Synthesis of Superabsorbent Polymers by Irradiation and Their Applications in Agriculture

Peng Chen, Wei'an Zhang, Wei Luo, Yue'e Fang

Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, China

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ABSTRACT: The superabsorbent polymers (SAPs) were synthesized by grafting copolymerization of acrylic acid and acrylamide onto starch by using γ-ray radiation technique and poly(ethylene glycol) (PEG) as a crosslinker. The samples were characterized by IR spectroscopy. The effect of various synthetic parameters such as irradiation dose, irradiation dose rate, monomer concentration, monomer/starch ratio, and PEG content were studied. The effects of different drying methods on water absorbency of the SAPs were also studied. The experimental results showed that the water absorbency of the SAPs depends largely on the specific conductance of water when the specific conductance is below 500 μs/cm. The water retention of sand and soil was enhanced by using the SAPs. Effects of the SAPs on the germination of seeds and growth of young plants were investigated. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1748–1755, 2004

Key words: irradiation; superabsorbent; graft copolymers; swelling

INTRODUCTION

Superabsorbent polymers (SAPs) are functional polymers with the ability to absorb large amounts of water including those with good water retention capacity even under high pressure or temperature. Because of their excellent properties, these SAPs were already well established in various applications such as disposable diapers,[1] hygienic napkins,[2] cement,[3] drug delivery systems,[4–6] sensors,[7] and agriculture.[8–10] These polymers have aroused considerable interest and many researchers have focused on modifying these absorbent polymers with a view to enhance their water absorbency, gel strength, and absorption rate.[11–13]

As starch is cheaper and more easily biodegradable than vinyl polymers, copolymerizing vinyl monomers in the presence of starch to fabricate a grafting copolymer composite is significant in biodegradation and reducing the product cost. Research on these polymers has been widely performed.[14–16] In this article, we reported the synthesis of SAPs by copolymerizing acrylate with acrylamide in the presence of starch by using γ-ray radiation technique with poly(ethylene glycol) (PEG) as a crosslinker. By selecting polymerization conditions, the water absorbency of the dry sample in distilled water could attain 2400 $\pm$ 10 g/g. The effects of SAPs on the water retention of sand and soil were studied. The experiment of using the SAPs for the germination of corn seeds (obtained from Fengle Co., Ltd., Hefei, China) and the growth of young plants showed satisfactory results.

Correspondence to: Y. Fang (fye@ustc.edu.cn).
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EXPERIMENTAL

Materials

Batata starch (Fuyang, Anhui, China) was used without further purification. All commercial grade reagents, acrylic acid and acrylamide (Radiation Chemistry Co., Ltd., USTC, Hefei, China), PEG (Fushun Jiahua Chemical Co., Ltd., Liaoning, China) with M_w = 10,000, were used as received. Sodium hydroxide, methanol, and acetone (A. R. Shanghai Chemical Reagent Co., Ltd., China) were used directly. Sand (Changjiang River, China) and soil (Fuyang, Anhui, China) were dried and screened by a 24-mesh screen before utilization.

Preparation of SAPs

Batata starch mixed with distilled water in a three-necked flask was stirred at 200 rpm and heated at 85 $\pm$ 5°C for 30 min to form a pastlike slurry. Then, the gelatinized starch was cooled to 40 $\pm$ 5°C. Acrylamide and PEG were dissolved in distilled water and mixed with acrylic acid solution that was neutralized by sodium hydroxide. This mixture was added into the gelatinized starch in the three-necked flask and stirred to equity, with nitrogen gas purged into it to remove oxygen. The mixture was placed into an airtight tube and irradiated in the field of 3.0×10^5 Bq ^{60}Co γ-rays source. After irradiation, the mixture turned into a gel. Finally, the gel was dried and crushed to obtain the final dry sample.

Water absorbency measurement

The dry sample was weighed and immersed in water for 24 h to reach absorption equilibrium. The fully swollen hydrogel was separated from the unabsorbed water with a 65-mesh screen. Then, the hydrogel was weighed. Relative water absorbency was calculated by

$$\text{Water absorbency (g/g)} = (\text{Mass of fully swollen hydrogel} - \text{Mass of dry sample})/\text{Mass of dry sample} \quad (1)$$

Measurement of grafting ratio

The dry sample (water absorbency = 2000 ± 20 g/g) was extracted with methanol for 24 h to remove the homopolymer of polyacrylate, and then, the extracted sample was washed with distilled water and acetone to remove the homopolymer of polyacrylamide.[17] Then, the sample was dried and weighed. The grafting ratio was calculated by

$$\text{Grafting ratio (wt \%)} = (\text{Mass of the sample extracted and washed}/\text{Mass of dry sample}) \times 100\% \quad (2)$$

Water absorption rate measurement

The dry sample with particle diameters between 0.8 and 0.25 mm was left to swell in water for some time, and then, the hydrogel was separated from unabsorbed water with a 65-mesh tubby screen. The excess water was left to drain away before the hydrogel was weighed. Water absorbency within the certain time was calculated by eq. (1).

By repeating the experiment with different soakage times, the relationship between water absorbency and soakage time could be obtained.

Water retention of the SAPs

Water retention of the SAPs was studied as follows.

(1) The fully swollen hydrogel was weighed and then put into an oven at 70°C. The hydrogel was weighed after various time intervals. Water retention was calculated by

$$\text{Water retention (wt \%)} = (\text{Mass of hydrogel dried after a certain time}/\text{Mass of fully swollen hydrogel}) \times 100\% \quad (3)$$

(2) One hundred grams of dry sand mixed with 0.1 g SAPs was placed in a cup (A), and the other 100 g sand without SAPs was placed in an identical cup (B). Three hundred milliliters of water was added into both cups, then, the cups were kept under identical conditions at room temperature (about 30 ± 2°C) for 15 days. The initial masses of the mixture in the two cups were measured after removal of excess water, and their masses were recorded daily to compare the water retention of SAPs. Water retention was calculated by

$$\text{Water retention (wt \%)} = (\text{Mass of the mixture dried after certain days}/\text{Initial mass of the mixture}) \times 100\% \quad (4)$$

(3) Experiments with five groups of dry soil mixed with SAPs (ratios of SAPs/soil0/100, 0.1/100, 0.2/100, 0.4/100) were performed according to the procedure described in (2) to study the water retention of the soil mixed with SAPs.

Applications in agriculture

The soil with 15% moisture was placed into two identical boxes (30 × 45 × 16 cm). The depths of the soil were 12 cm. One box was irrigated with 400 ml water; the other was irrigated with 400 ml water mixed with the weighed SAPs. The same amount of healthy corn seeds was placed in each box. Germination percentages were measured to testify that the seed qualities of two groups are identical, and germination energies were calculated to compare the effect of the soils on seeds germination.

Germination percentage of the seeds was calculated by

$$\text{Germination percentage (\%)} = \text{amount of germination seeds/total seeds} \times 100\% \quad (5)$$

Germination energy of the seeds was calculated by

$$\text{Germination energy (\%)} = \text{amount of germination seeds in first 3 days/total seeds} \times 100\% \quad (6)$$

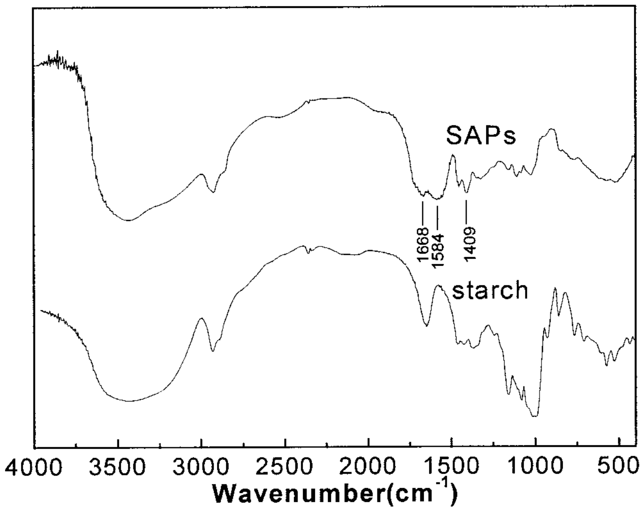

Figure 1 Infrared spectroscopy of the starch and the SAPs.

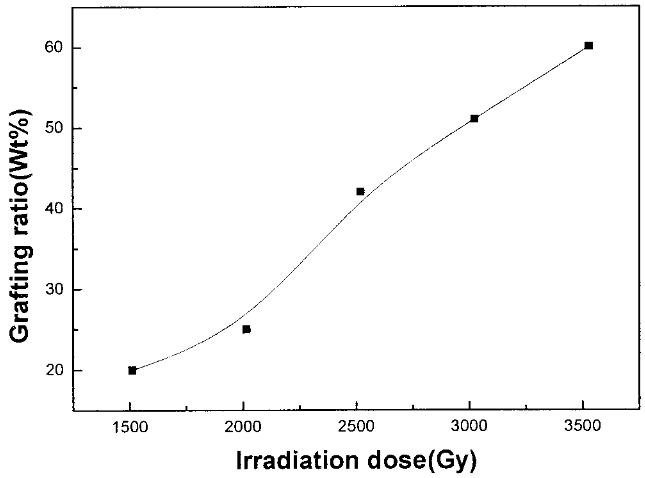

Figure 2 Effect of irradiation dose on grafting ratio. [monomer] = 15.5 wt %, AA/AM = 4 : 1 (wt/wt), [PEG] = 0.65 wt %, monomer/starch = 4 (wt/wt), irradiation dose rate = 24.5 Gy/min.

The young plants were studied to observe the effect of SAPs on growth of plants.

RESULTS AND DISCUSSION

IR spectra characterization

The IR spectra shown in Figure 1 were recorded with a Bruker Vector-22 FTIR spectrometer in the range from 4000 to 400 cm^{-1} by using KBr pellets at room temperature. Compared with the IR spectrum of starch, the SAPs' spectrum shows broad peaks at 1668 cm^{-1}, corresponding to the carbonyl group of the acidic moiety of the acrylate unit and that of the amide moiety of the acrylamide unit.[17] Peaks at 1584 and 1409 cm^{-1} correspond to the carbonyl group of the ester group of acrylate unit.[18] From the IR data, it can be concluded that the monomeric units were grafted onto the starch chains.

Effect of irradiation dose and dose rate on graft copolymerization

The effect of the irradiation dose on the grafting ratio is shown in Figure 2. In irradiation grafting copolymerization, the number of the grafting sites is basically determined by the dose, so the grafting ratio increases as the irradiation dose is increasing.[18] The long chains of PEG and starch tend to intertwine with those of the grafting copolymers to form a net. Owning to the function of hydrophilic groups such as ester and amide groups, these nets can absorb and hold a large quantity of water. There is a limiting crosslinking density for the maximal water absorbency according to Flory's theory.[19] When the crosslinking density is less than the appropriate density, the water absorbency of the SAPs increases as the degree of crosslinking increases. However, if the crosslinking density is higher than the appropriate one, the water absorbency of the SAPs decreases as the crosslinking density increases.[10,16]

As can be observed from Figure 3, the effect of grafting ratio on water absorbency of the SAPs has the same trend as that of radiation dose on water absorbency of the SAPs, which is shown in Figure 4. This is due to the approximately linear relationship of irradiation dose with grafting ratio.

Figure 5 shows the effect of the dose rate on the water absorbency. By increasing the irradiation dose rate, the water absorbency of the SAPs is reduced gradually. At a fixed dose, the grafting ratio and

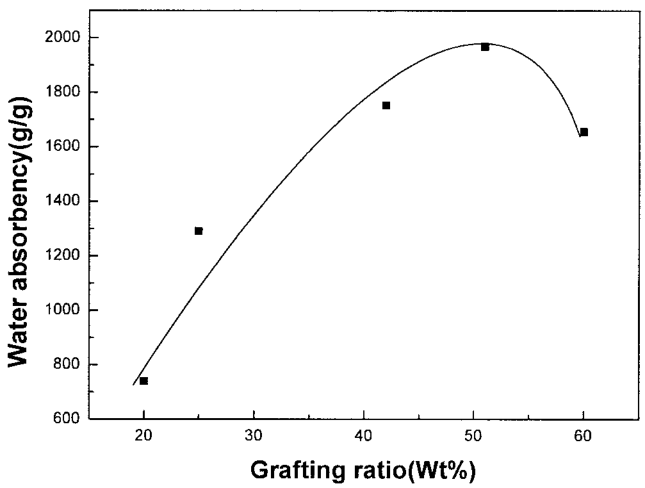

Figure 3 Effect of grafting ratio on water absorbency. [monomer] = 15.5 wt %, AA/AM = 4 : 1 (wt/wt), [PEG] = 0.65 wt %, monomer/starch = 4 (wt/wt), irradiation dose rate = 24.5 Gy/min.

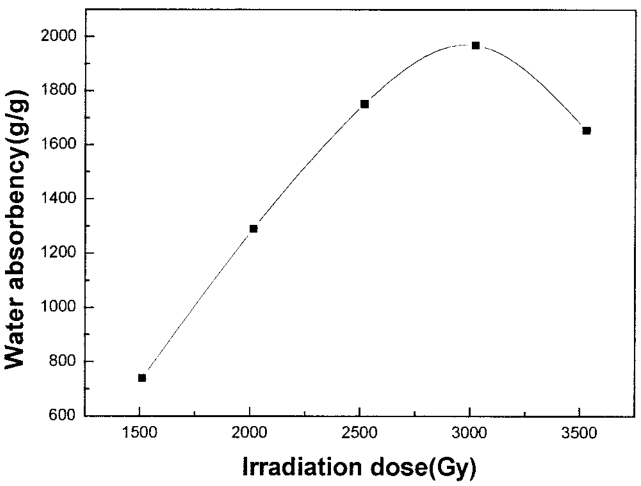

Figure 4 Effect of irradiation dose on water absorbency. [monomer] = 15.5 wt %, AA/AM = 4 : 1 (wt/wt), [PEG] = 0.65 wt %, monomer/starch = 4 (wt/wt), irradiation dose rate = 24.5 Gy/min.

monomer conversion ratio decrease with increasing dose rate, because the chain termination and transfer would occur easily with a high content of radicals.

Effect of reaction temperature on water absorbency

The effect of reaction temperature on the water absorbency is presented in Figure 6. With increasing temperature, the water absorbency of the SAPs decreases greatly. This is because the speed of chain termination and transfer reactions increase with increasing temperature,[20] thus shortening the molecule chains. The

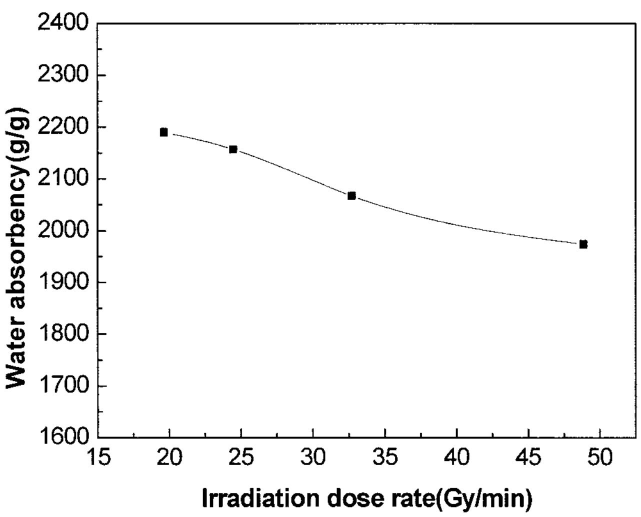

Figure 5 Effect of the dose rate on water absorbency. [monomer] = 15.5 wt %, AA/AM = 4 : 1 (wt/wt), [PEG] = 0.65 wt %, monomer/starch = 4 (wt/wt), irradiation dose = 3.0 kGy.

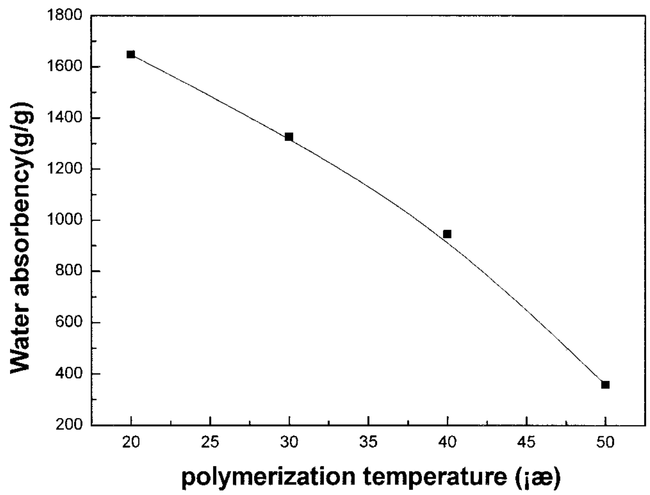

Figure 6 Effect of the reaction temperature on water absorbency. [monomer] = 15.5 wt %, AA/AM = 4 : 1 (wt/wt), [PEG] = 0.65 wt %, monomer/starch = 4 (wt/wt), with a irradiation dose = 3.0 kGy, irradiation dose rate = 24.5 Gy/min.

structure of the net with short molecule chains does not encourage water absorption and water retention.

Effect of monomers concentration on water absorbency

Figure 7 shows that with increasing monomer concentration the water absorbency decreases rapidly. This is caused by the fact that the networks of SAPs become denser with high monomer concentration, and consequently, would retain a lot of heat produced by polymerization. Hence, the temperature of the reaction

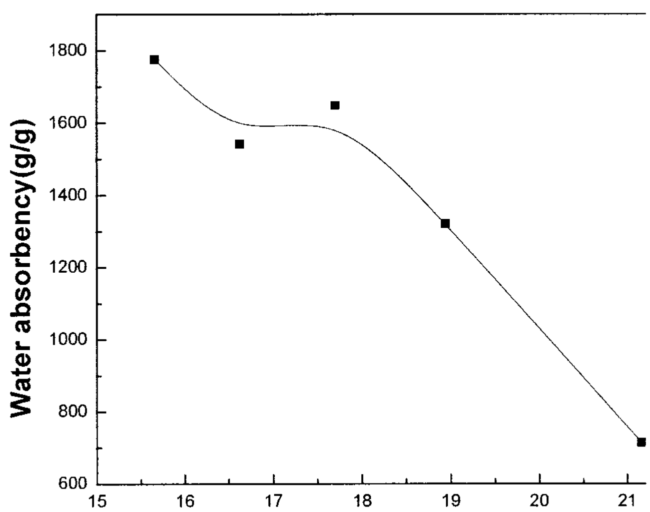

Figure 7 Effect of monomers concentration on water absorbency. AA/AM = 4 : 1 (wt/wt), [PEG] = 0.65 wt %, monomer/starch = 4 (wt/wt), irradiation dose = 3.0 kGy, irradiation dose rate = 24.5 Gy/min.

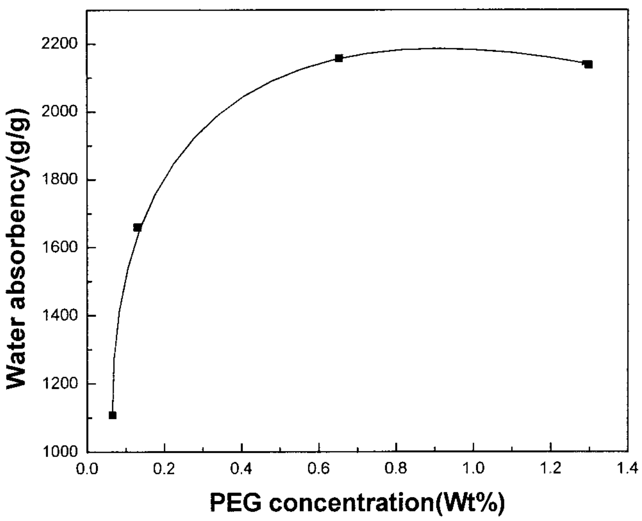

Figure 8 Effect of PEG concentration on water absorbency. [monomer] = 15.5 wt %, AA/AM = 4 : 1 (wt/wt), monomer/starch = 4 (wt/wt), irradiation dose = 3.0 kGy, irradiation dose rate = 24.5 Gy/min.

system would increase and in turn accelerate the chain termination and transfer speeds as discussed above. The high reaction temperature is known to decrease the water absorbency of the SAPs.[21]

Effect of PEG content on water absorbency

Figure 8 shows the effect of PEG content on water absorbency. At low content of the PEG, the water absorbency of SAPs increases rapidly with increasing content of PEG. The water absorbency reached saturation at about 0.65 wt % PEG. When the amount of PEG increases any further, there is little influence on water absorbency of the SAPs.

Effect of monomers to starch ratio on water absorbency

Figure 9 shows the effect of monomer/starch ratio on water absorbency. The water absorbency increases almost linearly with the increasing monomer/starch ratio. This is because the water absorbency of the starch is much lower than that of poly(acrylate-*co*-acrylamide). In this experiment, the introduction of starch into SAPs is to make the SAPs cheaper and easier to degrade.

Comparison of several methods for drying the hydrogel

Figure 10 shows the influence of different drying methods on the water absorbency. The same hydrogel was separated into five portions and each one was dried by a different method. The results showed that the water absorbency of the different final samples

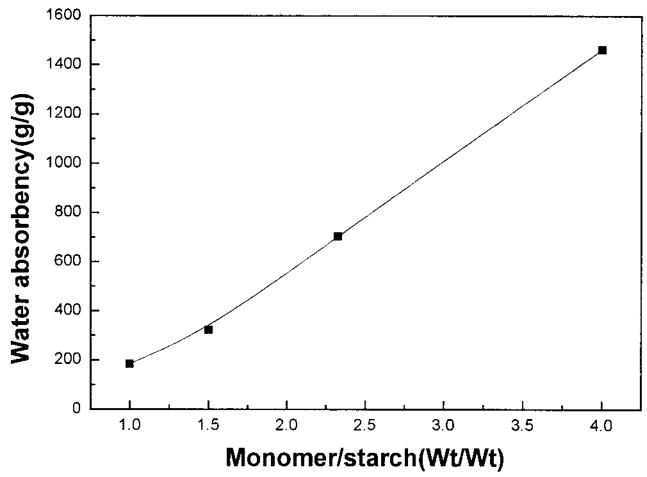

Figure 9 Effect of monomer/starch ratio on water absorbency. [monomer] = 15.5 wt %, AA/AM = 4 : 1 (wt/wt), [PEG] = 0.65 wt %, irradiation dose = 3.0 kGy, irradiation dose rate = 24.5 Gy/min.

varied from each other. Among these drying methods, the sample obtained by infrared baking (40°C) had the maximum water absorbency. Compared to the oven drying at different temperature (A and B), the lower drying temperatures (C and D, E) are suitable to obtain a higher water absorbency.

Study of the water absorbency of SAPs in waters with different specific conductances

As the specific conductances of different waters such as tap water, rain water, and river water vary with their electrolyte contents, the study of the variation of water absorbency of the SAPs in various waters is

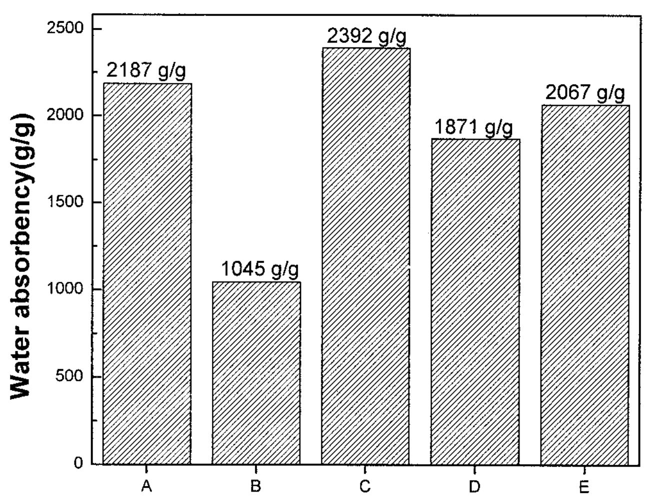

Figure 10 Influence of different dry methods on water absorbency. A: oven drying (60°C); B: oven drying (80°C); C: infrared baking (40°C); D: vacuum baking (40°C); E: freeze-drying.

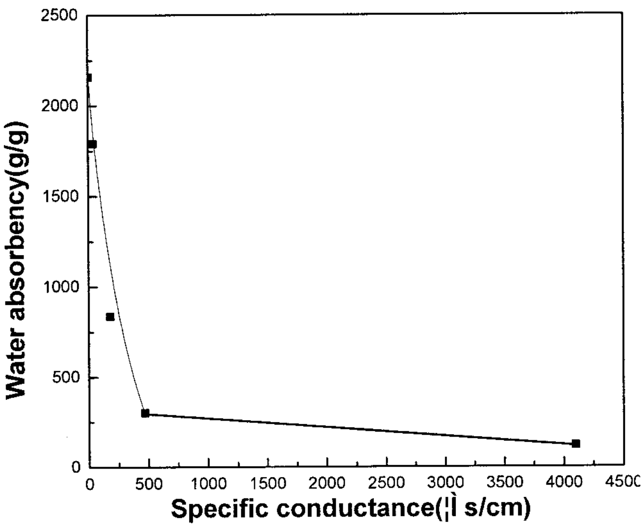

Figure 11 Effect of water specific conductance on the water absorbency.

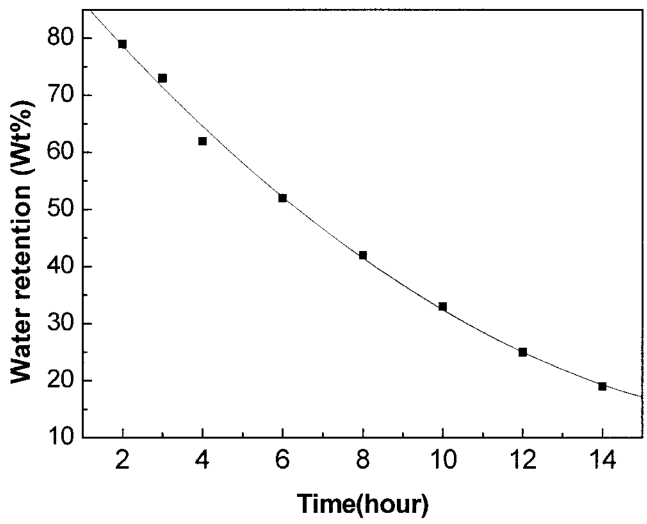

Figure 13 Water retention of the SAPs at 70°C.

significant for practical application. Figure 11 presents the variation of water absorbency of the SAPs as a function of the specific conductance. By increasing the water-specific conductance, the water absorbency of SAPs decreases rapidly below 500 μs/cm, whereas it decreases only slightly when the specific conductance exceeds 500 μs/cm.

Water absorption rate of the SAPs

The water absorption rate of the SAPs is shown in Figure 12. The water absorbency of the sample with particle diameter between 0.8 and 0.25 mm increased fast during the first 10 min and reached an approximate equilibrium after 30 min.

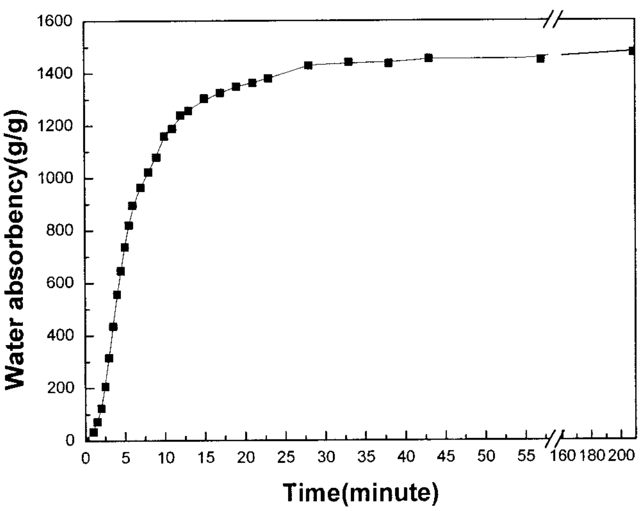

Figure 12 Water absorption rate of the SAPs.

Water retention of SAPs

(1) The swollen hydrogel showed good water retention capability at high temperature. Figure 13 shows the mass of the hydrogel reduced only by one-half of its initial value after 6 h at 70°C.
(2) As Figure 14 presents, the water retention of sand mixed with the SAPs was studied. The masses of two samples were compared within 15 days. Initially, the sand with 0.1 wt % SAPs can absorb more water than the sand without SAPs. After nine days the sand without SAPs had nearly given off all water, but the sand with 0.1 wt % SAPs still retained 10 wt % water.
(3) Figure 15(a) shows that the soils mixed with SAPs absorbed initially more water than the soils without the SAPs. The rate of water loss

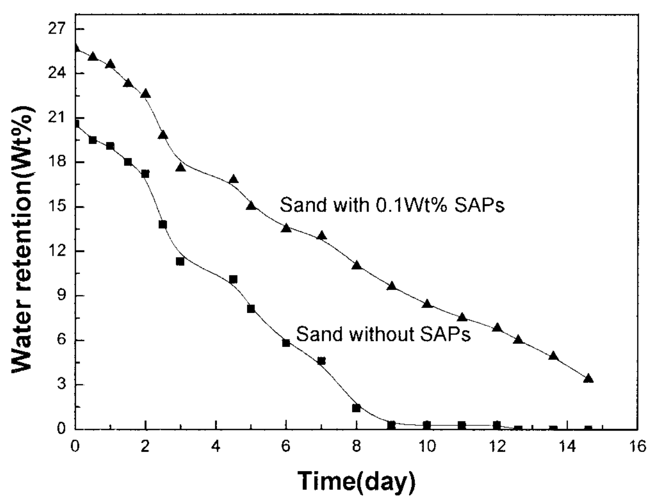

Figure 14 Water retention of the sand mixed with 0.1 wt % SAPs (environment temperature is 30 ± 3°C).

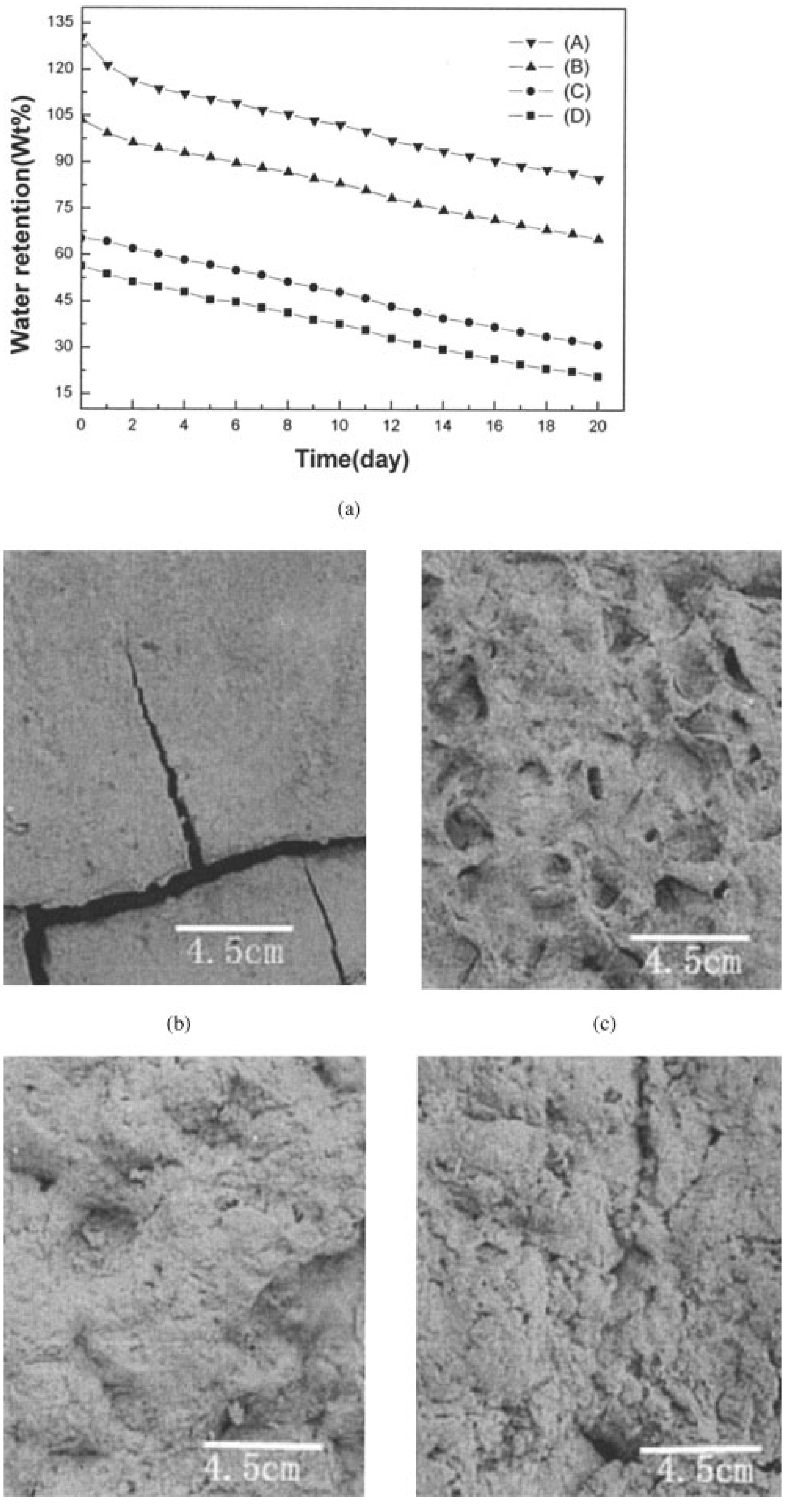

Figure 15 (a) Water retention of the SAPs in soil (environment temperature is 15 ± 3°C). (A) SAPs/soil = 0.4 g/100 g; (B) SAPs/soil = 0.2 g/100 g; (C) SAPs/soil = 0.1 g/100 g; (D) SAPs/soil = 0/100 g. (b) The soil without SAPs. (c) The soil with 0.1 wt % SAPs. (d) The soil with 0.2 wt % SAPs. (e) The soil with 0.4 wt % SAPs.

appears to be identical for all samples investigated. Samples A and B can hold more water than the sample C because A and B contain more SAPs than C. Sample B is more efficient than sample A considering the smaller content of the SAPs without significant decrease of water retention capability. As Figure 15(b) shows, the mere soil used in the experiment hardened and cracked after 20 days at room temperature, whereas the soils mixed with SAPs [Fig. 15(c, d, e)] still kept their moist and continuous configuration.

Applications of the SAPs in agriculture

The applications of SAPs in agriculture were studied with a view to promote the growth of plants.[22,23] In this experiment, the SAPs with water absorbency 2000 ± 20 g/g were synthesized and applied in agriculture to observe the effect on the germination of corn seeds and growth of young plants. From Table I, as all seeds used in the experiment were healthy and planted at random, the germination percentages of both group of seeds were almost the same. The germination energy of the seeds with SAPs was obviously higher than that of the seeds without SAPs. This is ascribed to the fact that the SAPs cannot only absorb large amounts of water but also have good water retention capability, which supplies plentiful water to promote the seeds' growth. After 15 days, soil with 0.2 wt % SAPs showed a favorable effect on the weights of leafages and roots of the plants (Table II). From the initial study, it can be concluded that the SAPs have potential for applications in agriculture, especially in arid and desert regions.

CONCLUSION

A new way was studied to synthesize SAPs by grafting copolymerization of vinyl monomers onto starch with PEG as a crosslinker by using γ-ray irradiation technique. The optimum synthesis parameters were [monomer] = 15.5 wt %, AA/AM = 4 : 1 (wt/wt), [PEG] = 0.65 wt %, monomer/starch = 4 (wt/wt), with a irradiation dose of 3.0 kGy and a irradiation dose rate of 24.5 Gy/min at room temperature. The sample with maximum water absorbency (2400 ± 10 g/g) was obtained by infrared baking (40°C). The SAPs will be saturated with water in ~30 min. At high temperature, the SAPs show good water retention. On addition of SAPs, the water retention capability of sands and soils was enhanced. The experimental results showed that the SAPs may have considerable effect on seed germination and young plant growth.

TABLE I
Effect of the SAPs on Germination of the Corn Seeds

SAPs content	Germination percentage (%)	Germination energy (%)
SAPs (0%)	98.0 ± 0.5	60.0
SAPs (0.2%)	98.0 ± 0.5	86.0

TABLE II
Effect of SAPs on Growth of the Young Corn Plants

SAPs content	Height of the plant (cm)	Weight of the leafage (g)	Weight of the root (g)
SAPs (0%)	3.6 ± 0.1	6.8 ± 0.1	1.0 ± 0.1
SAPs (0.2%)	3.5 ± 0.1	7.3 ± 0.1	1.3 ± 0.1

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