

4th International Conference on Process Engineering and Advanced Materials

Effect of Different Monomers on Water Retention Properties of Slow Release Fertilizer Hydrogel

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Abstract

The combination of hydrogel and fertilizer as slow release fertilizer hydrogel (SRFH) has become one of the promising materials to overcome the shortcomings of conventional fertilizer by decreasing fertilizer loss rate, supplying nutrients sustainably, and lowering frequency of irrigation. A comparative study on water retention and plant growth performances of SRFH made from three hydrophilic monomers; acrylic acid (AA), acrylamide (AAM) and AA-co-AAM was executed. PAA SRFH has smaller swelling rate constant, k as it required only 166.67 minutes to absorb 0.63 of its equilibrium capacity of swelling, followed by P(AA-co-AAM) SRFH and PAAm SRFH. Although PAAm SRFH has the lowest swelling rate constant, it has the most excellent water retention ability in soil followed by P(AA-co-AAM) SRFH. Additionally, the presence of PAA SRFH in soil has enhanced the plant growth performances of model plant (capsicum annum) in term of its average leaf width and plant height. The synergistic effects of acrylic acid and acrylamide in P(AA-co-AAM) SRFH could be utilized to produce hydrogel used in agriculture.

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Peer-review under responsibility of the organizing committee of ICPEAM 2016

Keywords: Hydrogels; water absorbency capacity; water retention; plant growth performance

1. Introduction

In agricultural area, as far as the plant growth performance is concerned, a suitable distribution of fertilizer and water plays a very significant role. However, about 40–70% of nitrogen, 80–90% of phosphorus and 50–70% of potassium of the conventional fertilizers are released to the environment through leaching or volatilization without being absorbed by plants [1, 2]. Excessive nitrogen can be lost via two pathways; it is released as gas during microbiological transformation or it undergoes leaching with the seepage water. Nitrogen leaching is accelerated in sandy soils due to high rates of precipitation [3].

Slow release fertilizer hydrogel (SRFH) is a combination of hydrogel and fertilizer mainly created to reduce evaporation losses and frequency of water irrigations [4]. The SRFHs act by helping the absorption of some nutrient elements into its structure, holding them tightly, and delaying their dissolution. Hydrogel has been used to improve water retention of soil and water managing materials for degraded land [5]. Hydrogels can be identified as hydrophilic polymeric materials with network structures and appropriate degree of crosslinking. Hydrogel has the ability to absorb large amount of water during a short period of time and

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hold the absorbed water even under pressure. When fertilizer is incorporated in hydrogel, it produces SRFH that can improve water retention in soil [6], lower death rate of plants, and increase the plant growth tremendously [7, 8].

Hydrogel can be loaded with the active component such as fertilizer by two techniques; absorption of the fertilizer solution by dried hydrogel until the equilibrium swelling is reached [9], or SRFH is prepared directly (*in-situ*) into the fertilizer solution [10]. In this research, the latter technique was employed as it give better absorption properties being reported in our previous research [11]. Different types of hydrophilic monomer have been used as starting raw materials to produce hydrogels that suitable for specific applications. SRFHs base acrylic acid or acrylate can be considered environmentally compatible to forest soil and it showed no adverse effects on the microbial community of forest floor [5]. On the other hand, SRFH based acrylamide and aldehyde derivatives are able to self-crosslink at high temperatures and can be considered economically attractive to reduce the usage of crosslinking agent. However, several side reactions are also involved, leading to the formation of formaldehyde by-products which is undesirable because of its toxicity [12].

There are wide choices of monomers employed to produce hydrogels, therefore a proper choice of monomer is very crucial for an effective SRFH. Thus, the aim of this research is to study the effect of hydrophilic monomers on the three main properties of SRFH which are swelling rate, water retention test and plant growth performance of a model plant. Three hydrophilic monomers; acrylic acid (AA), acrylamide (AAM) or acrylic acid-co-acrylamide (AA-co-AAM) were used to combine with liquid fertilizer to produce SRFH.

2. Materials and Method

2.1. Materials

5M Acrylamide (AAM), 5M acrylic acid (AA), sodium hydroxide (NaOH), urea fertilizer (diluted to 1%), ammonium persulphate (APS) and N'-N-Methylenebisacrylamide (NMBA) were purchased from Merck (M) Sdn. Bhd. All chemicals were used as purchased.

2.2. Neutralization of Monomers

At room temperature, NaOH was added into monomer to get the 60% degree of neutralization. After 30 minutes, the mixture was transferred into five-necked flask, which was equipped with a mechanical stirrer, a condenser and a nitrogen line. Water bath was used to supply heat into the flask at the temperature of 70 °C. Neutralization is important to increase the electrostatic repulsion in carboxylate anions of the SRFH networks. The negatively charged carboxylate ions attached to the polymer chains that will set up an electrostatic repulsion that tends to expand the network. This results in the increase of water absorbency with the increase of degree of neutralization.

2.3. SRFH Synthesis Reaction

The reaction was carried out in 500 ml five-necked round-bottom flask equipped with a mechanical stirrer, a condenser, a thermometer and a nitrogen gas supply. Memmert Water Bath was used to supply heat to the mixture. Once the temperature reached 70 °C, weighted amount of neutralized monomers, NMBA, APS, and urea were mixed together with distilled water. The mixture was vigorously stirred at 170 rpm and dissolved oxygen was flushed out by nitrogen gas throughout the process. After all materials have completely turned into hydrogel, the synthesis reaction was stopped. To remove any unreacted materials, the synthesized SRFH was then filtered and washed with distilled water for several times. The SRFH was dried in oven at 70 °C for 24 hours. To avoid any moisture contact, all products were stored in a desiccator.

2.4. Swelling Rate of SRFH

Absorbency rate test is important to study the absorbency tendency and the time needed for SRFHs to reach equilibrium water absorbency. 0.5 grams of sample with various particle sizes were poured into numbers of weighed tea bags and immersed in 200 ml distilled water at room temperature. At certain intervals, the water absorbency of the sample was measured according to Eq.1.

$$WAC = (W_2 - W_1) / W_1 \quad (1)$$

where W_1 and W_2 are the weights of the dry sample and water absorbed sample, respectively. WAC was calculated as gram of water per gram of sample (g/g).

2.5. Water Retention of SRFH

Water retention test was used to study the ability of SRFH to hold water inside its network structure for 30 days using the water evaporation ratio (WER). Four containers labelled as A (control), B (PAA), C (PAAm) and D (P(AA-co-PAAm)) were prepared. Initially, soil for this test was dried in an oven for two days at 60 °C. Two grams of SRFHs were well mixed with 200 grams of dried soil and kept in containers. Subsequently, the mixtures were irrigated with 200 ml of distilled water and weighed (M_i). The containers were placed in the laboratory at room temperature and weighed every 3 days for 30 days (M_t). Eq. 2 was used to determine the water evaporation ratio [1, 13]:

$$\text{WER} = (M_i - M_t) / 200 \times 100\% \quad (2)$$

2.6. Plant Growth Performance

300 grams of soil were placed into four containers; (A) PAA, (B) PAAm and (C) P(AA-co-AAm) SRFHs were mixed thoroughly with the soil and chili plant (*capsicum annum*) seeds were placed in all containers. Water irrigation remains constant starting day one for all containers and they were exposed to the actual environment condition. The growth patterns of all chili plants were observed at different time intervals. The plant height and the average of total leaf width of the chilli plant were determined using a ruler.

3. Result and Discussion

3.1. Swelling Rate of SRFHs

Swelling kinetics of a SRFH material are greatly influenced by varieties of features such as the types of hydrophilic monomers, composition of the hydrogel, the particle size, and the surface area [2]. Thus, the swelling rates of all SRFHs for 300 minutes are shown in Fig.1. All SRFHs gave the same absorbency pattern where water had been absorbed rapidly at the beginning and started to increase slowly after the first point. It shows that initial swelling process is slow. This is because; primarily slow water penetrating into the hydrogel through capillary and diffusion in the glassy state and then, swelling is higher at first because penetrated water is absorbed by hydrophilic groups such as carboxylate, amide and hydroxyl ethyl carboxylate through the formation of hydrogen bonds. The swelling is driven by repulsion of hydrophilic groups inside the network and osmotic pressure difference between the hydrogel and the external solution. Thus, subsequently, swelling gradually slows down until the swelling reaches up to equilibrium.

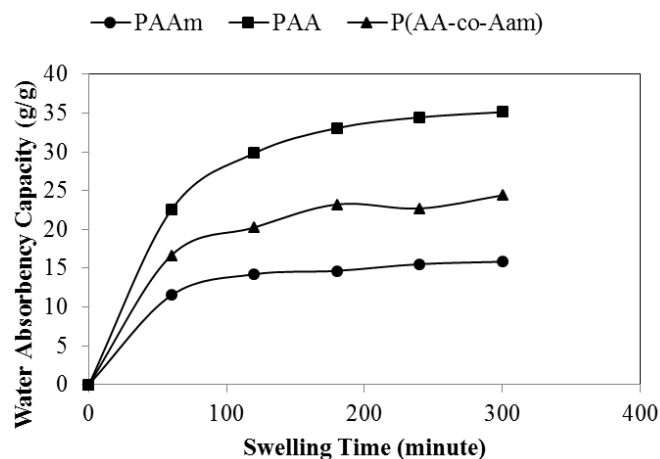


Fig. 1. Swelling rate of PAAm, PAA and P(AA-co-AAm) for 300 minutes

Similar phenomenon was observed by El-Mohdy and El-Rehim when the swelling rate of hydrolyzed and untreated kappa-carrageenan grafted acrylamide were sharply increased at initial time and then began to level off after 180 minutes [14]. From Fig. 1 it can be assumed that the swelling of the polymer fits the process of first-order dynamics. To calculate the swelling rate constant k , a Voigt-based viscoelastic model was applied [2, 15, 16]. The swelling rate of SRFH is written based on as in Eq 3:

$$dQ_t/dt = k(Q_e - Q_t) \quad (3)$$

where t is the swelling time, Q_t is the swelling ratio at that time, k is the swelling rate constant and Q_e is the equilibrium swelling ratio. Eq 3 is integrated and arranged as in Eq 4:

$$\int dQ_t/(Q_e - Q_t) = \int k dt \quad (4)$$

By integrating Eq. 4 swelling time, Q_t for theoretical value can be obtained from as in Eq 5. A graph $\ln[(1-Q_t-Q_e)]$ versus t to determine the swelling kinetics of PAAm, PAA, and P(AA-co-AAm) of experimental and theoretical values for 300 minutes is shown in Fig. 2.

$$\ln[(1-Q_t-Q_e)] = -t/k \quad (5)$$

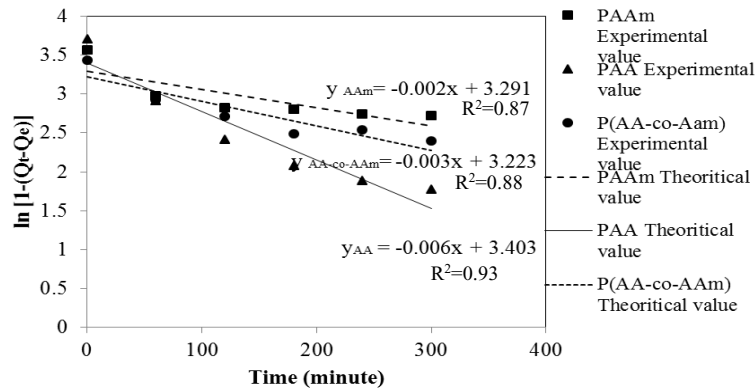


Fig. 2. Swelling kinetics of PAAm, PAA, and P(AA-co-AAm) of experimental and theoretical values for 300 minutes.

Based the graph the theoretical calculations and experimental values agreed well hence, the hypothesis that the swelling processes of the polymers fit the processes of first-order dynamics is correct. The slope of the straight line (slope $-1/k$) gives k value, the measurement of the swelling rate and the lower the k value, the higher the rate of swelling. k values for PAAm, P(AA-co-AAm), and PAA SRFHs are 500, 333.3, and 166.67 minute, respectively. This could be interpreted as PAA had better swelling kinetics properties as it required only 166.67 minutes to absorb 0.63 of its equilibrium capacity of swelling followed by P(AA-co-AAm) and PAAm required the longest time [15]. From the Fig. 2, the swelling rates of AA-based hydrogels were higher than AAm-based ones. This behaviour can be attributed to the increase in ionic groups existing in copolymer chains, which allows polymer coils to expand more easily.

3.2. Water Retention in Soil

Fig. 3 shows water retention behaviour of soil without SRFH (blank) and with three different types of SRFHs; PAA, PAAm, P(AA-co-AAm) for 30 days. From this data, it can be found that the water evaporation ratio in blank soil is obviously weaker than soil with SRFHs as it losy 43.53% and 74.43% on the 15th and 30th days, respectively. Evaporation is the direct loss of water from the soil to the atmosphere as water vapor and it is controlled by the water vapor deficit in the atmosphere such as humidity, temperature of the air and the water retention capacity of the soil. The blank soil water evaporation loss values were then used as the indicator to study the effect of SRFH produced from different monomers.

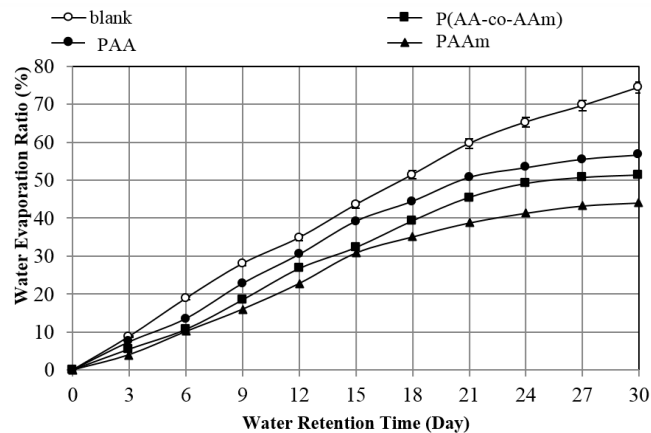


Fig. 3. Water retention behaviour in soil for blank soil, soil with PAA, PAAm and P(AA-co-AAm) SRFH for 30 days

From the results, PAAm had the most excellent water retention ability as it only lost 30.84% and 44.06% on the 15th and 30th days, respectively followed by P(AA-co-AAm) SRFH that had loss 32.18% and 51.30% on the 15th and 30th days, respectively. In contrast, PAA had the highest water evaporation lost compared to all SRFHs as it lost 39.17% and 56.62% of total water on the 15th and 30th days, respectively. However, the evaporation from all SRFH is significantly lower than the evaporation of free water from blank soil due to the macromolecular network hindrance and the interaction between water and polymer molecules. As the humidity content in the surrounding soil decreases, the absorbed water is then slowly released by the hydrogel, through a diffusion driven mechanism.

According to Marandi et al. (2008) the water in hydrogel can be classified into bound water, half-bound water and free water [17]. Compared to bound water and half-bound water, the free water in a hydrogel had high mobility and can easily be lost. The percentages of bound water and half-bound water in the swollen gels are related to the number of hydrophilic groups in a unit volume in the hydrogels, in this research they are $-\text{COOH}$ of acrylic acid, $-\text{CONH}_2$ of acrylamide and $-\text{COOH}/\text{NH}_2$ for acrylic acid-co-acrylamide. The hydrogen bonding is weaker than a normal covalent bond. When water outside of hydrogel was fully evaporated, at room temperature, thermal energy is enough to break hydrogen bonds between water inside the SRFH structure.

3.3. Plant Growth Performance

The successful planting system depends on an adequate supply of plant nutrients and other interaction factors such as plant species and variety, yield level, soil properties, environment and management. The urea slow release process of the SRFH can be described by the following five steps: Firstly, the water enters into the SRFH in the first stage. Then, the SRFH is slowly swollen by the water until the dynamic exchange between the free water in the SRFH and the outside water has developed. Continuously, the urea dissolved in the SRFH network has been slowly diffused out of the SRFH through this dynamic water exchange. The water entered into the SRFH core through the tiny pores and dissolved it. Finally, the dissolved urea diffuses out the outer layer, and then releases into the water through the dynamic exchange of free water and osmosis differences [18]. Nutrients shortage can be observed through the plant's changes in height and leaf width and the results of for this observation are shown Fig.4 and Table 1.

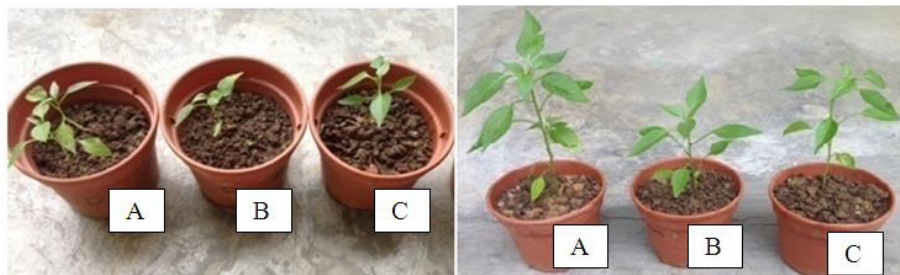


Fig. 4. The growth performances of chili plants in week 3 and week 7: (A) Soil + PAA, (B) Soil + PAAm and (C) Soil+P(AA-co-AAm)

Table 1. The Growth Differences of Chili (*capsicum annum*) for three different monomers

Duration (week)	Average Plant Height (cm)		
	PAA (A)	PAAm (B)	PAA-co-PAAm(C)
3	5.2	3.0	6.1
7	14.2	9.4	11.4
	Average Leaf Width (cm)		
3	2.1	2.7	3.1
7	5.1	3.8	4.0

From the tables and figures, it is clear that the presence of PAA SRFH in soil has enhanced the growth and performance of chili plant while chili plant in PAAm SRFH showed rather poor outcome. These results are related to the fertilizer salt index. As soon as the dried SRFH was put into soil, it began to swell and converted into SRFH. Once nutrients inside SRFH were dissolved in the soil, the salt concentration of the soil where the chili plant was is increased. Both PAAm and P(AA-co-AAm) contained extra N which has the higher possibility to produce free ammonia, which can cause poor germination or seedling death. Chilli plant in soil treated P(AA-co-AAm) SRFH developed more root and shoot biomass. This is favorable in dry environments where more root growth means increased capacity to take in the scarce water resources whereas increased shoot growth means a larger leaf area for photosynthesis with more growth and enhanced water use efficiency [19]. It may also has sufficient amounts of urea and water. Chili plant in soil treated PAA SRFH absorbed high amount of water thus releasing urea faster compared to other SRFHs through osmosis process [20]. While chilli plant in soil treated PAAm SRFH maybe has salt buildup that caused from excess fertilizer and interfered with plant growth. When water had a high salt level, the water cannot enter the cell membrane and the roots cannot take in water. Roots may be unable to find water and dehydrated [21].

4. Conclusion

An excellent choice of hydrophilic monomer combined with the optimum amount of crosslinking agent, initiator, and degree of neutralization are important in synthesizing a good hydrogel. In this research, a comparative study of SRFHs made from three hydrophilic monomers was thoroughly performed. The swelling kinetics study of PAA SRFH suggested that it has smaller swelling rate constant, k as it required only 166.67 minutes to absorb 0.63 of its equilibrium capacity of swelling followed by P(AA-co-AAm) SRFH and PAAm SRFH. Although PAAm SRFH has the lowest swelling rate, it has the most excellent water retention ability followed by P(AA-co-AAm) SRFH. In addition, the presence of PAA SRFH in soil has enhanced the plant growth performances of chili plant. From all these data, the synergistic effects of acrylic acid and acrylamide in P(AA-co-AAm) SRFH were clearly presented.

Acknowledgements

Great appreciations offered to Universiti Teknologi Petronas, Universiti Teknologi Malaysia and Ministry of Higher Education, Malaysia (R.J130000.7844.4L143) for the supports and funding.

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