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*Full Length Research Paper*

# Environmentally friendly superabsorbent polymers for water conservation in agricultural lands

**Fidelia Nnadi* and Chris Brave**

Department of Civil, Environmental and Construction Engineering, University of Central Florida, Orlando 32816, Florida.

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**Polymer complexes of crosslinked carboxymethyl cellulose (CMC) and starch were synthesized to form superabsorbent polymers (SAP) and their performances as a water retaining aid for irrigation were assessed. The SAP was crosslinked with aluminum sulfate octadecahydrate for optimum water retention. Starch from vegetables and chemically modified cellulose fibers were used as the basis for the polymer structure because of their biodegradability and the sustainability of their sources. The starch vegetables include potatoes, yam, cassava, and corn. Radish seeds were planted in pots that contained soil amended with the SAPs (as well as soils control with no amendment). For the first two weeks the plants were given a healthy amount of water, then watering was reduced to observe how the plants responded to drought. The plants with no amendment to the soil stopped growing after the first two weeks and showed signs of dehydration. All the plants in the amended soil continued to grow after the first two weeks and they looked much healthier. Performance evaluation of the response to the four starch types suggests that potato based SAP performed the best with 73% water retention, while corn gave 56%. The study also suggests that lower dosage of 0.12% by weight of the potato based SAP performed better than 0.24% when used for soil amendment.**

**Key words:** Carboxymethyl cellulose, starch, superabsorbent polymer, water retention, biodegradable.

## INTRODUCTION

Superabsorbent polymers (SAP) are a class of polymers that are able to absorb large amounts of water, typically more than traditional absorbent material (Esposito et al., 1996). Generally they consist of a network of polymer chains that are crosslinked to avoid dissolution. Usually there are ionic functional groups along the polymer chains to encourage diffusion of water within the network (Raju et al., 2003).

Polyacrylate is the principle material used in the SAP industry. Superabsorbent polyacrylates are prepared by polymerizing acrylic acid with a crosslinker (Heinze and Pfieffer, 1999). Acrylic acid is produced from propene, which is a byproduct of ethylene and gasoline production. Therefore, polyacrylate is a nonrenewable material that is dependent on the petroleum industry.

Personal hygiene products mostly control the market for SAPs. However there are a number of other applications in agriculture, horticulture, waste management, electronics and construction. Superabsorbents have been used as soil additives to increase the water retention of soils, which can replace peat, the traditional moisture retention aid for soil (Barbucci et al., 2000). Generally SAPs are applied to the soil at a concentration between 0.1 to 0.5% by weight (Buchholz and Graham, 1998). Below this range, the effect of the soil additive is negligible, and above this range the soil can become too spongy when it is fully saturated. Miller (1979) suggested that the performance of superabsorbent polymers as a water-retaining additive is greater in soils that are well draining such as sand.

Recently there has been a demand for biopolymers that are derived from feedstock such as starch or cellulose. The advantages of these biopolymers compared to petroleum-based polymers are their sustainability, biodegradation properties and base components as non-

*Corresponding author. E-mail: Fidelia.Nnadi@ucf.edu Tel: 407-823-6513. Fax: 407-823-3315.

toxicity (Stahl et al., 2000; Weerawarna, 2009). Biopolymers can be made from carboxymethyl cellulose (CMC), which has a naturally occurring polysaccharide cellulose base. CMC is made commercially by reacting chloroacetic acid with sodium cellulose in slurry with isopropanol and water. CMC based superabsorbent products were produced during the 1970s and early 1980s (Buchholz and Graham, 1998). However, while cost of the reactants required to produce CMC are relatively cheap, there is a significant cost for the purification needed for most applications. For this reason CMC based SAPs were mostly discontinued in favor of petroleum based SAPs. Studies have shown that the rate of biodegradation of CMC polymers increase when starch is introduced into the complex (Modelli et al., 2004). In this study CMC polymer complexes were crosslinked with aluminum ions to form non-permanent bonds when the complex is swollen with water. Crosslinked CMC and starch will create an environmentally friendly SAP that is based on biopolymers and could be an alternative to petroleum based SAPs as a water retaining aid in irrigation.

## MATERIALS AND METHODS

Commercial cassava starch powder (Ayoola Foods), commercial cornstarch powder (Pinnacle Foods), commercial potato starch powder (Bob's Red Mill), and commercial yam starch powder (Ayoola Foods) were used without further purification. Carboxymethyl cellulose sodium salt (Acros Organics) with an average molecular weight of 90000 and DS = 0.7 was used with starch to synthesize superabsorbent polymers (Zohuriaan-Mehr and Kabir, 2008). Aluminum sulfate octadecahydrate was used at reagent grade to crosslink the polymer complex (El Salmawi, 2007; Wang and Wang, 2010).

### Preparation of superabsorbent polymer

The preparation of the SAP follows a procedure described by Suo et al. (2007) and Weerawarna (2009). Carboxymethyl cellulose sodium salt (20 g) was mixed with 2.0 L of distilled water in a large beaker using a magnetic stirrer. Each of the four starches types (1.2 g) was gelatinized in 50 mL of distilled water at 80°C for 45 min. The gelatinized starch was added to the CMC solution and allowed to mix for 1 h. Then varying amounts of aluminum sulfate were added to the beaker to investigate the optimum crosslinkage, and the solution was allowed to mix for another 30 min. The solution was then spread on Teflon baking pans and dried at 70°C until a film is formed. The film was shredded with a blender and then ground into a powder with a mortar and pestle. This was repeated for each type of starch investigated.

### Water retention of hydrogels

The polymer samples (0.1 g) were immersed in 100 mL of distilled water. The slurry was then filtered through a course glass filter under a slight vacuum for 10 min. The amount of retained water is calculated as follows:

Water Retention = $(G_S - G_i) / G_i$,

Where $G_S$ is the weight of the swollen hydrogel and $G_i$ is the initial weight of the polymer sample.

### Testing of hydrogels

One gallon milk jugs with the top cut off and uniform holes drilled at the bottom were used as flower pots. A large batch of commercial top soil was thoroughly mixed together and 2.5 kg of the soil was placed in each pot to create about 150 cm depth of planning soil (Miller, 1979). For each of the four different polymers produced, 3.0 g was mixed in the soil of two pots and 6.0 g was mixed in the soil of two pots giving eight duplicate samples (Miller, 1979). There were six control samples that contained no polymer in the soil. In each pot 12 cherry bell radish seeds were evenly planted one and half inch deep in the soil. During the first watering period one teaspoon of phosphate rich vegetable fertilizer was mixed into the water. After the first watering, no more fertilizer was added for the rest of the experiment. Each pot received water according to the schedule in Table 2. Each plant in the pot was measured from the soil level to the top of the highest reaching leaf after 5, 14 and 35 days after planting. The measurements were made when appreciable difference was observed in the plants. The heights of each plant in the pot were averaged and the values are presented in Figures 2a, b and c. The plants were picked and weighed 35 days after they were planted. The results reported in Table 3 are the total plant mass in each pot.

## RESULTS AND CONCLUSION

### Crosslinking

Esposito et al. (1996) investigated cross linking density, presence of ionic groups on the backbone of hydrogels as well as the macroscopic morphology detected by electron scanning microscopy and suggested that in order to obtain hydrogels characterized by the desired water absorption there is evidence to bias the process parameters. Hence optimal water retention by the SAP investigated suggested that it optimized when 2.3% $Al_2(SO_4)_3.18H_2O$ was used in the crosslinking. Figure 1 shows the result for potato starch. It was observed that when less than 2.3% $Al_2(SO_4)_3.18H_2O$ was used the SAP was under-crosslinked, indicating that the complex does not have enough connections to create the appropriate sized void spaces for optimal water absorbance; while more than 2.3% $Al_2(SO_4)_3.18H_2O$ indicated that the polymer was over-crosslinked and the complex had too many connections making the void spaces too small for optimal water absorbency. Table 2 presents the optimal water retention of the four different hydrogels made with 2.3% $Al_2(SO_4)_3.18H_2O$ by weight.

### Flower pot experiment

Previous study on the impact of irrigation regime and soil additive (Aquasorb) on tomato growth suggested a better leaf-area increase and improved growth at 0.6% by weight of the additive (Al-Harbi et al., 1994). In the current

**Table 1.** Plant watering schedule.

| Number of days after planting | Amount of water per day (ml) |
|---|---|
| 0 | 200 |
| 7 | 100 |
| 14 | 50 |
| 21 | 50 |
| 28 | 0 |
| 35 | 0 |

**Table 2.** Water retention for hydrogels crosslinked at optimum with 2.3% wt. $Al_2(SO_4)_3.18H_2O$, (g/g).

| Cassava starch | Corn starch | Potato starch | Yam starch |
|---|---|---|---|
| 66 | 56 | 73 | 65 |

**Table 3**. Weight of radish plants at end of 35-day planting period, (g).

| Dose of SAP (g) | Cassava starch | Corn starch | Potato starch | Yam starch | Control |
|---|---|---|---|---|---|
| 3 | 3.3 | 4.4 | 5.6 | 4.4 | 1.5 |
| 6 | 4.9 | 4.4 | 3.2 | 4.0 | 1.5 |
| Increase in Wt (%) | 48.5 | 0.0 | - 42.9 | - 9.1 | 0.0 |

study, evaluation of the hydrogel with a complex of CMC and starch and crosslinked with aluminum suggested that at maturity of the relish plant, the samples with 3 g (0.12% by weight) of the hydrogel showed a better leaf-area increase and improved growth. Comparisons of the results for three measurement days (5, 14 and 35) for potato starch hydrogel are shown in Figures 2a, b and c, respectively. Further evaluation of the results suggests that plants with 6 g (0.24% by weight) of the hydrogel did not perform as well as the 3 g samples during the study period. The radish plants without additive (control condition) performed better than those of 6 g additive. This might be a case of excessive additive at 0.24% by weight of the hydrogel because at initial watering condition the soil was soggy and the plants were less healthy than the control soil. After day 14 when the plant's watering was reduced to 50 mL, the control plant stopped growing while the other plants continued to grow at similar rates, suggesting that the control plants were dehydrated while the other plants still had moisture stored in the soil due to the hydrogels (Table 1).

Considering the various hydrogels, the potato starch hydrogel appeared to have out performed the other ones at both 0.12 and 0.24% by weight of the additive. At both 0.12 and 0.24% additive the corn starch hydrogel performed the least and appear to have reduced rate of growth with reduction in watering, while the cassava starch and yam starch additives showed consistent growth up to the end of the study period. This again suggests that while the control plants were dehydrated with reduced watering, the plants grown in both 0.12 and 0.24% additive soils continue to receive moisture from the hydrogels.

Throughout the study period, all plants showed an upward trend in growth for all planting conditions. The final weights of the plants after the study period showed that those grown in the amended soils grew much larger than the control plants. In comparing the plants final weights in both doses, it was observed that there was no trend on the effect of the hydrogels when doses are increased. The plants grown in the cassava starch hydrogel increase by 48.5% in weight, while those in the potato and yam starch hydrogels decreased by 42.9 and 9.1%, respectively. There was no change in weight for those grown in both corn starch hydrogel and the control (Table 3). The variation in response to increased dosage could be explained by the effect of the molecular structure of the combination of the hydrogels/soil/water at different doses.

The ability of the larger dosage to store more moisture in the soil may have affected the plants in the potato and yam starch hydrogels due to excess water in the soil during the first 14 days. Hence the potato starch hydrogel amended soil showed a better performance with the 0.12% dose than the 0.24% dosage. Figures 3 and 4 showed that at the end of the experiment, plants grown in

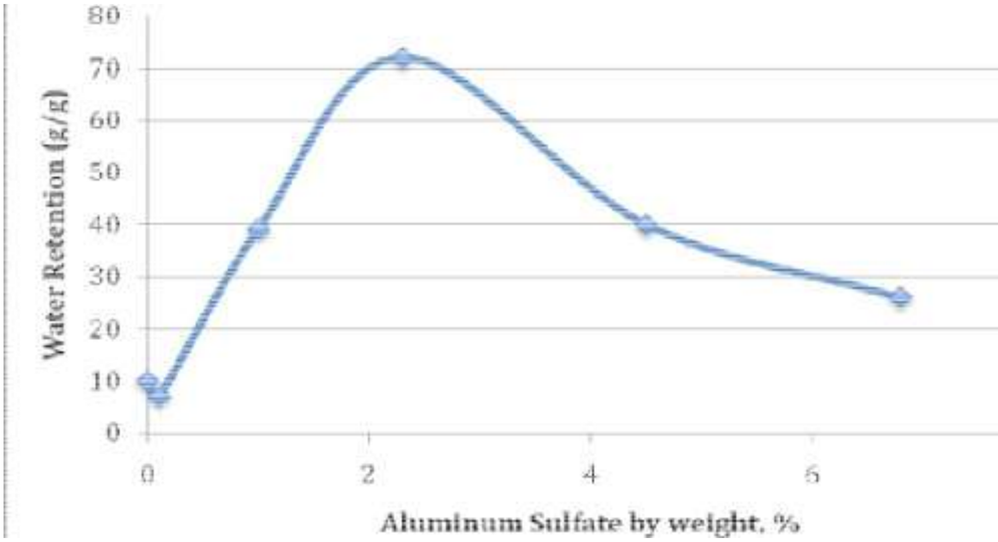


**Figure 1.** Optimization of water retention of potato starch hydrogel at various levels of crosslinking.


**Figure 2a.** Growth comparison for plants in all hydrogel-amended soils at day-5.

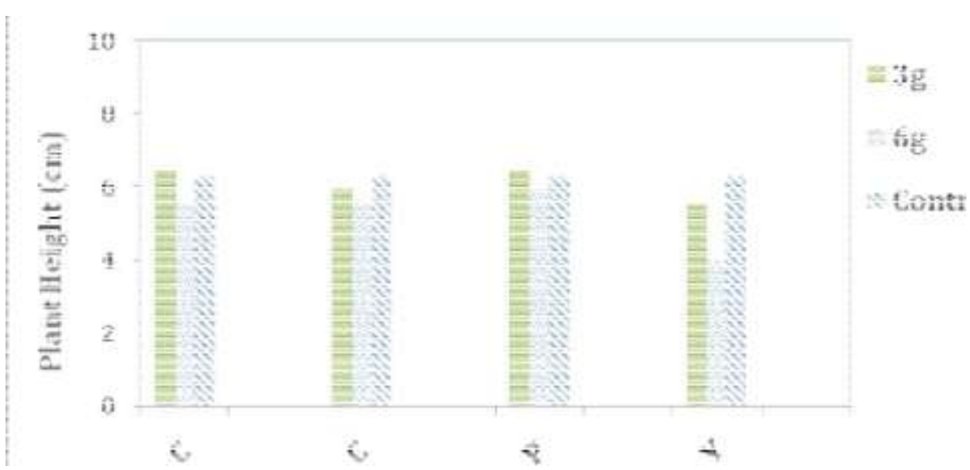


**Figure 2b.** Growth comparison for plants in all hydrogel-amended soils at day-14.

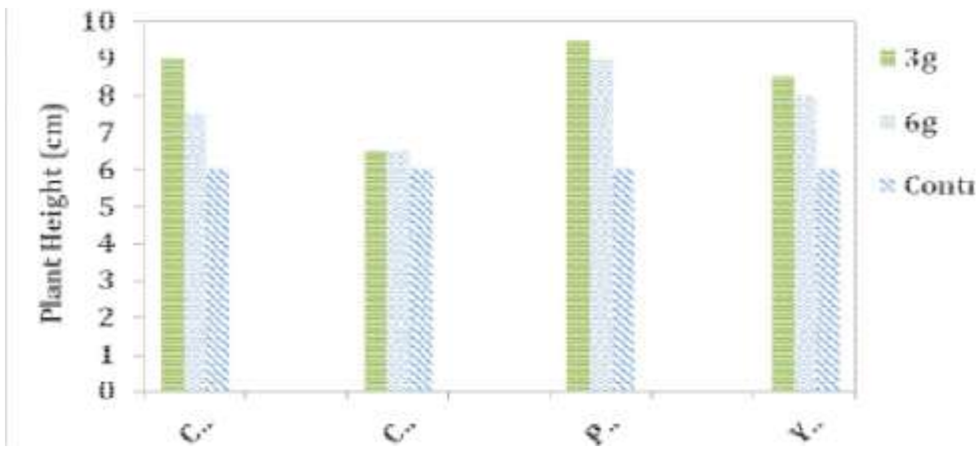


**Figure 2c.** Growth comparison for plants in all hydrogel-amended soils at day-35.

**Figure 3.** Photograph of relish plant control plants at day 35.

**Figure 4.** Photograph of relish plants in potato starch hydrogel-amended soil at day 35.

the potato starch hydrogel amended soil appear to have larger, healthier looking leaves than the control plants. It is the opinion of the authors that further studies be performed to investigate the molecular structure of these hydrogels and their response to water absorption.

Therefore, superabsorbent polymers with a complex of CMC and starch and crosslinked with aluminum showed promise as an environmentally friendly amendment in soil. When there was no polymer amendment in the soil, the plants show signs of dehydration during water stress, for the purpose of retaining water in soil during irrigation. while plants growing in amended soil were healthier. Overall, the potato starch hydrogel amended soil at 0.12% dosage performed better than those of cassava, corn and yam starch hydrogels. These results also suggest that soil amendment using a superabsorbent polymer composed of CMC and starch can be an alternative to petroleum based superabsorbent polymers for water retention during irrigation.

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