Synthesis and Properties of Starch Grafted Poly[acrylamide-*co*-(acrylic acid)]/Montmorillonite Nanosuperabsorbent via γ-Ray Irradiation Technique

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ABSTRACT: The novel nanosuperabsorbent copolymer (NSAP) was synthesized by grafting copolymerization of acrylamide (AM) and acrylic acid (AA) onto starch with montmorillonite (MMT) initiated using ^{60}Co γ-ray irradiation. NSAP was characterized by IR spectroscopy and X-ray diffraction (XRD). Different synthesis parameters were studied, such as AM-to-AA ratio, radiation total dose, radiation dose rate, crosslinker content, and clay content. NSAP can effectively improve the water retention capacity of soil. The effects of NSAP on crops were also studied, showing that NSAP has an encouraging potential for agricultural application. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1341–1346, 2005

Key words: superabsorbent; starch; clay; radiation; polymerization

INTRODUCTION

Superabsorbent polymer (SAP), as a functional polymer with the ability of absorbing and tightly holding a great amount of water, is widely applied in many fields, such as disposable diapers,[1] hygienic napkins,[2] cement,[3] drug delivery systems,[4–6] sensors,[7] and agriculture.[8–10] Since the first superabsorbent polymer was reported by the U.S. Department of Agriculture,[11] its research has aroused considerable interest.[12,13]

In previous reports, SAP has been shown to be synthesized in several ways. It can be prepared from monomers such as acrylonitrile, acrylic acid, acrylamide, and methyl methacrylate.[10,14,15] Producing these kinds of SAP is relatively costly and some even bring chemical pollution to the environment. As it is known that starch is able to biodegrade, graft-copolymerization of vinyl monomers onto starch is significant in biodegradation, which results in less remaining in the soil. Due to the presence of starch, which is abundant and low cost, the production cost is reduced. Much research about these polymers has been done.[16]

Polymer/clay nanocomposites have been receiving great attention because of their unusual properties.[17,18] Compared to the conventional polymers, these nanocomposites can exhibit increased modulus,[19] reduced gas permeability,[20] and enhanced thermal stability.[21] However, little research on the subject of clay/nanogel or nanosuperabosorbent (NSAP) has been reported.[22,23]

In this paper, a novel NSAP was synthesized by graft-copolymerization of acrylic acid/acrylamide onto starch with montmorillonite (MMT) initiated by a γ-ray irradiation technique.

MMT was incorporated into SAP to form NSAP, which can enhance gel strength and the water retention of the gel. Compared to chemical initiators such as Fe^{3+}, Cu^{2+}, Ce^{4+}, V^{3+}, Mn^{3+} and their complexes,[24] γ-ray irradiation is an effective and convenient technique for preparing SAP. The effects of synthesis parameters on the water absorbency were systematically studied. The experimental results show it has encouraging potential for use in agricultural applications.

EXPERIMENTAL PROCEDURES

Materials

Batata starch was obtained from Fuyang, Anhui, China. The Na^+–montmorillonite clay (Na–MMT), with a cation exchange capacity (CEC) value of about 100 mmol/100 g (Ling An Chemicals Co. Ltd., Hangzhou, China), was used as received. All commercial grade reagents, acrylamide, *N*,*N*′-methylenebisacrylamide (NMBA), and acrylic acid were obtained from Dongfanghong Chemical Factory in Beijing, China. Sodium hydroxide was purchased from the first Reagent Factory of Shanghai China.

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Preparation of NSAP

A series of NSAP were synthesized according to the following steps. A mixed solution of desired amounts of acrylic acid (neutralization degree of 80%, with sodium hydroxide solution), acrylamide, Na–MMT, NMBA, and distilled water (90 mL) was prepared after stirring and ultrasonic treatment at 25°C. Batata starch (10 g) mixed with distilled water (100 mL) in a three-neck flask was stirred magnetically at 80°C in an oil bath under nitrogen for about 30 min until the color of starch slurry turned from white to gray and then the paste-like slurry was cooled to 40 ± 5°C. Subsequently, the mixed solution was added into the paste-like starch in the three-neck flask. The system was stirred under a nitrogen gas atmosphere for about 1 h. It was then removed into tubes, which were tightly closed and irradiated under ^{60}Co γ-ray irradiation at the desired conditions. The products were obtained by freeze-drying under vacuum.

IR

The IR spectra of dried powdered sample and granular starch were run in the form of KBr pellets on a Bio-Rad WIN FTIR 4200 Spectrophotometer in the frequency range of 4000 to 400 cm^{-1}.

XRD

XRD patterns were obtained by using a Japanese Rigaku D/max γ_A X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 0.154178 nm). The scanning range was 1.5–10.2° with a scanning rate of 2°/min.

Measurement of water absorbency

The dried sample (0.15 g) was immersed in distilled water (300 mL) at room temperature. The gel was weighed after it reached absorption equilibrium.

Water absorbency was calculated using the following equation:

$$Q = (W_1 - W_0)/W_0 = W_1/W_0 (W_1 >> W_0) \quad (1)$$

where Q is water absorbency and W_1 and W_0 are the weights of the water-swollen gel and the dry sample, respectively.

Water retention of NSAP

The desired amount of dry soil mixed with NSAP(NSAP/soil = 0.2 wt %) was placed in a cup. The same amount of soil without NSAP was placed in the other cup. Subsequently, each cup was immersed in enough water for 30 min and the excess water that was not absorbed was filtered. The water retention ratio (R) was calculated using following equation:

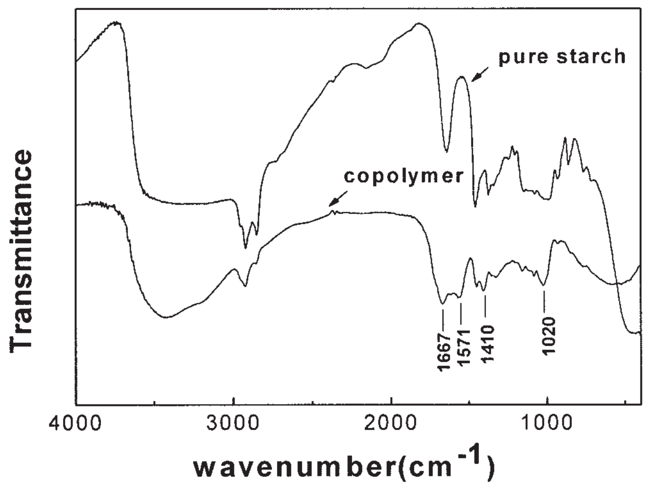

Figure 1 IR spectra of pure starch and graft copolymer.

$$R = (M - m)/M \times 100 \quad (2)$$

where M is the total weight of the wet clay at the time of measurement and m is the weight of the dry clay (100 g).

Applications in agriculture

NSAP suspension was prepared with 0.5 g of dried NSAP powder and 250 mL of H_2O. 370 g of soil and 20 greengrocery seeds were filled in 10 boxes, respectively. Five of the boxes were irrigated with 50 mL NSAP suspension, respectively, while the others were irrigated with 50 mL water. The seeds grew for a month without additional water.

RESULTS AND DISCUSSION

IR and XRD of NSAP

The IR spectra of pure starch and graft copolymer are shown in Figure 1. It can be seen that the graft copolymer has absorption peaks at 1571 and 1410 cm^{-1}, corresponding to the carbonyl group of the ester group of the acrylate unit.[25] The IR spectra of graft copolymer also shows the peak at 1667 cm^{-1}, which corresponds to the carbonyl group of the amide moiety of the acrylamide unit. This confirms that both acrylate and acrylamide have been grafted onto the starch. In addition, the peak at 1040 cm^{-1} corresponds to the Si–O stretching of MMT, implying MMT has been introduced into the compolymer matrix.

Figure 2 illustrates the X-ray diffraction of MMT and NSAP with 5 wt % MMT. There is intense diffraction for MMT, while no diffraction peak appears for

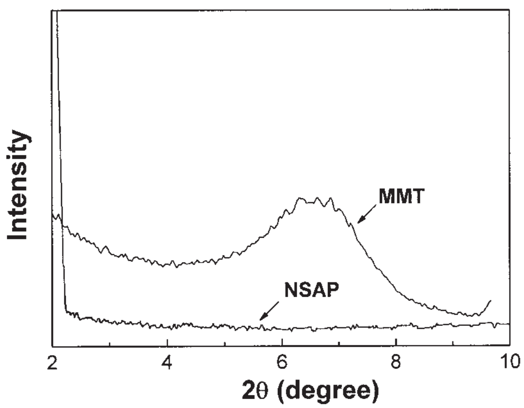

Figure 2 XRD spectra of MMT and NSAP.

NSAP in the experimental range of 2θ, suggesting that clay sheets are exfoliated and uniformly dispersed in the organic network. The network of NSAP is shown schematically in Figure 3.

Effect of the acrylamide-to-acrylic acid ratio on water absorbency of NSAP

The effect of different acrylamide-to-acrylic acid ratios on water absorbency is shown in Table I. It can be seen that the increase of AM content in the absorbent results in an increase of water absorbency. This is because the radiation can cause the monomers to produce a certain number of free radicals that are used both for homopolymerization and graft copolymerization of the monomers in a proper ratio at a given total dose. In the present system, the reactivity ratios of AA are lower than those of AM. Therefore the higher ratio of AA in the monomer mixture results in greater amounts of homopolymer and ungrafted copolymer. However, the polyacrylamide doesn't have a high water absorption capacity without the ionic functional group. Therefore, the acrylamide-to-acylate molar ratio was kept to 4 : 1 (AM/(AM+AA) = 80%) in the following work.

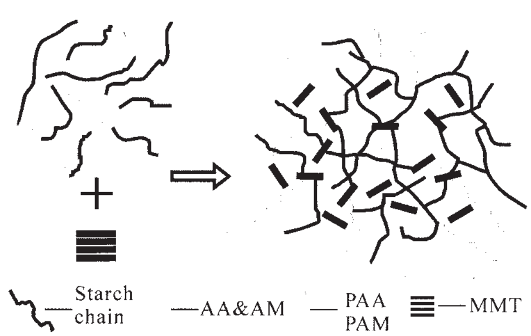

Figure 3 Schematic drawing of the process of the formation of NSAP.

TABLE I
Effect of Monomer Ratio on Water Absorbency of NSAP

AM/(AM + AA) (%)	550 Gy	1,100 Gy	1,650 Gy
0	—	—	—
20	34	77	159
40	202	315	531
60	474	787	930
80	717	1007	941
100	—	—	—

Reaction conditions: radiation dose rate = 27.5 Gy/min; clay content = 2.0%; crosslinker content = 0.027%.

Effects of radiation dose and dose rate on water absorbency of NSAP

The effect of radiation dose on water absorbency is shown in Figure 4. Below the dose of about 1,100 Gy, the water absorbency increases with the increasing dose; when radiation dose is beyond 1,100 Gy, the water absorbency decreases with the increasing dose. This is due to an increase of radicals as the radiation dose increases, which results in an increase of the active grafting sites on the starch backbone. However, when the dose is higher than the appropriate dose (1,100 Gy), the crosslink density of the network of the copolymer is so high that it is difficult to absorb a large amount of water. There is an appropriate crosslink density for the maximal water absorbency according to Flory's theory:[26]

$$Q^{5/3} = \left[(i/2VnS^{1/2})^2 + \left(\frac{1}{2} - X_1\right)/V_1 \right] / (V_e/V_u) \quad (3)$$

where Q is the water absorbency, $i/2V$n is the concentration of fixed charge referring to the unswollen network, S is the ionic strength of the swollen solution,

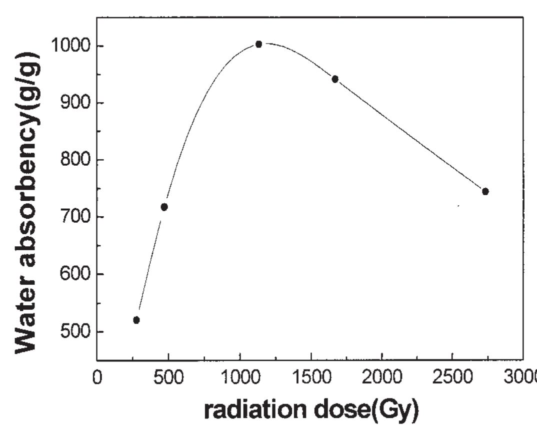

Figure 4 Effect of radiation dose on water absorbency of NSAP. Reaction conditions: radiation dose rate = 27.5 Gy/min, clay content = 2.0%, crosslinker content = 0.027%, AM/AA = 4 : 1.

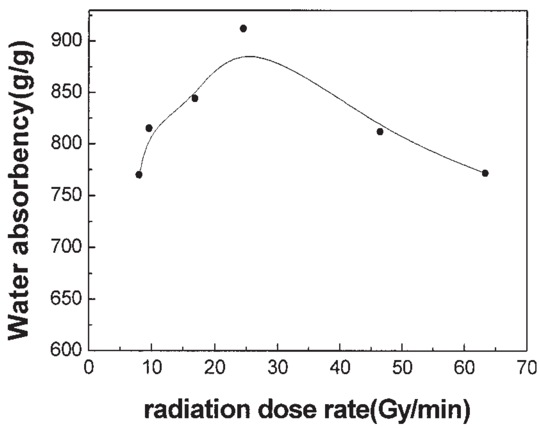

Figure 5 Effect of radiation dose rate on water absorbency of NSAP. Reaction conditions: radiation dose = 1,100 Gy, clay content = 2.0%, crosslinker content = 0.027%, AM/AA = 4 : 1.

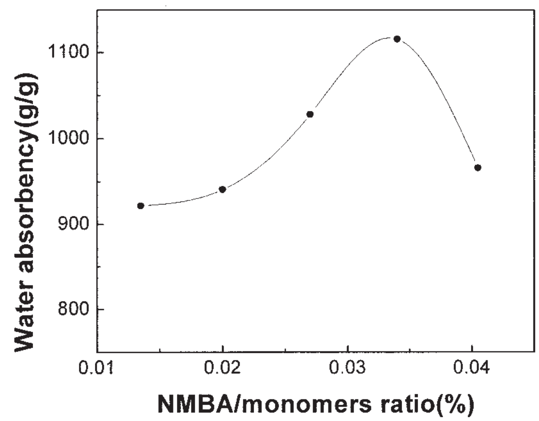

Figure 6 Effect of NMBA-to-monomers ratio on water absorbency of NSAP. Reaction conditions: radiation dose rate = 27.5 Gy/min, radiation dose = 1,100 Gy, clay content = 2.0%, AM/AA = 4 : 1.

$(1/2 - X_1)/V_1$ is the hydrophilic ability, and V_e/V_u is the crosslink density.

Figure 5 shows the effect of radiation dose rate on water absorbency of NSAP. There is also an appropriate dose rate for NSAP, because too low a dose rate results in a low concentration of radicals and therefore a low degree of grafting. In contrast, when the dose rate is too high, the concentration of the radicals is so high that chain termination and transfer can occur easily before obtaining adequate grafting.[27]

Effect of crosslinker content on water absorbency of NSAP

Crosslink density is an important swelling-control element, which plays a significant role in the formation of the chemically crosslinked network. The absorbed water is constrained among the polymer networks so that it's hard to remove even under some pressure. With a low concentration of crosslinker or no crosslinker, the absence of crosslinked networks limits the amount of water that can be absorbed. As shown in Figure 6, at low concentrations, the water absorbency increases with the increasing of crosslinker content. However, for a crosslinker content that is too high, the swelling capacity decreases drastically, which also can be explained by Flory's law. According to Flory's law, the water absorbency will decrease with an increase in crosslink density. A crosslink density of NSAP that is too high means there is not enough space for water molecules to enter the networks, resulting in lower water absorbency. Therefore there is an ultimate crosslink content to maximal water absorbency.

Effect of conductance of swollen solution on water absorbency of NSAP

Table II shows the effect of ionic strength of swollen solution on water absorbency of NSAP. Because the conductance is directly proportional to the square of the ionic strength, the water absorbency of NSAP will decrease with the increase of the ionic strength of swollen solution according to Flory's law. However, even in a solution of high ionic strength, NSAP can absorb a great deal of water. This is due to the high content of acrylamide, which is a nonionic monomer. Therefore, NSAP has a high resistance to ionic strength.

Effect of MMT content on water absorbency of NSAP

Conventional copolymers composed of chemically crosslinked polymer networks have severe limitations, such as morphological homogeneity and mechanical properties.[28,29] That is, conventional organic, crosslinked polymers always exhibit mechanically weak and brittle properties, for the polymer chains are molecularly restricted by a large number of chemical crosslinking knots.

To overcome these disadvantages, MMT was introduced into a copolymer matrix. The gel strength was obviously enhanced. In this system, clay is exfoliated and uniformly dispersed in an aqueous media, and the neighboring clay sheets are connected by polymer

TABLE II
Effect of Conductance on Water Absorbency of NSAP

	Distilled water	Rain water	Tap water
Water absorbency	844	767	512
Conductance (μs/cm)	5.0	16.5	46.0

Reaction conditions: radiation dose rate = 27.5 Gy/min; radiation dose = 1,100 Gy/min; clay content = 2.0%; crosslinker content = 0.027%; AM/AA = 4 : 1.

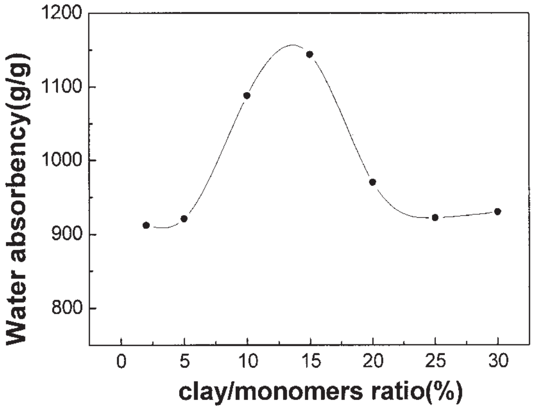

Figure 7 Effect of clay on water absorbency of NSAP. Reaction conditions: radiation dose rate = 27.5 Gy/min, radiation dose = 1,100 Gy, crosslinker content = 0.027%, AM/AA = 4 : 1.

chains (Fig. 3). The intercrosslinking distance then is equivalent to the neighboring clay–clay interparticle distance, which is greatly improved in contrast to conventional chemically crosslinked networks.[30] Therefore, the size of the polymeric network is improved, inducing the increment of water absorbency of NASP.

Figure 7 shows the influence of the content of MMT on the water absorbency of NSAP. Increasing the MMT/monomers ratio up to 15% causes an increment in water absorbency, which indicates that MMT can greatly improve the ability of to absorb water. But further increase of MMT causes a decrease in water absorbency. When the concentration of the clay is too high, the neighboring clay–clay interparticle distance will be too small, and thus make the size of the polymeric networks too small to absorb a large amount of water.

Water absorption speed of NSAP

Figure 8 illustrates the water absorption speed of NSAP. The dry NSAP powder absorbs water quickly at the beginning, and it reaches swelling equilibrium in 20 min.

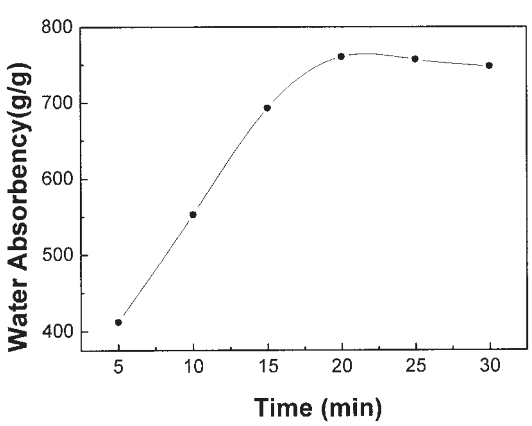

Figure 8 Water absorption speed of NSAP.

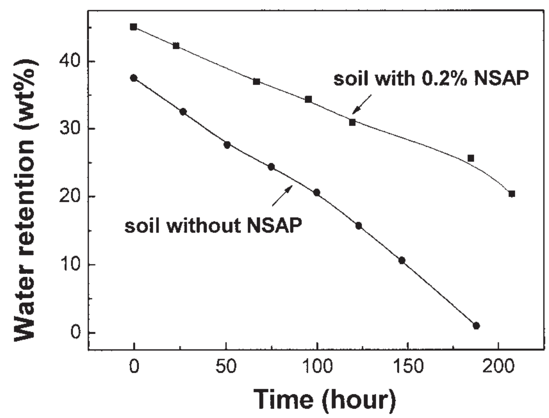

Figure 9 Water retention of soil with NSAP and soil without NSAP.

Effect of NSAP on water retention in soil

The water retention capacity of soil with NSAP and soil without NSAP was shown in Figure 9. The soil with 0.2% NSAP not only absorbs more water, but also evaporates water more slowly according to the two lines.

Application of NSAP in agriculture

The primary purpose of our research is to explore a product available for agriculture. So we measured the average height and weight of plants in each box and calculated the average output of five boxes. As shown in Table III, the crop planted in the soil with NSAP grew much better than that in the soil without NSAP. This is ascribed to the following: NSAP not only can absorb a large amount of water but also has good water retention capacity, which supplied the seeds with plentiful water. From the results above, we can conclude that NSAP can be widely used in agriculture, especially in dry and desert regions.

CONCLUSION

A novel nanosuperabsorbent was successfully sysnthesized by grafting copolymerization of AA/AM

TABLE III
Effect of NSAP on the Crop

Disposal method	No NSAP	0.2% NSAP
Height of the stem(cm)	5.7	6.3
Height of the root(cm)	2.6	3.1
Weight of the stem (g)	0.456	0.794
Weight of the root (g)	0.055	0.085

onto starch in the presence of montmorillonite and NMBA via γ-ray irradiation. The XRD pattens indicate the layers of MMT are exfoliated and uniformly dispersed in the polymer matrix. The best synthetic conditions were obtained by measuring the water absorbency of NSAP. Water absorbency of the product could reach up to 1,200 g/g. NSAP also has a high water absorption speed. The research on crops indicates that NSAP has great feasibility in agriculture.

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