SYNTHESIS AND PROPERTIES OF SUPERABSORBENT COPOLYMER OF ACRYLIC ACID, ACRYLAMIDE AND KONJAC GLUCOMANNAN POLYSACCHARIDE

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Abstract

The research was focused on synthesis and investigation of swelling behavior of konjac glucomannan (KGM)-based superabsorbent prepared by free radical graft copolymerization of acrylic acid and acrylamide onto polysaccharide in the presence of potassium persulfate as an initiator and N,N´-methylenebisacrylamide as a cross-linking agent. The swelling properties of KGM-*g*-poly(acrylic acid-*co*-acrylamide) hydrogels were studied, such as swelling ratios in water, the rate of swelling and drying, the dependence of swelling ratio on the number of swelling cycles. Moreover, the water retention of soil with the copolymer was investigated.

Introduction

Superabsorbent polymers (SAPs) are functional polymers which can absorb large amount of water, and therefore they are used as soil conditioners[1]. Nowadays, there are many types of SAPs as soil conditioners recommended, the most commercially used are copolymers of sodium or potassium acrylate and acrylic acid and cross-linked polymer of acrylamide and sodium/potassium acrylate[2]. Superabsorbent polymers act as a water reservoir, which allows controlled-release of water into the environment, which leads to reduced irrigation resulting in economic effect. Improved physical properties of the soil, increased plant production and lower mortality of plants are other positive effects of SAPs application[3].
Konjac glucomannan (KGM) is obtained from the tuber of Amorphophallus konjac[4] and it is a nature polysaccharide composed of repeating units of D-mannose and D-glucose in a specific molar ratio 1.6:1[5]. The backbone of glucomannan contains some branching points in C-3 position and acetyl substitutes approximately 5-10 % at C-6 position[6]. Glucomannan and its derivatives are widely used in various fields such as food and food additives, pharmaceutical, biotechnological, and chemical industries as films and membranes, cosmetic and coating materials etc[7].
The aim of this work was to synthesize SAPs hydrogels based on Konjac glucomannan (KGM) and evaluate their physicochemical properties and suitability as soil conditioners.

Experiment

Materials

Glucomannan was purchased from Now Foods (USA). Acrylic acid (AA), acrylamide (AAm) and N,N´-methylenebisacrylamide (MBAM) were supplied by Sigma-Aldrich (Steinheim, Germany). Potassium persulfate was obtained from Lachema (Brno, Czech Republic) and sodium hydroxide was purchased from Penta (Chrudim, Czech Republic).

Synthesis

The synthesis of hydrogel was carried out according to the literature with small modifications[8]. The thirty ml of distilled water was put into three-necked flask and before reaction, was bubbled with N_2 for at least 10 min to discharge oxygen and then KGM (0.42 g) was added and stirred 1h at 40 °C under an atmosphere of N_2. Then a predetermined amount of $K_2S_2O_8$ solution (0.5 wt. % of (AA + AAm)) was added into the flask as initiator agent, MBAM (0.04 wt. % of (AA + AAm)) as crosslinker, 2 g of AA (neutralization degree 75% with NaOH) as the monomer, and 1 g of AAm as the co-monomer. The copolymerization reaction was carried out for 3 hours at 60 °C after the flask was filled with N_2. The product was precipitated with ethanol, filtered, and dried to a constant weight at 60 °C in a vacuum. Scheme of the reaction is showed in the Figure 1.

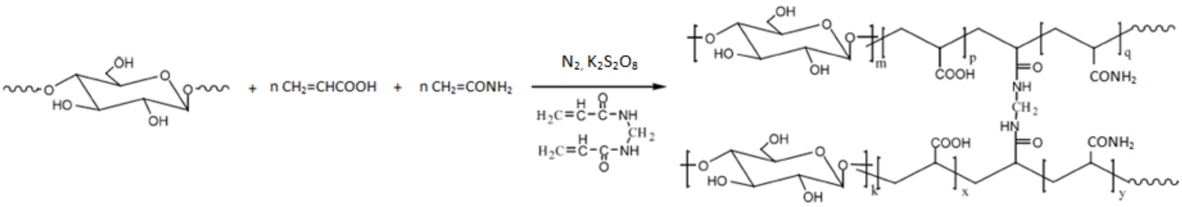

Figure 1. Scheme of graft radical copolymerization

Swelling studies

Swelling behavior of prepared hydrogel was measured by tea bag method. A tea bag (mesh) with weighed hydrogel (0.025 ± 0.001 g) was immersed into swelling medium at room temperature. At predetermined time intervals, the tea bag containing swollen hydrogels was removed from swelling medium to let drain the excess of water from the gel surface, blotted with filter paper and weighed. The swelling ratio (SR) [g H_2O/ g dry hydrogel] was calculated using equation:

$$SR = \frac{w_2 - w_1 - w_0}{w_0} \qquad (1)$$

Where w_2 is the weight of wet tea bag containing swollen hydrogel, w_1 is the weight of wet tea bag, w_0 is the weight of dry hydrogel.

Water retention of soils with SAPs

50 g of the air-dried soil was ground enough to pass through a 2 mm sieve, then put into a beaker and mixed with 0.05 wt. % of SAP (based on soil). A control experiment, i.e., without SAP, was also carried out. Then an equal amount of distilled water (wH_2O) was added according to the water capacity of soil and weighed (w_1). The beakers were placed in the laboratory at room temperature and weighed (w_i) approximately every day over a period of 20 days. The water evaporation ratio (W) was calculated according the following equation:

$$W(\%) = \frac{(w_1 - w_i) \times 100}{w_{H_2O}} \qquad (2)$$

Results and discussion

Swelling studies

The results of swelling ratio measurements for different SAPs hydrogels in distilled water are shown in Figure 2. The four hydrogel preparations were performed, and for each hydrogel its swelling ratio was determined three times. The average value is presented in the Figure 2. It can be seen from Fig. 2 that all four hydrogels reached at least 480 g H_2O/g with a swelling maximum about 570 g H_2O/g, which is sufficient for usage as a regulators of soil moisture.

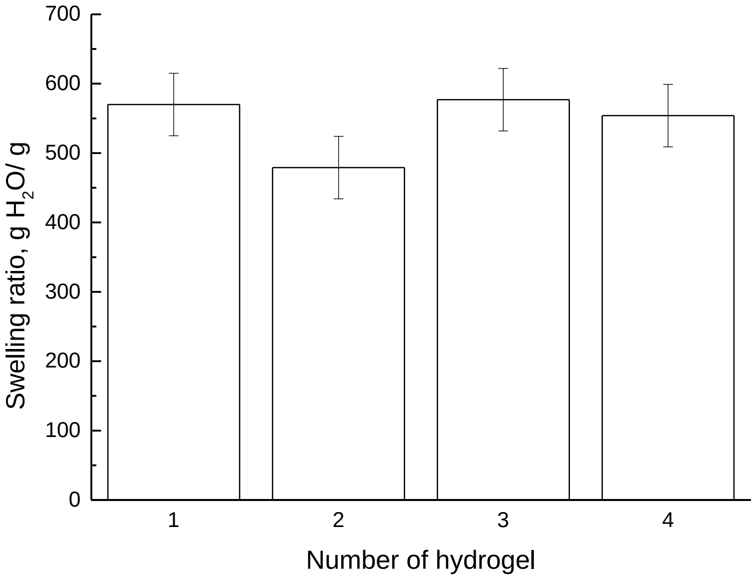

Figure 2. Swelling behavior of SAP hydrogels.

The swelling rate of SAP hydrogels

The high swelling rate of hydrogel is one of the most important properties of hydrogels used in agriculture, especially in case of raining or irrigation. The time required to achieve maximum swelling capacity of SAP hydrogels was studied and results are illustrated on the graphs in Figure 3. The results indicated that the samples reached 90% of the maximum swelling capacity approximately after 5 hours and the maximum swelling capacity was achieved after one day contact with water for all samples.

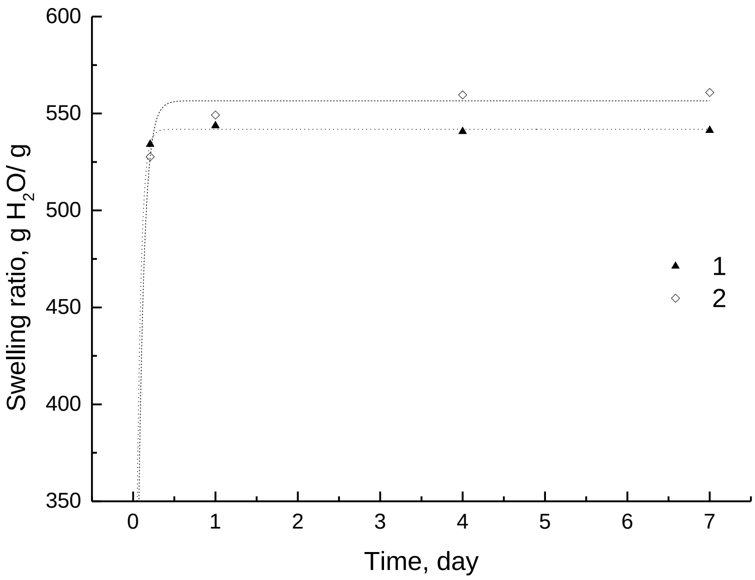

Figure 3. The swelling rate of SAP hydrogels.

Rate of dehydration

The time needed to reach total drying of swollen hydrogel at ambient temperature was investigated for two hydrogel samples, results are presented on the graphs in Figure 4. As can be seen, the results for both samples were very similar. The time of total dehydration was determined as 70 hours.

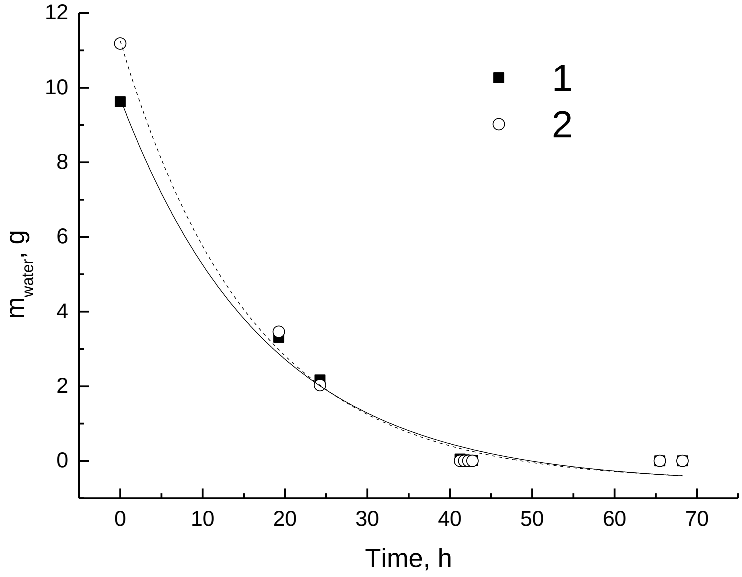

Figure 4. Time course of swollen SAP hydrogels dehydration.

The influence of swelling – drying cycles on hydrogel swelling ratio

The other equally important properties of hydrogel should be to preserve swelling capacity depending on the swelling – drying cycles. Therefore, the effect of number of swelling – drying cycles on the water capacity was studied. The experiment was repeated three times, the average values of swelling ratio were calculated and the results are illustrated on the graph in Figure 5. It can be seen that the swelling ability of hydrogel even after third swelling – drying cycle was preserved.

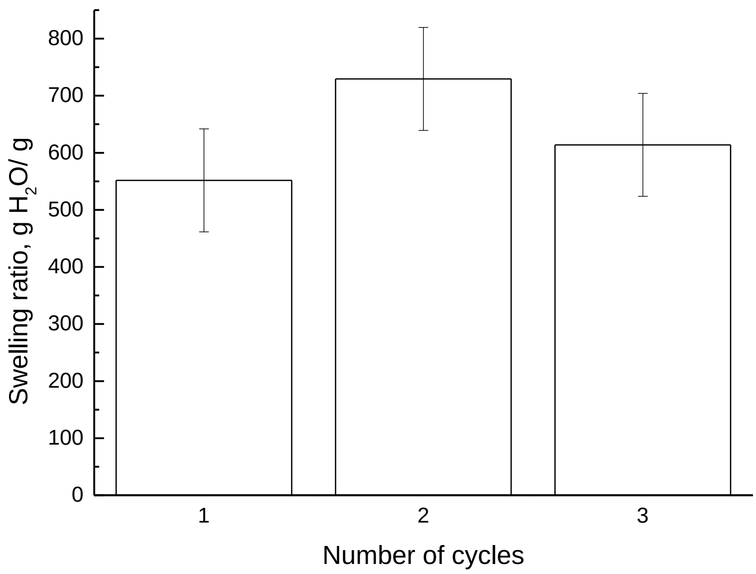

Figure 5. The influence of swelling – drying cycles on hydrogel swelling ratio.

The water retention behavior of soil with SAP hydrogel

The water retention of soil with SAP hydrogel was investigated, results are shown on the graph in Figure 6. The experiment was repeated three times. It is evident, that application of hydrogel into soil led to increasing water retention and decreasing water evaporation ability. The water evaporation ratio of soil without hydrogel reached 77 % after 5 days, while that of the soil with 0.05 wt. % of hydrogel was 51.4 %, respectively. The time required for 50 % water evaporation was 77 hours for the soil without hydrogel and 116 hours for the soil with 0.05 wt. % of hydrogel. After 300 hours, the soil with and without hydrogel has lost all water.

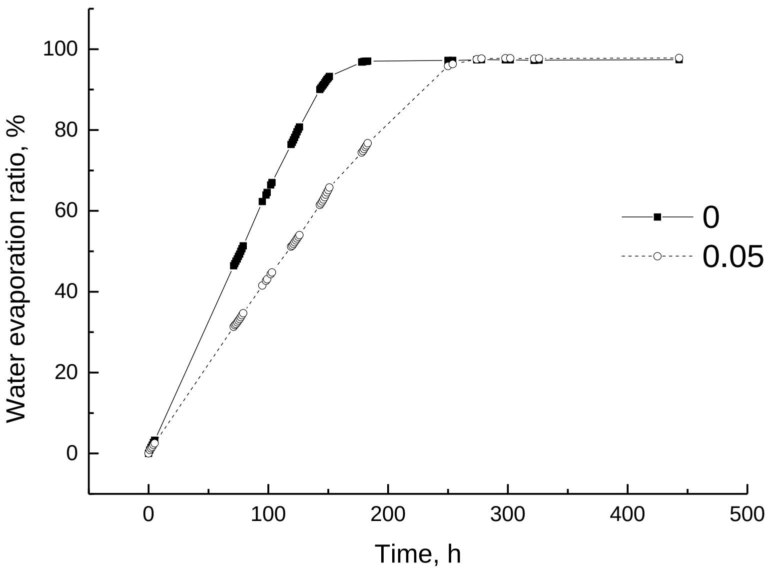

Figure 6. The water retention behavior of soil with and without SAP hydrogel.

Conclusion

Hydrogels were prepared by graft copolymerization of acrylic acid and acrylamide onto glucomannan. The experiments proved that the swelling ratio of prepared hydrogels reach 480 – 570 g H_2O/g, which is sufficient for usage as a regulators of soil moisture. Hydrogels achieved maximum swelling capacity after one-day contact with water, the swollen hydrogel lost all water during 70 hours at a laboratory temperature and retained its swelling properties at least during three swelling – drying cycles. The application of tested hydrogel greatly improves the water retention property of the soil.

Acknowledgement

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