

Hybrid Superabsorbent Polymers as “Water Reserve” in Agricultural field



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Abstract

In this study, acrylate-based SAP powder is analysed “as it is” (pristine SAP) and processed with silicate sodium (hybrid SAP) as “water reserve” in agricultural application. To do that, SAP powder is opportunely swelled in different aqueous alkaline media (NaOH or SiO₂/Na₂O) with a ratio SAP: water solution equal to 1:200. The produced hydrogels properties, such as water retaining and water adsorption/desorption capability along with the regeneration of pristine and hybrid samples are assessed without and within soil in a reduced scale. Furthermore, hydrogels are tested in a real scale system too and the water release is monitored over time starting from dried soil. The results show that hydrogels obtained with 0.5w/w% of SAP can release gradually water to the soil and/or to the plants when needed, more or less in 5 days in relation to environmental conditions, T=26°C and RH=50%. The adoption of the suggested SAP in cultivations could therefore represent a valid approach for the rationalization of water resources, mainly in desert areas or as “monitored water source” in flowerpots located within the “future smart cities” in which the concept of water efficiency represents a fundamental concept.

Keywords: Superabsorbent polymer; Sodium- silicate; Hybrid-hydrogel; Water reserve

Introduction

The circular economy and the need to decrease dependence on oil [1,2] and the growing awareness of environmental concerns have pushed industries and researchers to develop environmentally friendly strategies by promoting the search for sustainable paths in all sectors.

Among these, the theme of the “water reserve” has already constituted one of the most important areas of modern science and technology, even if the concept only emerged at the beginning of this century.

In the last years, the control and the management of agricultural water-saving irrigation is considered one of the major challenges within the policy of circular economy: by 2030 water demand is expected to be 50% higher than today. The agriculture sector is heavily dependent on water resources and, the water shortage has become a serious issue, especially in arid and semi-arid areas and in those regions that are exposed to the progressive desertification [3] or which have been gravely affected by the drought situation. In addition, the climate change

with rain deficiency could further worsen this condition. Then, unavailability of sufficient water for irrigation, loss of fertilizers, and increasing food demand requires proper management of water to conserve moisture and to increase water-holding capacity of the soil. Furthermore, the climate change could be one of the reasons for rain deficiency. Unavailability of sufficient water for irrigation, loss of fertilizers, and increasing food demand requires proper management of water to conserve moisture and to increase water-holding capacity of the soil. For this reason, it results mainly strategic for the long-term competitiveness of the agricultural industry and not only. In this respect, the severity of the subject has motivated constant interest in individuating effective technological and management solutions for water irrigation optimization. Among them the use of superabsorbent polymers (SAPs), able to absorb and retain large amounts of water, results a valid and innovative approach to the optimization of water consumption [4]. SAPs can reduce water loss and improve nutrient retention too and therefore minimize leaching and increase crop yields. SAPs hydrogels are a class of macromolecular

gels, obtained by chemical or physical crosslinking of linear (or branched) hydrophilic polymer molecules, in which the swelling phase (solvent) is water, present in high amount [4].

The application foresees that the SAPs granules swelled at suitable amount of water are put in contact with soil in given amounts, after watering the SAPs release water slowly through diffusive mechanism, as the soil gets dry. For this reason, it is of great significance to investigate the influencing factors and mechanisms of SAP effects on soil environments and crop growth. Furthermore, there is very little information in the scientific literature on the synthesis of hydrogels crosslinked with silicate source [4].

In this respect, in the present work hybrid polyacrylate-silicate based SAP (hybrid-hydrogel), is adopted as water-retaining material in agricultural field and its performances are compared with the pristine ones. Chemical and thermal degradation properties along with the water adsorption/desorption capability and the regeneration ability were analysed.

Moreover, a preliminary evaluation of the hybrid hydrogel as water reservoir in agriculture was performed by using the hydrogel in experimental greenhouses.

Experimental

Materials

The SAP used is Regel TH5P, provided by Cromogenia Units. Sodium Silicate (SS) ($\text{SiO}_2/\text{Na}_2\text{O} = 3.2$) [5] was provided by Prochin Italia Srl (27.40wt%, SiO_2 , 8.15wt%, Na_2O and 64.45wt% H_2O); tap water was used as dispersed media.

Hydrogels preparation

The hydrogel samples were obtained by mixing a suitable amount of SAP powder with water in a ratio equal to 1:200. The aforementioned mixtures, pristine- and hybrid-hydrogel, were neutralized with 1ml of a 10M NaOH solution and 3ml of SS,

respectively.

Characterizations

The chemical interactions/modifications occurred in each hydrogel sample were characterized by ATR-FTIR analysis by using a Nicolet apparatus (Thermo Scientific, Italy) from 4000 to 600cm^{-1} with a wavenumber resolution of 4cm^{-1} for 64 scans at room temperature. The thermal degradation of hydrogels was investigated by thermogravimetric analysis (TGA) with a TGA 2950 apparatus (T.A. Instruments, USA) under air atmosphere. The samples were heated on platinum pans from 30 to 1000°C with heating rate of 20 C/min [6,7].

Hydrogels regeneration capability was tested in 50mL Falcon tube at environmental condition with and without the presence of soil after dehydration.

The regeneration tests were conducted by placing in several Falcon tubes a suitable volume (10mL) of hydrogel in conditions of $T=26^\circ\text{C}$ and $\text{RH}=50\%$ and leaving them to de-hydrate until they reached a certain volume. Once that happened, each hydrogel was regenerated adding water to the starting volume of 10mL. This procedure was carried out with up to the identification of the critical volume (point of no return), as well as which the hydrogel can no longer be regenerated. The regeneration tests in the presence of the soil were carried out in experimental vessels equipped with a special compartment to house a known quantity of hydrogel. Once the hydrogel has transferred water to the soil, what remained of the gel has been recovered and added with water to restore the initial volume and verify its regenerability.

Finally, permeability test was performed putting the optimized hydrogel (hybrid hydrogel) in contact with soil in volumetric ratio equal to 1:1 in an experimental apparatus (as shown in Figure 1), which allow to see macroscopic changes in the hydrogel during its water releasing work. Moreover, using a data logger connected to moisture sensors, soil relative humidity was monitored over time.



Figure 1: Real-scale permeability test, experimental apparatus.

Results and Discussion

Firstly, visual macroscopic observation allows to investigate the effect of SS solution on the morphological aspect of hydrogels. SS, thanks to its own 3D network, improved the hybrid hydrogel structure, which appeared definitely more wrinkled and showed a double network nature.

These findings were confirmed by ATR-FTIR and t TGA-derivative TGA reported in Figure 2. In particular, for the FTIR spectra of SAP and pristine hydrogel the main peak at 1705cm^{-1}

¹ related to the C=O ester bond was highlighted along with the stretching vibrations of C-H and O-H at 2900cm^{-1} and 3100cm^{-1} respectively, the band at 1250 to 1200cm^{-1} was assigned to the stretching of C-O-C of acrylates. Conversely, for the hybrid-hydrogel sample a strong reduction of both C=O and the C-O-C absorption peaks were observed at the same time the characteristic stretching vibration of Si-O-Si at 1050cm^{-1} was detected [8]. These outcomes mean that a chemical interaction (crosslinking) between the silicatic with acrylate species occurred [4].

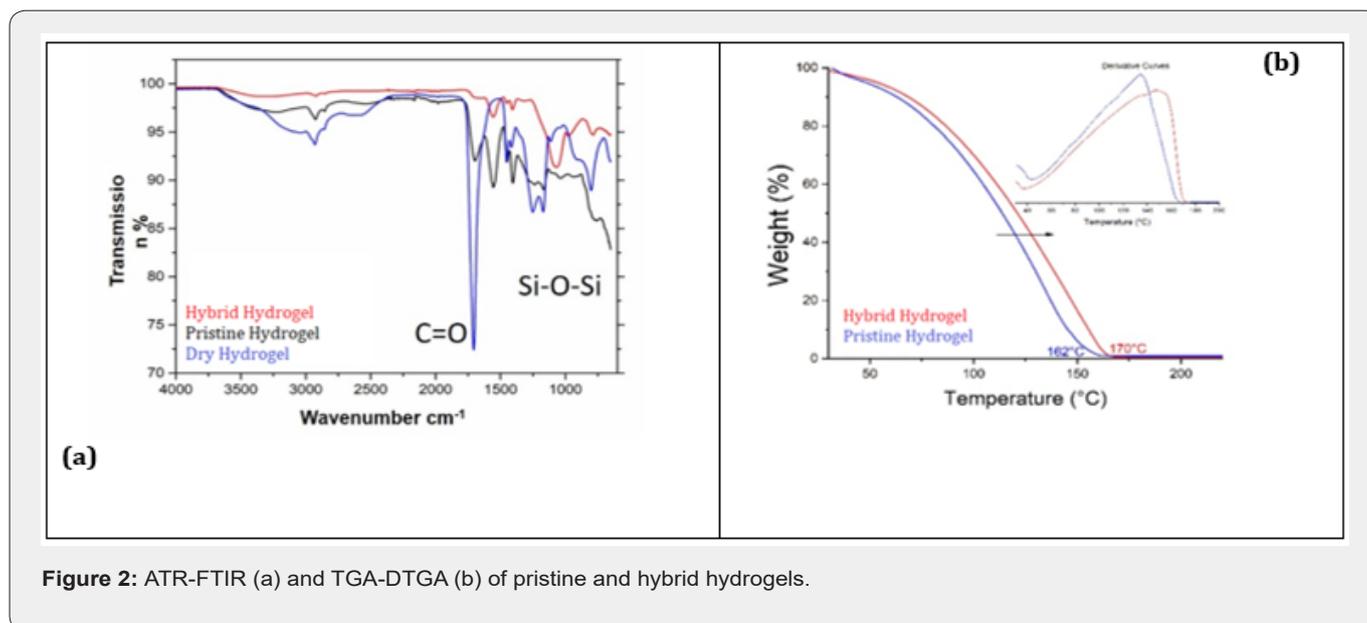


Figure 2: ATR-FTIR (a) and TGA-DTGA (b) of pristine and hybrid hydrogels.

Accordingly, from TGA-DTGA the water evaporation starting from room temperature ($>30^{\circ}\text{C}$) until 100°C was observed for both pristine and hybrid hydrogels. Subsequently a main degradation step related to the organic phase (acrylate) of SAP was detected. Furthermore, a higher thermal stability (around 30°C) for the hybrid-hydrogel is observed this behaviour can be correlated to the presence of inorganic structure (silicate) crosslinked with SAP.

Collected data showed that the functionalization of the hydrogel by SS led to a double network hybrid hydrogel with a stronger texture than pristine one. Moreover, the presence of this strong texture allows for easy handling as it has a more compact "shape" compared to the pristine hydrogel. Additionally, the presence of crosslinking could potentially play a superior and improved role in preventing nutrient loss during heavy rainwater flow from the soil surface because these hydrogels absorb water and swell to hold water longer and release it more slowly. Therefore, this kind of hybrid hydrogel can be proposed not only as direct addition in soil but also as independent water reservoir in agricultural real scenario.

As regards the regeneration capability, each hydrogel (pristine or hybrid) can be completely regenerated by adding water to the starting volume up to a dehydration of about 80%. Otherwise, working in contact with soil, hydrogels matrix needed a ratio equal to 1:80 to fully regenerate because of their electrolyte sensitivity. Acrylic acid-based hydrogel has shown a decrease in their water adsorption potential in presence of ionic strengthened solvent [9]. In this context, soil can actively exchange ions with hydrogel liquid phase increasing his ionic strength, therefore limiting the polymer storage capability and causing the extrusion of large amount of water from the network. Nevertheless, to hinder this process, it is possible to increase SAP concentration and preserve hydrogel texture.

In Figure 3 the results of soil hydration process by hybrid hydrogel are reported. Monitoring soil relative humidity over time showed a raising from 10% to 80% in 5 days, confirming the great hydration power of the SAP. Moreover, we can hypothesize that the using of hydrogel as water reserve allow to keep soil wet with low irrigation thanks to its water controlled-release over the time.

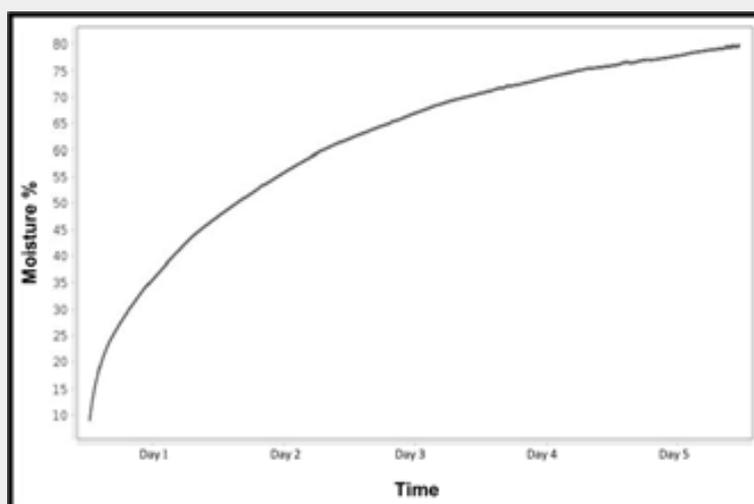


Figure 3: Hydration curve.

Conclusion

Superabsorbent polymers could store great amounts of liquid relative to its own mass, so they are widely used in agriculture as water reserve. In this work, pristine and modified polyacrylate-based hydrogels were characterized, and their regeneration capability was tested with and without the presence of soil. Using silicate sodium as neutralizer during swelling process led to a double network hybrid hydrogel with stronger texture than pristine one, which has a great hydration power and can be completely regenerated.

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