Journal of Physical Science, Vol. 26(2), 23–39, 2015

The Synthesis of Superabsorbent Polymers from a Carboxymethylcellulose/acrylic Acid Blend Using Gamma Radiation and its Application in Agriculture

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Abstract: *Superabsorbent polymers (SAPs) were synthesised from an aqueous solution of a carboxymethylcellulose (CMC)/acrylic acid (AAc) blend followed by neutralisation with alkali using Co-60 γ-irradiation source at room temperature (~27ºC). The preparation conditions, such as the irradiation dose and the variation of the CMC to AAc ratio (10:1.5, 1.0:2.0 and 1.0:3.0) in the feed solution, were investigated. Fourier Transform Infra-Red (FTIR) spectroscopy was used to investigate the molecular interactions of CMC/AAc SAP. The influence of the radiation dose and the concentration of AAc on the gel content and the swelling behaviour was also investigated. The gel fraction of SAP increases with an increase in the radiation dose and the concentration of each component and attains maximum value at a 5 kGy radiation dose. The water absorption capacity of SAP decreases with an increased radiation dose and AAc content. SAP enhances the water retention of sand and soil. SAP also influences germination of wheat and lady's finger seeds and the growth of young plants. The biodegradation of SAPs was also investigated.*

Keywords: Superabsorbent polymer, gamma radiation, carboxymethylcellulose/acrylic acid, gel fraction, swelling behaviour, germination

1. INTRODUCTION

Superabsorbent polymers (SAP) are a class of three-dimensional, hydrophilic, functional polymeric network systems with the ability to absorb large amounts of water, including those with good water retention capacity even under high pressure or temperature.[1] Usually ionic functional groups along the cross-linked polymer chains encourage the diffusion of water within the network without allowing the substance to dissolve in water.[2] SAPs are widely used in various applications such as drug delivery, hygiene, foods, cosmetics and agriculture.[3–8]

Ionising radiation is very convenient technique for the preparation of SAPs. In the radiation processing method, an initiator, catalyst and cross-linker are not required because ionising radiation is highly energetic.[9] Radiation processing has many advantages such as ease of process control, and the technology is environmentally friendly because it leaves no residue or environmental pollutants.[10–11]

A demand for biopolymers that are derived from feedstock such as cellulose has recently arisen. Compared to petroleum-based polymers, these biopolymers have the advantages of high hydrophilicity, sustainability, biodegradation properties and non-toxic base components.[12–13] Biopolymers can be made from carboxymethylcellulose (CMC), which has a naturally occurring polysaccharide cellulose base. CMC, a linear glycosidic macromolecule consisting of β- (1→4)-linked D-glucose, is the most popular, and the cheapest cellulose ether can also be used for this purpose. It is an anionic linear polymer in which the original H atoms on the cellulose hydroxyl groups are replaced by a carboxymethyl substituent $-CH_2COO$.[14–15] CMC hydrogel has been prepared by gamma radiation in the presence of mono- and divalent salts (NaCl and $CaCl_2$), and its swelling properties depend on the radiation dose and the ionic strength of the salts.[16] The swelling properties of an acrylamide/CMC blend hydrogen depend on the swelling medium (distilled water, buffer or salt solution).[17] The swelling behaviours of the superabsorbent polymers synthesised by graft copolymerisation of acrylic acid/acrylamide/2-acrylamido-2-methyl-1-propanesulfonic acid with CMC and montmorillonite (MMT) by using potassium persulfate (KPS) as a free radical initiator in the presence of N,N′-methylenebisacrylamide (MBA) as a crosslinking agent are dependent on the pH of the external solution, the particle size and the concentration of the salt solution.[18] However, a single study on carboxymethylcellulose/acrylic acid SAPs prepared by a radiation method is not sufficient to fully understand this process. Thus, in this study, the synthesis of SAPs by copolymerising acrylic acid with CMC using a γ-ray irradiation technique is reported. The effect of radiation dose and the concentration of acrylic acid on the properties of the prepared hydrogels were investigated. The hydrogels were characterised with respect to gel content, swelling properties and Fourier transform infra-red (FTIR) spectroscopy. The effects of SAP on the water retention of sand and soil and biodegradability of the SAP were studied. An experiment using the SAP for the germination of wheat and lady's finger seeds (obtained from Jessore Beej Bhander, Savar, Bangladesh) and the growth of young plants showed satisfactory results.

2. EXPERIMENTAL

2.1 Materials

Carboxymethylcellulose (purity 99.5%) obtained from Sigma-Aldrich, India was used without further purification. All commercial grade reagents, acrylic acid (purity 99.5% min-JDH, China), potassium hydroxide (assay 84%), methanol (assay 99.8%), and acetone (assay 99.5%) were purchased from Merck, Germany. Sand (Jamuna River, Bangladesh) and soil (Dhaka, Bangladesh) were dried and screened before utilisation.

2.2 Preparation of SAPs

CMC (5% wt) mixed with distilled water in a beaker (250 mL) was stirred with an electrical stirrer for one hour at room temperature to form a paste-like slurry. Then, various concentrations of acrylic acid (7.5 to 15.0%) were added to the paste-like slurry and partially neutralised by adding KOH. The mixture was poured into glass test tubes, sealed and finally irradiated by γ-rays from a Co-60 source with the radiation doses of 1, 2, 3, 5, 8, and 10 kGy at the dose rate of 3 kGy/h in air at room temperature (~27ºC). The CMC/acrylic acid SAP obtained in a cylindrical shape was cut into small pieces, air dried and then further dried in a vacuum oven to constant weight for measurement of the gel fraction and the swelling properties.

2.3 Determination of Gel Fraction

The SAP samples dried to constant weight (W_i) were immersed in distilled water for 24 hours to remove the soil fraction. They were removed from the distilled water, air dried and then further dried to a constant weight (W_1) in an oven. The experiment was repeated three times for each sample, and the average weight of the extracted sample was measured. The gel fraction was calculated as follows:

$$\text{Gel fraction (\%)} = \frac{W_1}{W_i} \times 100 \tag{1}$$

where W_1 is the weight of dry sample after extraction in water and W_i is the initial weight of dry sample.

2.4 Determination of Water Absorption

The swelling ratio of the SAP was determined by a gravimetric method. SAP samples dried to a constant weight were immersed in distilled water until maximum swelling was obtained at room temperature (~27ºC). The swollen samples were removed from distilled water and weighed after removing the surface water with a soft tissue paper. The experiment was repeated three times for each sample, and the average weight of the swollen sample was determined. The swelling ratio was calculated as follows:

$$\text{Water absorption } (\%) = \frac{W_2 - W_1}{W_1} \times 100 \qquad (2)$$

where W_2 is the weight of swollen sample and W_1 is the weight of dry sample.

2.5 Determination of Degree of Grafting

The SAP samples were dried to a constant weight and were extracted with methanol for 24 hours to remove the homopolymer of polyacrylic acid. The extracted samples were washed with distilled water and acetone to remove the water.[19] Then, samples were dried and weighed. The experiment was repeated three times for each sample, and the average weight of swollen sample was determined. The degree of grafting was calculated as:

$$\text{Degree of grafting } (\%) = \frac{\text{Weight of extracted sample in methanol}}{\text{Weight of dry sample}} \times 100 \qquad (3)$$

2.6 Water Retention of the SAPs

The 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 as:

$$\text{Water retention } (\%) = \frac{\text{Weight of hydrogel dried after a certain time}}{\text{Weight of swollen hydrogel}} \times 100 \qquad (4)$$

2. One hundred grams of dry sand mixed with 0.1 g SAPs was placed in a cup (A), and another 100 g of sand without SAPs was placed in an identical cup (B). Three hundred millilitres of water was added into both cups. The cups were incubated under identical conditions at room temperature (approximately 30 ± 2°C) for 15 days. The initial mass of the mixture in the cups was measured, and then the weight of cups was measured daily to compare the water retention of SAPs. Water retention was calculated as:

$$\text{Water retention} = \frac{\text{Mass of the mixture after certain days}}{\text{Initial mass of the mixture}} \times 100 \quad (5)$$

3. Experiments with four groups of dry soil mixed with SAPs (ratios of SAPs/soil: 0/100, 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.

2.7 Biodegradability

Biodegradability of a SAP film was studied in a composting environment. The composting environment was maintained at 30ºC, pH 6.0–8.5, and a moisture content ~60%, which is very favourable for the growth of microorganisms that play the active role in biodegradation.

2.8 Applications in agriculture

Soil with 15% moisture was placed into six identical bowls (diameter 30 cm). The soil depth was 12 cm. Three bowls were irrigated with 800 ml water without SAPs, and the other three were irrigated with 800 ml water with 0.3% SAPs. The same amount (100 pieces) of healthy wheat seeds was placed in each bowl. Germination percentages were measured to verify that the seed qualities of the six groups were identical, and the germination energy was calculated to compare the effect of the soil on seed germination. The germination percentage of the seeds was calculated as:

$$\text{Germination percentage (\%)} = (\text{Amount of germinating seeds/Total seeds}) \times 100 \quad (6)$$

The germination energy of the seeds was calculated by:

$$\text{Germination energy (\%)} = \frac{\text{Amount of germinating seeds in first three days}}{\text{Total seeds}} \times 100 \quad (7)$$

3. RESULTS AND DISCUSSION

3.1 IR Spectra of SAP and Identification

IR spectroscopic analysis was used to illustrate the nature of the bond formation in the hydrogen and crosslinking moieties in the anhydroglucose units. The FT-IR spectra of pure CMC powder and CMC/AAc blend hydrogel are shown in Figure 1 (spectrum a and b). Pure CMC had absorption bands related to O–H stretching at 3462.22 cm^{-1} as well as intramolecular and intermolecular hydrogen bonds in cellulose, $-CH_2-$stretching on anhydroglucose units at

2926.01 cm^{-1}, C=O carbonyl stretching in the anhydroglucose unit of the cellulose at 1583.56 cm^{-1}, C–OH in the in-plane bend at 1419.61 cm^{-1}, an –OH bending vibration at 1327.03 cm^{-1}, C=O stretching from an asymmetric oxygen bridge at 1112.93 cm^{-1} and ring stretching at 904.61 cm^{-1}. These values were consistent with those reported by Rimdusit et al.[20] and Wang et al.[21]. As shown in Figure 1, the characteristic absorption bands of CMC at 1062.78 and 1112.93 cm^{-1} were obviously weakened after the reaction in the CMC/AAc blend hydrogel. The bands at 3664.75–2409.09 cm^{-1} (O–H stretching, usually very broad, strongly H-bonded) overlaps the –CH_2– stretching of CMC. In spectrum b (red colour), the new band at 1714.72 cm^{-1} (C=O stretching of –COOH groups) showed the C=O stretching of the carbonyl group of acrylic acid, which was absent in the spectrum of CMC (spectrum a-blue colour). The band shift towards a lower wave number apparent at 1529.55 cm^{-1} (which was at 1583.56 cm^{-1} for CMC) for CMC/AAc SAPs indicates the formation of copolymer hydrogels. These results also indicate that AAc monomers were grafted onto the CMC backbone.

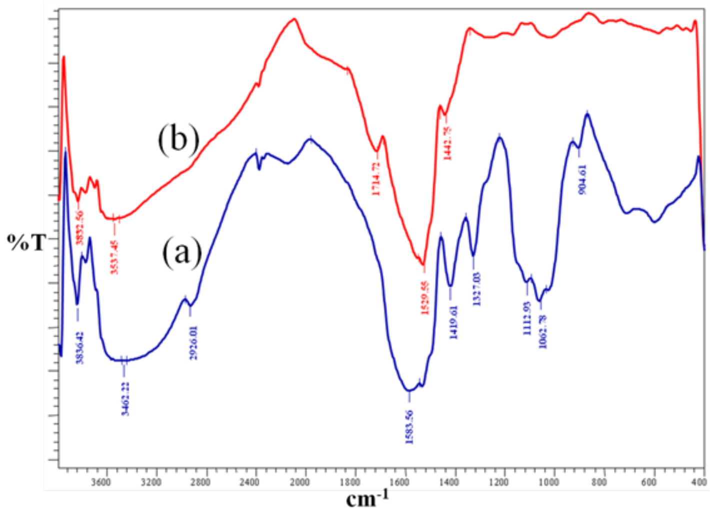

Figure 1: Infrared spectroscopy of (a) CMC powder (blue colour spectrum) and (b) SAPs of CMC/AAc (red colour spectrum).

3.2 Gel Fraction of SAP

The gel fraction of SAP prepared from the CMC/AAc blend with the various radiation doses and the variation of the AAc content in the feed solution is shown in Figure 2. The gel fraction of SAP increases with an increasing radiation dose. The maximum value of the gel fraction was obtained at the 5 kGy radiation dose. It has been reported that the maximum value of gel fraction was obtained at a 25 kGy radiation dose for a CMC/acrylamide blend hydrogel.[17] From Figure 2, it can be observed that a slight decreasing trend of the gel fraction occurred after irradiation at 5 kGy. This result might be due to the degradation of the cellulose molecules. In addition, the gel fraction increased with an increase of AAc content in the feed solution, and it increased from 55 to 89% following the variation of the ratio of CMC to AAc (1.0:1.5, 1.0:2.0 and 1.0:3.0) in the feed solution at a radiation dose of 5 kGy. When an aqueous solution of CMC/AAc is irradiated with gamma rays, free radicals are generated on the CMC and AAc. Random reactions of these radicals lead to formation of a graft copolymer of CMC and AAc. When the radiation dose increases beyond a certain value, the polymer chains become cross-linked, and a gel-like material is obtained. The subsistence of two radicals on neighbouring chains and their subsequent combination are required for the formation of cross-linked macromolecules. At a higher polymer concentration, the macromolecules come closer together, which facilitates cross-linking.

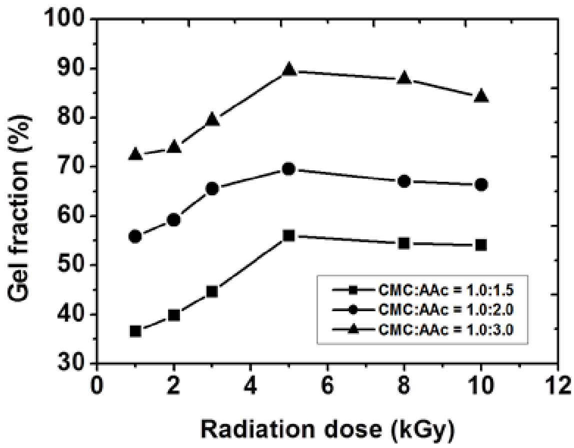

Figure 2: Effect of radiation dose and concentration of AAc on gel fraction of CMC/AAc SAP.

3.3 Grafting of AAc onto CMC

The effect of the concentration of AAc on the grafting percentage at a 5 kGy radiation dose is shown in Figure 3. It was found that the percentage grafting of AAc onto CMC increases the variation of the CMC to AAc ratio (1.0:1.5, 1.0:2.0 and 1.0:3.0). With an increased concentration of AAc in the feed solution, more monomer radicals may be available to interact with CMC macroradicals, which increases the percentage of grafting.

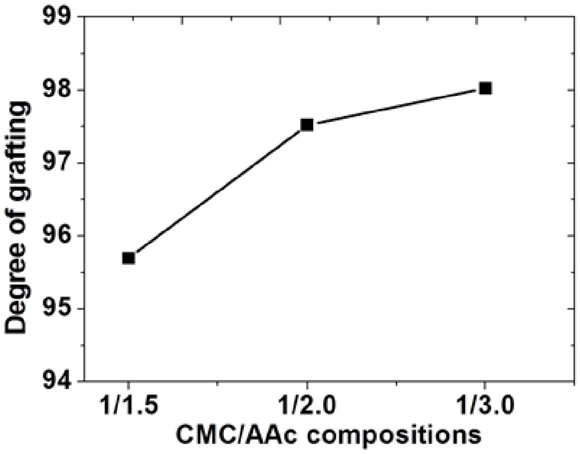

Figure 3: Effect of concentration of AAc in CMC/AAc SAP on degree of grafting at 5 kGy radiation dose.

3.4 Water Absorption of SAP

The swelling ratio indicates the extent of the cross-linking in a polymer. With an increased cross-linked density in a polymer, the swelling ratio decreased because less vacant space was available in the cross-linking network for free solvent to enter. The effects of the radiation dose and the concentration of AAc on the water absorption of SAP prepared from CMC/AAc are shown in Figure 4. The water absorption of the SAP decreased from ~16500 to ~11500% for a CMC/AAC ratio of 1.0:1.5, ~13800 to ~9700% for a CMC/AAC ratio of 1.0:2.0 and ~11200 to ~8900% for a CMC/AAC ratio of 1.0:3.0 with an increased radiation dose from 1 to 10 kGy. This result was due to the increased cross-linked density with the increase in the radiation dose. The swelling ratio of hydrogel also decreased with an increased concentration of AAc in a mixture of CMC/AAc. The swelling ratio of SAP was ~13075% for a CMC/AAC ratio of 1.0:1.5, ~10950% for a CMC/AAC ratio of 1.0:2.0 and ~9935% for a CMC/AAC ratio of 1.0:3.0 at a radiation dose of 5 kGy. Because the highest gel content was obtained at a 5 kGy radiation dose, the maximum cross-linking in the polymer chain was also obtained at a similar radiation dose, and the cross-linking density increased with an increased AAc content in the CMC/AAc SAP. As a result, the chain segments of the polymer chain shortened with increased cross-linking of the chain and reduced the swelling values of SAP because limited space was available for free water to enter into the vacant spaces of the cross-linked network.

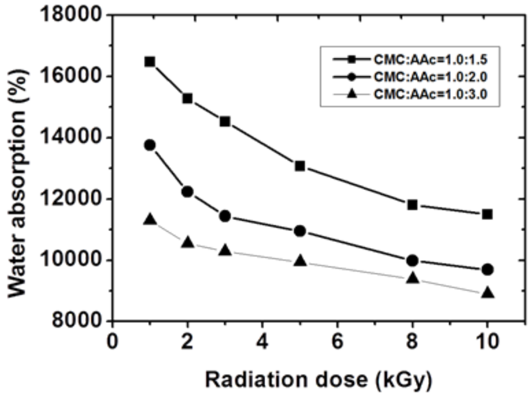

Figure 4: Effect of radiation and concentration of AAc on water absorption of CMC/AAc SAP.

3.5 Water Retention of SAP

The water retention of the swollen SAP is shown in Figure 5. It was found that the mass of swollen SAP was reduced with an increased incubation time for SAP at room temperature (27°C). The swollen SAP showed a good water retention capability at room temperature. The mass of SAP was reduced by only one-half of its initial value after seven days. Afterwards, the weight loss of the SAP was not significant.

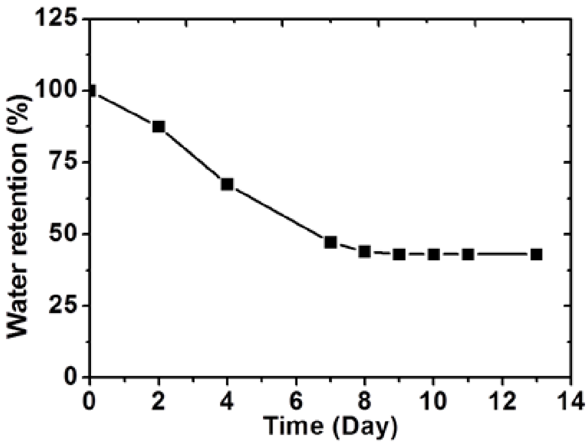

Figure 5: Effect of standing time of SAP on water retention (CMC/AAc = 1.0:1.5, room temperature = 27°C, dose = 5 kGy).

Figure 6 shows the water retention of sand with and without SAP. The masses of sand with and without SAP were compared within 18 days. The mass of sand decreased with an increased incubation time at room temperature. The decreasing trend of sand without SAP is higher than that in sand with SAP. After 18 days, the mass of sand without SAPs was nearly 82%, but that of the sand with 0.1 wet % SAP was nearly 88%.

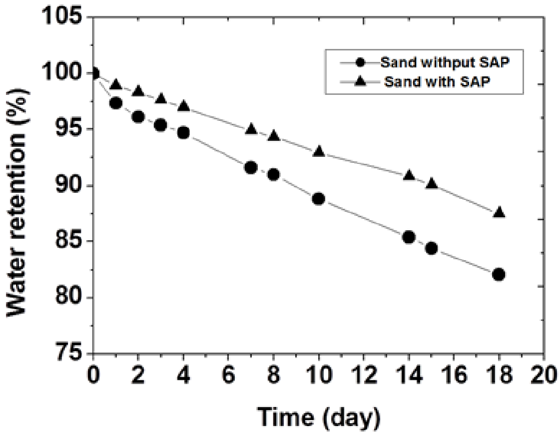

Figure 6: Effect of standing time of SAP in sand on water retention (CMC/AAc = 1.0:1.5, room temperature = 27°C, dose = 5 kGy, SAP = 1%).

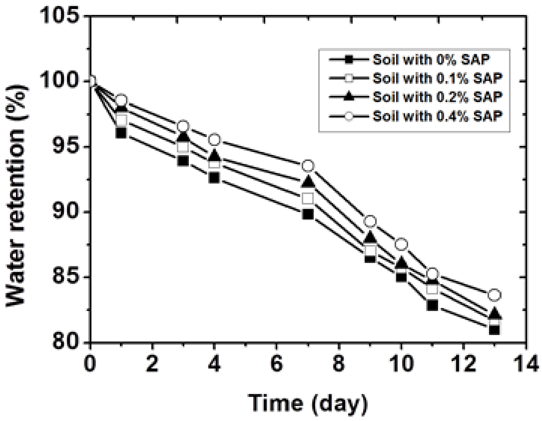

Figure 7: Water retention of soil with 0%, 0.1%, 0.2% and 0.4% SAP (CMC/AAc = 1.0:1.5, room temperature = 20°C, dose = 5 kGy).

Figure 7 shows the water retention of soil mixed with SAP and soil without the SAP. The rate of water loss increased with increased incubation time.

It is clear that soil mixed with SAP can hold more water than soil without SAP. The water holding capacity of the soil increased with an increased amount of SAP in the soil. After 13 days, the mass of soil was ~80% for 0.0% SAP, ~82% for 0.1% SAP, 83% for 0.2% SAP and ~84% for 0.3% SAP. Figure 8 (panels a, b, c and d) are photos of soil without SAP (panel a) and soil mixed with different amounts (wt%) of SAP (panel b, c and d). Panel a shows that soil alone became hardened and cracked after 13 days at room temperature but that the soils mixed with 0.1 wt% (panel b), 0.2 wt% (panel c) and 0.4 wt% (panel c) SAPs stayed moist and showed a continuous configuration under the same conditions.

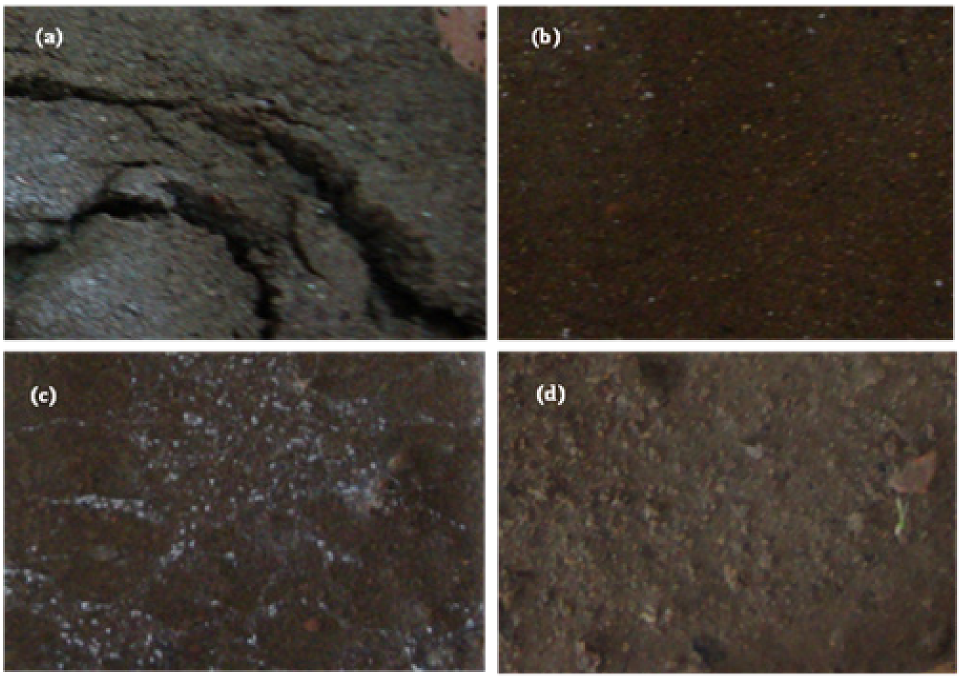

Figure 8: Photos of (a) the soil without SAP, (b) the soil with 0.1 wt% SAP, (c) the soil with 0.2 wt% SAP and (d) the soil with 0.4 wt% SAP.

3.6 Biodegradation of SAP

The biodegradability of the SAP was investigated with a soil-burial test. The SAP samples (diameter: 65 mm, thickness: 0.2–0.25 mm) were kept in a composting environment.[22] The composting environment was maintained at 30°C, pH 6.0–8.5 and a moisture content ~ 60%, which is very favourable for the growth of microorganisms that play the active role in biodegradation. Biodegradation was monitored for four weeks. The influences of microbial action on the morphology and weight loss were studied weekly. The effect of the standing time of SAP in a compost environment on degradation is shown in Figure 9. When the incubation time was increased, the weight loss of the SAP increased. After four weeks, the weight loss of the SAP was 40%. This result indicates that the CMC/AAc SAP is biodegradable. Figure 10 shows a photograph of CMC/AAc SAPs (a) before degradation, (b) SAP in a compost bed for degradation, (c) degraded SAP after three weeks in a swollen state and (d) after four weeks in a dried state. Some black and white spots were noted in the degraded SAP (Figure 10[c] and 10[d]). This result indicates that bacteria might attack SAP.

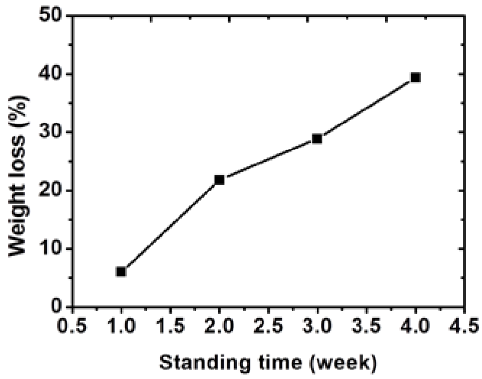

Figure 9: Effect of standing time of SAP in compost environment on degradation.

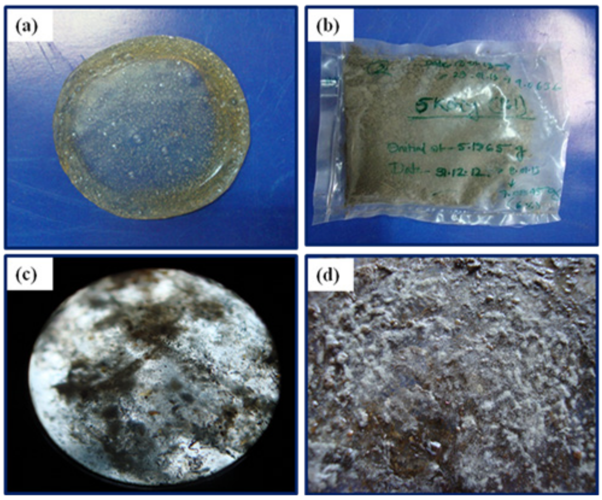

Figure 10: Biodegradation of SAPs film (a) before degradation, (b) compost bed for degradation, (c) degraded SAP after three weeks in a swollen state and (d) after four weeks in a dried state.

3.7 Application of the SAPs in Agriculture

The application of the SAPs in agriculture was studied with the purpose of promoting plant growth.[23,24] In this experiment, the synthesised SAPs were used agriculturally to determine the effect on the germination of wheat and lady's finger seeds and on the growth of young plants. All seeds used in the experiment were healthy and planted at random, and we found that the germination energy of the seeds in soil with SAPs was obviously higher and denser than that of the seeds in soil without SAPs (Figure 11). This is likely because the SAPs not only can absorb large amounts of water but also have good water retention capability, which supplies plentiful water to promote plant growth. After a few days, soil with 0.3% SAP showed a favourable effect on the length and weights of the wheat (Table 1 and Table 2; Figure 12) and lady's finger (Table 3 and Table 4; Figure 13) plants. In previous studies, starch/AAc grafted SAP showed a considerable effect on the germination of corn seeds and young plant growth.[25] Superwater absorbent obtained from cassava starch/acrylic acid blend showed a good effect on the growth of Chinese cabbage.[26] From our study and these other initial investigations, it can be concluded that the SAPs have a potential application in agriculture, especially in arid and desert regions.

Table 1: Effect of the SAP on germination of the wheat seeds (after three days).

SAPs content	Germination percentage (%)	Germination energy (%)
SAPs (0.0%)	70	58
SAPs (0.3%)	92	85

Table 2: Effect of SAPs on growth of the young wheat plants (after six days).

SAPs content	Height of the plant (cm)	Length of the root (cm)	Weight of fresh plant (cm)	Dry weight of plant (cm)
SAPs (0.0%)	18.1 ± 0.1	2.40 ± 0.1	0.2203 ± 0.1	0.0397 ± 0.1
SAPs (0.3%)	21.5 ± 0.1	3.78 ± 0.1	0.2532 ± 0.1	0.0446 ± 0.1

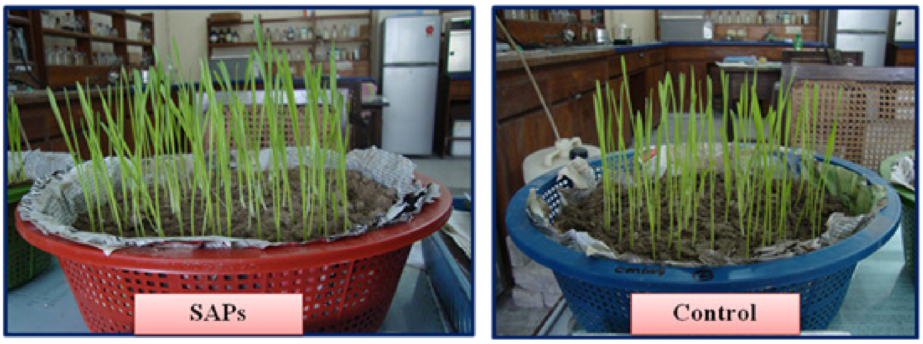

Figure 11: Photos of the wheat plants after six days.

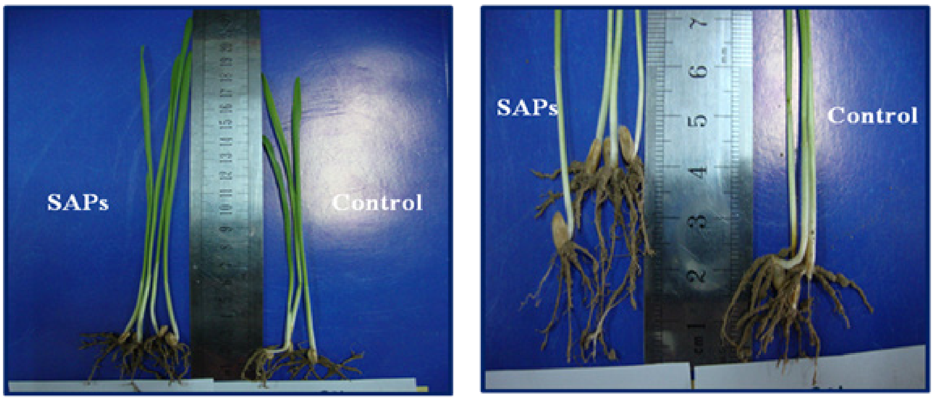

Figure 12: Photos of measurement of the height of the wheat plants and roots after six days.

Table 3: Effect of the SAPs on germination of the lady's finger seeds (after three days).

SAPs content	**Germination percentage (%)**	**Germination energy (%)**
SAPs (0.0%)	40	60
SAPs (0.3%)	60	80

Table 4: Effect of SAPs on growth of the young lady's finger plant (after 15 days).

SAPs content	Height of the plant (cm)	Length of the root (cm)	Weight of fresh plant (cm)	Dry weight of plant (cm)
SAPs (0.0%)	10.4 ± 0.1	1.0 ± 0.1	0.3043 ± 0.1	0.0365± 0.1
SAPs (0.3%)	16.5 ± 0.1	2.1 ± 0.1	0.4254 ± 0.1	0.0261 ± 0.1

Figure 13: Photos of measurement of the height of the lady's finger plants and roots.

4. CONCLUSIONS

The synthesis of SAP from a CMC/AAc blend can be performed with a radiation processing technique using a Co-60 gamma source. With respect to gel fraction, a 5 kGy radiation dose can be considered suitable for the preparation of SAP from a CMC/AAc blend. The grafting percentage of AAc on to CMC increases with an increased concentration of AAc in the feed solution at a 5 kGy radiation dose. The addition of SAP increases the water retention capacity of soil and sand. The water retention capacity of the soil increases with an increased amount of SAP in soil. The CMC/AAc SAP was found to be biodegradable. The experimental results show that the SAP has a positive effect on the germination of wheat and lady's finger seeds and young plant growth due to its good water retention capability. Thus, it can be concluded that CMC/AAc SAPs with different properties can be used as a soil conditioner in agriculture, especially in arid and desert environments.

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