

## **Application of Superabsorbent Hydrogels for the Optimization of Water Resources in Agriculture**

*Alessandro Sannino*

Department of Innovation Engineering, University  
of Salento, Monteroni, Italy

### Abstract

The 'Colgel' is a project founded by the Italian Ministry of Research and co-founded by the University of Naples 'Federico II (Italy), the University of Lecce (Italy), the University of Bari (Italy), the National Research Council (CNR) in Italy and three floricultural enterprises in the Salento Region, in the South-East of Italy. The work presents a novel technology developed for the optimization of water resources in agriculture, horticulture and, more in general, for the stimulation of a novel approach of human habit and culture towards the water to be treated as a benefit to save and not an excess to waste. The internationally patented technology is represented by a novel class of macromolecular superabsorbent hydrogels, able to absorb more than 1.5 liters of water per gram of dry material, once in contact with liquid water or water solutions. During the sorption process, the material turns from a glassy state to a gel-like material, able to store the water even under significant compression. The water can be released from the material under a diffusion mechanism, activated by a gradient of humidity between the inside and the outside of the material, or by phase inversion in a non solvent for the polymer. The application of such a technology which have been tested is a 'water reservoir' in agriculture to be used in arid and desert Regions of the World, where scarcity of water resources is a relevant issue. To this aim, the hydrogel is mixed, in the dry form, to the soil in the area close to the plant roots. The soil is watered and the water not absorbed by the plant roots is stored in the hydrogel which swells, and releases water to the cultivation as far as the soil is de-watered. This process allows an high saving of water resources and a re-distribution of water available for cultivation in other human-related applications. Different classes of superabsorbent hydrogel have been developed and patented by prof. Sannino and co-workers. In this work we present the last generation, which is a cellulose-based hydrogel crosslinked by citric acid, and using only 'food grade' reagents. Synthesis reaction mechanism is a double esterification carried out by means of citric acid. Reaction parameters have been controlled; results are not reported in this work for the sake of reading and are available under request.

Hydrogel sorption capacity has been tested by gravimetric measurements and results have been reported and discussed as a function of the synthesis parameters variation. Preliminary results in agricultural application of this technology, presented in this work, are most promising and, if data will be confirmed on the large scale, this would be a breakthrough in water resources management in agricultural applications and, more in general, in all human ethic relation to water resources management. The soil with the

addition of small quantities of the product is able to remain humid for periods also more than four times longer than the soil watered without the presence of the hydrogel.

A pilot scale production plant has been developed to produce the amount of product necessary for the studies carried out in the arid and desert regions of the South of Italy, in experimental Greenhouses. The production plant and tests are carried out also to prove the feasibility and the efficacy of the proposed technology.

### The Technology

Superabsorbent hydrogels are a particular class of macromolecular gels, obtained by chemical stabilization of hydrophilic polymers in a tridimensional network, in which the dispersed phase is water, present in substantial quantity. They are widely used nowadays as absorbent core for hygiene products, such as baby diapers, and this attractive business pushed multinational groups toward the development of new technologies both in the chemistry definition and the production processes of these materials [1-11]

However, superabsorbents on the market nowadays are mainly acrylate-based products, thus not biodegradable and toxic if used in agriculture or water preservation for all the applications related to human consumption. The renewed attention of institutions and public opinion towards environmental protection issues sensitized some producers to development of biodegradable superabsorbents.

Prof. Alessandro Sannino and co-workers developed and patented a novel class of cellulose-based superabsorbent hydrogels, totally biodegradable and biocompatible. They are able to absorb up to 2 liters of water or water solution per gram of dry material, without releasing it under compression. In the dry form it has the appearance of a soft sponge, in the swollen form it is like a food gelatin. It can be produced both in form of powder or of a bulky material with a well defined shape, and it has a strong memory of its shape after swelling (figure 1). The material can be charged with small molecules, such as nutrients, to be released under a controlled kinetic [12, 13].



Figure 1: Dry and swollen hydrogel

The investigated application is a system of water and nutrients release for agriculture and horticulture in arid and desert areas. To this aim, the hydrogel is produced in form of powder, charged with nutrients and/or plants pharmaceuticals, and mixed to the soil near plant routes. The cultivation is then watered only once, the hydrogel absorbs the water and swells, releasing the water and nutrients and keeping the soil or the substrate humid over long periods of time.

The liquid is absorbed or released under a diffusion mechanism when the hydrogel is in contact with a more humid (during watering) or drier (after watering) environment.

Moreover, hydrogel granules which in the dry form have almost the same dimensions of the substrate granules, increase their dimension after swelling, thus increasing soil porosity and providing a better oxygenation to the roots (see figure 2).

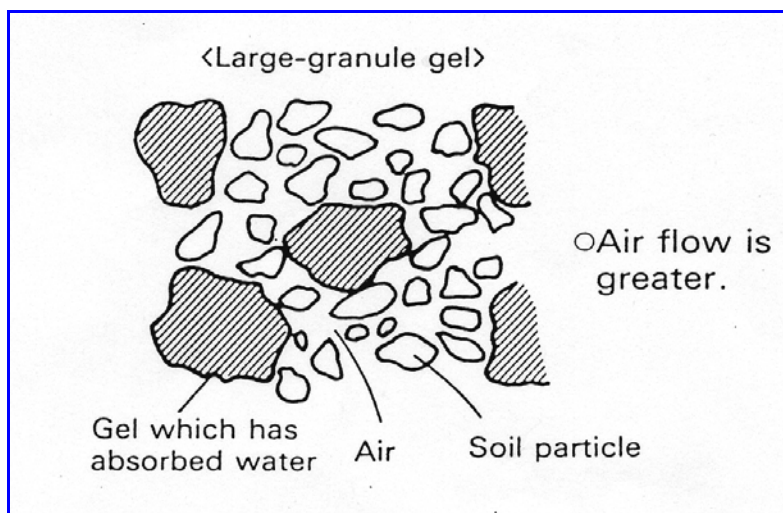
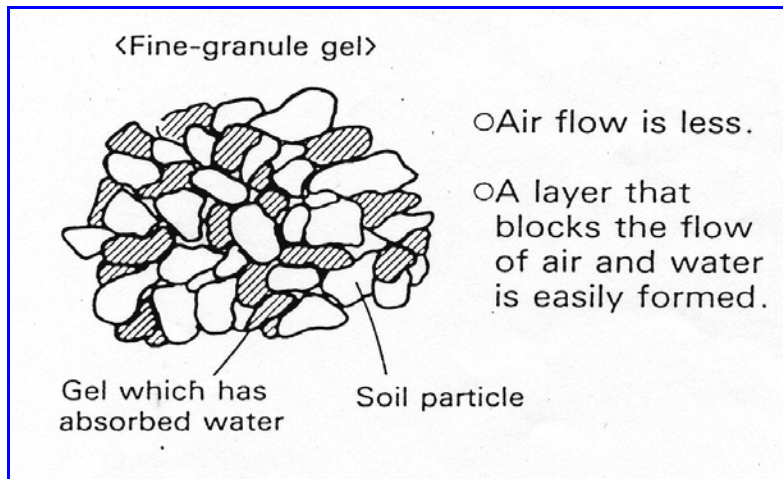


Figure 2. Dry and swollen hydrogel in the soil

### Hydrogel Synthesis

In previous works (attached to the nomination form), cellulose-based superabsorbent hydrogels, with sorption properties similar to those displayed by traditional acrylate-based products were synthesized and characterized by reacting in water mixtures of CMCNa and HEC crosslinked with divinylsulphone (DVS) or with a carbodiimide crosslinking agent.

Here we present a third generation synthesis carried out with citric acid, a new crosslinking agent able to further reducing costs and complexity compared with the former reagents. As no complete data are available in the literature, CMCNa, HEC, CA hydrogels were synthesized and characterized through DSC and FT IR techniques. For the sake of simplicity, we will not present here the chemical characterization analysis and physical analysis; we will give information on the reaction mechanism and on the swelling capacity. Further information on the whole characterization study are in press and are available under request.

Citric acid (CA), widely used in food and drug industry, is an excellent candidate as crosslinking agent. CA, extensively widespread in nature (lemon juice contains approximately 5% of CA), is prepared commercially by fungal fermentation of glucose. CA and its salts, with a good affinity for metal ions, are used in a wide variety of applications: in soft drinks and effervescent salts, as an antioxidant in food, as a sequestering agent for metal ions, as a cleaning and polishing agent for metals, as a mordant in dyeing. Moreover, CA and its salts have fundamental biological functions. For example, CA is involved as intermediate in the “Krebs cycle” in all living cells, also known as “citric acid cycle”, for the production of usable energy.

Recently, CA was used as crosslinking agent in various cellulose derivative systems and different mechanisms have been proposed in the literature to explain the crosslinking reaction of cellulose polymers with CA [14-18]. When CA is heated it will dehydrate to yield the cyclic anhydride that reacts with starch; than, another cyclic anhydride function can be achieved into CA structure through the other two non reacted carboxylic groups, allowing the attachment of another hydroxylic starch group (figure 3). This mechanism is based on an anhydride intermediate formation.

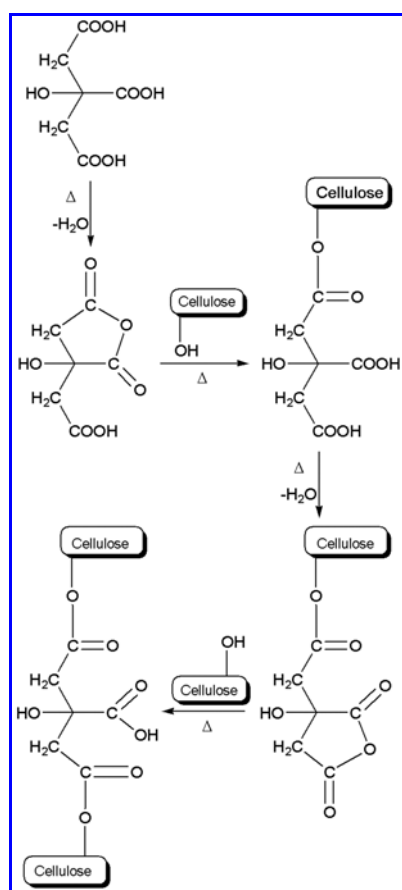


Figure 3. Hydrogel network formation by esterification with citric acid.

Attachment of the carboxylic acid moiety to celluloses hydroxyl group *via* esterification reaction of the first cyclic anhydride would expose a new carboxylic acid unit in citric acid, which has the proper chemical connectivity to form a new intra molecular anhydride moiety with the adjacent carboxylic acid unit. Further reaction with a cellulose hydroxyl of another chain can then lead to crosslinking.

Hydrogel samples were obtained reacting, in water, CMCNa and HEC with citric acid as a crosslinking agent according the following procedure. Firstly, a total polymer

concentration of 2% by weight of water, using a mixture of CMCNa and HEC, with weight ratio equal to 3/1, was dissolved in distilled water by stirring gently at room temperature until a clear solution was obtained. CMCNa dissolution is slow at the concentration adopted; thus, first HEC was added to water till, after 5 min, a clear solution was obtained with a slight increase of viscosity; then, CMCNa was added, and the stirring was kept on till a clear solution was obtained (24h), with a significant increase of viscosity. Finally, CA was added at different concentrations (1.75%, 2.75%, 3.75%, 10% and 20% w/w polymer) in order to obtain samples with various crosslinking degrees. This final solution was used to mold 10 mm thick samples. All samples were first pre-dried at 30°C for 24 h to remove absorbed water and then kept at 80°C for the crosslinking reaction.

Moreover, samples containing neat HEC or neat CMCNa samples crosslinked with CA were also prepared following exactly the same experimental conditions used for HEC/CMCNa mixtures.

### Swelling studies

Equilibrium swelling measurements for all the samples were carried out in water using a Sartorius microbalance ( $10^{-5}$  sensitivity). The swelling ratio was measured by weighing samples before and after their immersion in distilled water for about 24 h. The swelling ratio (SR) is defined as following:

$$SR = (W_s - W_d) / W_d$$

where  $W_s$  is the weight of the swollen hydrogel and  $W_d$  is the weight of the dried sample.

Swelling ratio was calculated as a function of the reaction time for: (a) CMCNa with 10% or 20% of CA concentration (Fig 4); (b) HEC with 10% or 20% of CA concentration (Fig 5); (c) the mixture of CMCNa and HEC (3/1) with 10% or 20% CA concentration (Fig 6); (d) the mixture of CMCNa and HEC (3/1) with 1,75%, 2,75% or 3,75% CA concentration (Fig 7).

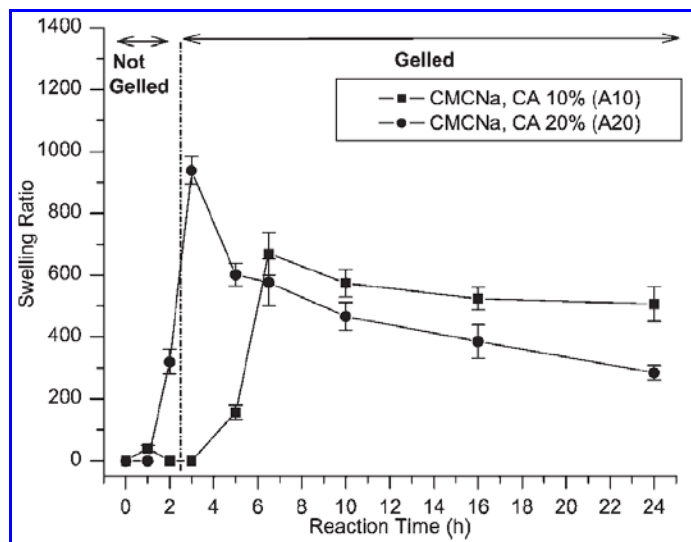


Figure 4. Equilibrium swelling ratio versus reaction time of CMCNa polymer with 10% w/w or 20% w/w of CA crosslinker concentration (both samples were dried under vacuum at 30°C for 24 h and then reacted at 80°C)

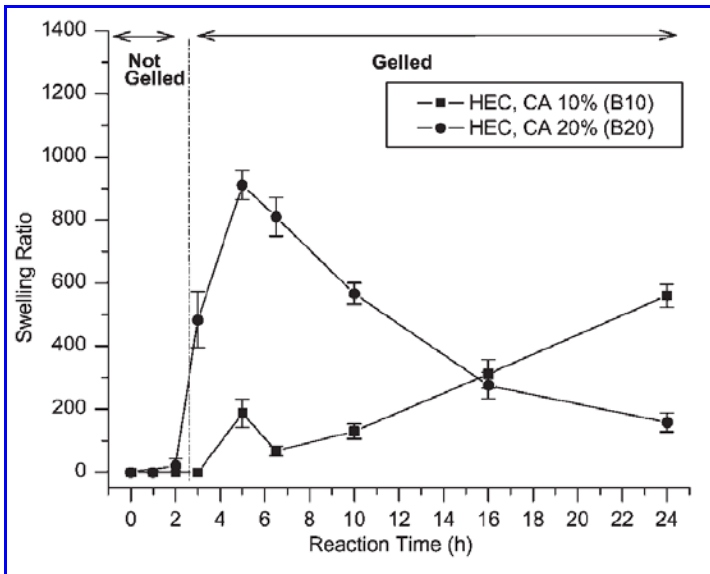


Figure 5. Equilibrium swelling ratio versus reaction time of HEC polymer with 10% w/w or 20% w/w of CA crosslinker concentration (both samples were dried under vacuum at 30°C for 24 h and then reacted at 80°C)

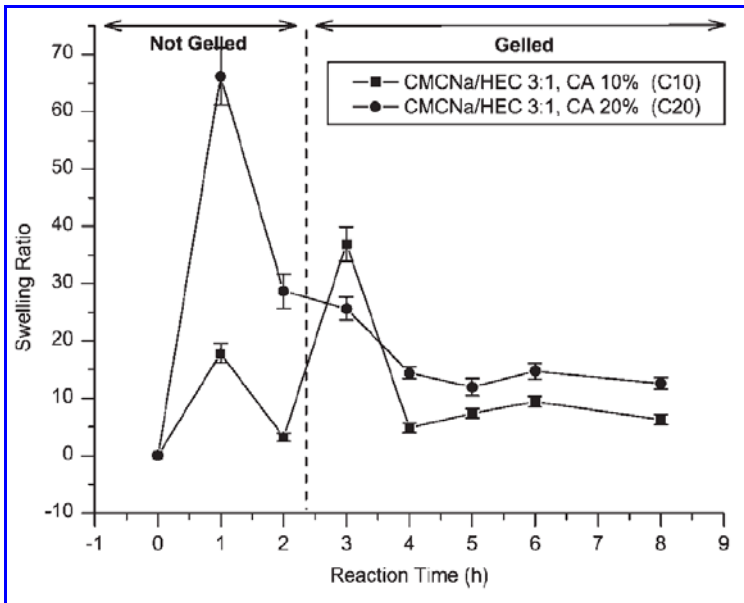


Figure 6. Equilibrium swelling ratio versus reaction time of CMCNa/HEC weight ratio 3/1 mixture with 10% w/w or 20% w/w of CA crosslinker concentration (both samples were dried under vacuum at 30°C for 24 h and then reacted at 80°C)



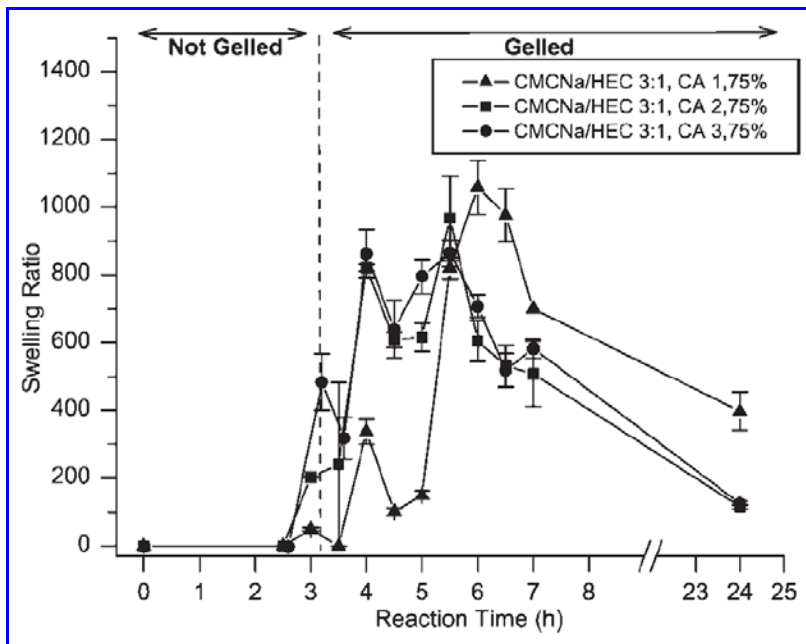


Figure 7. Equilibrium swelling ratio versus reaction time of CMCNa/HEC weight ratio 3/1 mixture with 1.75% w/w, 2.75% w/w or 3.75% w/w of CA crosslinker concentration (all samples were dried under vacuum at 30°C for 24 h and then reacted at 80°C).

According to the results of Figs. 4-5 the swelling of CMCNa crosslinked with 10% of citric acid is higher than HEC with the same citric acid concentration after 24 h. When 20% of citric acid was added to the celluloses, the shape of the swelling curves are similar for HEC and CMCNa. In this case, as crosslinking proceeds the swelling of HEC based samples decreases faster than CMCNa samples indicating that a higher rate of reaction between CA and HEC. This probably occurs because HEC is less sterically hindered than CMCNa and can react more quickly than CMCNa chains.

The maximum swelling of CMCNa/CA sample is observed at the gelation onset, after 3 h, when the second esterification reaction, those leading to crosslinking, begins (Figure 4). Then as the crosslinking process increases the corresponding equilibrium water sorption decreases.

The same reaction mechanism can be assumed for neat HEC crosslinked with CA (Fig 5). However in this case the overall behaviour is slightly different as a consequence of the absence of carboxylic groups bonded to the polymer. The results of swelling experiments must be interpreted taking into account that the CA introduces the high hydrophilic carboxylic groups that are responsible of the formation of a polyelectrolyte network. Therefore the water sorption is significantly increased as carboxylic groups are linked first to the HEC chains and then to the gelled network. This effect cannot be appreciated in CMCNa hydrogels since a large amount of  $-\text{COOH}$  groups, those linked to the CMCNa chains, is already bond to the network at gelation onset. Similar trend is observed for the mixtures of HEC and CMCNa in Figure 6.

Hydrogels of practical use presenting a high degree of swelling were obtained with a reduced concentration of citric acid (1.75%, 2.75%, 3.75% by weight of polymer). Figure 7 shows that with a citric acid concentration of 3.75% the swelling ratio value is 900. This hydrogel, after swelling, is characterized by adequate stiffness and it is capable to keep the same shape of the synthesis vat. At concentrations lower than 1.75% of CA a weak crosslinking associated with insufficient mechanical property is observed.

Agricultural preliminary observations.

In its application as water reservoir in agriculture and horticulture, the hydrogel, in dry powder form, has been mixed to the soil in the area closed to the plant roots. Then the soil has been watered once and the soil humidity has been monitored for long periods, until a fixed lower humidity level is reached.

Different hydrogel powder amount were added to the soil, up to a concentration equal to 0.2%, 0.5% and 1% of the soil. A soil without the addition of the hydrogel was used as a control. Different horticultural species and flowers, specialty from the South of Italy, have been tested. In Figure 8 the results related to a cultivation of 'cherry tomato', a small rounded tomato, are reported.

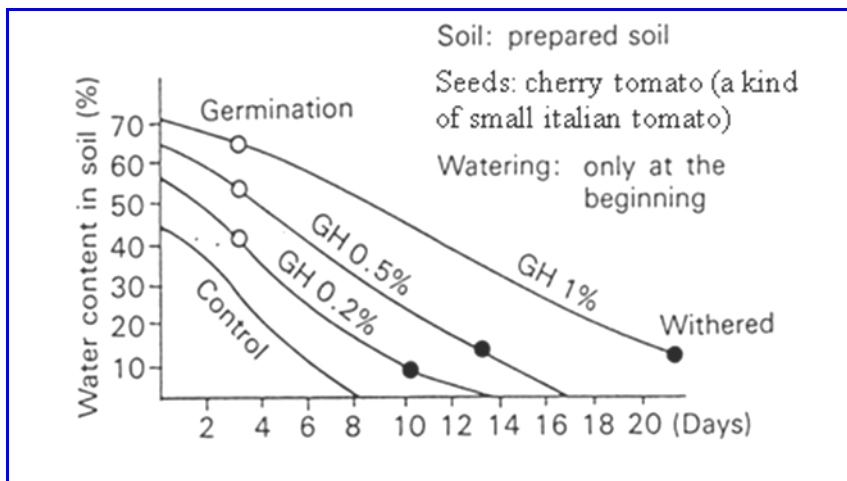


Figure 8. Water content in the soil during time with and without hydrogel addition

It can be observed that increasing the hydrogel concentration in the soil, it increases the period of time at which the humidity reaches a certain level. It is interesting that after the addition of small hydrogel amounts (up to a maximum of 1%), the period of time at which the soil remains humid almost triplicates, even in presence of a cultivation. Moreover, the initial humidity, right after watering, is substantially higher for a soil where the hydrogel has been added, thus confirming the 'water reservoir' mechanism cited above. This allows the irrigated water not to be wasted after irrigation, but stored in the soil and released under a mechanism controlled by diffusion and driven by roots absorption and evaporation. It is worth noting that the evaporation mechanism depends upon the climate conditions; however, the evaporation of water from a macromolecular hydrogel is significantly slower than the evaporation of free water from a soil exposed to atmosphere, due to the macromolecular network hindrance and the interaction between water and polymer molecules.





Figure 9: The Greenhouses in the South of Italy where the hydrogel is tested.

In Figure 9 a picture of the experimental tomato cultivation in the South of Italy is shown. A humidity sensor has been developed which has a sensitivity device the hydrogel itself. It is thus able to measure the humidity conditions of the hydrogel in the soil and allow to understand the moment at which it is necessary to perform an irrigation.

In Figure 10 the preliminary results of the humidity content in the soil are shown. It is evident the effect of hydrogel concentration in the soil capability to preserve water.

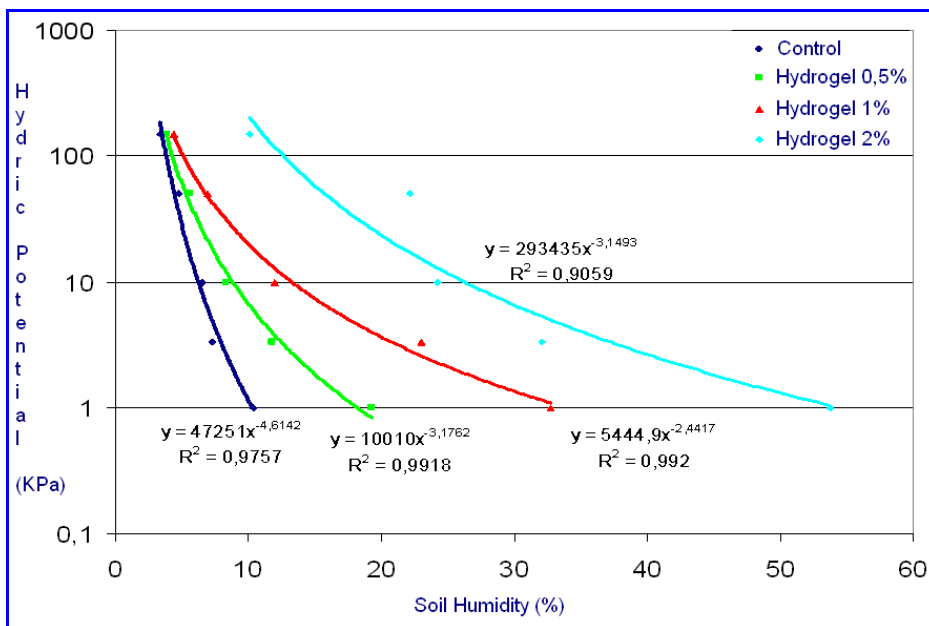


Figure 10: Effects of hydrogel concentration on soil humidity

In the long run, this sensor system can be integrated with a computer software able to activate an automatic irrigation mechanism when the humidity content in the hydrogel is low.

Preliminary analyses on the soil chemistry assessed that the hydrogel does not alter the soil chemistry, and the hydrogel is totally digested by the soil in a period of approximately 6 months.

Further study concerning the biocompatibility of the CMC/HEC hydrogel with respect to fibroblast cell line has been performed in this work with the aim of acquiring more information concerning the hydrogel biocompatibility. 3T3 fibroblasts have been used to perform biocompatibility studies in terms of cell viability and proliferation after contact with media conditioned by the material.

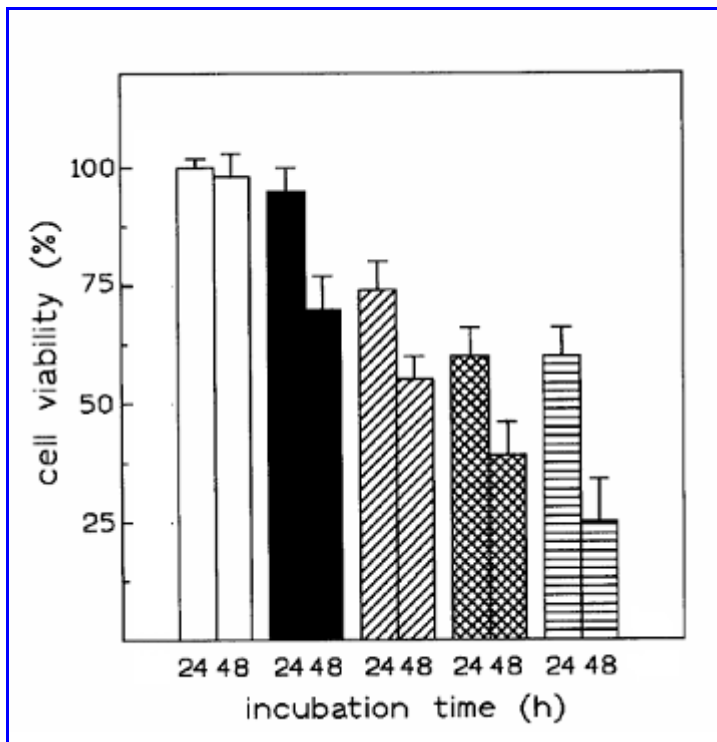


Figure 11: Cell viability

Figure 11 shows cell viability versus incubation time with either different concentrations of hydrogels (5 mg, diagonal bars; 10 mg, criss-crossed bars; 15 mg, horizontal bars) or 10 ng/mL LPS (solid bars). Untreated cells are shown as open bars. It is evident a decreasing trend in cell viability by increasing hydrogel concentration, but this behaviour can be considered not significant if applied to our hydrogel application.

### Conclusion

This work shows that CA can be successfully used as crosslinking agent of CMCNa/HEC mixtures. An esterification mechanism based on an anhydride intermediate formation was proposed to explain the reaction of cellulose polymers with CA.

The swelling ratio, monitored at different reaction times, confirmed the reaction path figured out from FTIR analysis. An optimal degree of swelling (900) for practical applications was achieved using low CA concentrations. The hydrogel obtained through the method described here has the great advantage to reduce primary and production costs and avoid any toxic intermediate during its synthetic process.

Preliminary studies using the hydrogel as a water reservoir in agriculture applications show interesting results in terms of water saving after irrigation and water conservation in the soil.

Further studies can be specifically addressed to the application of superabsorbents in agriculture wherein it is strategic to optimize water where water scarcity is a common problem.

## References

1. Buchholz, F. L. In *Superabsorbent Polymers: Science and Technology*, ACS Symposium Series 573, Buchholz, F. L.; Peppas, N. A., Eds.; American Chem Society: Washington, DC, 1994; p 27.
2. Sakiyama, T.; Chu, C. H.; Fujii, T.; Yano, T. *J Appl Polym Sci* 1993, 2021, 50.
3. Yoshida, M.; Asano, M.; Kumakura, M. J. *Eur Polym Mater* 1989, 25, 1197.
4. Shiga, T.; Hirose, Y.; Okada, A.; Kurauchi, T. *J Appl Polym Sci* 1993, 47, 113.
5. Hogari, K.; Ashiya, F., Eds. *American Chem Society: Washington, DC, 1994; Vol. 1, p 12.*
6. Ericksen, P. H.; Nguyen, H. V.; Oczkowski, B.; Olejnik, T. A. *Eur. Pat. 40087 (1981)*
7. Kobayashi, T.; Kobunshi, T. *J Appl Polym Sci* 1987, 36, 612.
8. Benhur, M.; Keren, R. *Soil Sci Soc Am J* 1997, 61, 565.
9. Levin, J.; Benhur, M.; Levy, G. J. *Aust J Soil Res* 1997, 29, 455.
10. Al-Harbi, A. R. *HortScience* 1999, 34, 223.
11. Raju, K. M. *J Appl Polym Sci* 2001, 80, 2635.
12. Esposito, F.; Del Nobile, M. A.; Mensitieri, G.; Nicolais, L. *J Appl Polym Sci* 1996, 60, 2403.
13. Sannino, A.; Nicolais, L. *Polymer* 2005, 46, 4676.
14. Glusker, J. P. *Acc Chem Res* 1980, 13, 345.
15. Wang, C. C.; Chen, C. C. *Appl Catal A* 2005, 293, 171.
16. Coma, V.; Sebti, I.; Pardon, P.; Pichavant, F. H.; Deschamps, A. *Carbohydr Polym* 2003, 51, 265.
17. Xie, X. S.; Liu, Q.; Cui, S. W. *Food Res Int* 2006, 39, 332.
18. Yang, C. Q.; Wang, X. J. *J Appl Polym Sci* 1998, 70, 2711.

## Appendix

### Hydrogel production plant

To witness the feasibility of the implementation of this technology, hydrogel synthesis scale up process has been performed with the aim of producing the material in a quantity able to satisfy the requirements for the agricultural studies in all the Greenhouses involved in the test.

The process consists mainly in four steps: 1) mixing the cellulose derivatives, the citric acid and water; 2) performing the crosslinking reaction to chemically stabilize the polymer network; 3) hydrogel purification; 4) hydrogel desiccation.

In the following, some pictures of the first generation pilot plant are reported. A second generation, with higher production capacity, is under construction.



Figure 12. The mixing stage (up, left); the crosslinking stage (up, right); the desiccation stage (down).