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Preparation and Properties of Biodegradable Slow-Release PAA Superabsorbent Matrixes for Phosphorus Fertilizers

B. Tyliszczak, J. Polaczek, J. Pielichowski, K. Pielichowski*

Summary: Biodegradable superabsorbent matrixes for a slow-release fertilizer were prepared by using crosslinked acrylic acid and water-soluble granular phosphorus fertilizer KH_2PO_4. The effects of the amount of crosslinker, initiator and phosphorus fertilizer concentration on water absorption were investigated and optimized. The products show excellent slow release and water-retention capacity, being nontoxic in soil and environment-friendly, and could be useful especially in agricultural and horticultural applications. The results showed that the hydrogel structure and swelling capacity was affected by various factors, such as concentration of crosslinker and initiator, as well as by the amount of KH_2PO_4.

Keywords: hydrogels; PAA; slow release fertilizers; superabsorbents

Introduction

Superabsorbent polymers were defined as three-dimensional networks of hydrophilic polymers that can absorb and retain a significant amount of water. They have been attracting the interest of researches in the field of functional polymers. Hydrogels have found application in a variety of fields, such as medicine and pharmaceuticals, food, agriculture and chemical engineering.[1–4] One of the possible applications of superabsorbent polymers was the controlled release fertilizers. Slow release fertilizers were made to release their nutrient contents gradually and to coincide with the nutrient requirement of a plant.[5–7]

Increasing attention was being directed to reducing the amount of fertilizers and other biologically active agents used in modern agricultural crop management. One method for reducing the amount of such agents, while still maintaining effectiveness, was to encapsulate or otherwise incorporate the active agent into some form of plastic. By being incorporated into the plastic, the active agent diffuses slowly, but continuously, from the plastic matrix. It has been found in numerous instances that this use of controlled release delivery systems results in using less amount of the active agent A new type of controlled release fertilizer which enables control over both release rate and release pattern was developed. A dry mixture of soluble fertilizer was contained in polymeric matrix. Two main processes govern the release of nutrients from the hydrogels matrix: water penetrates through the pores into the dry mixture forming a distinct and sharp wetting front. The process starts with a 'burst' of water into the matrix; fertilizers leave the matrix through the pores either by diffusion alone or by diffusive and convective flows.

Several factors which affect both the water penetration and the nutrients release were investigated: fertilizer type, cross-linking of hydrogel, the chemical composition of the polymer chains and the type of the functional groups. It was found that the rate of wetting and the magnitude of the 'burst' effect increase with fertilizer solubility.

Department of Chemistry and Technology of Polymers Cracow University of Technology ul. Warszawska 24, 31-155 Krakow, Poland
E-mail: pielich@usk.pk.edu.pl

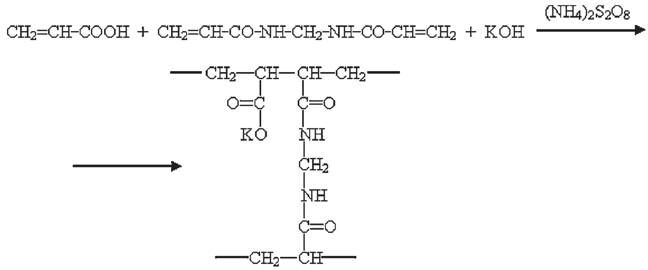

Figure 1.
Synthesis of PAA hydrogel.

Consequently, the release itself was affected in a similar manner. Reducing the diameter of the pores, reduces significantly the wetting rate and even more so the release of nutrients. The ability to control both the rate and the time pattern of the release through different combinations of the main factors was discussed and demonstrated.[5–9]

In this work we report on the preparation and properties of acrylic hydrogels, obtained under microwave irradiation, containing phosphorus-based fertilizers.

Experimental Part

Materials

Analytical grade acrylic acid, ammonium persulfate, N,N-methylene-bisacrylamide, phosphorus fertilizers (KH_2PO_4) and KOH were purchased from POCh Gliwice, Poland, and used without further purification.

Hydrogel Preparation

The synthesis of poly(acrylic acid) (PAA) hydrogel was performed as follows (Figure 1): an appropriate amount of monomer acrylic acid (AA) was added to the solution containing KOH. The mixture was then cooled slowly until the temperature drop to 30 °C, then an initiator ammonium persulfate (APS) and crosslinker N,N-methyleno-bisacryloamide (NMBA) were added. The synthesis of hydrogel in aqueous environment was carried out under microwave irradiation (300 W, 5–7 min.)

The synthesis of PAA with phosphorus fertilizer was performed using the mixture of PAA and KOH which was cooled slowly until the temperature drop to 30 °C, then an agrochemical, an initiator and crosslinker were added. After polymerization dry hydrogel samples were disintegrated into fraction 0.5–2.0 mm. Description of samples used in this work is given in Table 1.

Table 1.
Description of PAA/KH_2PO_4 samples.

Sample No.	Initiator concentration [wt.]	Crosslinker concentration [wt.]	KH_2PO_4 concentration [%]					
			a	b	c	d	e	f
1	0.2	0.10	–	10	–	–	–	–
2	0.2	0.25	–	10	–	–	–	–
3	0.2	0.35	0	10	20	30	40	50
4	0.2	0.50	0	10	20	30	40	50
5	0.2	0.75	0	10	20	30	40	50
6	0.3	0.35	–	10	–	–	–	–
7	0.4	0.35	–	10	–	–	–	–
8	0.5	0.35	–	10	–	–	–	–

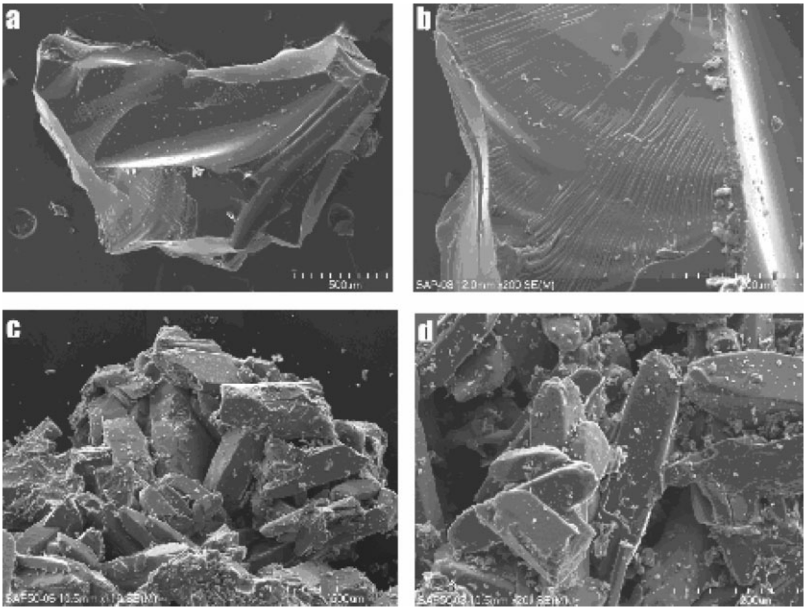

Figure 2.
SEM microphotograph of dried hydrogel: a) and b) PAA hydrogel (sample 3a), c) and d) PAA hydrogel with KH_2PO_4 (sample 3d).

SEM

Structures of silver-coated hydrogels were examined using a scanning electron microscope Hitachi S-4700.

It has been found that PAA layers of "fibril-like bundles" in the polymer networks are formed, where by for PAA hydrogels with KH_2PO_4 overlapping strands of bundles occur (Figure 2).

Determination of Water Swelling Ratio of Hydrogel

1 g of dry hydrogel was put into 500 ml distilled water (or 500 ml 0.9% NaCl solution) for 24 h to reach swelling equilibrium at room temperature. The swelling ratio Q (g/g) was calculated by the equation

$$Q = (W_1 - W_0)/W_1$$

where W_1 (g) was the weight of the swollen hydrogel after swelling equilibrium and W_0 (g) was the weight of dry hydrogel (Figure 3).[10–27] The swelling behaviour of the absorbent polymer depends on the composition of the polymer and the characteristic of the external solution.

Result and Discussion

Effect of Initiator

In the present work the amount of initiator has been varied in the feed mixtures in the concentration range 0.20–0.5 [wt. %] and the effect of this variation on the swelling ratio of the hydrogel has been studied. The results are shown in Figure 4 which reveal that with increasing concentration of APS, the swelling ratio increases. On increasing the APS concentration the molecular weight of the resulting crosslinked PAA will decrease thus shortening the macromolecular chains and increasing the available free volumes within the hydrogel. This clearly brings about an increase in the swelling ratio of the hydrogel.[10–15]

Effect of Crosslinker

To investigate the effect of crosslinker on the swelling characteristics of the gel, the concentration of NMBA in the feed mixture was varied in the range 0.10–0.75 [wt. %], the results are shown in Figure 5. At higher amounts of NMBA the hydrogel

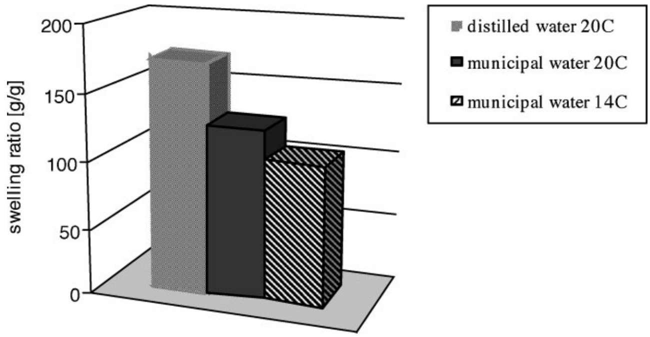

Figure 3.
Swelling ratio of PAA superabsorbent (sample 3a).

network chains became less flexible. It causes about a decrease in the swelling ratio of the hydrogel.[10–15]

Effect of Ionic Strength

The presence of ions in the swelling medium has a profound effect on the swelling behaviour of the hydrogel (Figure 6). The underlying principal behind this ionic dependence of swelling was that it was the balance between the osmotic pressure of the swelling system and elastic response of the polymeric material that was controlled the extent of swelling. The osmotic pressure results from the difference between the mobile ion concentrations in the interior of the hydrogel network and the external immersion medium. By increasing the ionic concentration the mobile ion concentration difference between the polymer gel and external medium (osmotic swelling pressure) was reduced which, in turn, reduces the gel volume, i.e. the gel shrinks.[1–4,7–16]

Release Study

The release kinetics of a loaded hydrogel was closely related to its water sorption kinetics since a highly swelled hydrogel should release a greater amount of solute

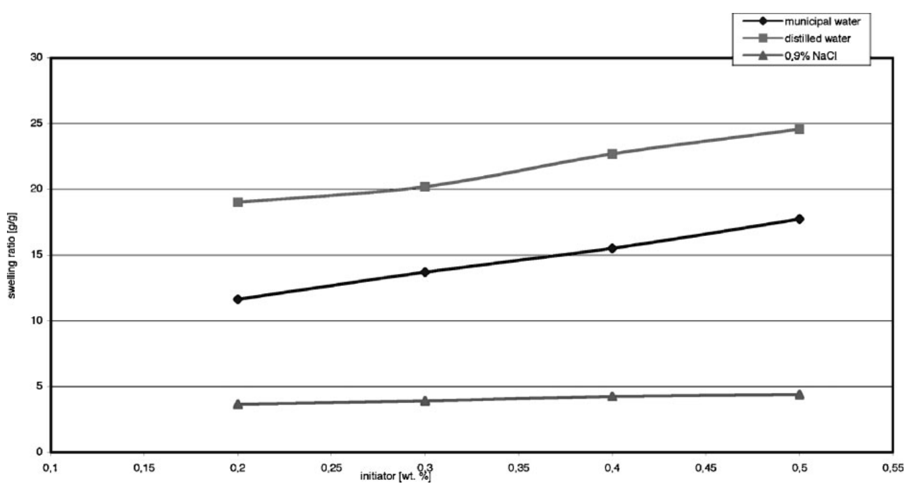

Figure 4.
The dependence of swelling ratio upon the concentration of initiator in dried hydrogels (sample 3b,6b,7b,8b,).

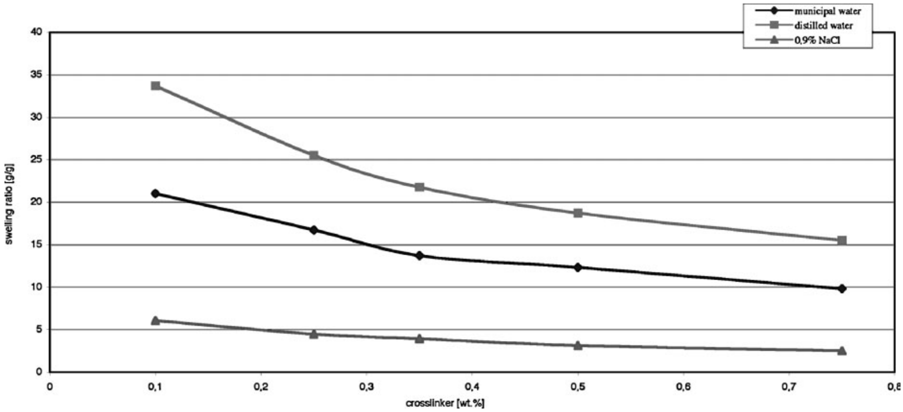

Figure 5.
The dependence of swelling ratio upon the concentration of crosslinker in dried hydrogels (sample 1b,2b,3b,4b,5b).

entrapped within the gel. Our results on release also supported the above fact and were consistented with the water-sorption results (Figure 7). The net release of nutrients from the device is a mere result of two main processes which occur concomitantly: water penetrating into the device and dissolving the fertilizer, and nutrients leaving the device. Immediately after placing the device in a wet surrounding, water penetrates into it, causing in many cases a 'burst' effect. The water dissolves the fertilizer and forms a gel with the thickener.

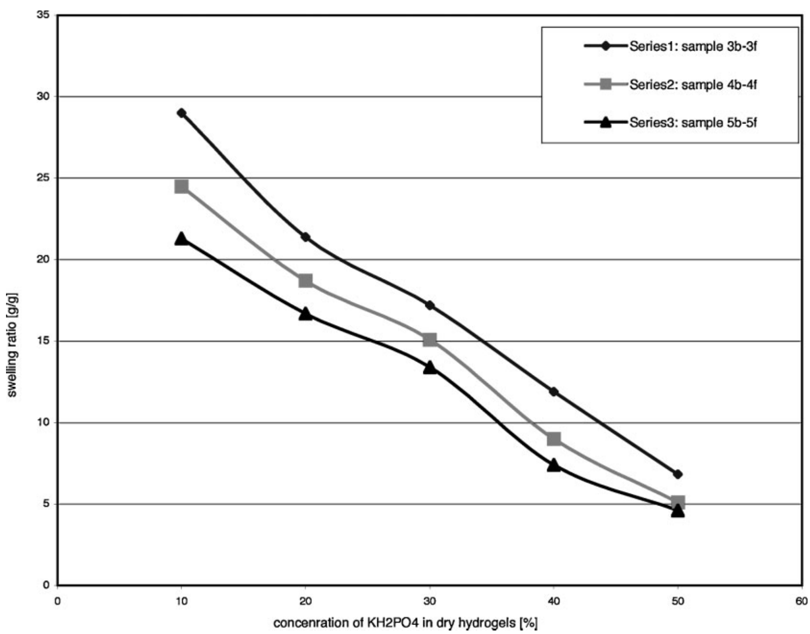

Figure 6.
The dependence of swelling ratio upon the concentration of KH_2PO_4 in dried hydrogels.

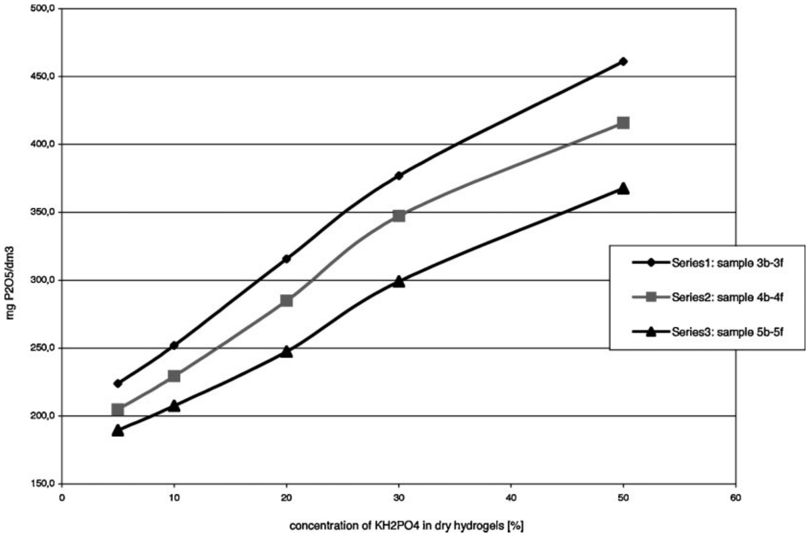

Figure 7.
The dependence of release ratio upon the concentration of KH_2PO_4 in dried hydrogels.

Conclusions

A new concept of controlling release of nutrients from macromolecular matrix was investigated. The dissolved nutrients left the hydrogel by diffusion thus inducing the formation of three distinct zones in the matrix: a transparent gel which contained a concentrated solution of nutrients, a second zone which consisted of un-dissolved fertilizer particles dispersed in a gel (containing a saturated solution of nutrients) and a third zone, so called dry zone.

It has been found that the rate of release, its pattern and its reproducibility can be reasonably governed by a proper choice of the several control parameters, such as initiator and crosslinker concentrations.

The dry PAA hydrogel loaded with phosphorus fertilizer swells in aqueous medium releasing the salt entrapped within the matrix in the controlled way.

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