Synthesis of a Superwater Absorbent and Studies of its Properties

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Abstract

The synthesis of superwater absorbent (SWA) from aqueous solution of potato starch/acrylic acid blend by irradiation with gamma radiation from Co-60 source at ~27ºC was carried out. Where the preparation conditions, such as irradiation doses (2-15 kGy) and potato starch to acrylic acid composition ratios (1.0:1.0, 1.0:1.5 and 1.0:2.0) in the feed solution were investigated for their optimization. The study of some properties of prepared SWA, such as gel fraction and swelling behavior showed that the gel content of SWA increased with increasing radiation dose and attained the maximum value at 5 kGy radiation dose. It also increased with increasing acrylic acid content in potato starch/acrylic acid blend. Swelling ratio of SWA increased with increasing radiation dose until it attained the maximum value at 5 kGy radiation dose. Then it started to decrease with increasing radiation. But it increased with increasing acrylic acid content in SWA. Water retention capacity of soil improved with addition of SWA with it. The storage modulus of SWA investigated using dynamic mechanical analyzer (DMA) decreased with increasing acrylic acid content in blend solution as well as increasing temperature. Soil mixed with SWA enhanced germination of chilli seeds and growth of young chilli plants.

Keywords: Potato starch, acrylic acid, superwater absorbent, swelling behavior, water retention, gel content, radiation.

1. Introduction

The superwater absorbent (SWA), an important class of cross-linked hydrophilic polymeric materials can absorb water from aqueous medium in the amount many hundred times its dry weight due to a considerable number of hydrophilic groups in its structure [1]. There is a wide application of SWA in various fields including drug delivery, hygiene, foods, cosmetics and agriculture [2-7].

The cross-linked structures of hydrophilic polymers can play a vital role in the absorption of a plentiful amount of water and the cross-linking can be introduced into the polymer structure by both chemical and radiation methods of which the radiation processing method does not require any initiator, catalyst and agent for cross-linking of polymers due to high energetic ionizing radiation [8]. The advantages of a radiation processing technique are easy process control, cross-linking of polymer, sterility of the product and the environment friendly technology leaving no residue or pollutant in the environment [9-10]. The cross-linking of polymer by radiation technique with or without cross-linker is much durable with respect to chemically cross-linking materials [11].

Graft copolymerization of an acrylic acid monomer onto a polysaccharide is an efficient route to the preparation of SWA in which the polysaccharide acts as the main part because of its exceptional properties like biocompatibility, biodegradability and non toxicity. Starch is a polysaccharide which consists of the linear D-glucan amylose and the highly branched amylopectin. Acrylic acid, an unsaturated carboxylic acid (CH_2=CHCOOH) consisting of a vinyl group connected directly to a carboxylic acid terminus acts as a monomer which can easily polymerize to poly(acrylic acid). Poly(acrylic acid) and its derivatives are popular as a thickening, dispersing, suspending and emulsifying agents in pharmaceuticals, cosmetics and paints [12]. SWA prepared from graft copolymerization of acrylamide/itaconic acid onto cassava starch and found that it is biodegraded by α-amylase enzyme [13]. The swelling behavior of SWA obtained from acrylic acid grafted Carboxyle Methyle Cellulose (CMC) and acrylonitrile and acrylic acid co-monomer grafted chitosan by chemical method has been described [14-15]. A porous hydrogel has been prepared from graft copolymerization of acrylic acid/2-hydroxy ethyl methacrylate onto starch by a free radical polymerization technique with sodium bicarbonate as foaming agent and found that it could potentially be a useful local drug delivery system to release drug at a specific site of body [16].

In the present investigation, SWA was prepared from potato starch/acrylic acid blend solution using gamma radiation. The effect of radiation dose, and potato starch/acrylic acid composition on gel content, swelling ratio, water retention capacity and storage modulus of SWA were investigated. The effect on the addition of SWA with soil in seed germination as well as growth of young plants was also studied.

2. Materials and Method

2.1 Raw materials

Potato starch (SIGMA-ALDRICH, India)), acrylic acid (JHD, China) and Potassium hydroxide (MERCK, India) were used as main chemicals for synthesis. Chilli seeds collected from the local market were used for germination test. Distilled water was used as a solvent.

2.2 Preparation of superwater absorbent (SWA)

An aqueous solution of potato starch was prepared by dissolving 10 g of potato starch in 100 mL distilled water in a 250 mL beaker by stirring with a glass rod on water bath at 80ºC for one h. In order to obtain blend solutions of

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potato starch and acrylic acid with the composition ratios of 1.0:1.0, 1.0:1.5 and 1.0:2.0, 10g, 15g and 20g of acrylic acid were added separately to the aqueous solution of potato starch followed by mechanical stirring for 0.5 h. Each of the blend solutions was partially neutralized by adding potassium hydroxide (KOH) and poured in a glass test tube, sealed and finally irradiated by gamma-rays from Co-60 source with the total dose of 2.0, 5.0, 7.0, 10.0, 12.0 and 15.0 kGy at the dose rate of 3 kGy/h. The potato starch/acrylic acid SWA thus obtained in cylindrical shape was cut into small pieces, dried in air and vacuum oven to a constant weight for measurement of various properties.

2.3 Determination of gel content

The SWA samples dried to constant weight were extracted with distilled water for 24 h to remove the soil fraction. The water extracted insoluble gels were taken out from water and dried to constant weight in a vacuum oven at 50°C. The experiment was repeated three times for each sample and the average weight of the extracted sample was taken to calculate gel content as follows:

Gel content (%) = $[W_1/W_i] \times 100$, where W_1 is the weight of dry SWA sample after extraction in water and W_i is the initial weight of dry SWA sample.

2.4 Determination of swelling properties

The SWA samples (dried to constant weight) were immersed in distilled water at room temperature (~27ºC). The swollen SWA samples were periodically taken out from distilled water and weighed after removing the excess surface water with tissue paper. The experiment was repeated three times for each sample and the average weight of the swollen sample was determined. The water absorption capacity of SWA was calculated as follows:

Water absorption capacity (%) = $[(W_t – W_1)/W_1] \times 100$, where W_t is the weight of swollen SWA sample at time ‘t’ and W_1 is the initial weight of dry SWA sample.

Swelling ratio of SWA sample was calculated as follows:

Swelling ratio = $(W_t – W_1)/ W_1$, where W_t is the weight of swollen SWA sample for ‘t’ hour swollen period and W_1 is the weight of dry SWA sample. The swelling ratios were calculated for 5 h swollen period.

2.5 Determination of water retention

0.0g, 0.3g and 0.5g of SWA were kept in three similar weighed plastic pots to each of which 100g soil was added and mixed homogeneously and then 300 mL of water was added into each pot. The pots were kept on laboratory bench under identical conditions at room temperature for 14 days. The initial and final masses of the mixture in each pot were measured. The water retention was calculated as follows:

Water retention (%)

= (Mass of the mixture after certain days /Initial mass of the mixture) ×100

2.6 Dynamic mechanical analysis

The storage modulus of SWA samples were studied from 27 to 195ºC at a heating rate of 4ºC/min and at oscillating frequency of 1 Hz using a dynamic mechanical analyzer (DMA) Triton Technology TTDMA, UK.

2.7 Application of SWA in agriculture

Soil with 15% moisture was placed into six identical bowls (diameter 30 cm) up to the depth of 12 cm. Three bowls were irrigated with 800 mL of water without SWA and other three were irrigated with 800 mL of water with 0.5% (wt.) SWA. 100 pieces of healthy Chilli seeds were placed in each bowl and allowed to germinate. Germination percentage of the seeds was calculated as follows:

Germination (%) = (Number of germinated seeds/Total number of seeds sown) ×100

3. Results and Discussion

Gel content of SWA was measured after removing the soluble part through extraction with distilled water as solvent. It depends on many factors such as polymer compositions, irradiation dose, cross-linking etc. The variation of gel content of SWA at different radiation doses and composition ratios of potato starch to acrylic acid in the feed solution is shown in Fig.1. The gel content of all potato starch to acrylic acid composition ratios in SWA was found to increase with increasing radiation dose and reached a maximum value at 5 kGy radiation dose due to cross-linking of polymer chains by the action of radiation dose. It was also found that gel content of SWA increased with increasing amount of acrylic acid in the blend solution. It has been reported that the maximum value of gel fraction is obtained at 25 kGy radiation dose from carboxymethyl cellulose/acrylamide blend SWA [17]. By the action of high energy radiation, the molecules of polymer are excited and turn to free radicals through energy transfer leading to cross-linking reaction between polymer chains [18]. The acrylic acid molecules also excited by radiation and formed graft copolymer with potato starch, cross-linking and homopolymer itself [19]. These may be the cause of increase in gel content with increased acrylic acid in the feed solution.

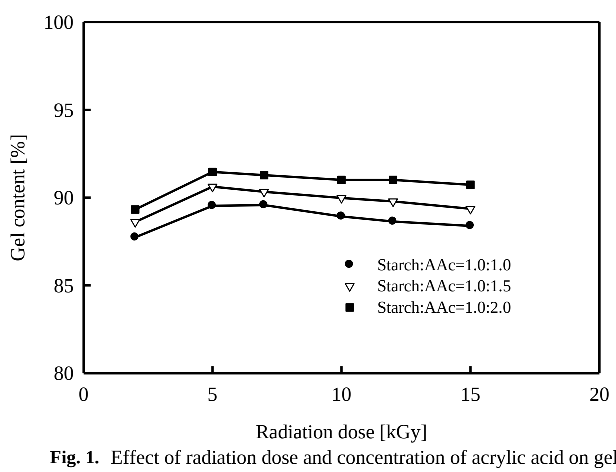

Fig. 1. Effect of radiation dose and concentration of acrylic acid on gel content of potato starch/acrylic acid SWA.

SWA has an ability to absorb and hold significant amount of water in its network structure due to the presence of hydrophilic groups like –OH, –O–, $–NH_2$, –CONH–, –CHO, $–SO_3H$, –COOH, –COONa, etc. SWA shows an important characteristic called swelling when it absorbs water. The swelling ratio reflects the density of cross-linking in the polymers. It decreases with increasing cross-linking density due to reducing size of void spaces in the polymer network for free water entrance. Fig. 2 shows the effect of radiation dose and composition (ratio) of starch to acrylic acid on swelling ratio of SWA. It was found that the swelling ratio of all potato starch to acrylic acid composition ratios increased with increasing radiation dose until it reached its maximum value at 5 kGy. Then it started to decrease with increasing radiation dose but it increased with increasing concentration of acrylic acid in the blend solution. Fig. 3 represents the effect of standing time of SWA in distilled water prepared at 5 kGy radiation dose on water absorption capacity. The water absorption capacity increased with increasing standing time of SWA in water. The increasing trend of water absorption is fast up to 4 h standing time and the maximum value of water absorption is obtained at 5 h. The maximum value of water absorption capacity of potato starch/acrylic acid SWA for the ratio (1.0:1.0), (1.0:1.5) and (1.0:2.0) are ~4592%, ~5504% and ~8080%, respectively. The water, absorption capacity increases with increasing amount of acrylic acid in SWA. This result can be explained as increased amount of acrylic acid content having increased number of hydrophilic group (-COOH) in SWA. The carboxylic group (:COOH) on SWA network ionizes in water and form electrostatic repulsion between COO^- groups causes an enhancement of water absorption capacity.

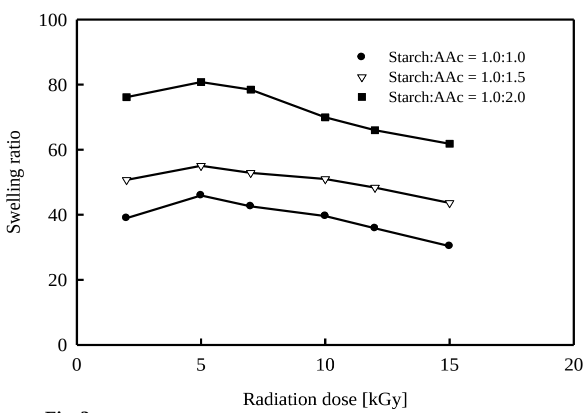

Fig. 2. Effect of radiation dose on swelling ratio of potato starch/acrylic acid SWA.

Fig. 4 represents the water retention of soils with SWA and without SWA. The rate of water loss increased with the increase in standing time of soil with and without SWA at room temperature. It was also found that soil mixed with SWA could hold more water than that without SWA. Water holding capacity of soil increased with increasing amount of SWA in soil. After 14 days, the weight loss of soil is ~23.35%, ~21.51%, and 19.53% for 0.0%, 0.3% and 0.5% content of SWA in soil, respectively.

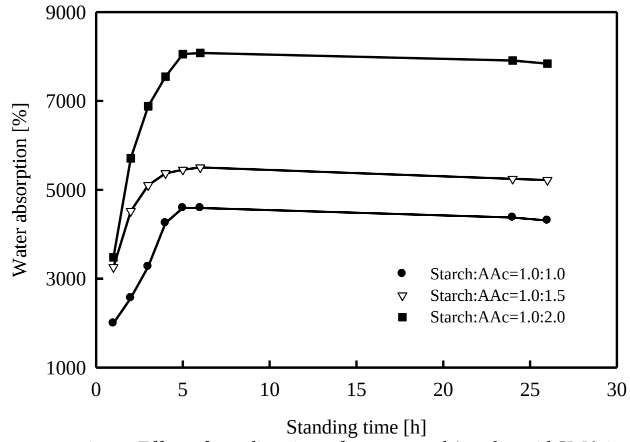

Fig. 3. Effect of standing time of potato starch/acrylic acid SWA in water on water absorption [Dose = 5 kGy].

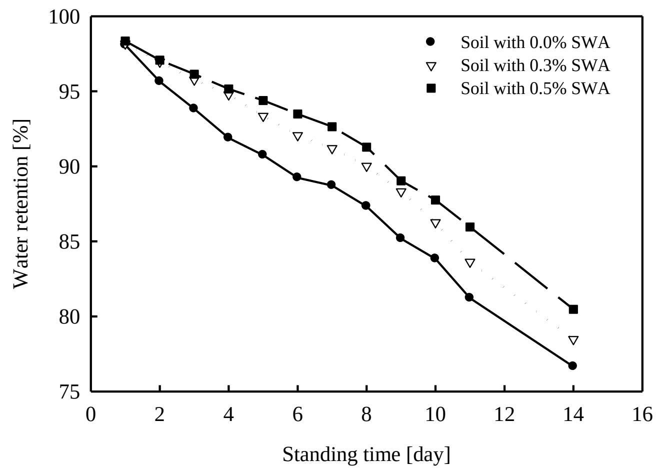

Fig. 4. Water retention capacity of soil with and without potato starch/ acrylic acid SWA prepared at 5 kGy radiation dose.

The storage modulus in viscoelastic materials measure the stored energy, representing the elastic portion, and the energy dissipated as heat, representing the viscous portion. The effect of temperature on the storage modulus of SWA prepared from potato starch/acrylic acid blend solution at 5 kGy radiation dose was studied. The curves as shown in the Fig. 5 show that the initial values of storage modulus are not same for all SWA. It is found that the initial value of modulus for potato starch/acrylic acid ratio (1.0:1.0) is higher than that of potato starch/acrylic acid ratios (1.0:1.5 and 1.0:2.0). The glassy region is extended and the leathery state plateu region (after 130ºC for potato starch/acrylic acid ratios, 1.0:1.0) occurs at higher temperature with decreasing the ratio of acrylic acid in SWA. For potato starch/acrylic acid ratios (1.0:1.5 and 1.0:2.0), the curves become almost flat and for the ratio (1.0:1.0) there is a sharp decrease of modulus in glassy transition region (30ºC to 130ºC). This result indicates that acrylic acid interacts with potato starch by the action of gamma radiation.

The synthesized SWA is applied in agriculture to observe the effect on the germination of chilli seeds and growth of young plants. All the seeds used in the experiment were healthy

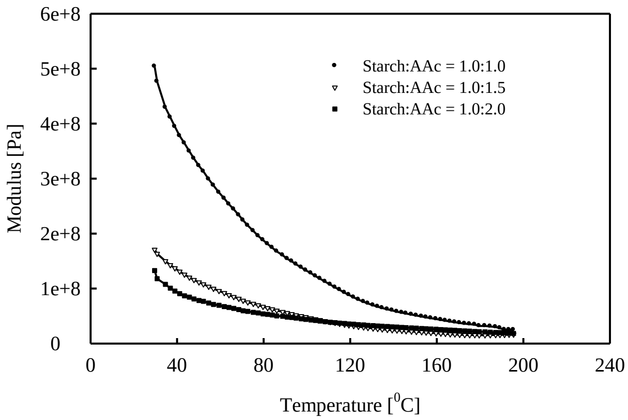

Fig. 5. Storage modulus curves for potato starch/acrylic acid SWA [Radiation dose = 5.0 kGy]

and planted at random. It was found that the germination of seeds in soil with SWA was obviously higher and denser than that of seeds in soil without SWA (Fig. 6).

(a) (b)

Fig. 6. Photo of chilli seeds germination without (a) SWA and with (b) SWA after 7 days.

The germination percentage of seeds in soil without and with SWA was 80% and 94%, respectively. This explains that the SWA can not only absorb large amounts of water but also have good water retention capability and can supply plenty of water to promote the growth of plants. After 14 days, soil with 0.5wt % SWA showed a favorable effect on the length and weight of the chilli plants (Table 1). SWA obtained from cassava starch/acrylic acid blend showed a good effect on growth of chinese cabbage [20]. From the initial investigation, it can be concluded that the SWA obtained from potato starch/acrylic acid blend solution has potentiality of applications in agriculture.

Table 1. Effect of SWA on growth of Chilli plants after 14 days

SWA content	Weight of fresh plant (gm)	Height of the plant (cm)	Length of the root (cm)	Number of leaves
Soil without SWA	0.0531	6.4	2.1	2
Soil with 0.5% SWA	0.1243	8.7	2.7	3

4. Conclusion

For synthesis of superwater absorbent (SWA) from potato starch/acrylic acid blend solution by the application of gamma radiation from Co-60 source at room temperature (~27ºC), the suitable potato starch to acrylic acid composition ratio and irradiation dose were found to be 1:2 and 5 kGy, respectively, indicating maximum gel content and swelling ratio of SWA. Water absorption capacity of SWA increases with increasing acrylic acid content in the blend solution. The maximum value of water absorption was obtained at 5 h. The storage modulus of SWA decreased with increasing acrylic acid content in potato starch to acrylic acid blend solution and also decreased with increasing temperature indicating that acrylic acid interacted with potato starch by the action of gamma radiation. The water retention capacity of soil increased with increasing amount of SWA in soil. Higher percentage of germination obtained for chilli seeds in soil with SWA indicated that SWA might have considerable effect on seed germination and growth of young plants and could contribute greatly to agriculture from the economical point of view.

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