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# Hydrogels based on starch from various natural sources: synthesis and characterisation

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## Abbreviations

AA, acrylic acid; AAm, acrylamide; H, cross-linked hydrogel; MBA, methylene-bis-acrylamide; NH, non-cross-linked hydrogel; PSA, ammonium persulfate; SR, swelling ratio; WS, water solubility; TGA, thermogravimetry analysis

## Keywords

Acrylamide, Acrylic acid, Starch, Starch-graft-copolymer, Swelling of hydrogel

## **Abstract**

Hydrogels based on a graft copolymer of acrylic acid (AA) and acrylamide (AAm) on a backbone of starch, obtained from different natural sources, have been prepared and characterised for potential agricultural use, as soil moisture regulators and nutrient sources for plant nutrition. Five types of starch were used: corn, waxy corn, wheat, potato and rice starch. Hydrogels were prepared by a solution polymerisation method, in the presence of ammonium persulphate (PSA) as initiator and *N,N'*-methylene-bis-acrylamide (MBA) as a cross-linking agent. Thermal and physico-chemical properties, such as TGA and DSC data and swelling properties of hydrogels, were observed. The influences of the cross-linking agent on the swelling ratio (SR) and solubility of prepared hydrogels were studied and optimised. The highest SR observed in water corresponded to non-cross-linked hydrogels prepared with waxy corn starch (780 g water/g dry matter), and the SR of these hydrogels in ammonium sulphate and calcium nitrate solutions were 9.6 g and 1.2 g/g dry matter, respectively. Higher thermal stability was observed with cross-linked starch-g-(AA-AAm) hydrogels. The non-cross-linked hydrogels had a higher SR, but also had significant solubility in water.

## 1. Introduction

Hydrogels are physically- or chemically-cross-linked hydrophilic polymers with three-dimensional network structures, and can absorb large amounts of water or aqueous solutions.<sup>[1-4]</sup> For this reason, hydrogels are used for applications in drug delivery, tissue engineering, wastewater treatment and food chemistry.<sup>[5-10]</sup> In recent years, there has been an effort to replace synthetic hydrogels, which have high production costs, are non-renewable, difficult to degrade and environmentally unfriendly, with hydrogels of natural origin. Natural hydrogels do not contain harmful substances, which may pollute the environment, and are readily biodegradable.<sup>[11-16]</sup> Hydrogels based on biodegradable polymers, mainly polysaccharides, are frequently used in agriculture. In particular, polysaccharides containing a high amount of hydroxyl and carboxyl groups, including starch, chitosan or cellulose, represent biodegradable hydrogels with adequate swelling properties. For instance, starch-based hydrogels may be prepared via graft polymerisation of acrylic acid (AA) or/and acrylamide (AAm), either with a chain of starch or with interpenetration and *in situ* simultaneous cross-linking.<sup>[17-19]</sup>

Starch is a polymeric carbohydrate found in seeds and tubers of plants like maize (corn), rice, wheat, potato and cassava. Starch consists of two major components, amylose (AM) and amylopectin (AP), which are organized into a semi-crystalline structure in the starch granules.<sup>[20]</sup> AM is a linear polymer of  $\alpha$ -D-glucose units bonded to each other through  $\alpha(1\rightarrow4)$  glycosidic bonds. AP creates a highly branched structure of short  $\alpha$ -1,4 glucose chains that are connected by  $\alpha$ -1,6 branch linkages.<sup>[21]</sup> The ratio of AP to AM strongly depends on the natural source of the starch in most cases. Regular starches contain approximately 70–80 % of AP and 20–30 % of AM, waxy starches less than 10 % of AM and high-AM starches more than 40 % of AM.<sup>[22]</sup> It is well known that not only the ratio of AP to AM but also botanical origin of starch has a great influence on the properties of products made from the starch. Olad (2020) reported starch based hydrogel from potato peel waste with good swelling properties which make it a potential candidate for agricultural and horticultural applications.<sup>[23]</sup> In contrast, Parvathy (2012) reported the water sorption kinetics of cassava starch hydrogels under different conditions of swelling.<sup>[24]</sup> Moreover, Zou (2012) studied the effect of AM/AP ratio in corn starch on swelling of hydrogels prepared from this starch and found that a higher amylose content led to higher water absorption, which corresponds with its higher grafting ratio and grafting efficiency.<sup>[25]</sup> Previously reported studies were mainly focused on synthesis of hydrogels based on the starch from one type of natural source. Till this

time there has been no report published on the effect of different natural origin of starch on swelling properties of the starch based hydrogels prepared by graft-copolymerization technique.

In agrochemistry, hydrogels are investigated for two reasons. The first reason is for improvement of the water-holding capacity of soil in areas with unfavourable climatic conditions. Incorporating hydrogels into the soil improves the utilisation of soil water by plants, reducing the cost of irrigation.<sup>[17, 26, 27]</sup> The second reason is that hydrogels also act as a slow-release system, by favouring the uptake of some nutrient elements, holding them tightly, and delaying their dissolution. Hydrogels with a slow release of nutrients prevent over-fertilisation of the soil, thus avoiding salinisation and subsequent contamination of groundwater.<sup>[16, 28, 29]</sup>

In this work, hydrogels were synthesised by grafting AA and AAm on starches, obtained from different natural sources, using ammonium persulphate (PSA) as initiator and methylene-bis-acrylamide (MBA) as cross-linking agent. The aim of this study was to find conditions for preparation of hydrogels with properties suitable for agricultural applications; in particular, high swelling and low solubility. Variables such as MBA content, AAm content, type of starch, and temperature and time of preparation, were examined and optimised. To the best of our knowledge, no previous report describing such a comparison of five different starch hydrogels, synthesised with or without cross-linking agent, has yet been published. The obtained hydrogels were characterised via thermogravimetry analysis (TGA), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). Swelling of the hydrogels was explored, in fertiliser solutions or in water at different pH levels.

## **2. Materials and methods**

### **2.1. Materials**

Starches (corn S4126, waxy corn S9679, potato S4251, rice S7260 and wheat S5127), AA 147230, AAm 01700 and MBA 146072 were purchased from Sigma-Aldrich. PSA, urea and barium chloride were purchased from Lachema N.P. (Czechia). Calcium nitrate tetrahydrate and hydrochloric acid were purchased from Penta (Czechia). Potassium hydroxide and ammonium sulphate were purchased from Lach-Ner, s.r.o. (Czechia). Nitrogen and argon (99.996% purity) were purchased from Linde Gas, a.s (Czechia).

## 2.2. Preparation of hydrogels

Starch from different natural sources, such as corn (22–28 % of amylose), waxy corn (less than 5 % of amylose), potato (23–29 % of amylose), rice (20–29 % of amylose) or wheat (20–25 % of amylose), was used for the hydrogel preparation.<sup>[30-35]</sup> The AAm solution was prepared by dissolving AAm (0.5 g or 1.0 g) in 10 mL of deionised water, under constant stirring at room temperature. Then, the AAm solution was blended with AA (1.9 mL) and the mixture was neutralised with KOH (2.5 mL, 45 wt. %) to pH = 6–7. The neutralised mixture was then heated in a water bath at 40 °C and bubbled with nitrogen for 12 min. Subsequently, starch (2.0 g) was added into the mixture, and the outflowing nitrogen tube was placed above the surface of the reaction mixture during stirring for 10 min. After that, the gelatinised starch solution was heated to 50 °C. Various amount of 1 wt. % MBA solution (0; *non-cross-linked*, 0.50, 0.75, 1.00 mL) and 1 wt. % PSA (0.5 mL) was added to generate free radicals, after which the mixture was kept in a water bath under nitrogen atmosphere for 30–35 min. The gelatinised mixture was transferred to an oven and kept there at 75 °C for 2 h, in order to complete the polymerisation reaction. The obtained gel was cooled at room temperature and washed thoroughly by acetone. The final starch-g-(AA-AAm) hydrogel was cut into small pieces (1–2 mm) and dried at room temperature for 1–2 d until constant weight was achieved. The same procedure was repeated for preparing the hydrogel under an air atmosphere.

## 2.3. Characterisation of hydrogels

### 2.3.1. FTIR Spectroscopy

The FT-IR spectra of the prepared samples were measured by Nicolet iS20 spectrometer (Nicolet CZ s.r.o.) in the range of 4000–500 cm<sup>-1</sup>. The spectra were recorded at resolution of 4 cm<sup>-1</sup> accumulating 128 scans and treated first with the Omnic program supplied by Nicolet CZ s.r.o. KBr was used as a background.

### 2.3.2. Scanning electron microscopy (SEM)

A scanning electron microscope (LYRA3, Tescan Orsay Holding, a.s.) was used for studying the surface morphology of hydrogel samples, at an accelerating voltage of 10 kV. The swollen hydrogels were freeze-dried and coated with a thin 25 nm layer of gold under vacuum (Leica EM ACE200, Leica Microsystems GmbH) prior to observation.

### 2.3.3. Thermal stability

Thermal properties of AA, AAm, starches and prepared hydrogels were studied using simultaneous thermogravimetry with differential scanning calorimeter (TG-DSC, Labsys, Setaram). Dry sample (approximately 5 mg) was measured within the temperature range of 25–650 °C in a corundum crucible, at a heating rate of 10 °C min<sup>-1</sup> and under air atmosphere, with a flow rate of 50 mL min<sup>-1</sup>. Under the same conditions, but an argon rather than air atmosphere, the sample overflowed from the crucible at temperatures above 350 °C. Thus, the measurements under argon atmosphere were only done up to 350 °C. Unfortunately, the combined TG-DSC technique uses small crucibles (100 µL) and the thermocouple is close to them, therefore it was not possible to measure under argon atmosphere over a wide temperature range due to the overflow of the sample from the crucible during pyrolysis. The sample weight loss was analysed as a function of temperature as well as the heat flow dependence on temperature.

### 2.4. Swelling study

The T-bag method was used for determination of swelling behaviour of the starch-g-(AA-AAm) hydrogels in distilled water.<sup>[36]</sup> Dried samples (25 mg) were placed in monofilament bags and immersed in 100 mL of water (distilled or with pH 3–8). Prior to measuring, KCl (0.1 mol L<sup>-1</sup>, 1 mL) was added to water, in order to increase the conductivity of water for improvement of pH measurements. The weight of the swollen hydrogel in the bag was measured at room temperature until the swelling equilibrium was reached (3 h). Separately, dried samples (500 mg) were placed into 100 mL of fertiliser solutions (4 mol L<sup>-1</sup> aqueous solutions of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O or urea). The swollen hydrogels were filtered using a Büchner funnel prior to weighing, then dried in a vacuum dryer at 85 °C. The swelling in fertiliser solutions was complete within 3 h for all fertilisers. The swelling ratio (SR) was calculated as follows:

$$SR = \left[ \frac{\text{water(g)}}{\text{dry mass(g)}} \right] = \frac{(m_1 - m_2) - (m_3 - m_4)}{m_3 - m_4}$$

Where  $m_1$  is the weight of swollen gel in the bag (g),  $m_2$  is the weight of the wet bag (g),  $m_3$  is the weight of the dried bag with dried gel (g) and  $m_4$  is weight of the dried bag (g).

In addition, the influence of pH on SR was monitored in solutions of pH = 3–8, according to the T-bag method described above.

### 2.4.1. Determination of water solubility

The starch-g-(AA-AAm) hydrogel swollen in water was dried at room temperature ( $23 \pm 1^\circ\text{C}$ ) until constant weight was achieved. The water solubility (WS) was obtained on the basis of differences in weight before and after swelling of hydrogel in 100 mL of distilled water, according to:

$$WS = m_0 - m_3 - m_4$$

Where  $m_0$  is the weight of the original dry gel (g), and  $m_3$  and  $m_4$  are the weights previously mentioned.

### 2.5. Statistical analysis

All experiments were repeated three times ( $n = 3$ ) and results presented as average values (mean  $\pm$  SD).

## 3. Results and discussion

### 3.1. Synthesis and mechanism

The hydrogels were synthesised by graft copolymerisation of AA and AAm monomers onto starches, obtained from different natural sources, in the presence of MBA as a cross-linking agent and PSA as initiator. The proposed mechanism of the synthesis is illustrated in Fig 1. The PSA initiator decomposes under heating at  $50^\circ\text{C}$  to generate sulphate anion radicals ( $\text{SO}_4^{\cdot-}$ ), which subsequently react with water molecules producing hydroxyl radicals ( $\text{OH}^\cdot$ ). These radicals attract the hydrogen atoms in starch -OH groups, resulting in the formation of other active groups, such as alkoxy radicals, in the starch.<sup>[37, 38]</sup> Then, the macro-radicals react with monomers of AA and AAm to generate monomer radicals. Simultaneously, the AA and AAm monomer radicals become free-radical donors to neighbouring monomer molecules, resulting in the formation of polymer chains, eventually generating graft copolymers.<sup>[2, 39, 40]</sup> During chain propagation, the polymer chains may react synchronously with vinyl groups in MBA, allowing the formation of a three-dimensional network. The amorphous structure of hydrogels was confirmed by XRD (Fig. S1).

**Figure 1.** Proposed reaction mechanism for the synthesis of starch-g-(AA-AAm) hydrogels: a) initiation, b) co-polymerisation, c) starch macroradical formation, d) grafting and cross-linking.

### 3.2. Spectral characterization

The FTIR spectra of starch and starch-g-(AA-AAm) hydrogel are shown in Fig 2. The characteristic bands of starch within 3750–3100  $\text{cm}^{-1}$  corresponded to O–H bonds stretching and peak at 2934  $\text{cm}^{-1}$  was due to the stretching vibrations of C–H on the polymer backbone.<sup>[41, 42]</sup> The absorption peak at 1650  $\text{cm}^{-1}$  was due to the O–H bending vibration of water absorbed in the amorphous region of starch.<sup>[20]</sup> The IR spectra of all starches (such as corn, waxy corn, potato, rice or wheat) were similar to those shown in Fig. 2a. The IR spectra of starch-g-(AA-AAm) hydrogels show four new characteristic absorption peaks at 1710, 1673, 1561 and 1403  $\text{cm}^{-1}$  verifying the formation of graft copolymer product.<sup>[42]</sup> The three peaks at 1710, 1561 and 1403  $\text{cm}^{-1}$  were related to the stretching of COOH, asymmetrical and symmetrical stretching of  $-\text{COO}^-$  groups, respectively. Finally, the absorption peak at 1673  $\text{cm}^{-1}$  was attributed to amide group.<sup>[41, 43]</sup> The IR spectra of other hydrogels prepared without MBA were similar to those shown in Fig 2b.

**Figure 2.** FTIR spectra of a) starch and b) starch-g-(AA-AAm) hydrogel.

### 3.3. Thermogravimetric analysis (TGA)

The thermal stability of the starting materials (Fig. 3) and starch-g-(AA-AAm) hydrogels (Fig. 4) were investigated, using thermogravimetric analysis (TGA) under an air atmosphere in the temperature range up to 650 °C. The measurements under the inert atmosphere were also performed (Fig. S2), but only up to 350 °C (above this temperature the pyrolysis caused a partial overflow of the sample from the crucible which distorted the measurement).

TGA curves of natural starches from different natural sources showed three distinct stages, as seen from derivative curves (dTG; Fig. 3c). Decomposition begins right at the beginning of heating, with initial weight loss due to the presence of moisture (endothermic dehydration can be seen from DSC curves in Fig. 5a,b), then the main weight loss occurs at approximately 300 °C, followed by the stage with maximum weight loss at approximately 500 °C (Fig. 3a). The thermal stability of the starches depends on the content of amylose and amylopectin. Thermal stability was increased with a decreasing amount of amylopectin, in line with previous work.<sup>[30]</sup> Based on a previous report <sup>[44]</sup>, it was observed that the

second process stage does not occur under inert atmospheres, and, therefore, it indicates oxidation of the partially decomposed starch. The thermal degradation of starch in air appears as an exothermic process (as described later in Fig. 5), due to ignition occurring; therefore, this stage is termed as “flaming combustion”. The carbonaceous residue formed may also react with oxygen to produce simple gases, such as CO, CO<sub>2</sub> and H<sub>2</sub>O; this stage is termed as “glowing combustion”.

Subsequently, three-stage decomposition was also observed in the TGA of AA, with maximum rate of the weight loss occurring at approximately 350 °C (Fig. 3b). The TGA of AAm showed a five-stage degradation process with main dTG peaks at approximately 160 and 375 °C (Fig. 3b,d), in agreement with previous work.<sup>[45]</sup>

The onset temperatures ( $T_{\text{ons}}$ ) and the temperatures corresponding to the maximum on dTG curves ( $T_p$ ) for all effects mentioned above are summarised in Table 1 (signal with three effects, i.e. data from Fig. 3c and AA from Figure 3d) and Table 2 (signal with five effects, i.e. data from Fig. 4c, d and AAm from Figure 3b). Comparing the results for natural starches and AA (Table 1), the dTG curve for starches shows narrower and stronger effects.  $T_p$  values are for all starches and the effects lower compared to those for AA. Similarly, the  $T_{\text{ons}}$  values for all starches are stronger than those for AA, except the second effect.

**Table 1.** Temperatures corresponding to the onset and maxima on dTG curves shown in Fig. 3c, d (AA), referred as the first, second and third peak in accordance with the text and in the order of increasing temperature

**Figure 3.** TGA: a) starches, b) AAm and AA, c) dTG of starches, d) dTG of AAm and AA. The measurement conditions: 10 °C/min, 25–650 °C under air atmosphere.

The TGA curves for all starch-g-(AA-AAm) hydrogels (Fig. 4) show five different weight loss steps, where the 2<sup>nd</sup> and 4<sup>th</sup> steps are not completely separated. The values of the characteristic temperatures determined from dTG of hydrogels (Fig. 4c, d) are given in Table 2. The first small step is observed within the range of 40–220 °C, corresponding to loss of water from the hydrogel (with significantly lower mass change and lower dTG peak in comparison to the starch). The second weight loss is likely caused due to the loss of CO<sub>2</sub> from the polysaccharide <sup>[46]</sup>, followed by the third stage, which is also associated

with starch decomposition.<sup>[29, 47]</sup> This thermal decomposition step was also observed in the TGA curves of neat starches in the range of 290–355 °C, with a maximum at approximately 300 °C (Fig. 4a, Table 2). The fourth stage corresponds to the degradation of grafted AA and with decomposition of amide groups from grafted AAm chains in starch-g-(AA-AAm).<sup>[46, 47]</sup> The final decomposition step can be also seen on the TGA curves of AA and AAm, with a dTG maximum above 550 °C (Fig. 4b). The lowest temperatures are observed for NH-rice and NH-waxy corn hydrogels which are close to  $T_p$  value for AAm (Table 2). Similar results were also obtained from TGA curves performed under an argon atmosphere. A comparison of TGA curves of starch-g-(AA-AAm) hydrogels prepared with corn starch, recorded under argon and air atmospheres, is shown in Fig. S2. The shift of the decomposition temperature in the TGA curves of starch-g-(AA-AAm) hydrogels is due to the presence of the cross-linking reagent (MBA) in the hydrogel structure, as observed in TGA curves of starch-g-(AA-AAm) prepared in the absence (Fig. 4a) and presence (Fig. 4b) of MBA. The thermal stability of starch-g-(AA-AAm) increased with the addition of MBA (shown by the slight shift of the decomposition step to higher temperatures, see Table 2).

**Table 2.** Temperatures corresponding to the onset and maximum of dTG curves given in Fig. 3d (AAm) and 4c,d, referred as the first, second, third, fourth and fifth peak in accordance with the text and in the order of increasing temperature

**Figure 4.** TGA of hydrogels: a) non-cross-linked (NH), b) cross-linked H). dTG of hydrogels: c) NH, d) H. The measurement conditions: 10 °C/min to 650 °C under air atmosphere.

### 3.4. Differential scanning calorimetry (DSC)

The DSC curves of AAm, AA, neat starches and starch-g-(AA-AAm) hydrogels are shown in Fig. 5. In the DSC curve of starch-g-(AA-AAm), one endothermic and two exothermic peaks are observed (Fig. 5c,d). The first endothermic peak at approximately 250 °C corresponds to either the formation of AA anhydride, or to ammonia loss and the formation of imine from AAm.<sup>[45, 48]</sup> The second exothermic effect of multiple structure with peak at approximately 370 °C corresponds to several processes connected either with the degradation of the AA anhydride, or with the second stage of polymer decomposition with imine group degradation.<sup>[48]</sup> The third exothermic peak at 625 °C corresponds to the thermal degradation of AA and AAm.<sup>[45]</sup> The endothermic and exothermic peaks are observed also in DSC curves of the

starting materials (Fig. 5a,b). However, the DSC curve of AA in the range of 350–600 °C is composed of several reactions, and the shape of the AA DCS curve is comparable to the final section of the AAm curve (Fig. 5a). The combination of these effects may also be observed in the DSC curve of starch-g-(AA-AAm) hydrogels, due to the simultaneous degradation and decomposition of AA and AAm originating from starch-g-(AA-AAm) chains. An increase of heat flow in DSC curves of starch-g-(AA-AAm) hydrogels within the temperature range of 300–500 °C may be attributed to the degradation of starch, as shown in DSC curves of neat starches in Fig. 5b. Although the prepared hydrogel samples are amorphous, no endothermic effect associated with the glass transition was observed – it should be masked by the other endothermic processes accompanied by the mass change described above.

**Figure 5.** DSC: a) AA and AAm, b) starches, c) non-cross-linked hydrogel (NH), d) cross-linked hydrogel (H).

### 3.5. Morphological analysis (SEM)

Scanning electron micrographs of prepared corn starch-g-(AA-AAm) hydrogels are shown in Fig. 6, where the differences between non-cross-linked and cross-linked hydrogels can be clearly observed. The SEM images suggested that the cross-section of cross-linked hydrogel was porous. Micrographs of the other hydrogels were similar to those of the corn starch-g-(AA-AAm) hydrogels.

**Figure 6.** SEM of corn starch-g-(AA-AAm) hydrogels: a) non-cross-linked, b) cross-linked. View field: 1000 µm.

### 3.6. Influence of reaction conditions on hydrogel swelling ratio

The corn starch-g-(AA-AAm) hydrogel was used as a reference material for the optimisation of swelling ability for all hydrogels.

It is known that SR depends on the composition of polymers, and this effect of increasing SR may be explained by the fact that the use of a nitrogen atmosphere does not allow reaction of free radicals from the initiator with oxygen, which has a negative influence on radical polymerisations due to its reaction with radicals present in the reaction mixture. The influence of inert atmosphere and of reaction time on SR is shown in Fig. S3.

### 3.6.1. Effect of cross-linking reagent content

The effect of MBA as a cross-linking agent on SR was tested on a corn starch hydrogel prepared under a nitrogen atmosphere. The dependence of SR of the hydrogel on MBA content (0–1 mL of 1 wt.% MBA) in the reaction mixture is illustrated in Fig. 7. The addition of MBA does not improve SR, and even a small amount (0.5 mL of 1 wt.% MBA) negatively affected the SR. The highest SR value (432 g water/g dry matter) was obtained for the hydrogel prepared without MBA, the reason for which may be that a higher content of MBA results in tighter cross-linking of copolymers that decreases the penetration of water into the hydrogel network.<sup>[49]</sup>

**Figure 7.** The dependence of SR of hydrogel on MBA content (0–1 mL of 1 wt.% MBA). The hydrogels were prepared with 1 g of AAm, 1.9 ml of AA, 2 g of starch, 0.5 mL of 1 % PSA, neutralization pH 6–7, 3 hours.

### 3.6.2. Effect of starch type and AAm content

The dependence of the SR of starch-g-(AA-AAm) hydrogels on AAm content (1 g or 0.5 g) is shown in Fig. 8a. The SR was improved using 0.5 g of AAm, with the highest SR (780 g water/g dry matter) observed for the hydrogel prepared with 0.5 g AAm and waxy corn starch. Influence of different amount of AAm (0.2–1.5 g) investigated for hydrogels prepared from corn starch (Fig. 8b) confirmed these results. The high SR of the waxy corn starch hydrogel is, in all likelihood, due to the high content of amylopectin (up to 99%), whereas the content of this polysaccharide in other starches is about 20% lower.<sup>[30]</sup> Accordingly, hydrogels prepared using these starches had SR values almost 200–250 g water/g dry matter lower, which can be explained by the formation of gel particles from starch granules during gelatinisation. The swollen granules are mainly composed of amylopectin, whereas the linear amylose molecules leach out and become part of the continuous phase. Therefore, waxy starches have a higher degree of swelling, and amylose is proposed to act as a swelling inhibitor.<sup>[39, 50]</sup> The short branched chains of amylopectin form gel-balls when swollen, and amylopectin molecules can form separated super-globes.<sup>[49, 51]</sup> These tight structures caused by the short branched chains likely hinder the grafting reaction.<sup>[49]</sup>

The SR of all grafted starch hydrogels (with the exception of potato starch hydrogel) decreased by about 20–35% with increasing AAm content (0.5 g to 1 g). The largest difference in SR was observed for the

hydrogel prepared from waxy corn starch. The SR was reduced from 780 to 502 g water/g dry matter with increasing AAm content, likely due to the lower density of the hydrogel network in the case of the lower AAm-containing polymer, where water can penetrate more easily into its structure and hydrophilic functional groups are available to bind water.

The SR of hydrogel prepared from potato starch was unaffected by the amount of AAm (0.5 or 1.0 g), which may be due to the different effects of AAm on the density of polymer networks of hydrogels from starches of different origin.

**Figure 8.** The dependence of the SR of hydrogels on content of AAm: a) for all starches (1 g or 0.5 g), b) for corn starch hydrogel (0.2–1.5 g). Reaction conditions: 1.9 ml of AA, 2 g of starch, 0.5 mL of 1 % PSA, neutralization pH 6–7, 3 hours.

### 3.7. Swelling of hydrogels in water at various pH levels

The aim of this experiment was to determine the effect of varying the pH (between 3–8) of water on the swelling behaviour of the hydrogel. Hydrogels used as soil improvers should have good stability in slightly acidic-to-neutral soil reactions, as this is the pH range most commonly measured in cultivated soils.<sup>[52]</sup> The SR values of hydrogels prepared with and without MBA are shown in Fig. 9a,b. The maximum SR was obtained at slightly acidic-to-neutral pH values (5–7). Up to pH = 8, carboxylate anions are protonated, eliminating the main anion-anion repulsive forces and, conversely, decreasing SR.<sup>[2, 53, 54]</sup> At low pH (3), SR is reduced due to protonation of the carboxylate groups (from  $\text{COO}^-$  to  $\text{COOH}$ ) and to physical crosslinking as a result of H-bond formation in the hydrogel structure.<sup>[39]</sup> These results are in good agreement with previous reports.<sup>[2, 41, 49]</sup> Differences between SR of non-cross-linked and cross-linked hydrogels can be associated with pKa of the polymer and pH of the surrounding medium. When the pKa is higher than the pH of the surrounding medium, the ionized structure will provide increased electrostatic repulsion of the network and, thus, enhance the swelling properties.<sup>[55]</sup> The relation between SR at different pH and cross-linking degree of hydrogel network was also shown in study of Mahkam (2005): with higher percentage of crosslinking agent, SR of hydrogels decreases, which is in agreement with our results.<sup>[56]</sup>

In summary, the optimal pH is between 5–7, and it follows that these hydrogels are suitable for application as soil moisture regulators on agriculturally utilised soils.

**Figure 9.** Influence of pH on SR of starch-g-(AA-AAm) hydrogels: a) non-cross-linked (NH), b) cross-linked hydrogels (H).

### 3.8. Swelling of hydrogels in fertiliser solutions

The starch-g-(AA-AAm) hydrogels were swollen in unsaturated solutions of urea, ammonium sulphate and calcium nitrate (all 4 mol L<sup>-1</sup>), in order to determine whether the hydrogels could be used as nutrient sources for plants in agriculture. These substances were selected as nitrogen sources, the most commonly used nutrient.<sup>[57]</sup>

The non-cross-linked hydrogels exhibited a slightly higher SR in all fertiliser solutions in comparison with cross-linked hydrogels. In general, the lowest SR values were observed with hydrogels swollen in calcium nitrate solution (Fig. 10a,b), which may be explained by the fact that divalent Ca<sup>2+</sup> cations form complexes with the carboxyl groups, and provide an additional ionic cross-linking which may reduce SR. It can be clearly seen that SR increased in solutions containing monovalent cations (e.g., NH<sub>4</sub><sup>+</sup>). However, this effect also depends on the cation ionic radius, as penetration of water into the hydrogel decreases with increasing ionic radius.<sup>[29]</sup> The highest SR values were observed for hydrogels swollen in urea solutions. The SR of the non-cross-linked hydrogel prepared with waxy corn starch was 327 g urea solution/g dry matter, and the same cross-linked hydrogel absorbed only 135 g urea solution/g dry matter. The high SR are likely due to the interaction of urea with polar hydrogel groups to form hydrogen bonds.<sup>[29]</sup> From these results, it can be concluded that the tested hydrogels can be saturated in neutral compounds, as shown in the case of urea solutions, and, thus, can be used as sources for release of fertilisers.

**Figure 10.** SR of a) non-cross-linked, b) cross-linked starch-g-(AA-AAm) hydrogels in fertiliser solution.

### 3.9. Water solubility of hydrogels

#### 3.9.1. Influence of amount of cross-linking agent

Hydrogels used as soil conditioners should have minimal solubility in water. The solubility of the cross-linked corn starch-g-(AA-AAm) hydrogel prepared with 1.0 g of AA and 1 wt.% MBA solution as cross-linking agent (0–1 mL) is shown in Fig. 11a, where it can be seen that the water solubility increased with decreasing amounts of MBA. It follows that cross-linking of the structure may play an important role in the water solubility of hydrogels. Non-cross-linked hydrogels absorb more water, but have higher water

solubility in comparison with cross-linked hydrogels. This is in accordance with a previous report [58], where it was claimed that MBA concentration up to 10%, in a mixture of reaction components for preparation of polymer latexes, enables the reduction of water-soluble polymer formed during polymerisation, down to a minimum value of approximately 10%.

### 3.9.2. Influence of amount of AAm

The solubility of non-cross-linked hydrogels prepared from different types of starches with AAm (0.5 g or 1 g) is shown in Fig. 11b. It appears that the type of starch did not significantly affect the solubility of starch-g-(AA-AAm) hydrogels, which is confirmed in Fig. 11c, where the solubility of non-cross-linked and cross-linked hydrogels from different types of starch are shown. Therefore, the solubility of hydrogels prepared from corn starch and different amounts of AAm (0.2–1.5 g) was explored, with results shown in Fig 10d. The solubility plays an important role in the degree of polymerisation. A low degree of cross-linking of the network increases the solubility of the hydrogel due to the content of water-soluble monomers and polymer chains. Lanthong (2006) reported that the cross-linked hydrogel was insoluble in water while the non-cross-linked hydrogel was found in the water extract,<sup>[59]</sup> which confirmed higher solubility in water of non-cross-linked hydrogels.

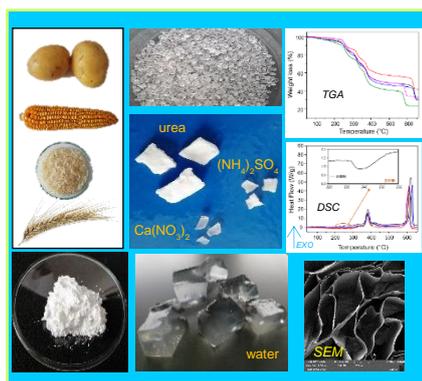
**Figure 11.** WS of starch-g-(AA-AAm) hydrogel: a) different volume of MBA, b) different amount (0.5 g or 1.0 g) of AAm for all starches, c) non-cross-linked and cross-linked starch-g-(AA-AAm) hydrogel, d) different amount of AAm (0.2 g to 1.5 g) for corn starch hydrogel. For synthesis, 0.5 mL of MBA was used.

## 4. Conclusion

Starch-g-(AA-AAm) hydrogels were synthesised via a cross-linking graft copolymerisation of AA, AAm and MBA onto starches from different natural sources. The synthesis of hydrogels was optimized using various parameters effecting the final product. Many factors, including type of starch, ratio of AAm/AA, degree of cross-linking and pH of water used in swelling experiments, have a significant influence on the SR of hydrogels. The maximum water absorbency was achieved under optimum conditions that were determined as 0.5 g AAm, 1.9 mL of AA, 2 g of starch, 0.5 mL of 1 % (w/w) PSA, 0.5 mL of 1 % (w/w) MBA, neutralization to pH 6–7 and reaction temperature of 50°C. SR was improved by decreasing MBA and AAm contents in the reaction mixture; however, the water solubility of the prepared hydrogels

increases as the degree of cross-linking decreases. The highest SR in water (780 g water/g dry matter) was observed for the non-cross-linked hydrogel prepared from waxy corn starch, using 0.5 g AAm. SR also significantly depends on the cation type in fertilisers. It was found that starch-g-(AA-AAm) hydrogels are stable, and have a maximised SR within the pH range of 5–7, which is the range where soil reactions occur in agriculturally used soils. Due to their high SR values, these hydrogels may be useful as alternative materials for the regulation of soil moisture during the dry season. The solubility of grafted starch hydrogels in water depends on the cross-linking degree – with increased cross-linking, hydrogel solubility decreases.

## Graphical abstract



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## Figure and legends

**Figure 1.** Proposed reaction mechanism for the synthesis of starch-g-(AA-AAm) hydrogels: a) initiation, b) co-polymerisation, c) starch macroradical formation, d) grafting and cross-linking.

**Figure 2.** FTIR spectra of a) starch and b) starch-g-(AA-AAm) hydrogel

**Figure 3.** TGA: a) starches, b) AAm and AA, c) dTG of starches, d) dTG of AAm and AA. The measurement conditions: 10 °C/min to 650 °C under air atmosphere.

**Figure 4.** TGA of hydrogels: a) non-cross-linked (NH), b) cross-linked (H). dTG of hydrogels: c) NH, d) H. The measurement conditions: 10 °C/min to 650 °C under air atmosphere.

**Figure 5.** DSC: a) AA and AAm, b) starches, c) non-cross-linked hydrogel (NH), d) cross-linked hydrogel (H).

**Figure 6.** SEM of corn starch-g-(AA-AAm) hydrogels: a) non-cross-linked, b) cross-linked. View field: 1000 µm.

**Figure 7.** The dependence of SR of hydrogel on MBA content (0–1 mL of 1 wt.% MBA). The hydrogels were prepared with 1 g of AAm, 1.9 ml of AA, 2 g of starch, 0.5 mL of 1 % PSA, neutralization pH 6–7, 3 hours.

**Figure 8.** The dependence of the SR of hydrogels on content of AAm: a) for all starches (1 g or 0.5 g), b) for corn starch hydrogel (0.2–1.5 g). Reaction conditions: 1.9 ml of AA, 2 g of starch, 0.5 mL of 1 % PSA, neutralization pH 6–7, 3 hours.

**Figure 9.** Influence of pH on SR of starch-g-(AA-AAm) hydrogels: a) non-cross-linked (NH), b) cross-linked hydrogels (H).

**Figure 10.** SR of a) non-cross-linked, b) cross-linked starch-g-(AA-AAm) hydrogels in fertiliser solution.

**Figure 11.** WS of starch-g-(AA-AAm) hydrogel: a) different volume of MBA, b) different amount (0.5 g or 1.0 g) of AAm for all starches, c) non-cross-linked and cross-linked starch-g-(AA-AAm) hydrogel, d) different amount of AAm (0.2 g to 1.5 g) for wheat starch hydrogel. For synthesis, 0.5 mL of MBA was used.

**Figure S1.** XRD curves of corn starch-g-(AA-AAm) hydrogels: a) non-cross-linked, b) cross-linked. The X-ray diffraction patterns were determined using  $K\alpha, Cu$  radiation. The voltage and current used were 40 kV and 15 mA, respectively.

**Figure S2.** TGA and dTG curves of non-cross-linked hydrogels (NH) recorded under an argon atmosphere. The measurement conditions: 10 °C/min to 350 °C.

**Figure S3.** Influence of a) nitrogen atmosphere, b) reaction time in dryer (under air atmosphere) on swelling ratio of corn starch-g-(AA-AAm) hydrogel.

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## **Conflict of interest statement**

The authors have declared no conflict of interest.

## **Novelty statement:**

Till this time there has been no report published on the effect of different natural origin of starch on swelling properties of the starch based hydrogels prepared by graft-copolymerization technique. To the best of our knowledge, no previous report describing such a comparison of five different starch hydrogels, synthesised with or without cross-linking agent, has yet been published.

## Tables

**Table 1.** Temperatures corresponding to the onset and maxima on dTG curves shown in Fig. 3c, d (AA), referred as the first, second and third peak in accordance with the text and in the order of increasing temperature

| sample    | 1 <sup>st</sup> $\Delta m$ step <sup>a</sup> |                     | 2 <sup>nd</sup> $\Delta m$ step <sup>b</sup> |                     | 3 <sup>rd</sup> $\Delta m$ step <sup>a</sup> |                     |
|-----------|--|---------------------|--|---------------------|--|---------------------|
|           | T <sub>ons</sub> (°C)                        | T <sub>p</sub> (°C) | T <sub>ons</sub> (°C)                        | T <sub>p</sub> (°C) | T <sub>ons</sub> (°C)                        | T <sub>p</sub> (°C) |
| Potato    | 41   | 79                  | 287  | 300                 | 426  | 494                 |
| Corn      | 39   | 72                  | 294  | 311                 | 439  | 507                 |
| Wheat     | 46   | 72                  | 295  | 304                 | 442  | 502                 |
| Rice      | 39   | 72                  | 291  | 313                 | 464  | 487                 |
| Waxy corn | 47   | 60-78<br>(plateau)  | 293  | 319                 | 453  | 501                 |
| AA        | 37   | 78                  | 207  | 345                 | 470  | 536                 |

The error limit of T<sub>ons</sub> and T<sub>p</sub> is about: <sup>a</sup>2 °C, <sup>b</sup>0.5 °C

**Table 2.** Temperatures corresponding to the onset and maximum of dTG curves given in Fig. 3d (AAm) and 4c,d, referred as the first, second, third, fourth and fifth peak in accordance with the text and in the order of increasing temperature

| sample       | 1 <sup>st</sup> $\Delta m$ step <sup>a</sup> |                     | 2 <sup>nd</sup> $\Delta m$ step <sup>b</sup> |                     | 3 <sup>rd</sup> $\Delta m$ step <sup>b</sup> |                     | 4 <sup>th</sup> $\Delta m$ step <sup>b</sup> |                     | 5 <sup>th</sup> $\Delta m$ step <sup>b</sup> |                     |
|--------------|--|---------------------|--|---------------------|--|---------------------|--|---------------------|--|---------------------|
|              | T <sub>ons</sub> (°C)                        | T <sub>p</sub> (°C) |
| Potato NH    | 47   | 86                  | 232  | 253                 | 269  | 315                 | 360  | 379                 | 619  | 635                 |
| Potato H     | -  | -                   | 232  | 260                 | 257  | 310                 | 379  | 357                 | 600  | 618                 |
| Corn NH      | 53   | 105                 | 238  | 256                 | 306  | 323                 | 357  | 378                 | 615  | 630                 |
| Corn H       | -  | -                   | 236  | 252                 | 306  | 324                 | 356  | 374                 | 594  | 610                 |
| Wheat NH     | 42   | 94                  | 237  | 264                 | 306  | 322                 | 356  | 379                 | 625  | 640                 |
| Wheat H      | -  | -                   | 244  | 257                 | 301  | 320                 | 360  | 384                 | 609  | 628                 |
| Rice NH      | 30   | 97                  | 239  | 264                 | 298  | 326                 | 347  | 368                 | 568  | 586                 |
| Rice H       | 48   | 68                  | 232  | 253                 | 309  | 330                 | 357  | 377                 | 588  | 606                 |
| Waxy corn NH | -  | -                   | 246  | 262                 | 316  | 333                 | 349  | 370                 | 563  | 581                 |
| Waxy corn H  | 48   | 68                  | 236  | 254                 | 306  | 328                 | 355  | 373                 | 589  | 608                 |
| AAm          | 125  | 157                 | 227  | 240                 | 270  | 307-323             | 364  | 387                 | 456  | 558                 |

<sup>a</sup>Only rough estimation of T<sub>ons</sub> and T<sub>p</sub>; <sup>b</sup>the error limit of T<sub>ons</sub> and T<sub>p</sub> is about 0.5 °C

**Table S2.** Temperatures corresponding to the onset and maximum of dTG curves given in Figure S2, referred as the first, second and third peak in accordance with the text and the order of increasing temperature

| sample    | 1 <sup>st</sup> $\Delta m$ step <sup>a</sup> |                     | 2 <sup>nd</sup> $\Delta m$ step <sup>b</sup> |                     | 3 <sup>rd</sup> $\Delta m$ step <sup>b</sup> |                     |
|-----------|--|---------------------|--|---------------------|--|---------------------|
|           | T <sub>ons</sub> (°C)                        | T <sub>p</sub> (°C) | T <sub>ons</sub> (°C)                        | T <sub>p</sub> (°C) | T <sub>ons</sub> (°C)                        | T <sub>p</sub> (°C) |
| Potato    | 121  | 128                 | 228  | 236                 | 311  | 327                 |
| Corn      | 121  | 129                 | 230  | 255                 | 306  | 328                 |
| Wheat     | 123  | 129                 | 246  | 260                 | 317  | 330                 |
| Rice      | 121  | 129                 | 241  | 264                 | 310  | 328                 |
| Waxy corn | 121  | 128                 | 229  | 254                 | 307  | 321                 |

The error limit of T<sub>ons</sub> and T<sub>p</sub> is about: <sup>a</sup>0.5 °C, <sup>b</sup>1 °C

## Supporting Information

**Figure S1.** XRD curves of corn starch-g-(AA-AAm) hydrogels: a) non-cross-linked, b) cross-linked.

The X-ray diffraction patterns were determined using  $K\alpha, Cu$  radiation. The voltage and current used were 40 kV and 15 mA, respectively.

**Figure S2.** TGA and dTG curves of non-cross-linked hydrogels (NH) recorded under an argon atmosphere. The measurement conditions: 10 °C/min to 350 °C.

**Table S2.** Temperatures corresponding to the onset and maximum of dTG curves given in Figure S2, referred as the first, second and third peak in accordance with the text and the order of increasing temperature.

### Effect of nitrogen atmosphere and reaction time

Corn starch was used for preparation of cross-linked hydrogel under a nitrogen atmosphere, in order to eliminate the reaction of atmospheric oxygen with radicals originating from the PSA initiator, and to evaluate the effect of these conditions on the swelling ratio of the product (Fig.S3a). As expected, the swelling ratio of the prepared hydrogel was improved when the synthesis was performed under a nitrogen atmosphere.

The reaction time required for completion of polymerisation reaction in a dryer on the SR of the hydrogel is shown in Fig. S3b. The optimum time was established to be 2 h at 75 °C. The SR of the hydrogel prepared under these conditions was enhanced from 126 to 170 g water/g dry matter at the same temperature (75 °C). Longer reaction times led to a higher degree of cross-linking of the hydrogel network, which reduces the penetration of water into the hydrogel structure and decreases the SR.<sup>[60]</sup>

**Figure S3.** Influence of a) nitrogen atmosphere, b) reaction time in dryer (under air atmosphere) on swelling ratio of corn starch-g-(AA-AAm) hydrogel.