Properties of Polyacrylamide-Based Hydrogels Prepared by Electron Beam Irradiation for Possible Use as Bioactive Controlled Delivery Matrices

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Received 17 April 2004; accepted 9 February 2005
DOI 10.1002/app.22167
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polyacrylamide/poly(ethylene oxide) (PAAm/PEO) crosslinked hydrogels were designed for controlled delivery of an herbicide, Atrazine, which is used in the agricultural field. Atrazine was incorporated into a PAAm/PEO matrix during an electron beam irradiation process. The Atrazine release rate from matrices prepared under different conditions was studied to determine which factors have the most affect and control over the PAAm/PEO matrix release property. The copolymer blend composition, copolymer gel content, and irradiation dose greatly affected the Atrazine release rate. In addition, its release rate was influenced by the pH and temperature of the matrix-surrounding medium. The Atrazine release rate decreased as the pH increased, but it increased as the temperature increased. The properties of the prepared crosslinked hydrogels may make them acceptable for practical use as bioactive controlled release matrices.
 J Appl Polym Sci 98: 1262–1270, 2005

Key words: electron beam; pesticide; controlled release; irradiation; polyacrylamide/poly(ethylene oxide) hydrogels

INTRODUCTION

The ways in which chemicals or agricultural bioactive agents are administered have gained increasing attention in the past two decades.[1–3] In all the main agricultural areas of the world, farmers heavily rely upon crop protection chemicals to help them meet the ever increasing demand for food and other materials, especially natural fibers. However, chemicals at a high dose are not economical and sometimes result in damaging side effects. In addition, there is increasing pressure from government regulatory authorities to reduce the application load of active ingredients on the environment. As a consequence, increasing attention has been focused on new biotechnological methods for bioactive agents that are released continually for prolonged time periods, which is more environmentally friendly in terms of ecotoxicity, and usable in a controlled fashion.[4,5]

In the last few years, use of controlled delivery systems for bioactive agents has proven to be a very attractive solution to problems associated with bioactive agent application and contamination.[6] The application of controlled release technology has been slow to reach commercialization, despite interesting research and development work by the major agrochemical companies over the last 10 years.[7] This technology now spans many fields and includes pharmaceuticals,[8] food,[9] agricultural applications,[10] pesticides,[11–15] and cosmetics and household products.[16,17]

Controlled release systems for pesticides involve advances in pesticide delivery technologies, highlighting new means of reducing toxicity, increasing efficacy, lessening environmental impact from pesticides and pesticide application, reducing evaporation, leaching, UV light and soil pesticide degradation, reducing hazards in transportation, and facilitating new product development.[14] Rather than applying one large dose of pesticide, the same amount released over a period of time will have a much greater pesticidal effect.[18]

According to the main mechanism of active agents transport, controlled release systems can be classified into three systems. The first is carrier systems, which are prepared by uniform dispersion of active agent particles throughout a solid nonerodible polymer matrix.[19] The main process for active agent release is diffusion through the matrix or leaching by the fluids. The second is bioerodible polymer systems, which are susceptible to degradation.[20,21] Degradation can be due to hydrolysis or enzymatic scission of polymeric chains and the ingredient release rate is controlled by the kinetics of degradation of the polymeric system itself. The third is swelling control systems in which the transport of active material throughout the system is controlled by the degree of swelling of the matrices.[22]

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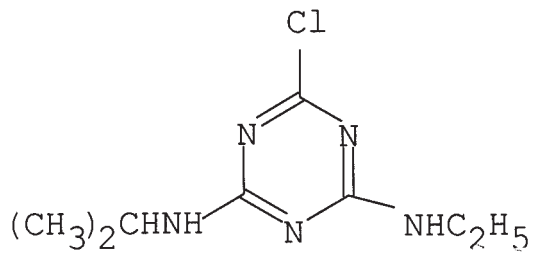
Based on the above-mentioned classifications, it seems important to investigate the intrinsic properties of matrices, such as the chemical structure, solubility, crosslinking, and so forth, that contribute to the design of tailor-made active agent delivery systems with tight control of their characteristics. There are relationships between the ways in which matrix bioactive formulations are synthesized and their controlled release properties. Radiation processing may be one method for designing matrices with controlled release properties. These techniques seem to be promising for preparation of crosslinked polymeric materials. This is because a polymer, which is in aqueous solution or a water-swollen state, undergoes crosslinking on irradiation to yield a gel-like material that is not contaminated with foreign additives. Radiation crosslinking must be composed of chemically stable C—C bonds.

Atrazine is an herbicide compound that binds strongly with clay and organic materials in soil.[23] This allows time for Atrazine to be broken down chemically and microbially. However, in sandy soil, Atrazine is prone to leaching into groundwater with excessive irrigation.[24] An ideal strategy for effective and safe use of agrochemicals would be one that limits the amount available at any time to be adequate for weed control but not for degradation or leaching into groundwater. In this respect, the objective of this study was to prevent the Atrazine compound from soil leaching or binding and control its release rate by incorporating it into radiation crosslinked copolymers such as polyacrylamide/poly(ethylene oxide) (PAAm/PEO). The factors influencing the swelling and controlled release properties of the prepared copolymers were determined.

EXPERIMENTAL

Materials

Commercial PAAm granules (molecular weight = 5,000,000–6,000,000), PEO (molecular weight = 6000.00, Acros Organics), and Atrazine (6-chloro-*N*-2-ethyl-*N*-4-isopropyl-1,3,5-triazine 99%, molecular weight = 215.69, Nihon Nohyaku Co. Ltd.) were used as received. The chemical structure of Atrazine is the following:



The chemicals, such as solvents, inorganic salts, organic compounds, and other reagents, were reagent grade and used without further purification.

Preparation of hydrogels

To prepare a PAAm/PEO hydrogel (polymeric composition, 50:50 w/w), 0.5 g of PAAm, 0.5 g of PEO, and an appropriate amount of *N*,*N*′-methylene bisacrylamide (0.005–0.03 g) were mixed with 20 mL of distilled water. The mixture was stirred until it completely dissolved at 50°C, and then it was mixed with an appropriate amount of Atrazine (≤0.02 g). The mixture was poured into a petri dish (poured mixture thickness = about 3 mm) and irradiated at doses ranging from 10 to 50 kGy with an electron beam of 1.5 MeV, a maximum beam current of 25 mA, and a power of 37.5 kW. The irradiated copolymer was cut into small pieces, left to dry at room temperature for 24 h, and then stored at 35°C in a vacuum oven.

Water absorbancy measurements

The hydrogel sample (0.05 g) was immersed in distilled water or buffer solutions with different pHs for 24 h at room temperature. The swelled gel was picked up from the solution and then weighed. The equilibrium absorbancy (Q_{eq}) was calculated by the following equation:

$$Q_{eq} = \frac{\text{weight swollen gel} - \text{weight dry gel}}{\text{weight dry gel}}$$

Release measurements

The hydrogel incorporating Atrazine (about 0. 1 g) was soaked in 20 mL of distilled water. The concentration of Atrazine released from the hydrogel was measured at time intervals using a UV spectrophotometer (Milton Roy Spectronic 1201) in a range of 190–900 nm. The UV absorbancy corresponding to the Atrazine concentrations was measured at 208 nm. Standard calibration curves were performed to determine the concentration of these solutions. The release rate of Atrazine was determined relative to the total amount of Atrazine incorporated into the hydrogel, according to the following equation:

$$\text{release (\%)} = C_r/C_t \times 100$$

where C_r and C_t are the released and total concentrations of Atrazine, respectively.

Gel determination for hydrogels

In order to determine the insoluble parts of the hydrogels, copolymers of known weight were placed in stainless steel net bags and immersed in distilled water for 48 h at 90°C. The gelled part was taken out, washed with hot water to remove the soluble fraction,

dried, and weighed. The gel percent in the sample was calculated from the following equation:

$$\text{gel (\%)} = (W_E/W_G) \times 100$$

where W_E and W_G are the dry hydrogel weights after and before extraction, respectively.

For accuracy, the water absorbency, release of Atrazine, and gel percent measurements were determined 5 times for each sample and the main average was taken. Each datum represents the mean of five determinations ($n = 5$) and the standard deviation ($\pm$SD) ranges for water absorbency, release of Atrazine, and gel percent were 3–5, 1–6, and 2–5%, respectively.

X-ray diffraction (XRD)

The XRD patterns of the copolymers were measured with a modern Shimadzu XD-D1 series diffractometer. The X-ray copper target tube was operated at 40 kV and 30 mA. All the diffraction patterns were examined at room temperature under constant operating conditions.

Thermogravimetric analysis (TGA)

A Shimadzu TGA-50 TGA system was used to study the thermal stability of the prepared copolymers under a nitrogen atmosphere. The temperature range was from ambient temperature to 600°C at a heating rate of 10°C/min.

Differential scanning calorimetry (DSC) measurements

The thermal parameters of the hydrogels [melting temperature (T_m) and heat of melting (ΔH_m)] were determined by DSC on a PerkinElmer apparatus equipped with a DSC-7 data station. An ~5-mg specimen of the Atrazine was used for DSC measurements. The measurements were carried out in an N_2 atmosphere at a heating rate of 10°C/min.

Scanning electron microscopy (SEM)

The lyophilized dried hydrogels were examined with a Jeol JSM-5400 SEM microscope. The surfaces of the polymers were sputter coated with gold for 3 min.

^{1}H-NMR spectroscopy

The ^{1}H-NMR spectra of the prepared samples were run on a Bruker 300-MHz NMR spectrometer.

RESULTS AND DISCUSSION

The preparation conditions of the PAAm/PEO crosslinked matrix, such as the effect of the irradiation dose and the copolymer composition on the matrix gel content, were thoroughly investigated.[25] We found that, as the irradiation dose and the PAAm content in the blend increased, the copolymer crosslinking content increased. The present work was designed to incorporate Atrazine into the PAAm/PEO matrix. The PAAm/PEO copolymer prepared by electron beam irradiation completely dissolved in water because of its low gel content. However, the irradiation dose reached 70 kGy. (Conversely, in the absence of Atrazine, the gel content of the copolymer was very high and reached >85%.) Therefore, we expected that the Atrazine release rate from such matrices would be very high. The presence of Atrazine molecules in the blend solution may trap the blend radicals formed by radiation, which is responsible for the crosslinking between the blend components. Thus, it is essential to use a crosslinking agent such as *N*,*N*′-methylene bisacrylamide to enhance PAAm/PEO crosslinking network formation and control the Atrazine release rate. The postulated mechanism for the formation of a PAAm/PEO crosslinked matrix containing Atrazine is shown in Scheme 1.

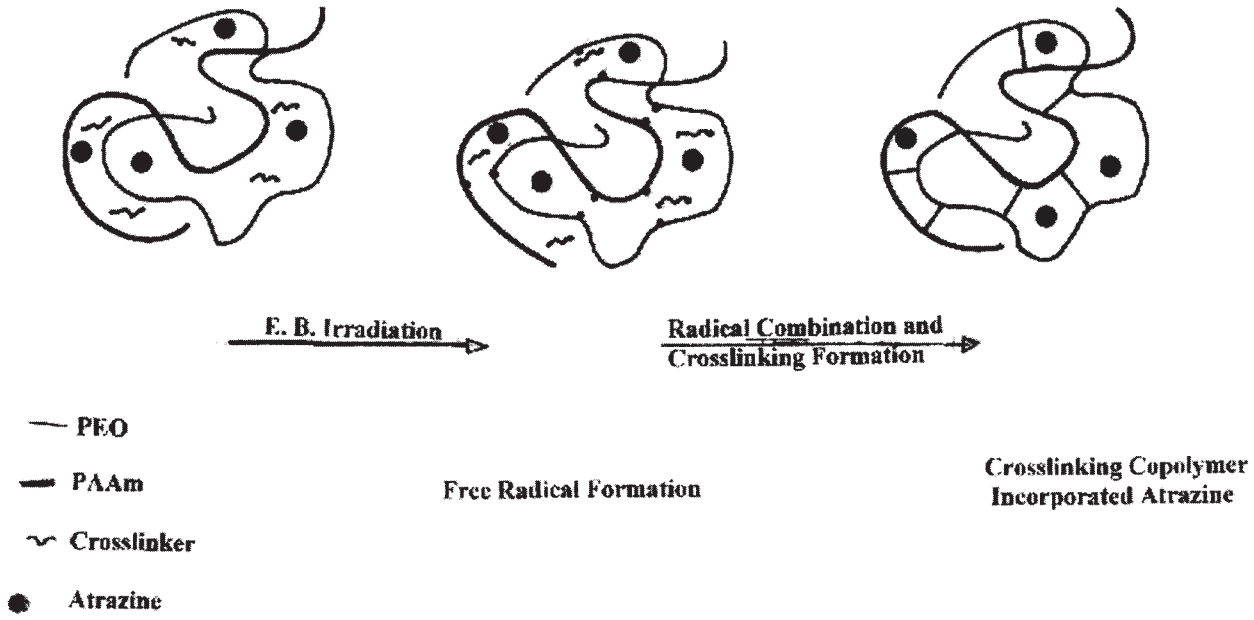
Properties of PAAm/PEO copolymer

Blend compatibility

The degree of miscibility and the affinity of PAAm and PEO to form physical intermolecular interactions reflect the extent to which the radiation can affect such a blend. The PAAm/PEO compatibility can be determined by measuring the change in thermal properties, melting temperature (T_m), and heat of fusion (ΔH) of blend components using DSC. Figure 1 and Table I show the thermal diagram and thermal parameters of PAAm/PEO copolymers with different blend compositions, respectively. It is clear that by blending PEO with PAAm, the T_m and ΔH values of PEO decrease.

The results obtained reflect the miscibility between the two polymers and suggest interactions between them. The interactions between the blend components (PAAm and PEO) may be attributable to the ether oxygen atoms of PEO, which may have the potential to form intermolecular hydrogen bonds with the NH groups of PAAm.[26,27] Such interactions may change the chain orientation of PEO. As a result, the original degree of crystallinity of PEO, as well as the ΔH, decreased.

The occurrence of intermolecular associations between PEO and PAAm can be estimated by using TGA to show to what extent the addition of PEO affects the thermal stability of PAAm. Figure 2 shows the TGA curves of PAAm/PEO blended at different



Scheme 1 The postulated mechanism for the formation of the PAAm/PEO crosslinked matrix containing Atrazine.

compositions. It is clear that the thermal stability and decomposition temperature of PAAm were improved when blended with PEO. The temperature required for the first stage of decomposition of pure PAAm is lower than that of the PAAm/PEO blend with different compositions. Conley and Malloy reported that PAAm undergoes thermal degradation at 175–300°C.[28] At these temperature imides are formed and ammonia is released. (Above 300°C, hydrogen and carbon dioxide are driven off, followed by chain session of the polymer.) When the PEO is mixed with PAAm (even at a lower PEO percent), the PEO polymer chains intertwine with the PAAm chains. This allows the adjacent amino groups for different PAAm chains to locate further from each other and distribute randomly. Therefore, the PAAm decomposition was retarded and required a higher temperature to allow NH_3 gas liberation. As a result, the thermal stability of the PAAm improved. This confirmed the above-mentioned assumption that there are intermolecular interactions between the PAAm and PEO that reflects the compatibility between them.

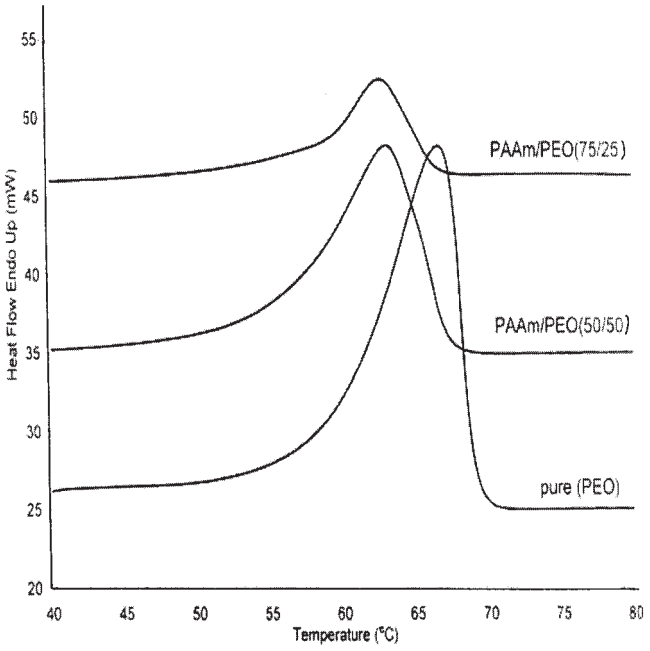


Figure 1 A DSC diagram for PEO after mixing with different amounts of PAAm.

Swelling behavior of PAAm/PEO matrix

For use in swelling controlled delivery systems, it is important to determine the amount and character of the imbibed water in hydrogels, which affects the diffusion of incorporated active materials throughout the hydrogels. In fact, the polymer type and degree of

TABLE I
Melting Temperature and Heat of Melting of PEO Mixed with Different Amounts of PAAm

PAAm/PEO composition (wt/wt)	T_m (°C)	ΔH (J/g)
0.0/100	66.7	147.0
25/75	63.0	91.5
50/50	62.6	64.8
75/25	61.5	26.5
100/0.0	—	—

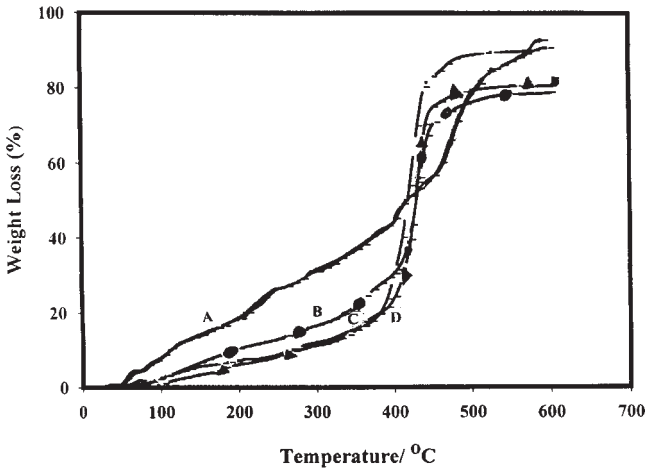


Figure 2 Thermal diagram curves for PAAm/PEO with compositions (w/w) of 100/0 (curve A), 75/25 (curve B), 50/50 (curve C), and 25/75 (curve D).

crosslinking mostly influence the swelling character. In this respect, the swelling behavior of the PAAm/PEO copolymers, which were prepared with different compositions and various amounts of crosslinking agent, was investigated and the results are shown in Figure 3(a,b). Observe that the swelling of hydrogels was decreased by increasing the PEO in the copolymer, as well as *N*,*N*′-methylene bisacrylamide crosslinking agent.

The results assume that the equilibrium swelling state depends on the polymer/water interaction and degree of crosslinking of the copolymer. The presence of a crosslinking agent creates regions, often called clusters, with a high degree of crosslinking and low water swelling. These regions increase as the crosslinking agent concentration increases, resulting in a decrease in the swelling of the copolymer.

Moreover, it is well known that water molecules first hydrate the most polar hydrophilic groups such as $CONH_2$ in PAAm. Consequently, the PAAm chains are greatly expanded. When the PAAm was mixed with the flexible PEO, which possesses relatively hydrophobic ether groups, physical interactions took place between them. As a result, the interaction between the water and the PAAm/PEO copolymer decreased. Thus, increasing the PEO content in the PAAm/PEO blend resulted in a decrease in copolymer swelling.

Practical evaluation of Atrazine entrapment systems

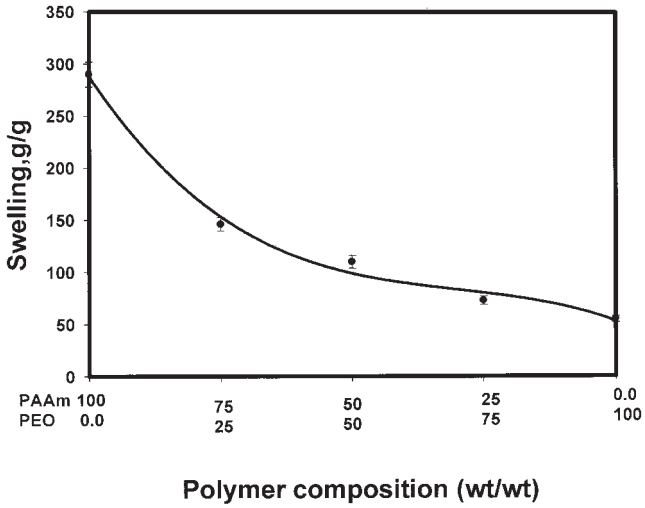
PAAm/PEO–Atrazine systems were evaluated on the laboratory scale. The Atrazine release rates were determined as a function of the matrix preparation factors and environmental conditions, such as pH and temperature.

Factors affecting release rate of Atrazine

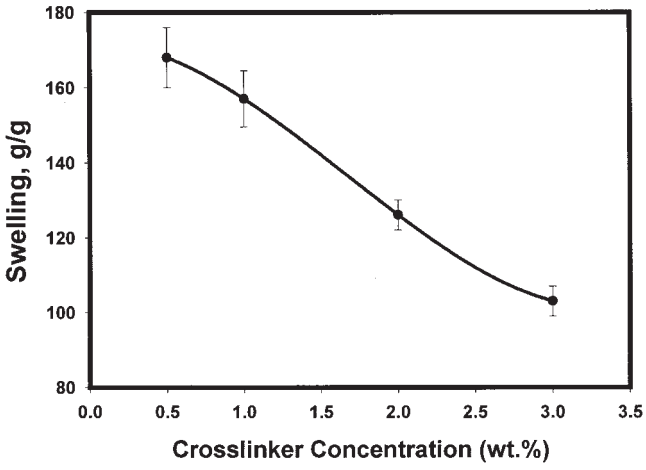
The properties of the macromolecule blends play an important role in determining the release rate of Atrazine. In particular, the average pore size, pore size distribution, and pore interconnections are important factors in Atrazine permeation. These factors, in turn, are mostly influenced by the composition and crosslinking degree of the copolymer.

Copolymer composition

Figure 4 shows the percentage of release of Atrazine incorporated into PAAm/PEO versus the time with



(a)



(b)

Figure 3 (a) The effect of different copolymer compositions on the swelling of the PAAm/PEO copolymer in distilled water; irradiation dose = 20 kGy, copolymer concentration = 5%. (b) The swelling behavior of the PAAm/PEO copolymer prepared with different amounts of crosslinking agent; PAAm/PEO composition = 50/50 (w/w), irradiation dose = 20 kGy, copolymer concentration = 5%.

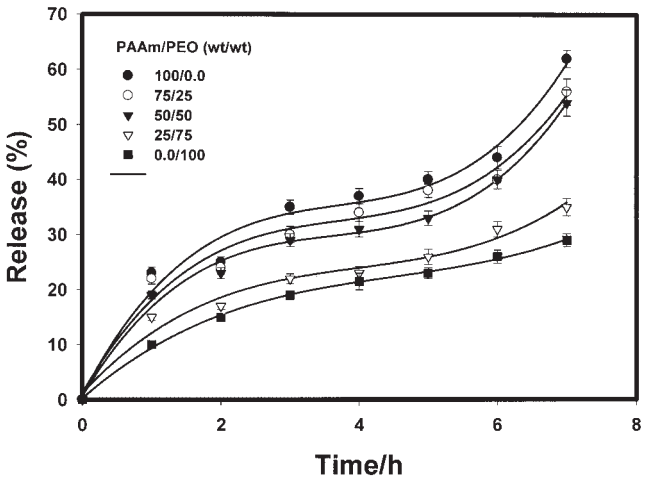


Figure 4 The release rate of Atrazine from PAAm/PEO in distilled water prepared with different compositions; copolymer concentration = 5 wt %, irradiation dose = 30 kGy, Atrazine concentration = 0.6%, crosslinker concentration = 2.5%.

different blend compositions in distilled water. The results indicated that the release of Atrazine increases with time. It was also observed that the release of Atrazine increases as the PAAm content increases in the copolymer.

By increasing the PAAm content in PAAm/PEO, the copolymer swelling increases and the diffusion and liberation rate of Atrazine throughout the matrix improved.

The morphology of the PAAm/PEO copolymer prepared with different compositions was studied by using SEM (Fig. 5). Homogeneous, deeply high porous structure, and randomly relatively aggregated granules were observed for PAAm-rich copolymers, which swelled significantly in water. By increasing the PEO content, the blend exhibited a honeycomb-like structure. These results may be due to the differences in the expansion of the copolymer network and its affinity magnitude for water; that is, PAAm has a great affinity to swell in water, whereas PEO is a linear polymer and has no tendency to randomly aggregate. Therefore, its affinity to swell in water is lower than that for PAAm. The permeation results confirmed the assumption that the PAAm-rich copolymers possess higher affinity to swell in water compared with PEO-rich ones.

Irradiation dose

The degree of crosslinking of the copolymer may control the release rate of entrapped active agent. It is well known that the polymerization and crosslinking processes are governed by the irradiation dose and crosslinker concentration. Thus, the crosslinking copolymerization of PAAm and PEO was studied in order to obtain polymeric matrices with different degrees of crosslinking and hydration.

Figures 6 and 7 show the release rate of Atrazine from PAAm/PEO hydrogels prepared with different irradiation doses and crosslinker concentrations, respectively. The release of Atrazine is decreased with increasing irradiation dose and crosslinker concentrations.

The results can be explained according to the following: when the irradiation dose and/or crosslinker concentration increases, the crosslinking density be-

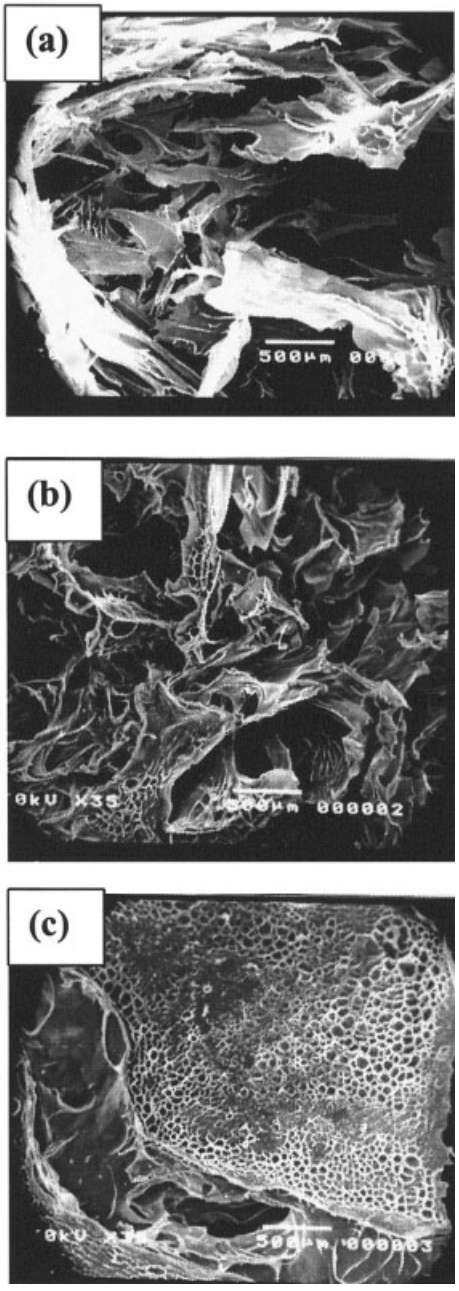


Figure 5 SEM photos for the PAAm/PEO hydrogel prepared with compositions (w/w) of (a) 75/25, (b) 50/50, and (c) 25/75.

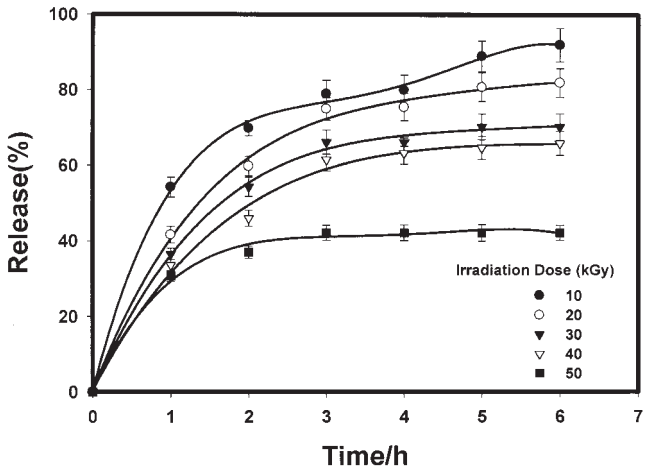


Figure 6 The release rate of Atrazine from the PAAm/PEO hydrogel in distilled water and prepared with different irradiation doses; polymer concentration = 5 wt %, PAAm/PEO composition = 50/50 (w/w), Atrazine concentration = 0.6%.

tween the resultant copolymer chains increases. This restricts the expansion of the chains of the prepared copolymer and decreases the swelling of the hydrogel. As a result, the dissolution, diffusion, and release rates of Atrazine from the PAAm/PEO hydrogel decrease.

XRD studies were performed in order to detect the morphological changes occurring in the copolymer structure during the irradiation process. PAAm/PEO samples, which were prepared at various irradiation doses, were examined by using XRD (Fig. 8). We observed that the intensity of the peak at 2θ 22°, which may represent the polymer crystal region of PEO, decreases as the irradiation dose increases.

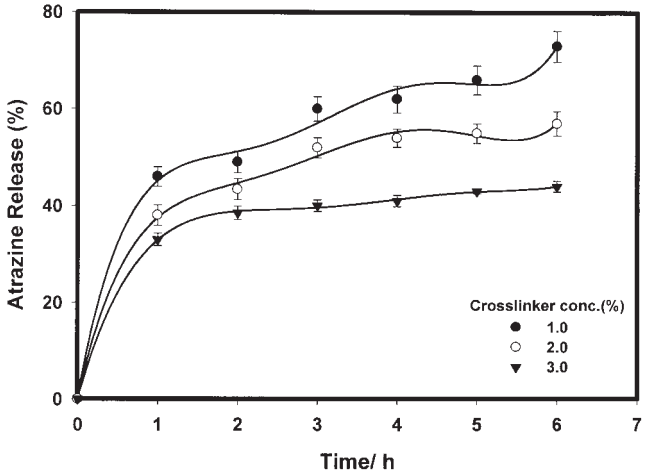


Figure 7 The release rate of Atrazine in distilled water from the PAAm/PEO hydrogel prepared with different crosslinking agent concentrations; polymer concentration 5 wt %, PAAm/PEO composition 50/50 (w/w), irradiation dose 20 kGy, Atrazine concentration 0.6%.

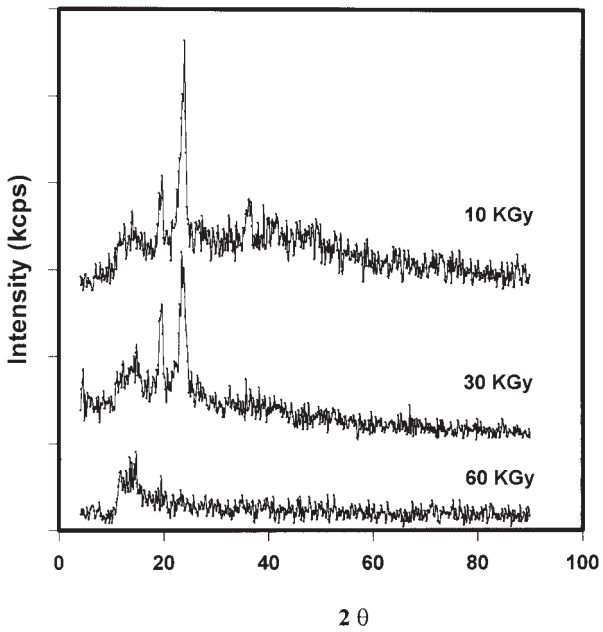


Figure 8 XRD patterns for the PAAm/PEO copolymer prepared at different irradiation doses.

The degree of crosslinking of the copolymer, which was irradiated in swollen form, was increased by increasing the irradiation dose. When the crosslinked copolymers were left to dry in air, the rearrangement and recrystallization of PEO polymer chains from the amorphous state was restricted by such crosslinked chains. Consequently, the crystal regions of PEO decreased.

From the previous results, it can be concluded that it is possible to modulate the active materials release to the medium by variation of the PAAm/PEO copolymer composition and/or its crosslinking degree.

Concentration of Atrazine

Figure 9 shows the release rate of Atrazine from the PAAm/PEO hydrogel prepared with different Atrazine concentrations. The concentration of active material incorporated into the PAAm/PEO hydrogel can affect its release rate in distilled water. The Atrazine release rate increased with its increased concentration incorporated into the PAAm/PEO matrix.

Effect of temperature on Atrazine release

The effect of the temperature on the release of Atrazine was investigated, and the results are presented in Figure 10. The temperature of the release medium was found to have a significant effect on the Atrazine release rate: the higher the temperature was, the higher the release rate. The swelling behavior of the PAAm/PEO hydrogel is closely related to the

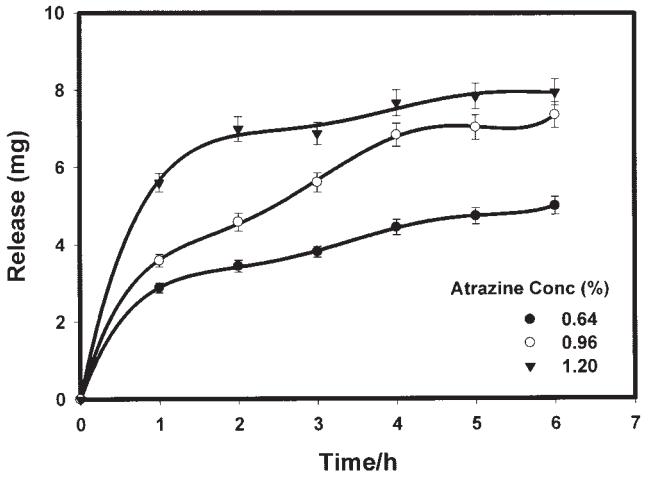


Figure 9 The release rate of Atrazine from the PAAm/PEO hydrogel containing different Atrazine concentrations in distilled water; polymer concentration = 5 wt %, PAAm/PEO composition = 50/50 (w/w), irradiation dose = 20 kGy.

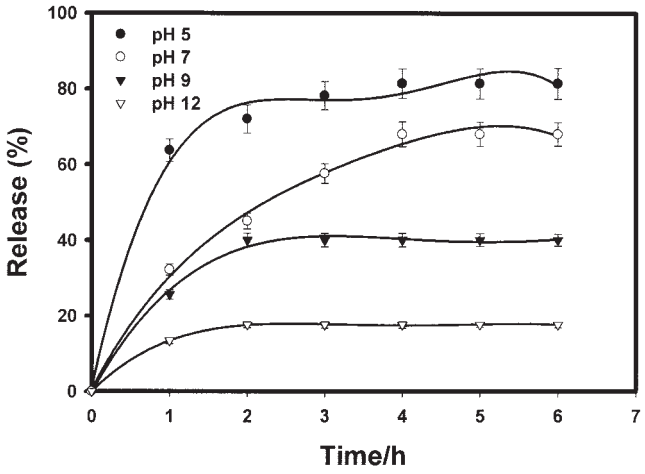


Figure 11 The effect of different pH media on the release rate of Atrazine from the PAAm/PEO hydrogel; polymer concentration = 5 wt %, PAAm/PEO composition = 50/50 (w/w), irradiation dose = 20 kGy, Atrazine concentration 0.6%.

temperature of the swelling medium. With a rise in temperature, the diffusion rate of water molecules into the PAAm/PEO hydrogel increased. Consequently, the matrix network chain relaxation increased, resulting in an increase in the Atrazine release rate.[29]

Effect of pH on Atrazine release

Because of the difference in pH values of various types of soils, it is essential to study the effect of the pH on the delivery of Atrazine incorporated into PAAm/PEO. The release rate characteristic of PAAm/PEO was studied in neutral, alkaline, and acidic media and the results are shown in Figure 11. It is obvious that the Atrazine release rate decreases as the surrounding pH increases. The results assume that the release of Atrazine from a polymer matrix depends on the characteristics of the active agent. Solubility of Atrazine in water is very poor. Therefore, a high release of Atrazine that is incorporated into PAAm/PEO in an acidic pH medium may be attributable to the basic character of Atrazine and its ability to be protonated in an acidic medium. The protonation of Atrazine improves its solubility in water and facilitates its diffusion throughout the matrix.

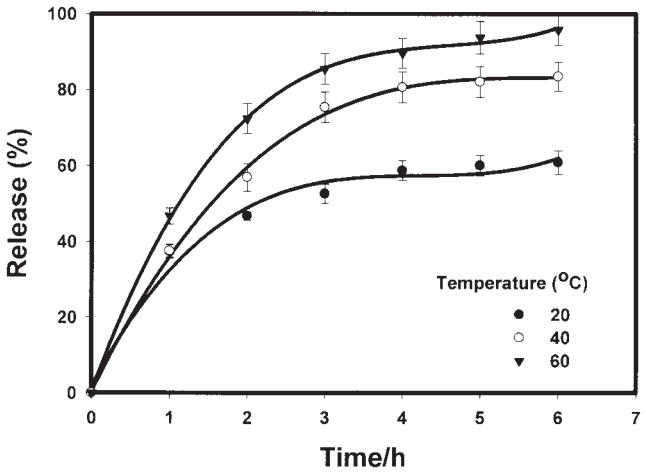


Figure 10 The effect of temperature on the release rate of Atrazine in distilled water from the PAAm/PEO copolymer; polymer concentration = 5 wt %, PAAm/PEO composition = 50/50 (w/w), irradiation dose = 20 kGy, Atrazine concentration 0.6%.

Effect of radiation on Atrazine stability

Because electron beam irradiation might lead to changes in the structure and activity of Atrazine, it was important to study its effect on the stability of Atrazine. The Atrazine released from the irradiated matrix as well as the control were investigated by using NMR and DSC. We found that the structures of both were not affected by irradiation doses up to 40 kGy. The presence of the PAAm/PEO matrix, which surrounded the Atrazine during the radiation process, protected the Atrazine from degradation by consuming the radiation energy in the copolymer crosslinking process.

CONCLUSION

Controlled delivery systems for agricultural active agents were designed. Atrazine was selected as a model herbicide and incorporated into a chemically stable crosslinked PAAm/PEO matrix prepared by electron beam irradiation. The structure of the copol-

ymers, as well as the environmental conditions surrounding them, play an important role in determining the release rate of Atrazine. The composition and degree of crosslinking of the copolymer control the Atrazine release rate. The release rate of Atrazine was decreased by increasing the pH of the medium. A temperature rise improved the diffusion of Atrazine throughout the matrix. The obtained results may make the prepared PAAm/PEO–Atrazine controlled delivery system acceptable for practical use in the agricultural field.

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