ denote the amounts of the solvent diffused into the gel at time t and infinite time (at

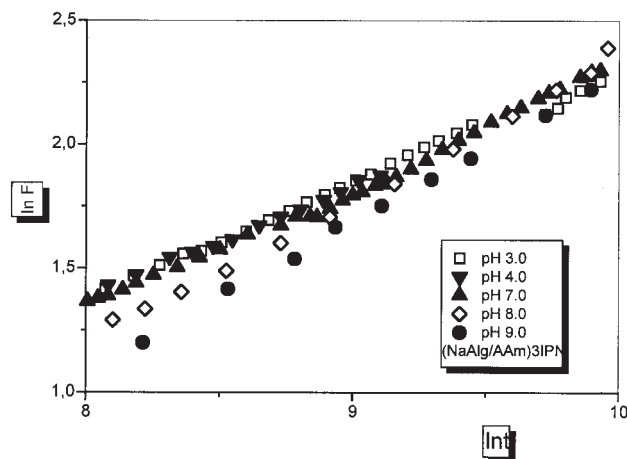


Figure 8 Linear fitted line of $\ln F$ versus $\ln t$ at different pHs for the NaAlg/AAm 3 IPN hydrogel ($I = 0.05$, dose = 10.0 kGy).

TABLE II
Values of n at Different pH Values for NaAlg/AAm IPN Hydrogels

pH	n		
	NaAlg/AAm 1 IPN	NaAlg/AAm 2 IPN	NaAlg/AAm 3 IPN
3.0	0.45	0.46	0.52
4.0	0.48	0.48	0.60
7.0	0.56	0.54	0.62
8.0	0.60	0.59	0.62
9.0	0.58	0.63	0.64

equilibrium), respectively; k is a constant related to the network; and exponent n is a number determining the type of diffusion. If during the swelling a non-Fickian process occurs, n will have a value between 0.45 and 1.0. To get n , $\ln F$ was plotted versus $\ln t$ (values of t should be expressed in seconds), and the slope was the value of n . This equation was applied to the initial stages of swelling; plots of $\ln F$ versus $\ln t$ are shown in Figure 8, and the values of n are shown in Table II. The n values were greater and less than 0.45, depending on the pH and NaAlg content. The pH had a great influence on the swelling. As the pH decreased, the swelling process became closer to non-Fickian kinetics. The swelling ratios of the NaAlg/AAm 1–3 IPN hydrogels increased with the pH. The presence of $-\text{NH}_2$ and $-\text{COO}^-$ groups in these IPN hydrogels strongly affected the swelling ratio. The values given in the table show that n was between 0.45 and 0.64. The fixed charge group ionization rates must be considered in addition to solvent diffusion. If the ionization rate is much slower than diffusion, then one can conclude that the ionization process is rate-limiting and the swelling kinetics will be non-Fickian. As the pH was increased, more $-\text{COOH}$ groups were ionized. Therefore, ionization became partially rate-limiting. Thus, as the pH was increased, the kinetics tended to become non-Fickian.

Figure 9 shows the equilibrium swelling behavior for the hydrogels measured as a function of the pH and composition of the IPN hydrogels. The $\text{p}K_a$ values of alginic acid were in the range of 3.3–4.0 (3.65 for guluronate and 3.38 for mannuronate).¹³ As can be seen from Figure 9, at a lower pH and lower alginate composition of the IPN hydrogels, the minimum values of swelling were reached. As the pH of the medium was acidic, the ion concentration difference decreased, and the hydrogels shrank. This figure shows that the swelling ratios increased with an increase in the concentration of NaAlg and $-\text{COO}^-$ groups in the hydrogels.

The swelling percentages of the NaAlg/AAm 3 IPN hydrogels containing 3% (w/v) NaAlg as a function of the ionic strength at 25°C and pH 7.0 are shown in Figure 10. As the ionic strength increased, the swelling

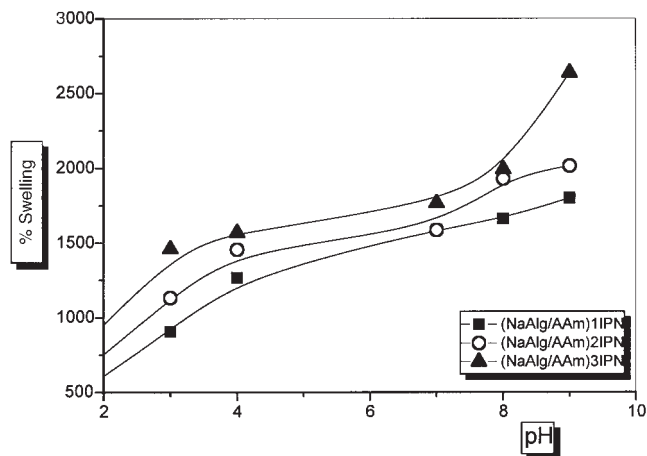


Figure 9 Influence of the pH on the swelling ratio of the NaAlg/AAm IPN hydrogels.

percentage decreased because of the increased counterion concentration shielding the charges on the polymer chain and the high ion concentration outside the gel. As the concentration of ions outside the hydrogel became equal, the osmotic pressure inside the hydrogel decreased.

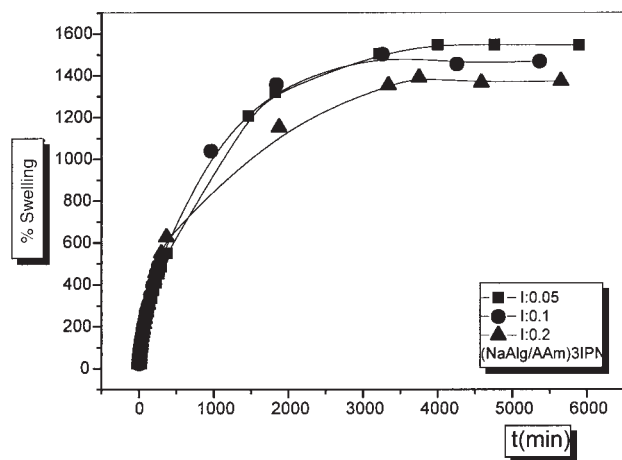


Figure 10 Influence of the ionic strength on the swelling ratio of the NaAlg/AAm 3IPN hydrogel at 25°C and pH 7.0 (dose = 10.0 kGy).

CONCLUSIONS

1. NaAlg/AAm IPN hydrogels were prepared at three different compositions and irradiated with a ^{60}Co γ source at different doses.
2. The 100% conversion of NaAlg/AAm mixtures into IPNs was achieved at 10.0 kGy.
3. Spectroscopic analyses were performed to investigate the structure of the NaAlg/AAm IPNs.
4. T_{max} of the NaAlg/AAm IPNs was found to be between those of PAAm and NaAlg.
5. The NaAlg/AAm 3 IPN hydrogel, containing more NaAlg, showed the maximum swelling percentage in distilled water at pH 7.0.
6. The diffusion of water into the NaAlg/AAm IPN hydrogels was non-Fickian in character.
7. The NaAlg/AAm IPN hydrogels were pH-sensitive. They swelled in the pH range of 7–9 in water.
8. Swelling decreased with the increasing ionic strength of the solutions.

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