Preparation and Characterization of Interpenetrating Network Beads of Poly(vinyl alcohol)-grafted-Poly(acrylamide) with Sodium Alginate and Their Controlled Release Characteristics for Cypermethrin Pesticide*

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ABSTRACT: Interpenetrating network polymeric beads of poly(vinyl alcohol)-grafted-acrylamide with sodium alginate have been prepared by crosslinking with glutaraldehyde. Cypermethrin, a widely used pesticide, was loaded with 80% efficiency in these hydrogel beads. The beads were characterized by Fourier transform infrared spectroscopy to confirm the grafting. Scanning electron microscopy was used to know the morphology of the beads. Equilibrium swelling experiments indicated that swelling of the beads decreased with an increase in crosslinking. The *in vitro* release studies were performed under static conditions and the release data have been fitted to an empirical relation to estimate the transport parameters. The diffusion coefficients have been calculated for the transport of pesticide through the polymeric beads using the initial time approximation method. These values showed decrease with increasing crosslinking as well as increasing pesticide loading. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 552–560, 2002; DOI 10.1002/app.10306

Key words: poly(vinyl alcohol)-grafted-poly(acrylamide); sodium alginate; hydrogel; interpenetrating polymeric network beads; cypermethrin

INTRODUCTION

In order to control pests like flies, nematodes, fungi, white grub, and the larva of chaffer beetles that are considered to be the serious soil pests for groundnut and several other crops, it is necessary to apply cypermethrin to the soil. Under soil conditions, the residual toxicity of the pesticide used should be minimum in order to avoid the possible cytotoxicity of the plants as well as to alleviate the environmental pollution problems. In our earlier papers[1–4] published from this laboratory, several hydrophilic polymers have been used in the controlled release (CR) of pesticides. The parameters that affect the properties of such CR formulations are dependent upon the nature and type of the polymer used. Further investigations are being carried out in our laboratory to use the appropriate polymeric matrices in order to achieve an effective CR of drugs and pesticides.[5,6] The inter-

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Table I Synthetic Details of the Graft Copolymer

Polymer	Density (g/cm^3)	Mass (in g)	Mass of AAm (in g)	Con. of CAN (mol/L)	% Grafting	Grafting Efficiency	% Conversion of AAm
PVA	1.0387	10	0	0	0	0	0
PVA-*g*-PAAm	1.2610	10	10	0.1	93	100	93

penetrating polymeric networks (IPNs) were found to be the quite useful matrices[7–10] in the CR of agrochemicals; however, a careful monitoring of the release of toxic pesticides in such systems is important in view of the present-day trends of green chemistry.

Earlier, it was shown[11–13] that one of the easiest ways to control the release of bioactive molecules through polymeric matrices is to use the blend systems. Among the various polymers used, crosslinked poly(vinyl alcohol) has been extensively used in the CR of pesticides.[14–16] Studies have also been made on the use of acrylamide grafted copolymers with different types of starches,[17–19] cellulose,[20] and guar gum[21], which indicated improved properties such as flocculation, solubility, binding strength, water retention, and drag-reducing effectiveness of the substrate upon grafting. The crosslinked sodium alginate (Na-Alg) has also been used as a CR matrix in medicine[22] and in agriculture.[5] Recently, the blends of sodium alginate with deoxycholate, pluronic F68LF, dodecyltrimethyl ammonium bromide, poly(vinyl alcohol), and poly(ethyloxazoline) have been used along with gelatin, poly(allylamine), and chitosan as the coating materials[14] to control the release of bioactive molecules. The present study is an extension of our earlier research[7] on the use of polymeric Na-Alg based matrices for the release of cypermethrin. The encapsulation efficiency, release kinetics, equilibrium water uptake, and release parameters have been evaluated to study their usefulness as the matrix materials in the effective release of pesticides.

EXPERIMENTAL

Materials

A 94.4 mass % pure grade cypermethrin (CPN) was received as a gift sample from Rallis India Limited, Bangalore. This compound was further purified by dissolving in an AR grade acetone and precipitated in double-distilled water to obtain the pure product. Poly(vinyl alcohol) (PVA; MW of 125, 000), acryl amide (AAm), sodium alginate (Na-Alg), ceric ammonium nitrate (CAN), glutaraldehyde (GA) (25% w/v) solution, acetone, and the AR grade methanol were all purchased from s.d. Fine Chemicals, Mumbai, India.

Synthesis of Graft Copolymer of PVA and Aam

The grafting of PVA by AAm was done by adopting the method reported in the literature.[23–25] The grafted copolymer of PVA with acrylamide, i.e., (PVA-*g*-PAAm) was prepared by polymerizing acrylamide in a 10% (w/w) PVA solution using CAN.[26] The reaction was carried out in a three-necked flask fitted with a condenser, a gas inlet, and a thermometer to monitor the temperature. The synthetic details are given in Table I.

A 10 g of PVA was dissolved in 100 mL of deareated distilled water at 60°C with a constant stirring under a slow stream of nitrogen gas. After cooling the solution, a 0.12*M* of AAm dissolved in 75 mL of deareated distilled water was mixed with the above PVA solution by stirring. The nitrogen gas was then purged into the solution for 20 min. A 5 mL of 0.1*M* of CAN was added by further purging with nitrogen gas for another 10 min. The temperature of the reaction mixture was maintained at 25°C. The copolymerization reaction was continued up to 24 h and the reaction was terminated by adding hydroquinone. An excess amount of acetone was added to precipitate the polymer, which was then filtered through the suction and dried in a vacuum oven at 60°C. The polymer was dissolved in dimethylsulfoxide and filtered to remove the undissolved polyacrylamide. The filtrate was concentrated and the dissolved graft copolymer was again precipitated in an excess amount of acetone.

The percentage grafting was estimated from the mass of the polymer before and after grafting using the relation

$$\% \text{ Grafting} = \frac{W_g - W_o}{W_o} \times 100 \quad (1)$$

where W_g and W_o are the masses of the graft copolymer and the PVA backbone. The % grafting of AAm onto PVA and the grafting efficiency were calculated as

$$\text{AAm \% grafting} = \left(\frac{\text{Mass of PVA-}g\text{-PAAm} - \text{Mass of PVA}}{\text{Mass of PVA-}g\text{-PAAm}}\right) \times 100 \quad (2)$$

$$\text{Grafting efficiency} = \left(\frac{\text{Mass of PVA-}g\text{-PAAm} - \text{Mass of PVA}}{\text{Mass of PVA-}g\text{-PAAm} + \text{Mass of PAAm homopolymer}}\right) \times 100 \quad (3)$$

Viscosities of the solutions of homopolymers and copolymers in water were determined[27] using an automated Ubbelhode viscometer (Schott Gerate, AVS 350, Germany) thermostated at 30°C. The unit performs automated measurements of the flow-through times in capillary viscometers and the efflux times were determined on a digital display within an accuracy of ±0.01 s. Four different concentrations of PVA solutions in the mass % ranging from 0.5 to 5 were used to calculate the specific viscosities. The intrinsic viscosity [η] of polymer solutions was calculated as

$$[\eta] = \lim_{C \to 0}\left(\frac{\eta - \eta_o}{\eta_0 C}\right) \quad (4)$$

where η_o , η, and C are, respectively, the solvent viscosity, solution viscosity, and concentration (g/dL) of the polymer. The intrinsic viscosity was determined by extrapolating the linear portion of the reduced viscosity vs concentration plot to the zero concentration (see Fig. 7). From the values of [η], the viscosity average molar mass, $\overline{M}\eta$ was calculated using the Mark Houwink-Sakurada (MHS) relation:

$$[\eta] = k(\bar{M}_\eta)^a \quad (5)$$

The values of the MHS parameters, k and a were taken from the literature[28,29] [$k = 45.3 \times 10^{-3}$ (mL/g) and $a = 0.64$]. The values of $\overline{M}\eta$ calculated were found to be 40,165 for PVA and 1,25,000 for the grafted copolymer.

Preparation of IPN Beads

The blends of PVA-*g*-PAAm with Na-Alg containing cypermethrin were prepared by dissolving 2.5 g of PVA-*g*-PAAm in hot water at 80°C. After cooling to room temperature, 3.0 g of Na-Alg was added and stirred to form a homogenous mixture. To this solution, different amounts (20, 30, and 40 mass % of dry mass of the polymer) of cypermethrin were added and mixed thoroughly on a magnetic stirrer to ensure complete mixing. The polymer solution containing cypermethrin was then added dropwise into water containing different volume % (5, 10, and 15) of glutaraldehyde and 3 % of 1.0 N HCl using a 25 mL hypodermic syringe (needle with an internal diameter of 1 mm) under constant stirring. The beads thus formed were removed from the antisolvent after 30 min and were washed with water repeatedly to remove the adhered glutaraldehyde and the acid; the beads were then dried completely.

In order to estimate the size of the beads, five samples of the completely dried beads from different formulations were selected and their sizes were measured by using a micrometer screw gauge (Sargent, USA) with an accuracy of ±0.01 mm

Equilibrium Swelling Study of the Beads

The equilibrium swelling of the beads was done in water and the % water uptake was measured gravimetrically at 35°C. Three different beads exposed to different amounts of GA at three different loadings of cypermethrin were selected and incubated by placing them in distilled water on a watch glass. The mass measurements were taken until an attainment of constant mass and the average value was considered for the calculations. During this process, the handling of the swollen beads should be smooth so as to avoid any mass loss due to breaking or erosion of solvent from the beads. All the mass measurements were done on a Mettler single pan balance (Model AE 240, Switzerland). The % water uptake Q was calculated by using the relation

$$Q = \left[\frac{\text{Mass of swollen beads} - \text{Mass of dry beads}}{\text{Mass of dry beads}}\right] \times 100 \quad (6)$$

Content Uniformity

Beads were evaluated for the pesticide content by refluxing a known mass of the beads with 100 mL of methanol at 70°C for 4 h to ensure the complete extraction of cypermethrin from the beads. Then the absorbance of methanol containing the extracted amount of cypermethrin was measured at the λ_{max} of 230 nm using a UV spectrophotometer (Secomam, Anthelie, France) with methanol as a blank.

Fourier Transform Infrared (FTIR) Measurements

FTIR (Nicolet, Model Impact 410, USA) was used to confirm the grafting reaction of acrylamide onto PVA as well as to find any possible chemical interactions between cypermethrin and PVA-*g*-PAAm, Na-Alg, or the crosslinking agent. Three samples were analyzed for FTIR: the first sample is PVA-*g*-PAAm and Na-Alg beads crosslinked with GA in the absence of cypermethrin. The second sample is that of cypermethrin loaded IPN beads crosslinked with GA, while the third sample was just the cypermethrin itself. The FTIR samples were prepared in KBr pellets under a hydraulic pressure of 400 kg and the FTIR spectrum of cypermethrin was obtained by taking a thin film of pesticide in between the two KBr plates.

Dissolution Studies

The static dissolution experiments were carried out in 250 mL conical flasks containing 40% (w/v) solution of methanol in distilled water as the dissolution media with the closer caps, and kept in an incubator (WTB Binder, Germany) maintained at 35°C. The beads weighing about 150 mg were taken in the dissolution media and the flasks were shaken well. Each time, 10 mL aliquot samples were removed at regular intervals and analyzed for cypermethrin using the UV spectrophotometer at a λ_{max} value of 230 nm. Experiments were performed in triplicate, and the average value was considered while data treatment and plotting.

Scanning Electron Microscope (SEM)

SEM was used to gather information on the topography of the beads. The instrument used was a JSM 6400 Scanning Microscope (Japan) and the SEM photographs were taken on the samples by depositing them on a brass hold and sputtered with gold at the required magnification. The working distance of 39 mm was maintained using an acceleration voltage of 5 kV, with the secondary electron image (SEI) as a detector.

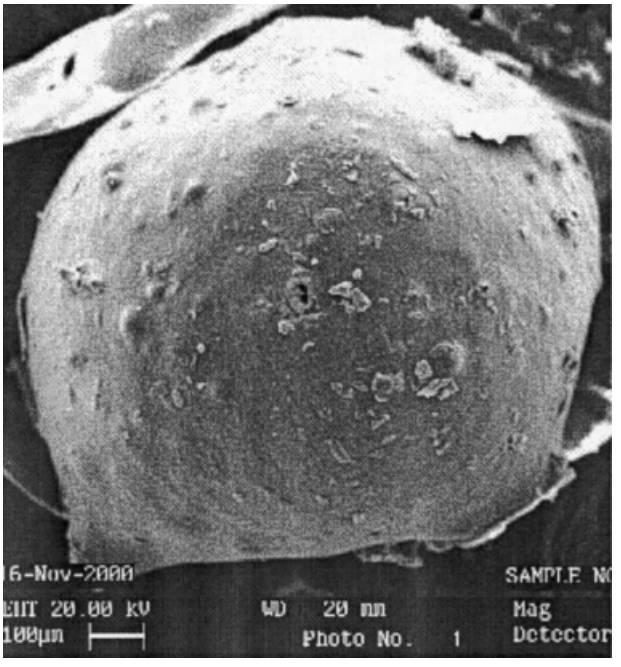

Figure 1 SEM micrograph of a single bead.

RESULTS AND DISCUSSION

The grafting efficiency of acrylamide onto PVA was up to 100 with a 93 % of grafting (see data in Table I). Cypermethrin was successfully encapsulated by using PVA-*g*-PAAm and Na-Alg matrices. The beads formed have the spherical shapes with the smooth surfaces as revealed by SEM (see Fig.1).

The grafting reaction was confirmed by FTIR (see Figs. 2 and 3). FTIR spectra of PVA (Spectrum A) and PVA-*g*-PAAm (Spectrum B) are presented in Figure 2. A broad band around 3400 cm^{-1} in both the cases is attributed to the O—H stretching vibration of hydroxyl group of PVA. Similar O—H stretchings can be seen in the grafted copolymer spectra, indicating that all the hydroxyl groups of PVA are not involved in the grafting reaction. A sharp band at 1252 cm^{-1} corresponds to an acetyl C═O group present on the PVA backbone because PVA is prepared by 80% hydrolysis of poly(vinyl acetate). However,

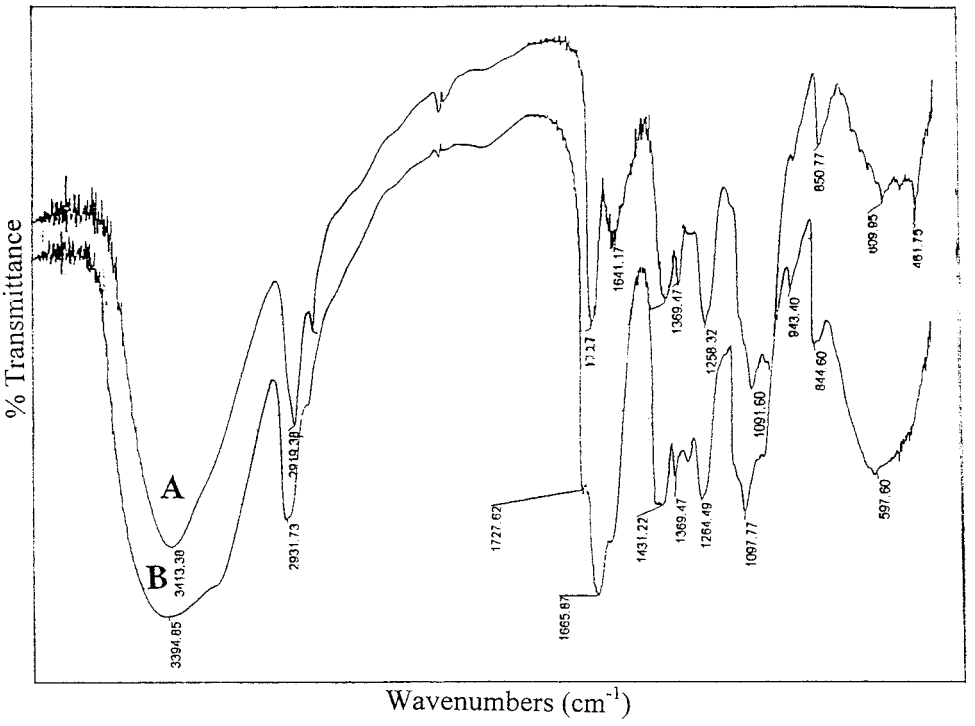

Figure 2 FTIR spectra of PVA (Spectrum A) and PVA-*g*-PAAm (Spectrum B).

some of the acetate groups might not have been fully converted into the hydroxyl groups. The peak due to N—H stretching vibrations of the primary amide overlaps with the O—H stretching vibrations, and the aliphatic C—H stretching vibrations appeared around 2931 cm^{-1}. A characteristic peak observed at 1728 cm^{-1} may be due to the carbonyl (C═O) stretching of the polyacrylamide chain in the grafted copolymer, thus confirming the grafting reaction. Further grafting was confirmed by the appearance of strong bands at 1666 and 1431 cm^{-1} corresponding to an antisymmetric N—H bending and C—N stretching, respectively.

In Figure 3, the spectrum A represents that of the IPN of PVA-*g*-PAAm and Na-Alg while B represents the IPN beads loaded with cypermethrin. The characteristic peaks appearing at 3067, 1584, 1407, and in the range 782–652 cm^{-1} did not alter even after the formation of beads, thereby indicating the absence of chemical interactions between cypermethrin and the polymer matrix.

The results of viscosity along with the viscosity average molecular masses are presented in Table II. The observed increase in molecular mass for the PVA-*g*-PAAm ($\overline{M}\eta$ = 1, 25, 101) is the result of grafting reaction. However, for the neat PVA ($\overline{M}\eta$ = 40,165), a one-third lower value than that found for PVA-*g*-PAAm is observed.

The results of % entrapment efficiency, bead size, and % equilibrium water uptake as a function of the amount of GA used, % loading, and entrapment efficiency of the pesticide are presented in Table III. The spherically shaped beads have the diameters ranging from 1.36 to a maximum of 1.44 mm. This means that the particle size did not vary significantly either by increasing the % loading of pesticide or by increasing the extent of crosslinking. On the other hand, the % entrapment efficiency varied from 80 to 91% by the variation of both the % loading as well as the % of crosslinking agent (GA) used in the matrices. Similarly, an increase in the extent of crosslinking from 5 to 15% also increases the % entrapment efficiency of the beads. The % equilibrium water uptake values show a decrease with an increase in crosslinking (i.e., with increasing amount of % GA used to crosslink the matrices) as well as with an increase in the % loading of the pesticide. The % equilibrium water uptake values vary from 20 to 43, suggesting a widely varying hydrophilic nature of the matrices.

In Vitro Release Kinetics

The *in vitro* release studies were performed in 40% methanol in water. The plots of % release vs

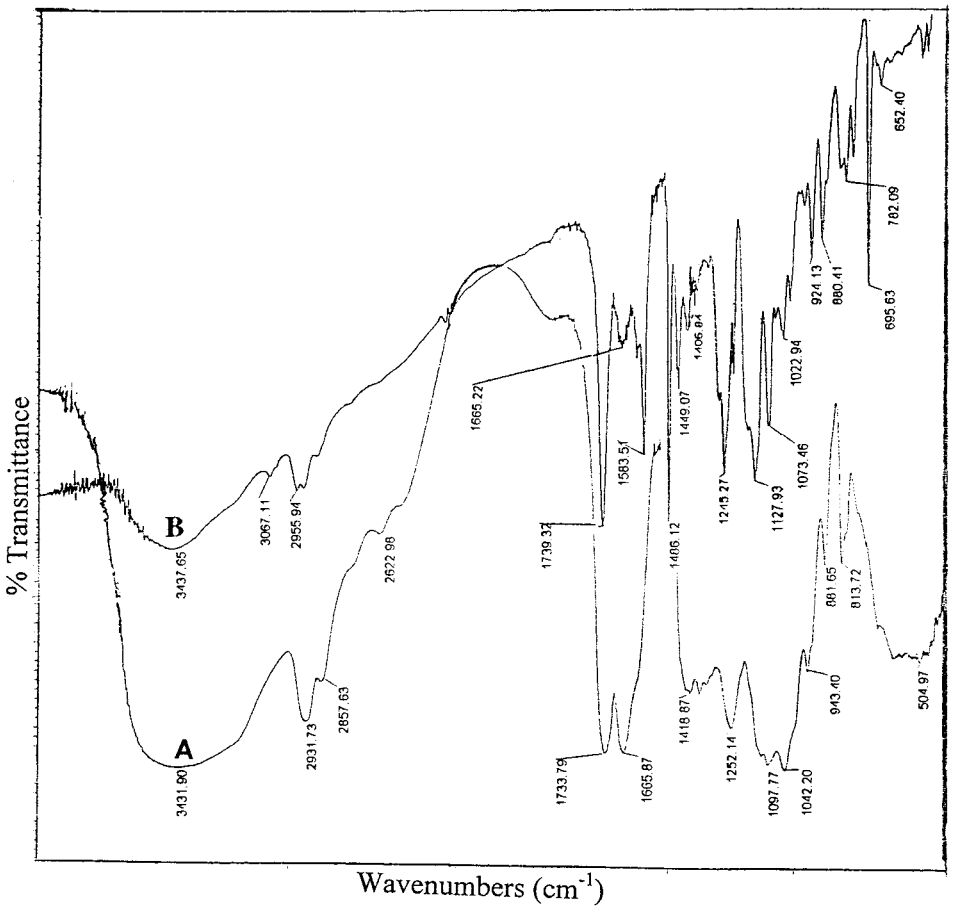

Figure 3 FTIR spectra of PVA-*g*-PAAm crosslinked with GA (Spectrum A) and CPN-loaded PVA-*g*-PAAm crosslinked with GA (Spectrum B).

time are presented respectively, in Figures 4, 5, and 6 for the 20, 30, and 40% cypermethrin-loaded beads with three different extents of crosslinking, viz., 5, 10, and 15 % GA. In all the cases, the results of % release decrease systematically with an increase in crosslinking of the matrices. The release of cypermethrin from the beads depends upon the type of the matrix used

Table II Viscosity and Viscosity Average Molar Mass of the Polymers

Polymer	Con. (g/dL)	Mean Time of Flow	Reduced Viscosity	$[\eta] \cdot$ (g/dL)	$\bar{M}_\eta$
PVA	0.01	17.1	119.5	40.05	40,165
	0.015	26.6	160.9		
	0.02	39.2	201.6		
	0.025	54.3	238.9		
	0.03	73.6	281.6		
PVA-*g*-PAAm	0.005	13.1	136.8	82.86	1,25,100
	0.01	23.1	196.5		
	0.015	36.8	250.3		
	0.02	55.2	304.5		

Also see Fig. 7.

Table III Some Pertinent Data on Entrapped Beads

% Amount of GA Used	% Loading of Cypermethrin	Bead Diameter (mm)	% Entrapment Efficiency	% Equilibrium Water Uptake
5	20	1.38 ± 0.11	85.31 ± 0.19	42.72 ± 2.15
10	20	1.42 ± 0.13	87.64 ± 0.24	38.61 ± 3.1
15	20	1.43 ± 0.21	91.33 ± 0.37	35.14 ± 3.67
5	30	1.36 ± 0.37	79.58 ± 0.63	41.33 ± 4.46
10	30	1.43 ± 0.26	81.81 ± 0.29	38.97 ± 2.31
15	30	1.37 ± 0.38	84.67 ± 0.15	35.47 ± 3.15
5	40	1.38 ± 0.31	81.69 ± 0.27	31.67 ± 3.8
10	40	1.44 ± 0.43	84.24 ± 0.31	25.88 ± 4.3
15	40	1.43 ± 0.39	86.69 ± 0.69	19.55 ± 6.83

as well as its rigidity. The release of cypermethrin involves first the matrix swelling and then its erosion. Among the three matrix systems investigated, the 20% cypermethrin loaded 15% GA-crosslinked beads have shown the least release (i.e., 69% up to 537 h), but the maximum release was observed for the 40% cypermethrin-loaded 5% GA-crosslinked (i.e., 91% up to 537 h) matrix. The release data for other systems are intermediary between the two extremes as shown above. These data are also in agreement with the equilibrium water uptake data presented in Table III. The release pattern in all the three matrices appears to be quite identical as seen in Figures 4–6.

The *in vitro* release data have been analyzed using an empirical equation of the type[30,31]

$$\log\left(\frac{M_t}{M_\infty}\right) = \log k + n \log t \qquad (7)$$

Here, the values of n indicate the type of diffusion mechanism while the values of k indicate the solute–solvent interaction. Here, M_t and M_∞ represent, respectively, the release of pesticide at time t and at infinite time. The logarithmic fractional release data, i.e., $\log (M_t/M_\infty)$ vs $\log t$ can be plotted up to 60% of the release and the initial linear portions have been fitted by the least squares method to estimate the values of k and n at 95% confidence limit. A value of $n = 0.5$ indicates the Fickian mechanism, $n = 1$ indicates Case II transport for slab geometry, and the intermediary values are indicative of the non-Fickian (anomalous) transport.[30,31] Fickian trends are generally exhibited by the nonsigmoidal shapes of the release curves shown in Figures 4–6. Generally, the limiting values of n depend upon the geometry of the matrices. In the case of polydisperse system of microspheres, these values could be even lower. For certain specific geometries, Ritger and Peppas[31] computed the values of n as

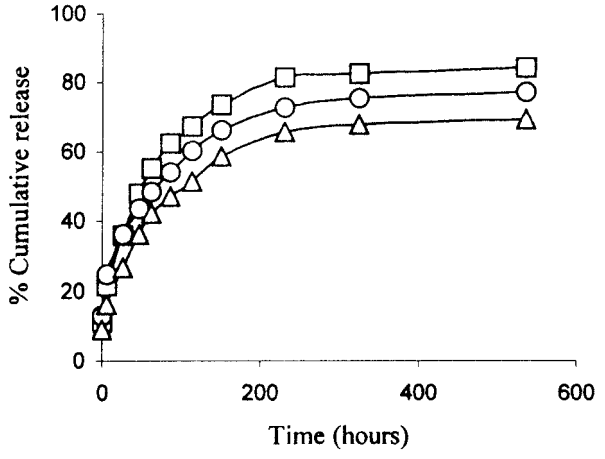

Figure 4 Percent cumulative release of 20% cypermethrin-loaded beads crosslinked with GA at: (□) 5%, (○) 10%, and (△) 15%.

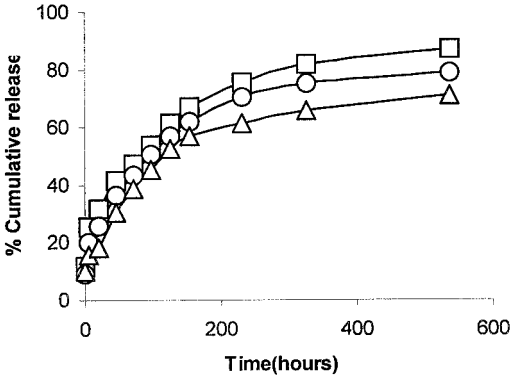

Figure 5 Percent cumulative release of 30% cypermethrin-loaded beads crosslinked with GA at: (□) 5%, (○) 10%, and (△) 15%.

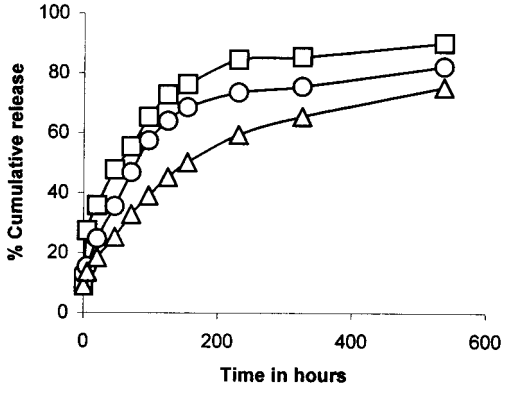

Figure 6 Percent cumulative release of 40% cypermethrin-loaded beads crosslinked with GA at: (□) 5%, (○) 10%, and (△) 15%.

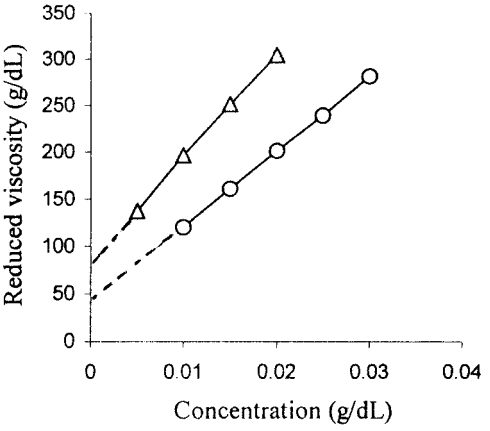

Figure 7 Reduced viscosity vs. concentration of polymer solution of PVA (○) and PVA-*g*-PAAm (△).

low as 0.3 and 0.45 for the Fickian and Case II transport, respectively. Our data of n and k are presented in Table IV. The n values in the present study vary between 0.26 and 0.31, indicating that the pesticide transport is not affected by crosslinking of the matrix materials. The values of n (0.26–0.31) indicate that the transport could be either Fickian or anomalous, but not Case II as suggested in the literature.[8,32] The k values for all the formulations at different loadings decrease with an increase in crosslinking (Table IV), suggesting varying interactions.

In order to calculate the values of apparent diffusion coefficients, D, of cypermethrin from the IPN hydrogel beads, the initial portion of the release profile, i.e., M_t/M_∞ fractional release, from 0 to 0.4 (minimum of 4–6 points are taken into consideration). A simplified equation for the calculation of initial time approximation as proposed by Baker and Lonsdale[33] has been used to calculate D as

$$\frac{M_t}{M_\infty} = \left(\frac{36Dt}{\pi r^2}\right)^{1/2} - \left(\frac{3Dt}{r^2}\right) \tag{8}$$

Here, r is the average radius of the bead. The diffusion coefficients are reported in Table IV. These values show a dependency on the extent of crosslinking. For instance, D decreases with increasing crosslinking as well as increasing cypermethrin loading.

CONCLUSIONS

In the present study, suitable wall materials are developed by grafting of AAm onto PVA in order to encapsulate the toxic pesticide, cypermethrin. The IPNs formed by using PVA-based copolymer and sodium alginates appear to be useful in encapsulating cypermethrin. The grafting reactions and possible interactions between the polymer and the pesticide were confirmed by FTIR and viscometry. Equilibrium water uptake values showed a decrease with increasing amount of crosslinking as well as % loading of cypermethrin. However, particle size and entrapment efficiency did not vary much even at higher crosslinking. The probable reason for higher entrapment efficiency may be that the polymer precipitation media used was that of acidified water rather than dilute alcohol in which cypermethrin is soluble to a very lesser extent. The *in vitro* static dissolution experiments have been performed to study the release kinetics of cypermethrin, and these data indicated that the release deviates from the Fickian transport. The diffusion values decrease with increasing crosslinking as well as increasing cypermethrin loading. The present paper is a continuation of our ongoing research on the development of environmentally friendlier matrices for the release of toxic pesticides. However, the fieldwork studies on these matrices will be the goal of our future research activity.

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Table IV Values of *k*, *n*, and *r* Calculated from Eq. (7) and Apparent Diffusion Coefficients (*D*) Calculated from Eq. (8)

% Amount of GA Used	% Loading of Cypermethrin	$D \cdot 10^8$ $cm^2\ s^{-1}$	*k*	*n*	*r*
5	20	1.268	0.15	0.30	0.989
10	20	0.759	0.17	0.26	0.995
15	20	0.678	0.12	0.30	0.984
5	30	1.126	0.21	0.25	0.996
10	30	0.628	0.13	0.26	0.996
15	30	0.525	0.12	0.28	0.947
5	40	1.110	0.15	0.31	0.997
10	40	0.822	0.14	0.27	0.989
15	40	0.168	0.11	0.27	0.955

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