

Synthesis and Analysis of Swelling and Controlled Release Behaviour of Anionic sIPN Acrylamide based Hydrogels

Atefeh Hekmat, Abolfazl Barati, Ebrahim Vasheghani Frahani, and Ali Afraz

Abstract—In modern agriculture, polymeric hydrogels are known as a component able to hold an amount of water due to their 3-dimensional network structure and their tendency to absorb water in humid environments. In addition, these hydrogels are able to controllably release the fertilisers and pesticides loaded in them. Therefore, they deliver these materials to the plants' roots and help them with growing. These hydrogels also reduce the pollution of underground water sources by preventing the active components from leaching. In this study, sIPN acrylamide based hydrogels are synthesised by using acrylamide free radical, potassium acrylate, and linear polyvinyl alcohol. Ammonium nitrate is loaded in the hydrogel as the fertiliser. The effect of various amounts of monomers and linear polymer, measured in molar ratio, on the swelling rate, equilibrium swelling, and release of ammonium nitrate is studied.

Keywords—Hydrogel, controlled release, ammonium nitrate fertiliser, sIPN.

I. INTRODUCTION

FERTILISER and water are two factors which put limitations on the agricultural products [1]. Therefore, improving the utilisation of water resources and nutritive fertilisers are of a high importance. Studies show that between 40-70% of the nitrogen loaded in the fertilisers is not absorbed by the plants' roots and is permeated to the environment. This results in economical losses as well as environmental pollution. This research shows that a controlled release process can solve this problem and reduce the pollution considerably. Another problem is that in most farms located in dry lands, there is a water shortage specifically in the dry seasons while they cannot take advantage from water sources in rainy seasons due to the lack of managerial skills. An appropriate solution to this problem is to use a component which can provide water and release fertiliser in a controlled way simultaneously.

Hydrogels are cross-linked polymers able to absorb and hold great amounts of water. These polymers are synthesised by using water soluble monomers through a free radical polymerisation with the help of a suitable cross linking agent.

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The water absorption characteristic of hydrogels is based on its contact with a thermodynamically fitted solution and is formed by transmitting from crystalline condition to rubbery condition. This characteristic of the hydrogels has many applications in the biomedicine production [2,3,4,5,6,7,8], tissue engineering technology [3], contact lenses production [4], and controlled release in agriculture and drug delivery systems [5,8]. Controlled release polymeric systems have many advantages in comparison with normal systems. In addition to their application in drug delivery systems, these hydrogels are used in agriculture as they reduce water consumption by reducing the numbers of irrigation [4,6]. They also reduce the plants' death due to dehydration [3,6,7,8], stabilise fertilisers in soil, prevent active component from leaching to underground water [2,7], and improve the plants' growth.

The substitution of controlled release method with the traditional fertilizing methods have resulted in development of the best technical solution to provide local concentration of the active agents and reduction of drain piping.[1,5,8]

Fertiliser release systems must be able to control the amount of leaving fertiliser as time goes by. Thus, amount of water inside the polymer network should be somehow controlled. Among the advantages of using hydrogels in controlled release of fertilisers in agriculture, mention can be made of:

1. As the water diffuses into the network, the loaded fertiliser exits slowly and feeds the plants' roots in a longer period of time. In addition, the amount of permeation can be controlled by changing the network structure.[9]
2. Since the interactions between the fertiliser and polymeric network are weak, a higher amount of fertiliser is released by the hydrogel in comparison with the zeolites which hold the fertiliser by adsorption.[9]

This article studies the water absorption and the release of ammonium nitrate as the sample chemical fertiliser in acrylamide based hydrogels. Linear polyvinyl alcohol monomers increase the strength of the gel by forming semi-interpenetrating polymer networks (sIPN) which are able to carry out the controlled release of fertilisers. The effects of changes in the amount of acrylamide monomer, ionized co-monomer, polyvinyl alcohol (PVA), and cross linking agent on the swelling rate and fertiliser release from the network have been studied. In the end, the best composition for a rigid

network with a high swelling ratio and a long fertiliser releasing time has been determined in each stage.

II. EXPERIMENTS

A. Materials

Table I shows the materials of the experiments briefly. [9]

TABLE I
REACTING MATERIALS IN HYDROGEL SYNTHESIS

Component	Chemical Formula	Application	Manufacturer
Acrylamide	C_3H_5NO	base monomer	Merck
Acrylic acid	$C_3H_4O_2$	base monomer	Merck
Polyvinyl alcohol	$(C_2H_4O)_n$	base monomer	Fluka
Potassium hydroxide	KOH	Hydrolysing agent	Merck
Methylene-bis-Acrylamide	$C_7H_{10}N_2O_6$	Cross-linking agent	Merck
Ammonium nitrate	NH_4NO_3	Chemical fertiliser	FAM Chemical
Tetra-Methyl Ethylene	$C_6H_{16}N_2$	Accelerator	Merck
Ammonium per-sulphate	$(NH_4)_2S_2O_8$	Initiator	Merck

B. Unloaded Hydrogel Synthesis

Hydrogels are synthesised through a free radical polymerisation with various molar composition of acrylamide, potassium acrylate, polyvinyl alcohol, and the cross linking agent. As it is demonstrated in Table II, in each step after adding specific amounts of acrylamide, bis-potassium acrylate and polyvinyl alcohol to water, solution is mixed 30 minutes by a 300 rpm magnetic mixer. Solution is deoxygenated by means of nitrogen during the mixing process. Casting process is begun after adding accelerator and initiator to the solution. Total volume of solution is 15 ml in each step. PVC disk shape casts ($L/D=1$) are used for gel-casting. Gels are separated from the moulds two to five minutes after gel-casting, their surface are rinsed with plenty amount of distilled water and they are dried 72 to 96 hours in laboratory condition.[9]

TABLE II
COMPOSITION OF REACTANTS AND DIFFUSION SWELLING

Am/AA/PVA×10 ⁻⁴ /Bis (mole ratio)	n	Mechanism
0.05/2.0/1.0/0.0	0.2337	Completely Fickian
0.05/2.0/1.0/0.5	0.4165	Completely Fickian
0.05/2.0/1.0/1.0	0.5256	Tend to non-Fickian
0.05/2.0/1.0/1.5	0.6256	Non- Fikian
0.05/2.0/1.0/2.0	0.7165	Non- Fikian
0.05/2.0/1.0/2.5	0.8337	Completely non-Fickian
0.05/2.0/0.0/1.5	0.3588	non-Fickian
0.05/2.0/0.5/1.5	0.5283	Tend to non-Fickian
0.05/2.0/1.0/1.5	0.6276	Non-Fickian

0.05/2.0/1.5/1.5	0.7286	non-Fickian
0.05/2.0/2.0/1.5	0.8614	Completely non-Fickian
0.05/2.0/2.5/1.5	0.9057	Completely non-Fickian
0.05/0.0/2.0/1.5	0.9574	Completely non-Fickian
0.05/0.5/2.0/1.5	0.6437	non-Fickian
0.05/1.0/2.0/1.5	0.5472	Tend to non-Fickian
0.05/1.5/2.0/1.5	0.5790	Tend to non-Fickian
0.05/2.0/2.0/1.5	0.8284	Completely non-Fickian
0.05/2.0/2.0/1.5	0.8284	Tend to non-Fickian
0.10/2.0/2.0/1.5	0.7250	non-Fickian
0.15/2.0/2.0/1.5	0.5500	Tend to non-Fickian
0.20/2.0/2.0/1.5	0.5000	Fickian

C. Synthesis of Ammonium Nitrate Loaded Hydrogels

The synthesis of loaded hydrogels is similar to that of the unloaded ones. The difference is, after complete mixing of the monomer solution, different amounts of ammonium nitrate are added and mixing operation continues for another 20 minutes. Then sample is separated from the mould after one to two minutes, its surface is washed, and it is dried for 96 hours in laboratory condition. In this method, total volume of solution is 15 ml either. Loaded amount of fertiliser on gels is 50 percent. Loading percentage is calculated by Equation (1).

$$\%Loading = \frac{\text{weight of } NH_4NO_3 \text{ Loaded}}{\text{weight of dry gel}} \times 100 \quad (1)$$

D. Swelling Studies

Water diffuses into the hydrogel network when it is immersed into water. Water diffuses into the network due to the osmotic pressure difference and it enters the empty space between the chains. In order to study the hydrogel swelling, the dried sample is weighted, immersed in 100 ml of distilled water in a 250 ml beaker. After a while, the sample is brought out, the excess water on its surface is dried with a tissue, and the sample is weighted again in particular time intervals. The final amount of swelling is obtained after 36 hours, when no significant weigh difference was observed in two successive weighing.

E. Ammonium Nitrate Release

A loaded hydrogel sample is used in order to determine the amount of ammonium nitrate released from the polymer network. The sample is dried and weighed, and then immersed in 100 ml of distilled water. A conductometer (Metrohm 712) measured the conductivity of the ions in the liquid around the hydrogel in different times.

III. RESULTS AND DISCUSSION

A. Determination of Diffusion Mechanism inside the Gel Network

Water absorption kinetics is determined by weighing different amounts of absorbed water by gel in various time steps. Equation (2) is used to calculate the swelling kinetics.

$$\frac{M_t}{M_\infty} = kt^n \quad (2)$$

Where k is the hydrogel swelling constant, n is the swelling ability, M_t is the amount of absorbed water at time t , and M_∞ is the amount of absorbed water by the network at equilibrium time. When n is equal or less than 0.5, the diffusion mechanism is Fickian, it is case II when n is equal to 1, and for values of n between 0.5 and 1, the mechanism is non-Fickian. Equation 2 is applicable to the first 60% of swelling process.

The slope of the line obtained by plotting $\ln(M_t/M_\infty)$ versus $\ln(t)$ shows the values of n and k . [3,4,7,8]

B. Effect of Composition on Swelling Behaviour and Fertiliser Release

As it was mentioned before, the sample is synthesised by changing one monomer composition when the others are constant in each step. This changing in one monomer composition leads to developing optimized composition of synthesised gel. Thus, optimized gel not only has a higher swelling rate in swelling experiments, but also creates maximum fertiliser release from network in releasing experiments. In order to achieve the optimized composition, swelling and releasing experiments are done after the synthesis of the sample, gel-casting, and drying. Next step is done by changing another component composition when the others are constant.

1. Effect of Acrylamide on Swelling and Release Behaviour

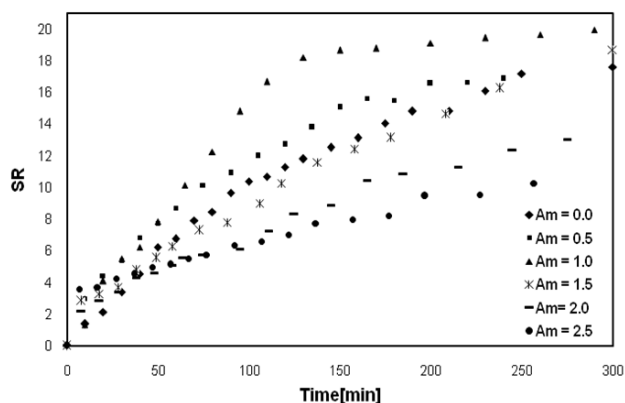


Fig. 2 (a) Chart of Swelling Ratio vs. Time for Different Compositions of Acrylamide

A sample with the molar ratio of acrylamide ranging from 0-2.5 is used to study the effect of the amount of acrylamide on the network and the swelling behaviour of the hydrogel (Table II). Fig. 2 (a) demonstrates water absorption tendency ratio of hydrogel for different acrylamide composition versus time. As it is shown, the swelling rate increases as the amount of acrylamide increases up to molar ratio of 1. For the higher molar ratios, the swelling rate decreases. Therefore, molar ratio of 1 leads to maximum amount of swelling rate. In

addition, experimental observations show that network does not have appropriate stability with lower percentage of acrylamide. Network dissociates in acrylamide composition below one percent.

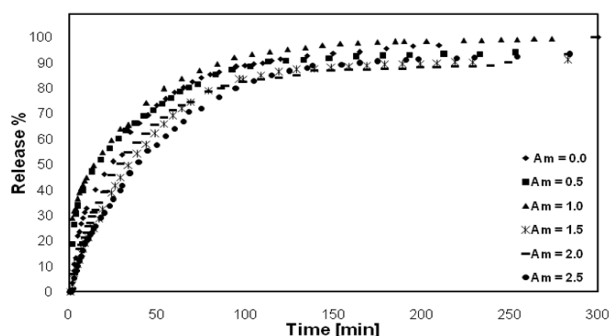


Fig. 2 (b) Chart of Release Percentage vs. Time for Different Compositions of Acrylamide

Fig. 2 (b) shows the release of fertiliser from the hydrogel network in the distilled water. As the amount of acrylamide increases, the release decreases in the beginning, and then increases. As the amount of acrylamide increases, repellent forces between COO^- and NO_3^- groups increase and fertiliser release from network increases consequently. Acrylamide composition of 1.5 is chosen due to its effect on network stability. Increasing acrylamide composition higher than 1.5 percent does not have any significant effect on either swelling or releasing ratios.

Thus, studying swelling and releasing amounts simultaneously results in choosing 1.5 percent as the optimized composition of acrylamide in hydrogel. This composition is used in the following steps.

2. Effect of Acrylic Acid on Swelling and Release Behaviour

Fig. 3 (a) demonstrates swelling rate of network versus time for different composition of acrylic acid. As the amount of acrylic acid increases to 2 percent, swelling rate increases. Besides, swelling rate increasing becomes gradually. It seems, as the amount of acrylic acid increases within the network, a positive osmotic pressure is formed due to the presence of positive ions in the network chains (COO^- group). This osmotic pressure leads to an increase in the swelling rate. In addition, formation of electro static repellent due to existence of similar charges on network polymeric chain leads to more extensivity of network and less Brownian movement of chains. Brownian movement decreasing leads to molecular relaxation time increasing and diffusion mechanism is changing from Fickian to case II. Table II explains this issue completely. Therefore, the potassium acrylate composition of 2 percent is chosen in this step due to its maximum swelling tendency rate and non-Fickian diffusion mechanism.

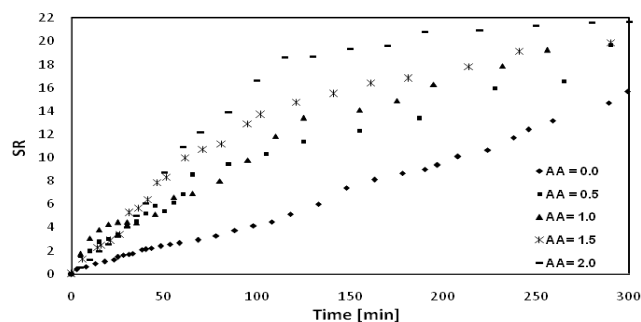


Fig. 3(a) Chart of Swelling Ratio vs. Time for Different Compositions of Potassium Acrylate

Fig. 3 (b) represents the release of fertiliser from the hydrogel into the distilled water. The amount of release changes in the beginning as the amount of acrylic acid increases; it first decreases and then increases. However, the amount of release decrease continuously as the amount of acrylic acid increases after a short while. As it is illustrated in Fig. 3(b), control of network on fertiliser release is much more efficient in the acrylic acid composition of 2 percent. In this composition, fertiliser releases gradually. Formation of repellent between similar charges (NO_3^- , COO^- , OH^-) leads to abovementioned decrease of release.

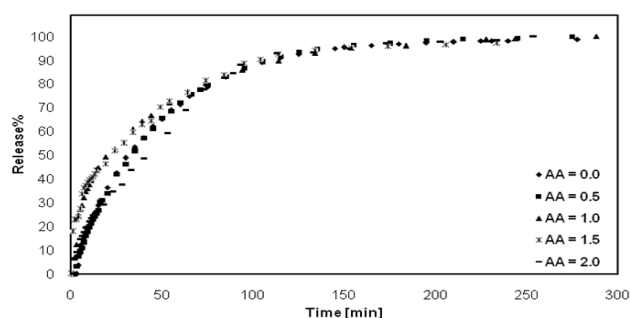


Fig. 3 (b) Chart of Release Percentage vs. Time for Different Compositions of Potassium Acrylate

3. Effect of PVA on Swelling and Release Behaviour

Fig. 4 (a) shows the tendency to equilibrium swelling of the synthesised hydrogels with various amounts of polyvinyl alcohol. As the amount of polyvinyl alcohol increases – up to molar ratio of 2×10^{-4} – swelling rate decreases but the final amount of swelling is remained constant. The amount of swelling rate decreases less than before as the amount of polyvinyl alcohol increases. It seems the increase of the amount of polyvinyl alcohol up to 2×10^{-4} has maximum effect on the swelling ratio. In addition, diffusion mechanism changes from non-Fickian to Fickian by increase of the amount of polyvinyl alcohol.

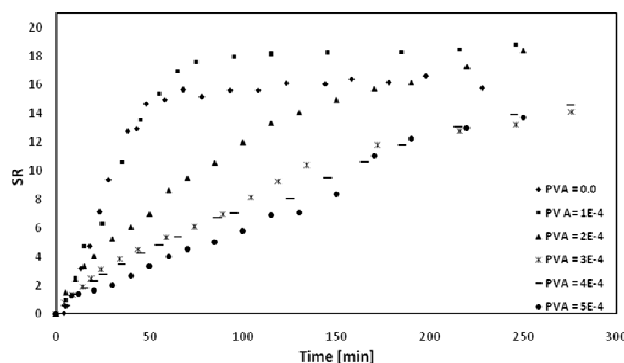


Fig. 4 (a) Ratio of Swelling to Time for Different Compositions of PVA

Fig. 4-b shows the percentage of release to time for different composition of polyvinyl alcohol. Results obtained from releasing tests show that decreasing the amount of swelling, i.e. increasing the amount of PVA, leads to a slower release of fertiliser in a higher period of time and in a more homogeneous way. However, mentioned reasons of swelling rate and changing non-Fickian diffusion mechanism to Fickian in the higher amount of composition simultaneously results in the optimized amount of polyvinyl alcohol of 2×10^{-4} .

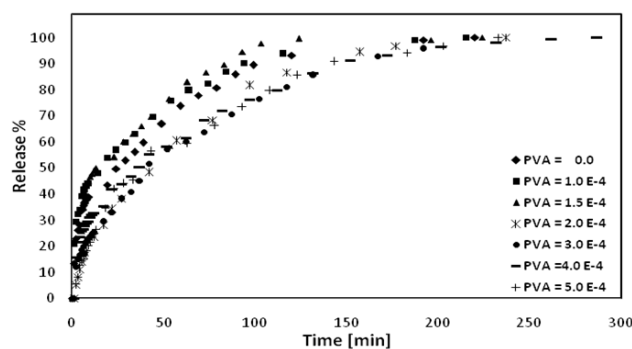


Fig. 4 (b) Percentage of Release to Time for Different Compositions of PVA

4. Effect of Bis-Acrylamide on Swelling and Release Behaviour

Fig. 5 (a) represents the swelling ratio to time for different compositions of bis-acrylamide. As the amount of bis-acrylamide increases from 0.05 to 0.15, the swelling rate increases and in the amount of 0.2 it decreases. More amounts of bis-acrylamide does not have significant changes in swelling rate of network. It seems that swelling rate increases due to the hydrophilic characteristic of this monomer. However, more increasing in the amount of cross linking agent (bis = 0.2) results in formation of more branches on network, which decrease free volume for water diffusion. Hence, swelling rate decreases as well. In addition, increasing the amount of bis-acrylamide leads to a stronger but less flexible network, resulting in a decrease in the swelling rate. However, the equilibrium swelling rate is obtained sooner at the least amount of cross linking agents.

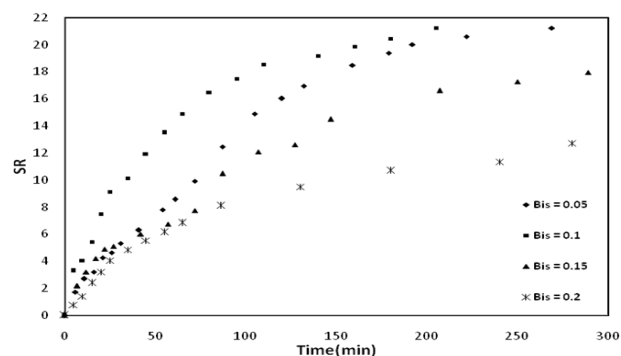


Fig. 5 (a) Swelling Ratio to Time for Different Compositions of Bis-Acrylamide

Fig. 5 (b) represents fertiliser release to time for different composition of bis-acrylamide. In one hand as the amount of cross linking increase, fertiliser release increase continuously. In the other hand as the amount of swelling decreases, i.e. the least amount of bis-acrylamide, the fertiliser releasing process occurs slower, in a higher period of time, and more homogeneously. Since the controlled release should be taken into consideration in addition to greater amounts of swelling in order to reach the optimised hydrogel, a composition of 0.05 of the cross linking agent is chosen as the optimised value.

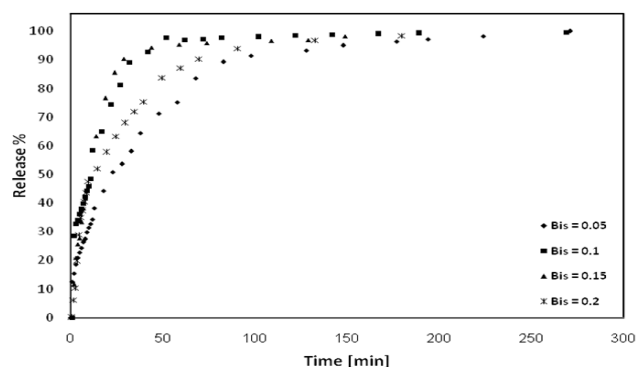


Fig. 5 (b) Percentage of release to Time for Different Compositions of Bis-Acrylamide

IV. CONCLUSION

Acrylamide based semi interpenetrating polymer networks are synthesised in the presence of ionisable monomers of potassium acrylate and linear polyvinyl alcohol. The swelling rate and equilibrium swelling are measured by gravimetric methods, and the results are reported as the tendency to equilibrium swelling. The amount of realising of the active component (ammonium nitrate fertiliser) is studied by conductometric method. Although increasing the amount of initial acrylamide leads to a stronger structure, it results in a decrease in the swelling rate and in an increase in the release rate. Higher amounts of potassium acrylate increase the swelling rate but decrease the release rate. As the concentration of the linear polymer and cross linking agent increases, the mechanical strength of the network increases.

However, the rate of release of ammonium nitrate decreases relatively.

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