Control Release of Some Pesticides from Starch/(Ethylene glycol-*co*-methacrylic acid) Copolymers Prepared by γ-Irradiation

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ABSTRACT: Starch/(Ethylene glycol-*co*-Methacrylic acid) [Starch/(EG-*co*-MAA)] hydrogels were designed for controlled delivery of pesticides, such as Fluometuron (FH); Thiophanate Methyl (TF) and Trifluralin (TI) which are use in the agricultural field. The delivery device was prepared by using γ-irradiation and was characterized by FTIR, DSC, and SEM. The swelling behavior of hydrogels as a function of copolymer composition and irradiation dose was detected. This article discusses the swelling kinetics of polymer matrix and release dynamics of Trifluralin from hydrogels for the evaluation of the diffusion mechanism and diffusion coefficients. The values of the diffusion exponent 'n' for both the swelling of hydrogels and the release of Trifluralin from the hydrogels have been observed between 0.56 and 0.86 when the MAA content in the polymers was varied from 20 to 80 wt %, respectively. It is inferred from the values of the 'n' that non-Fickian diffusion mechanism has occurred for different EG/MAA compositions. The release rate from matrices prepared under different conditions was studied to determine which factors have the most affect and control over the hydrogel matrix release property. The preparation conditions such as EG/MAA hydrogel composition, pesticide concentration, type of pesticide and irradiation dose greatly affect the pesticide release rate, which also influenced by the pH and temperature of the matrix-surrounding medium. The pesticide release rate decreased as the irradiation dose and pH increased, but it increased as the MAA content, pesticide concentration and temperature increased. The release rate of Trifluralin is the highest one, whereas the Fluometuron is the lowest. The properties of the prepared hydrogels may make them acceptable for practical use as bioactive controlled release matrices. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1500–1509, 2011

Key words: starch; ethylene glycol; methacrylic acid; γ-irradiation; hydrogels; control release

INTRODUCTION

Controlled-release technology has become increasingly popular as a means of delivering drugs, agrochemicals and other biologically active agents.[1–6] This technology can solve a variety of problems concerning the application of an active compound. Conventional treatment with such agents cause severe damage to the environment[7] since they migrate readily through water and air. The delivery of agrochemicals by controlled release formulations is a promising concept offering advantages for health, nutrition environmental pollution control, and economic development.[8–10] The controlled release systems are capable of delivering substances slowly and continuously up to several years. The release of active agent may be constant over a long period, or it may be triggered by the environment or other external events.[11] Furthermore, a controlled-release system not only increases the effectiveness of the active agents, but it also facilitates minimizing the amount of chemicals applied to the soil, and thus, decreases the likelihood of damage to the environment.[12] Unlike conventional products, controlled-release materials are safer for those who handle them or come in contact with treated crops during harvesting or storage.[13] 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.[14–17]

Starch is added to the synthetic copolymer due to a renewable, biodegradable, a naturally abundant polysaccharide and a low-cost material. In recent years, particular attention has been attached to synthesis of starch graft copolymer due to an increasing interest in the synthesis of new cost-effective polymer.[18,19] The aqueous copolymer systems have attracted much attention due to their environmental friendliness and biocompatibility compared with that formed in organic media.[20–22] The aqueous systems can be formed from double hydrophilic

copolymer (DHC) containing different hydrophilic segments. As the copolymer systems were formed by DHC in aqueous media, one hydrophilic segment undergoes physical or chemical transformations and becomes hydrophobic, whereas another hydrophilic segment remains soluble in water.[23–38] The DHC is an almost fully reversible process which is very sensitive to pH,[23–32] temperature,[23–25] and/or salinity.[24,25] The typical hydrophilic segments used in DHC include poly(acrylic acid),[23,24] poly(methacrylic acid),[25,26] poly (ethylene glycol),[27–30] poly(N-isopropylacrylamide),[32–34] poly(styrene sulfonic acid),[25] poly(N-alkylaminoethyl methacrylate),[30–32] poly(vinyl pyridine),[25] poly(vinyl ethers),[36] polyoxazoline,[37] polypeptides and RNA.[27,28] Poly(methacrylic acid) and poly(ethylene glycol) may associate to form hydrogen-bonded complexes under acidic conditions.[39–43] These complexes may be used to develop responsive polymers since the properties of the complex may be notably different than those of the constituent polymers. PMAA–PEG complex is considerably less hydrophilic in compared with the individual polymers, therefore a hydrogel containing a backbone of PMAA and grafts of PEG exhibits a relatively low degree of swelling under complex-promoting conditions (low pH when the acid is protonated), and a high degree of swelling when the complex is broken (high pH when the acid is neutralized).

Radiation polymerization/crosslinking has many advantages over conventional chemical and photochemical methods. It is a simple environmental friendly additive free process that occurs at room temperature and the degree of crosslinking can be easily controlled by altering the radiation conditions. The hydrogels prepared by the radiation method have potential for use in biomedical applications due to the absence of extraneous toxic additives (chemical initiators, crosslinkers, etc.). Another advantage of this method is that the resultant product is simultaneously sterilized during the irradiation process.[44,45] Crosslinking by radiation is an important method to obtain polymeric carrier for controlled release of bioactive agents.[46] Keeping in view the importance of pesticides and its adverse effect on environment, ecosystem and human health, controlled and sustained delivery devices are required for its release.

Therefore, this study is an attempt, to synthesize Starch/(EG-co-MAA) hydrogels, by using γ-irradiation to develop delivery devices. The polymeric networks Starch/(EG-co-MAA, thus formed have been characterized by FTIR, TGA, DSC, SEM, and swelling responses as a function of Starch/(EG-co-MAA) contents and irradiation doses. The swelling kinetics of hydrogels and release dynamics of pesticides from hydrogels have also been discussed for the evaluation of the release mechanism and diffusion coefficients.

EXPERIMENTAL

Materials

Methacrylic acid and ethylene glycole of purity 99% (Merck, Germany) were used as received. Water-soluble starch, ACS grade (Aldrich, Germany) was used as received. Analytical grade pesticides were purchased from El- Nasr for Chemical Industries, Egypt and used without further purification. Structure of pesticides is shown below: The concentration of the pesticide was measured and determined by UV-spectrophotometer. Family groups: (a) Urea (Herbicide), (b) Benzimidazole (Fungicide), and (c) Dinitroaniline (Insecticide) are shown below:

a. Herbicide (Urea): Fluometuron (FH); $C_{10}H_{11}F_3N_2O$ (N,N-dimethyl-N-[3-(trifluoromethyl) phenyl] urea) (M.wt 232.2) form colorless crystals. It was synthesized by Griffin; Makhteshim-Agan; Novartis; Nufarm GmbH. It is a crystalline solid, m.p 163–164.5°C. It's solubility is 110 mg/L at 20 C, $\lambda = 279$, in water and most organic solvents.

b. Fungicide (Benzimidazole precursor): Thiophanate Methyl (TF); $C_{12}H_{14}N_4O_4S_2$ (Dimethyl 4, 4-(o-phenylene) bis (imino-carbonothioyl) =bis [carbamate] (M.wt 342.4) form colorless crystals. It was supplied by Aimco; Elf Atochem; Nippon Soda; Rallis. It is a crystalline solid, m.p 172°C. It's solubility at 23°C is 58.1 mg/L, $\lambda = 267$, practically insoluble in water and soluble in most organic solvents.

c. Insecticide (2, 6-dinitroaniline): Trifluralin (TI); $C_{13}H_{16}F_3N_3O_4$ (2,6-dinitro-N,N-dipropyl-4-trifluoromethyl-benzenamine) (M.wt 335.3) form orange crystals (TI). It was introduced by Budapesti Vegymuvek. It is a crystalline soild, m.p 48.5–49°C, $\lambda = 252$. It's solubility is 30–67 mg/L at 25°C, in water and most organic solvents. The structures of previous pesticides are shown in Figure 1.

Hydrogel preparation

Hydrogel was obtained by gamma irradiation-induced copolymerization of 20 wt % aqueous solutions of EG and MAA with different weight ratio in small glass tubes with stirring at room temperature, using gamma rays with a dose rate was 4.25 kGy/h. 8 Grams of maize starch powder was first mixed with 70 mL of distilled water to form gel-like solution, and the system was stirred and heated at 80°C. The gelatinized starch was cooled at room temperature. Various EG : MAA ratios of (80 : 20), (60 : 40), (40 : 60) and (20 : 80) wt % were added into the gelatinized starch. The mixture was stirred at room
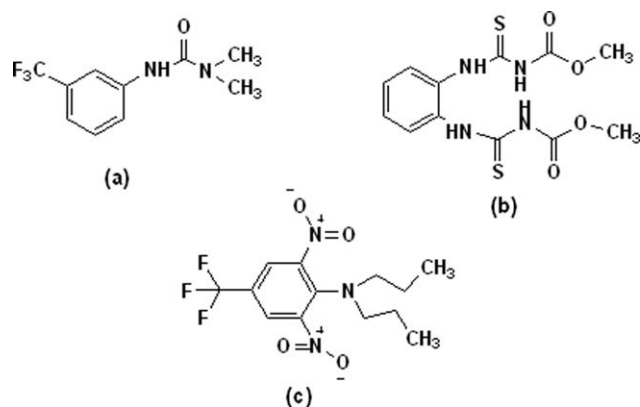
Figure 1 The structures of different pesticides, (a) Fluometuron, (b) Thiophanate and (c) Trifluralin.

temperature for 30 min. The gelatinized starch–monomer mixture was poured into a glass tube and then irradiated with gamma rays. After copolymerization, the tubes were broken, the formed polymeric cylinder were removed and cut into discs of 2-mm thickness. All samples were washed in excess water to remove the unreacted monomers then air-dried at room temperature and then dried in vacuum oven at 40°C.

Gel content

Dried hydrogels were extracted with distilled water for 24 h at 100°C to extract the insoluble parts of the hydrogel. The insoluble parts or gelled parts, were taken out and washed with hot distilled water for the removal of the soluble parts and then were dried and weighed. This extraction cycle was repeated until the weight became constant. The gel yield of hydrogel was determined as follows:

$$\text{Gel } (\%) = (W_e/W_d) \times 100 \qquad (1)$$

Where, W_d and W_e represent the weights of the dry hydrogel and the insoluble part after extraction, respectively.

Swelling and diffusion studies

Dried hydrogel discs (0.3–0.4 mm thickness, 4-mm diameter) were left to swell in distilled water or phosphate buffer solutions of desired pH (3, 5, 7, 9 and 11). Swollen gel removed from the swelling medium at regular time intervals and superficially dried with filter paper, then it was weighed and placed in the same bath. The measurements were continued until a constant weight was reached.

$$\text{Swelling } \% = (W_s - W_d/W_d) \times 100 \qquad (2)$$

where, W_s and W_d represent the weights of swollen and dry samples, respectively. To study the kinetic

of water- sorption mechanism; the water–intake process was monitored by the determination of the swelling ratio of the hydrogel at desired time intervals as previously described.

Pesticide loading into the polymer matrix

The loading of the pesticide in to Starch/(EG-*co*-MMA) polymers was carried out by swelling equilibrium method. The polymers were allowed to swell in the pesticide solution (in 10-mL water) of known concentration for 72 h at room temperature (23 ± 1°C) and then dried to obtain the release device. The loading % of pesticide in gel was calculated by the following equation:

$$\text{Loading } (\%) = m_1 - m_0/m_0 \times 100 \qquad (3)$$

where, m_1 and m_0 are the weights of gel loaded with pesticide and dry gels, respectively.

Release measurements

Release experiments were performed by placing the Starch/(EG-*co*-MAA) hydrogel loaded with pesticide in buffer solution of different pH. 1 mL sample was withdrawn at time intervals to follow the release process. The concentration of pesticide was measured by UV spectroscopy. Adsorption isotherm method by batching experiment were carried out using the bottle–pointed method where one gram of dry hydrogel discs (2 mm thickness and 4-mm diameter) of the four different EG/MAA compositions, (80 : 20), (60 : 40), (40 : 60) and (20 : 80) wt % were added into the gelatinized starch 40 wt % and the total volume is 100 ml for each EG/MAA composition in the hydrogel. A series number of concentrations; 0, 0.2, 0.4, 0.6, 0.8, and 1% of stock pesticide 250 mg/mL with constant volumes 20 mL (V) for each bottle containing the adsorbent polymeric hydrogel. The percentage release of pesticide at different pH was calculated according to the following equation:

$$\text{Releasing } (\%) = (C_r/C_t) \times 100 \qquad (4)$$

where C_r and C_t are the released and total loaded concentration of pesticide, respectively.

Differential scanning calorimetry

The thermal parameters of the hydrogels melting temperature (T_m) and heat of melting (ΔHm)] were determined by DSC on a PerkinElmer apparatus equipped with a DSC-7 data station. An 5-mg specimen of the pesticide was used for DSC

MAA/EG composition (wt %)	Gel (%) at		
	Irradiation dose (kGy)		
	20	30	40
0.0/100	60	65	65
20/80	64	68	70
40/60	81	84	85
60/40	87	91	93
80/20	93	95	96
100/0.0	91	93	94

measurements. The measurements were carried out in an N_2 atmosphere at a heating rate of 10°C/min.

Ultraviolet measurements

Determination of the permeated amount of pesticide was carried out using Perkin-Elmer, UV–vis spectrophotometer in the range of 190–900 nm.

Scanning electron microscopy

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.

RESULTS AND DISCUSSION

Gel content

The effect of preparation conditions of the Starch/(EG-co-MAA) hydrogels, such as irradiation dose and copolymer composition on the matrix gel content, was thoroughly investigated and shown in Table I. It was found that, as the irradiation dose and the MAA content increased, the gel content as well as the copolymer crosslinking increased. There are a low decrease in gel % in case of pure MAA, this is due to the crosslinking increased with increasing the copolymerization between MAA and EG and it reduced with pure MAA, so, it reduced with minute value.

FTIR spectroscopy

To study the modification of the starch, FTIR spectra of Starch/(EG-co-MAA) hydrogel and TI-loaded one are recorded in Figure 2(a,b), respectively. It shows a broad absorption band observed at 3200–3650 cm^{-1} due to OH stretching and glucosidic ring of starch [Fig. 2(a)]. In addition absorption band at 1760 cm^{-1} due to C=O stretching of carboxylic acid association in Starch/(EG-co-MAA) hydrogel. Other
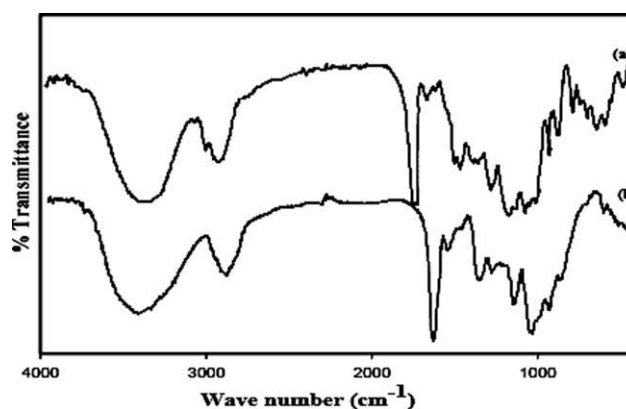

Figure 2 FTIR of (a) Starch/(EG-co-MAA) hydrogels and (b) TI-loaded hydrogels.

bands, such as those at 2931 and 2927 cm^{-1} (C—H stretching) and peaks around 1157.2 cm^{-1} (C—O stretching) due to hydroxyl groups, can also be seen. The absorption band due to C=O stretching of carboxylic acid association in Starch/(EG-co-MAA) hydrgels at 1760 cm^{-1} has been shifted to 1718 cm^{-1} and the band at 1157.2 cm^{-1} due to C-O stretching also shifted to 1134 cm^{-1} as a result of the interaction of Starch/(EG-co-MAA) with the TI [Fig. 2(b)].

Kinetic study of water swelling

The swelling rates of Starch/(EG-co-MAA) hydrogels in distilled water were investigated and shown in Figure 3. The hydrogels have various EG/MAA compositions. It can be seen that the swelling rate is significantly influenced by the MAA content into the Starch/(EG-co-MAA) hydrogels, it enhanced with increasing MAA content into the hydrogel. The swelling that controlled with diffusion is the most widely applicable mechanism for describing the pesticide release from hydrogels. Fick's law of diffusion with either constant or variable diffusion coefficients
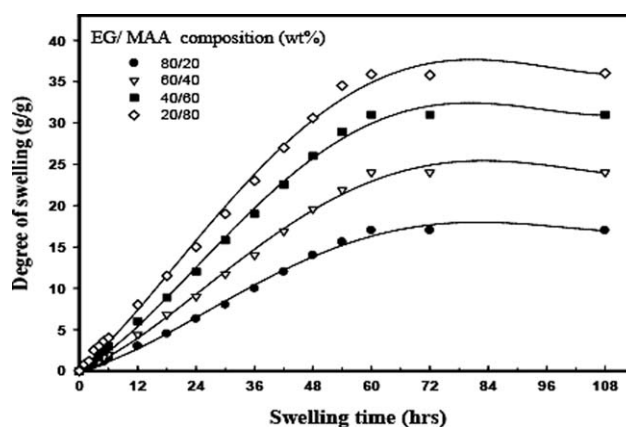

Figure 3 Swelling rate of different EG/MAA compositions of Starch (EG-co-MAA) hydrogel at starch content; 40 wt % and irradiation dose; 20 kGy.
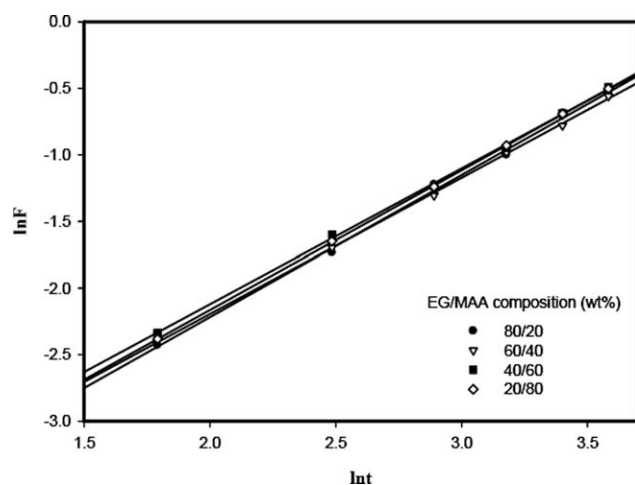
Figure 4 Plot of lnt against lnF for different EG/MAA compositions of Starch/(EG-*co*-MAA) hydrogel at room temperature and pH7.

is commonly used in modeling diffusion-controlled release.[47]

To determine the nature of water diffusion into the hydrogel, the following equation was used:

$$F = W_t/W_\infty = k \, t^n \tag{5}$$

$$\ln F = \ln k + n \ln t \tag{6}$$

Therefore,

where; F is the fraction of swelling due to the water uptake or denotes the amount of water absorbed at time t. W_t and W_∞ represent the amount of water absorbed by the Starch/(EG-*co*-MAA) hydrogel at time t and at equilibrium, k is a constant characteristic of the system, and n is an exponent which takes into account the mode of water transport. A value of $n = 0.5$ indicates a Fickian diffusion mechanism, whereas a value of $0.5 \leq n \leq 1$ indicates that diffusion is anomalous or non-Fickian. Above equation applies to initial swelling states and linearity is observed when ln F as a function of ln t as showed in Figure 4. From the intercept and the slope of the curves, the value of the kinetic constant, k and the diffusion exponent, n are obtained. In all cases, as the obtained n value is higher than 0.5, so it can be considered non-Fickian diffusion.[48] The diffusion increases with increasing MAA content. At higher swelling capacity the values of k increased. However, EG/MAA, (20/80) wt % composition shows an anomalous k value of 37.26, which is higher than the other compositions, (40/60) wt %; 30.15, (60/40) wt %; 25.71 and (80/20) wt %; 19.22, respectively. The results imply that the Starch/(EG-*co*-MAA) hydrogel swelling follow the anomalous diffusion mechanism.

For controlled diffusion process, the fraction of swelling due to the water uptake (F) through the

hydrogel can be expressed by the following equation:

$$F = 4(Dt/\pi\ell^2)^{1/2} \tag{7}$$

where D is the apparent diffusion coefficient of water through the hydrogel, ℓ is the thickness of the sample and t is the time. This equation is a solution of Fick's second law under simple boundary conditions such as swelling in water and biological fluids or simple geometric forms such as discs, cylinders and spheres. Plotting of water uptake fraction (F) against the square root of time ($t^{1/2}$), for different EG/MAA compositions in Starch/(EG-*co*-MAA) hydrogel where, S_1 (80/20) wt %, S_2 (60/40) wt %, S_3 (40/60) wt %, and S_4 (20/80) wt % respectively. According to Figure 4, the results imply that anomalous diffusion takes place in these gels as showed in Figure 5, linearity is obtained in the first stage of the process, this allow the calculation of the apparent diffusion coefficient from the slop of the straight line. These results are reported in Table II. D values increase by the increase of the methacrylic acid content in the hydrogel, could be attributed to the hydrophilic character of the hydrogel, supposes an increase of the network ionization, leading to higher water absorption and higher diffusion coefficients. Table II shows the values of non-Fickian diffusion parameters (n) and (k) which obtained after nonlinear regression that performed on the swelling data. As expected, the values of the swelling constant increases with the ionic strength resulted from the existence of water. The hydrogel compositions however show anomalous values for (n) and (k). The hydrogels that have values of (n) in the range more than 0.5, a non-Fickian diffusion can be assumed to be predominant in these gels. All the compositions
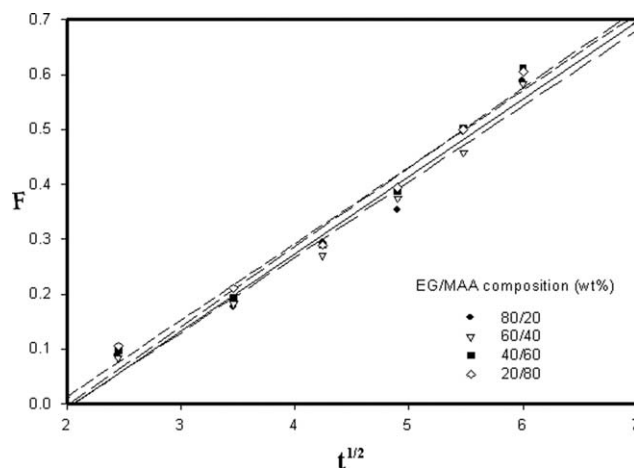

Figure 5 Plot of $t^{1/2}$ against F for different EG/MAA compositions of Starch/EG-*co*-MAA hydrogel at room temperature and pH7.

TABLE II
The Swelling Percent and Diffusion Parameters of Starch/(EG-co-MAA) Hydrogels with Different EG/MAA Compositions (wt %), S_1; (80/20), S_2; (60/40), S_3; (40/60) and S_4; (20/80) at Room Temperature, pH7 and Starch Content 40 wt %

Samples	EDS (g/g) at 60 h	Swelling constant ($k \times 10^2$)	Diffusion exponent (n)	Type of diffusion	Apparent diffusion coefficient of water through the hydrogel D(cm^2 min^{-1}) $\times 10^{-3}$
S_1	17	19.22	0.56	non- Fickian	0.08
S_2	24	25.71	0.69	non- Fickian	0.12
S_3	31	30.15	0.71	non- Fickian	0.19
S_4	38	37.26	0.86	non- Fickian	0.33

have values of (n) indicating that diffusion in these gels is anomalous. In these cases, the mesh size becomes so enough and thet penetration and diffusion of water molecules into the hydrogel network structure becomes easy. Thus, the higher MAA content in Starch/(EG-co-MAA) hydrogel can operate in the non- Fickian system, and allow significant diffusion to take place. So, there are a possibility for these gels to be utilize as agricultural controlled release systems.

Thermal properties of prepared hydrogels

The loading of pesticide into the prepared hydrogel can change the thermal parameters of it, so the thermal parameters of Starch/(EG-co-MAA) hydrogels and that loaded with TI can be determined by measuring the change in thermal properties such as melting temperature (Tm) and heat of fusion (ΔH) of these polymers using DSC. Figure 6 shows the thermal diagram of Starch/(EG-co-MAA) hydrogels and that loaded with TI. Tm and ΔH values for Starch/(EG-co-MAA) and that loaded with TI were 190°C &12 J/g and 110°C & 77 J/g, respectively. This occurred due to the interaction that occurred between Starch/(EG-co-MAA) hydrogel and TI .

Release of pesticides from polymer matrix

Hydrogels exhibit a thermodynamic compatibility with water, which allows them to swell in aqueous media and makes them potential candidates for agrochemicals release devices.[14] The release of chemicals entrapped in a hydrogels occurs only after water penetrates the network to swell the polymer and dissolve the chemicals, followed by diffusion along the aqueous pathways to the surface of the device. The chemicals release is closely related to the swelling characteristics of the hydrogels, which in turn, is a key function of chemical architecture of the hydrogels. In the present study, the release of pesticides from the hydrogels occurred in very controlled and sustained manner, which is the primary requi-

site for the use of agrochemicals to control the environment and health hazards.

Factors affecting release rate of pesticides

The release of pesticides through the swellable polymeric matrix is based on the glassy-rubbery transition of the polymer, which occurs as a result of water penetration into the matrix. Whereas interactions between water, polymer and pesticides are the primary factors in release control, the properties of the macromolecular copolymers and the environmental conditions surrounding them could influence the release rate to a greater or lesser degree. Therefore, the following factors which were expected to affect and control the release rate of pesticide from Starch/(EG-co- MAA) matrix in distilled water were investigated.

Copolymer composition

Figure 7 shows the release rate percentage of TI incorporated into Starch/(EG-co-MAA) versus the time with different EG/MAA compositions in distilled water. The results indicated that the release of TI increases with time. It was also observed that the release of TI increases as the MAA content increases in the copolymer. By increasing the MAA content in
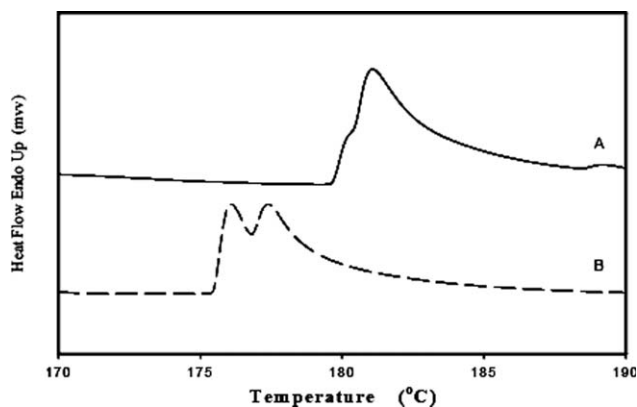
Figure 6 DSC of (A) Starch/Poly (EG-co-MAA) hydrogel and (B) Starch/ Poly (EG-co-MAA) hydrogel + TI.
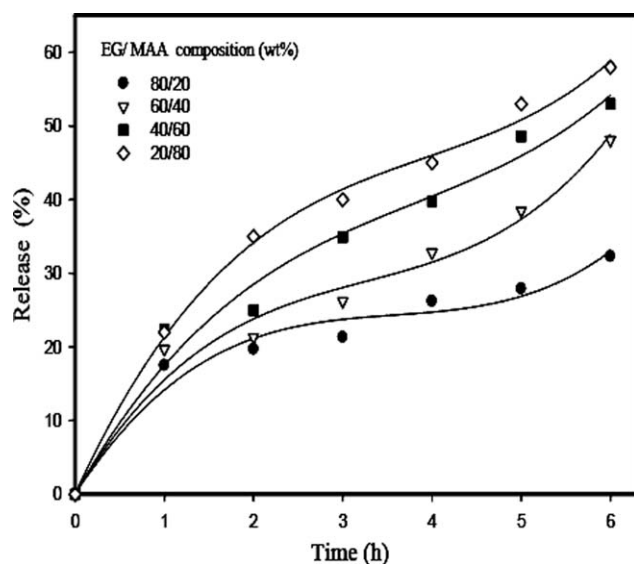
Figure 7 The release rate of TI from Starch/(EG-*co*-MAA) hydrogel at different EG/MAA compositions in distilled water and prepared with irradiation doses; 20 kGy starch concentration; 40 wt %, TI concentration; 1%.

Starch/(EG-*co*-MAA), the copolymer swelling increases as shown in Figure 8, the diffusion and liberation rate of TI throughout the matrix improved. The results assume that the equilibrium swelling state depends on the polymer/water interaction and degree of polymer crosslinking.

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 EG and MAA was studied to obtain polymeric matrices with different degrees of crosslinking and hydration. Figure 9 show the release rate of TI from Starch/(EG- co-MAA) hydrogels prepared with different irradiation doses. The release of TI is decreased with increasing irradiation as well as degree of crosslinking. The results can be explained according to the following: when the irradiation dose increases, the crosslinking density between the resultant copolymer chains increases. This restricts the expansion of the copolymer chains and this reduces the swelling of prepared hydrogels, as a result, the dissolution, diffusion, and release rates of TI from the Starch/(EG-*co*-MAA) hydrogel decrease.[49]

Effect of pH

Because of the difference in pH values of various types of soils, it is essential to study the effect of the
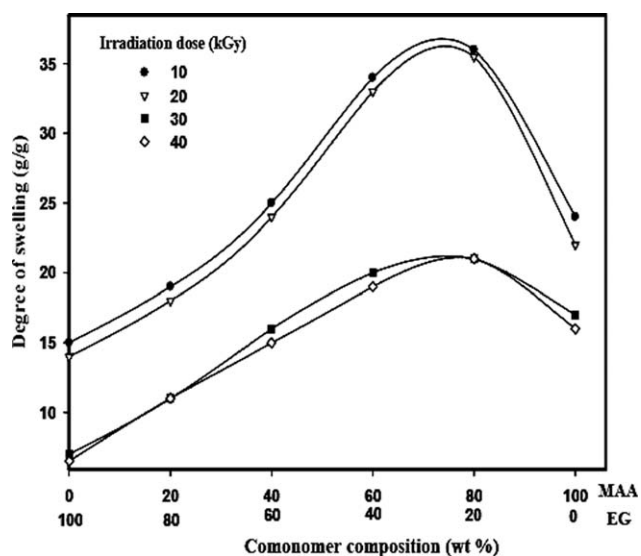

Figure 8 The effect of different EG/MAA compositions on the swelling of the Starch/(EG-*co*-MAA hydrogel in distilled water at different irradiation doses.

pH on the delivery of TI incorporated into Starch/(EG-*co*-MAA) matrix. The release rate characteristic of Starch/(EG-*co*-MAA) hydrogel was studied in neutral, alkaline and acidic media and the results are shown in Figure 10. It is obvious that the TI release rate decreases as the surrounding pH increases. The results assume that the release of TI from a polymer matrix depends on the characteristics of the active agent. Solubility of TI in water is very poor. Therefore, a high release of TI that is incorporated into the hydrogel matrix in an acidic pH medium may be attributable to the basic character of TI and its ability to be protonated in an acidic medium. The protonation of TI improves its
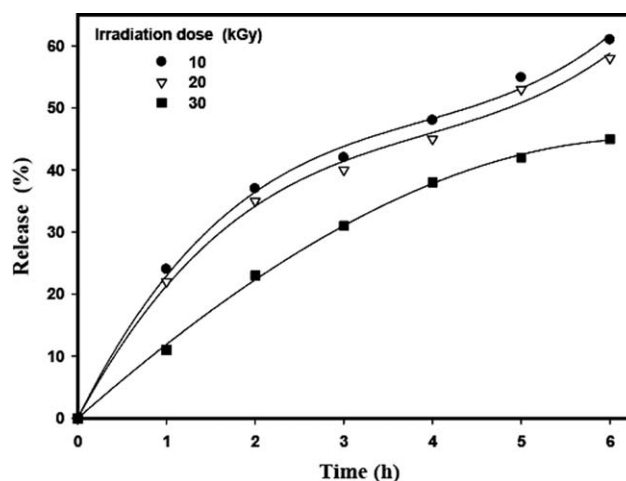

Figure 9 The release rate of TI from the Starch/(EG-*co*-MAA hydrogel in distilled water and prepared with different irradiation doses; EG/MAA composition; 20/80 (w/w), TI concentration; 1%.
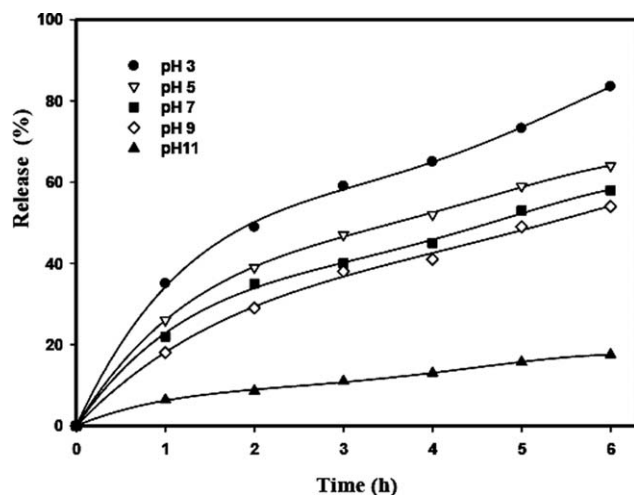
Figure 10 The effect of different pH media on the release rate of TI from the Starch/(EG-*co*-MAA) hydrogel; polymer concentration wt %, EG/MAA composition; 20/80 (w/w), irradiation dose; 20 kGy, TI concentration; 1%.

solubility in water and facilitates its diffusion throughout the matrix.

Environmental temperature

Due to the possible difference in environmental conditions, it is an important to investigate the influence of environmental temperature on the TI release throughout the Starch/(EG-*co*-MAA) matrices. Therefore, TI release rate was studied at various solution temperatures and was shown in Figure 11. Clearly, as the solution temperature increases the TI release rate increases. The high temperature may increase the total kinetic energy of the system, which leads to a greater random motion and a higher diffu-
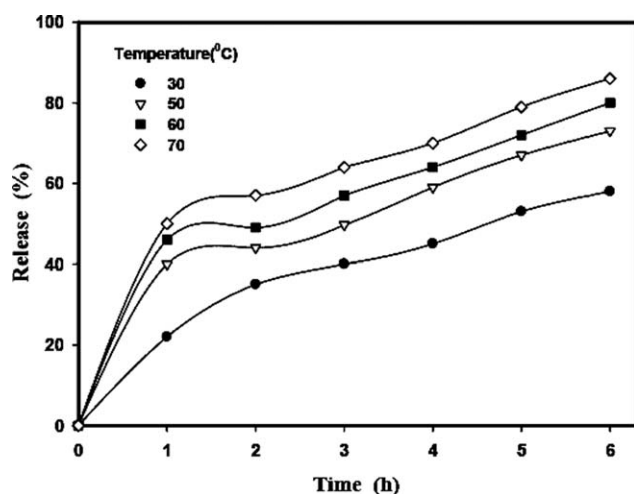

Figure 11 The effect of temperature on the release rate of TI from the Starch/(EG-*co*-MAA) hydrogel; EG/MAA composition; 20/80 (w/w), irradiation dose; 20 kGy, TI concentration; 1%.
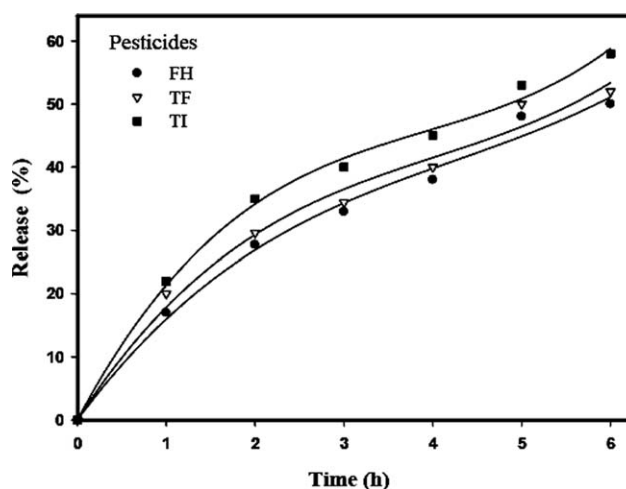

Figure 12 The release rate of FH, TF and TI from the Starch/ (EG-*co*-MAA) hydrogels in distilled water; EG/MAA composition; 20/80 (w/w), irradiation dose; 20 kGy, pesticide concentration; 1%.

sion rate of TI throughout the matrix imbibed with water.[49]

Concentration and type of pesticide

The release rate of pesticide can be influenced by it's concentration and structure. Figure 12 shows the release rate of different types of pesticides, Fluometuron, Thiophanate Methyl and Trifluralin from Starch/(EG-*co*-MAA) hydrogel. It showed that the release rate of Trifluralin is the highest one while it is the lowest for the Fluometuron, this is due to the structure of three types of pesticides (Fig. 1) and their interactions with the Starch/(EG-*co*-MAA) hydrogel. Strong intermolecular hydrogen band was occurred between –NH groups in Fluometuron, Thiophanate Methyl and – OH, -COOH in hydrogel
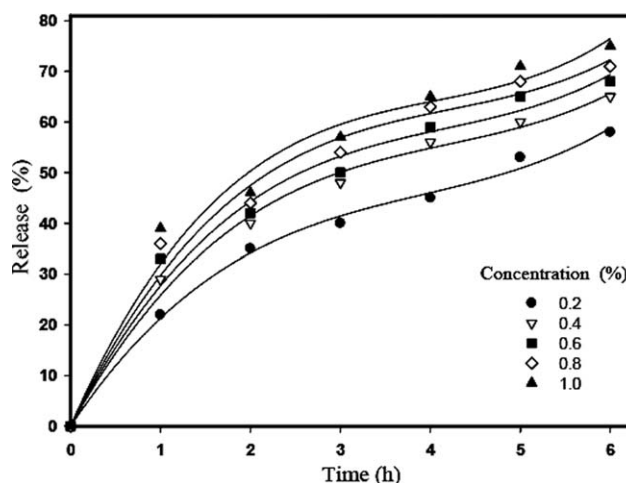

Figure 13 Scanning Electron Microscopy (SEM) of (a) Starch/(EG-*co*-MAA) (20/80) wt % and (b) Starch/(EG-*co*-MAA) (20/80) wt % hydrogel with TI.
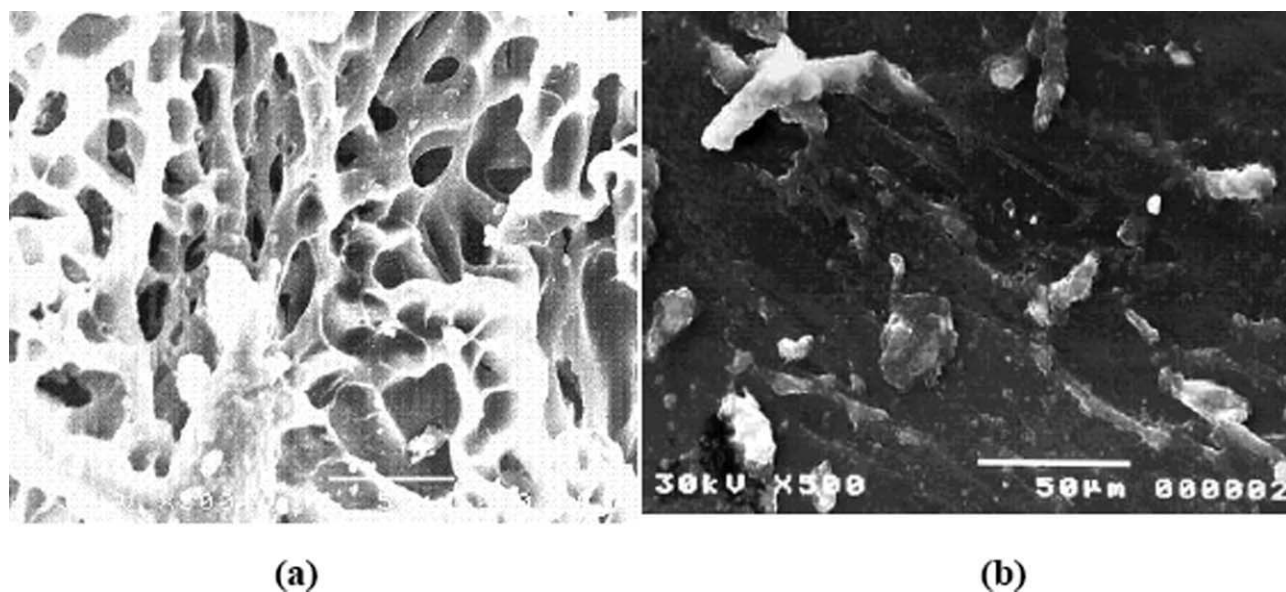
(a) **(b)**

Figure 14 The release rate of TI from the Starch/(EG-co-MAA) hydrogel containing different TI concentrations in distilled water; EG/MAA composition; 20/80 (w/w), irradiation dose; 20 kGy.

which stabilized by hydrophobic interactions, this reduces the pesticide release rate while low hydrogen bond was occurred between Trifluralin and hydrogel. SEM in Figure 13 showed that the incorporation of pesticide into the polymeric matrix can affect the morphology and the shape of surface pores which can affect the swelling rate that reflex on the release rate.

Figure 14 shows the release rate of TI from the Starch/(EG-co-MAA) hydrogel prepared with different TI concentrations that loaded into hydrogel matrix. The concentration of active material incorporated into the Starch/(EG-co-MAA) hydrogel can affect its release rate in distilled water. The release rate of TI increased with increased the concentration of soaked pesticide that incorporated into the Starch/(EG-co-MAA) matrix.

CONCLUSIONS

Starch/(EG-co-MAA) hydrogels were synthesized by γ-irradiation as controlled delivery systems for pesticides that used in agricultural field. The pesticides such as Fluometuron (herbicide); Thiophanate Methyl (fungicide) and Trifluralin (insecticide) were selected and incorporated with soaking into a chemically stable hydrogels. The swelling kinetics of polymer matrix of Trifluralin from hydrogels for the evaluation of the diffusion mechanism and diffusion coefficients were discussed. The values of the diffusion exponent 'n' for both the swelling of hydrogels and the release of Trifluralin from the hydrogels have been observed between 0.56 and 0.86 as the MAA content in the polymers was varied from 20 to 80 wt %, respectively. It is inferred from the values of the 'n' that non-Fick-

ian diffusion mechanism has occurred for different EG/MAA compositions. The structure and crosslinking of the copolymers as well as the EG/MAA compositions and irradiation dose control the pesticide release rate. Also, the environmental conditions such as temperature and pH of the medium affect the release rate of pesticides. The release rate of TI decreased by increasing the pH and increased with temperature rise. The release rate of Trifluralin is the highest one while the Fluometuron is the lowest. The obtained results concluded that the prepared Starch/(EG-co- MAA) controlled delivery systems have more advantages than the conventional ones to be acceptable for practical use in the agricultural field.

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