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# Synthesis and Properties of Novel Hydrogels from Cross-linked Starch Phosphates

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**Summary:** Starch based stable hydrogels providing high swelling and water storing capacity are not only of certain interest for the cosmetics and hygiene industry but also have the potential to become an effective tool in combating desertification and supporting cultivation in many regions of the world. It has been found that strong water adsorbing covalent networks with free swelling capacity (FSC) of up to 190 g water/g hydrogel can be obtained by cross-linking low-substituted mono-starch phosphates (MSP) in a semi-dry process with di- and tricarboxylic acids such as succinic acid (SA), adipic acid (AA) or citric acid (CA). The linear behaviour over a wide frequency range of the rheological parameters G′ and G″ which were determined by using a shearing disc viscosimeter clearly reveal that the cross-linked starch phosphates are stable hydrogels having stronger elastic than viscous properties.

**Keywords:** cross-linked starch; Hydrogels; rheology; starch phosphates

## Introduction

Modified starch is widely used in food[1–3] as well as non-food applications.[3] In non-food applications, modified starch finds wide application in pharmaceutical products,[4] cosmetics and as well as medical[4,5] and sanitary products,[6,7] where mechanically stable gels with high water storing capacity and swelling power are desired.

Modified starch products also have a big potential to be used as water storing soil amendment,[7–9] especially in arid regions where the climatic water balance is negative. Their applications could significantly improve the survival rate of new plantations, the growth and vitality of plants as well as the yields of economic plants. On the other hand, this could not only significantly reduce expenditure on irrigation, which is of economic importance, but also decelerate topsoil salinization. Furthermore, starch hydrogels could be an environmental friendly alternative to the utilization of so-called synthetic superabsorbants of the polyacrylate or polyacrylamide type, which possess some weaknesses such as low biodegradability, deterioration of the soil structure by very strong swelling and shrinking. Higher application rates can quickly lead to philistine conditions. In addition, there are some toxicological concerns, since polyacrylamides and polyacrylic acids usually contain a certain amount of the carcinogenic monomers from which they are made.[5,7]

However, two disadvantages have to be taken into consideration when starch is going to be used as soil improving material: partial solubility in water and easy degradation by soil microorganisms. It is known that more persistant starch derivatives can be obtained by cross-linking of the amylose and amylopectin chains with suitable bi- or polyfunctional reagents.[7]

Cross-linking of starch is simple and can be achieved by treating the corresponding

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native starch or starch derivatives with suitable bifunctional reagents. In order to obtain more defined products, the anhydroglucose units (AGU) are commonly modified by introducing functional groups such as carboxymethyl[10–13] or phosphate substituents[14,15] prior to cross-linking.

Carboxymethyl starch (CMS) and the corresponding cross-linked products[6,7,16] are probably one of the most comprehensively studied class of starch derivatives.

However, starch phosphates and the corresponding cross-linked derivatives also play an important role in food industry where they are used as thickeners, binders, stabilizers, gelating agents and emulsifiers.[17,18] In the paper industry they are used as additives to increase the strength of paper.[19]

Heinze et al.[20] found that starch carbamides, which can be obtained by cross-linking of starch phosphates with urea, have high swelling capacities (i.e. 300 g water/g starch phosphate carbamides) but have less favourable mechanical properties.

In nature only potato starch contains chemically bound phosphorus with a frequency of once every 20–300 glucose units[18] corresponding with phosphorus contents of 0.06 to 0.8%. Chemically, starch phosphates can be obtained by esterification of native starch with phosphorylating agents such as orthophosphates, metaphosphates, or phosphorous oxychloride.[21] Phosphorylation of starch under alkaline conditions gives cross-linked distarch phosphates which can be used as cation exchangers and flocculants due to their increased molecular mass and negative charge.[21] In acidic media, phosphorylation is carried out preferably by treating starch with sodium dihydrogen phosphate and/or disodium hydrogen phosphate under dry conditions at 150–180 °C. Under these conditions mono starch phosphates (MSP) with a higher degree of substitution ($DS_p$) are formed.[22] Atmospheric oxygen and moisture induce undefined side reactions i.e. the formation of di- and tri-starch phosphates as well as cross-linked starch phosphates or oxidation products.[22]

Several authors have found that starch phosphatation results in the cleavage of intermolecular bonds, tendency of gel formation as well as the formation of products having an enhanced hydratation capacity.[23,24] Starch phosphates in general show increased mechanical stability.[17]

However, cross-linked starch phosphate diesters which can be obtained from the reaction of starch with phosphorus oxychloride in pyridine[25] show a distinctly inhibited granule swelling. Since the reaction of starch with cross-bonding agents (polyfunctional compounds such as dicarboxylic acids, anhydrides, and aldehydes) cannot be controlled to give monoesters alone or even monoesters with a controlled degree of cross-linking, it is customary to mono-esterify and cross-link the starch in separate reactions.[19] For our investigations we followed this synthesis path in order to obtain stable hydrogels having suitable mechanical properties to be used as soil improving materials (Figure 1).

## Experimental

### Starch

Starch (soluble starch) was purchased from Merck, Darmstadt, Germany.

### Phosphorylation of Starch

Phosphorylation of starch was performed according to[14,22,26] with slight modifications and without using a vacuum oven. The amounts of sodium dihydrogen phosphate monohydrate $NaH_2PO_4 \cdot H_2O$ and disodium hydrogen phosphate dihydrate $Na_2HPO_4 \cdot 2H_2O$ which were used for the preparation of different starch/phosphate ratios can be seen in Table 1.

Prior to phosphorylation, both salts were dissolved in 20 ml of de-ionized water at 35 °C and a pH of 6 adjusted by adding a few drops of a 3.3 M aqueous NaOH solution. 10 g of starch were added to the salt solution and the mixture was stirred for 20 min at ambient temperature. The resulting slurry was vacuum filtered using a Büchner funnel and the filter cake was

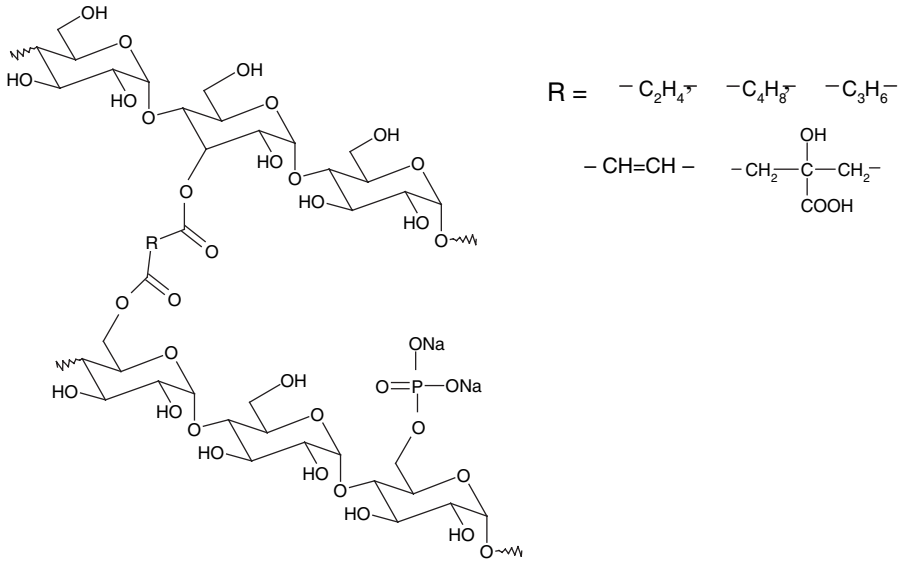



***Figure 1.***
Schematic representation of a section from cross-linked mono-starch phosphate.

crumbled and dried for 24 h at 55 °C. The crumbly mixture was then pulverized in a beetling mill and dried again at 65 °C for 90 min.

For starch phosphorylation, the dried mixture was "baked" at 150 °C for 3 h, cooled down to room temperature and stirred in 50 ml of 50% aqueous methanol for 30 min. After filtering (Büchner funnel), the crude product was dehydrated by washing with 20 ml of absolute ethanol. The resulting paste was washed with a ten-fold amount of water for 24 h. The starch phosphate was precipitated with acetone with about 75% yield. The product was vacuum-filtrated, repeatedly washed with absolute ethanol in order to remove water and acetone and finally dried at 45 °C before grinding.

### Determination of Phosphorus Content and Degree of Substitution $DS_P$

For the determination of the phosphorus content a method developed by Murphy and Riley[27] modified by Wongsagonsup et al.[28] was used with slight modifications:

***Table 1.***
Amounts of Phosphorylation Reagents, Phosphorus Contents and Values of Degree of Substitution ($DS_p$) of the Products.

| Molar ratio phosphate/starch | $NaH_2PO_4 \cdot H_2O$ [a] | | $Na_2HPO_4 \cdot 2H_2O$ [a] | | P [%] | $DS_p$ |
|---|---|---|---|---|---|---|
| | [g] | [mol] | [g] | [mol] | | |
| 0.125:1 | 0.69 | 0.005 | 0.69 | 0.04 | 0.69 | 0.04 |
| 0.25:1 | 1.38 | 0.01 | 0.76 | 0.05 | 0.76 | 0.05 |
| 0.5:1 | 2.76 | 0.02 | 1.13 | 0.09 | 1.13 | 0.09 |
| 1:1 | 5.52 | 0.04 | 2.12 | 0.14 | 2.12 | 0.14 |
| 1.5:1 | 8.28 | 0.06 | 3.26 | 0.21 | 3.26 | 0.21 |
| 2:1 | 11.04 | 0.08 | 3.74 | 0.24 | 3.74 | 0.24 |
| 2.5:1 | 13.80 | 0.1 | 5.59 | 0.35 | 5.59 | 0.35 |

[a] amounts of $NaH_2PO_4 \cdot H_2O$ and $Na_2HPO_4 \cdot 2H_2O$ related to 10 g starch.

A solution of 0.3 g $Na_2CO_3$ in 2 ml of de-ionized water was placed in a crucible, and 0.5 g of starch phosphate was than added and thoroughly mixed. The moist paste was dried at 100 °C prior to ashing in a muffle furnace at 550 °C for 9 h. After cooling down to room temperature, 2 ml of 25% HCl in 10 ml distilled water were added. The solution was then transferred into a beaker and filled up to a volume of 50 ml with distilled water. The mixture was stirred and filtered through a glass funnel with filter paper. The solution was diluted to 250 ml by addition of distilled water. 10 ml of this solution were mixed with 2ml of vanadate-molybdate reagent. The sulfuric acid containing vanadate-molybdate solution was purchased from Merck, Darmstadt, Germany. The absorbance of the sample at 435 nm was measured using a UV-VIS spectrophotometer (SHIMADZU UV-2101PC) 45 min after adding vanadate-molybdate.

The percentage of phosporous was calculated from a standard curve which was prepared from different amounts of $NaH_2PO_4 \cdot H_2O$.

The degrees of substitution by phosphate monoester groups were calculated according to Wongsagonsup[28] with P being the percentage of phosphorus content (dry basis) of the starch phosphate.

### FT-IR Spectroscopy

FT-IR spectra were recorded with a PERKIN ELMER FT IR Spectrometer 1725X. Potassium bromide pellets were prepared from a mixture of 1 mg of the absolute dry sample with 100 mg of dry potassium bromide.

### $^{31}$P- and $^{1}$H NMR Spectroscopy

$^{31}$P- and $^{1}$H NMR spectra were recorded with a BRUKER 500 DRX NMR spectrometer at 202.47 MHz ($^{31}$P) and 500.13 MHz ($^{1}$H), respectively. The corresponding starch samples were dried by repeatedly washing with absolute ethanol and removal of residual moisture traces by drying the samples in a desiccator in the presence of silica gel. 100 mg of dried MSP sample ($DS_p$ 0.14) were added to 750 μl $D_2O$ in a NMR tube. Phosphoric acid was used as external standard. The spectra were recorded at ambient temperature.

### Cross-linking of Starch Phosphate

Cross-linking of mono-starch phosphate was performed by using different polyfunctional carboxylic acids and anhydrides, i.e. citric, succinic, glutaric, adipic, maleic acid, and succinic anhydride. The aim was to investigate the influence of the amount of cross-linking agent and the influence of different spacers on gel structure and properties. The cross-linking of mono-starch phosphates was performed according to the method used for the preparation of hydrogels from carboxymethyl starch and polyfunctional carboxylic acids as cross-linking agents.[5–7,16,29] The cross-linking agent used was first dissolved in 10 ml of de-ionized water and then mixed vigorously with 10 g of the phosphorylated starch, resulting in a homogeneous syrup-like product. The latter was heated up to 150 °C for 3 h to accomplish cross-linking. The product obtained was pulverized in a mill, washed with de-ionized water and dried at 80 °C.

The following amounts of cross-linkers were used: 2.5–50 mg/g (0.013–0.26 mmol/g) MSP of citric acid, 11.69 mg/g (0.08 mmol/g) MSP of adipic acid, 9.45 mg/g (0.08 mmol/g) MSP of succinic acid, 10.58 mg/g (0.08 mmol/g) MSP of glutaric acid, 9.29 mg/g (0.08 mmol/g) MSP of maleic acid, and 1,5 mg/g (0.015 mmol/g) MSP of succinic anhydride.

### Determination of Free Swelling Capacity FSC

The swelling behaviour of the hydrogels was examined by placing 0.5 g of the corresponding sample into a G3 fritted glass filter of known weight. De-ionized water was then added over a time period of one hour until the sample was fully saturated with water. Excess water was dripped off from the swollen gel for ten minutes. The mass of the stored water was then determined by weighing the fritted

glass filter. The FSC values in g water/g dry hydrogel were determined as followed:

$$FSC = \frac{g(H_2O)}{g(sample)} = \frac{weight_{wet}(filter_{wet} + sample_{swollen}) - blank(filter_{wet})}{weight(sample_{dry})}$$

where *filter* is fritted glass filter.

#### Scanning Electron Microscopy SEM

Pictures of the dry hydrogel surface were obtained by using a JOEL scanning electron microscope unit T330A operating at 15 kV acceleration voltage. Pre-dried samples of the cross-linked starch derivatives were doubly-coated by vaporizing their surface with a 40 nm carbon layer under high-vacuum (vaporizing unit EMI-TECH K950) and finally sputter-coating with a 30 nm gold layer (ion sputter JOEL JFC 1100E). This technique was chosen with respect to the strongly rugged surfaces of the cross-linked starch derivatives.

#### Rheometry

It is common to use rheological measurements for characterizing network structures. The method of choice for cross-linked structures is a dynamic measurement. In dynamic oscillatory tests, a sinusoidal oscillation with defined deformation $\gamma$ and frequency $\omega$ is applied to the material and a resultant sinusoidal strain (or stress) is measured.[30,31]

From the oscillatory measurements, the viscous and elastic properties of investigated materials can be separately calculated by determining the storage modulus $G'$ (elastic component) and loss modulus $G''$ (viscous component). The tangent of phase difference, or tan $\delta$, is another common parameter that provides information on the relationship between the elastic and inelastic components.[29]

For rheological characterization total swollen hydrogels were used. The FSC values of gels investigated can be taken from Figures 3b and 4a. The rheological measurements were made at 20 °C with an oscillation rheometer (BOHLIN CVO, control system BOHLIN CS) and cone-plate geometry (Ø 40 mm; cone angle 4°). The manual shear stress was 0.2 Pa in a frequency region of $\omega = 0.02$–$20.0\ s^{-1}$ (frequency sweep).

## Results and Discussion

#### Starch Phosphates, Degree of Substitution $DS_p$

The introduction of anionic phosphate groups into the starch macromolecules increases the polar character of the starch. Hence, all starch phosphates obtained were easily soluble in cold water, giving clear colourless to light yellowish aqueous solutions.

The degree of substitution by phosphate groups $DS_p$ ranged between 0.04 and 0.35 (Table 1), corresponding to the different amounts of sodium phosphates which have been used for phosphorylation. $DS_p$ values were calculated according to Wongsagonsup[28] employing a modified version of the Paschall equation[26] and assuming that only primary phosphate esters were formed under the described reaction conditions.

#### FT-IR Spectroscopy

By comparing the FT-IR spectra of unmodified starch and the corresponding monostarch phosphates, minor spectral differences were observed in the region between 1180–1250 $cm^{-1}$ which are obviously caused by the P=O stretching vibration ($\nu$ P=O).[20] Other typical resonance signals such as the P-O-C bonding vibration could not be detected because of the dominating signals of the starch backbone (Figure 2a).

##### *$^{31}P$ and $^{1}H$ NMR Spectroscopy*

Figure 2b shows the $^{1}H/^{31}P$ HMBC spectrum of starch phosphate ($DS_p$ 0.14, solvent $D_2O$) with phosphoric acid as

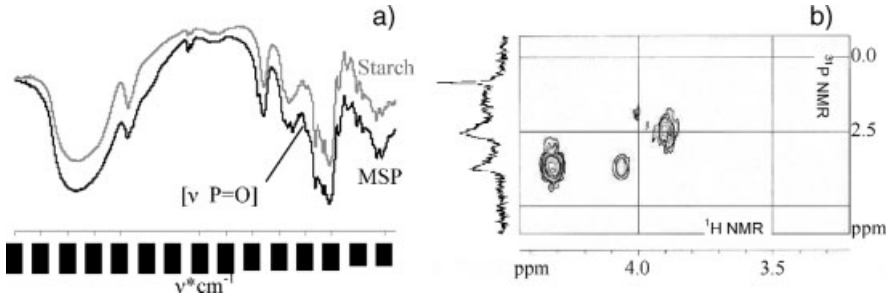



***Figure 2.***
(a) FT-IR and (b) $^{1}H/^{31}P$ HMBC NMR spectra of mono-starch phosphate (MSP) (degree of substitution 0.14, $^{1}H$ signal intensity not shown).

external standard. The most intensive signals were observed in the range from 0 to +5 ppm whereas a rather weak signal peaks at −8.5 ppm (not shown) indicating the presence of minor portions of di-starch phosphates which were reported to give resonance signals between −6 and −10 ppm.[20] The sharp signal at about 1 ppm is obviously caused by residual sodium dihydrogen phosphate.

The two broad peaks at about 2.5 and 3.6 ppm in the $^{31}P$ NMR spectrum clearly reveal that mainly mono-starch phosphates were formed under the selected reaction conditions. In principal, mono-starch phosphates usually give less sharp resonance signals in the range between 0 and +5 ppm. However, slightly different ranges for the $^{31}P$ NMR resonance signals of mono-starch phosphates were reported by several authors.[32–34] The differences may be caused by the known sensitivity of the chemical shift of $^{31}P$ NMR signals to pH changes near the pK values.[33] One of those sensitive ranges is pH 6 to 9 ($pK_{a2}$ of phosphoric acid) where starch phosphates are usually measured.

Furthermore, from the $^{1}H/^{31}P$ HMBC spectrum one may conclude that the broad signal at higher field (2.5 ppm) is rather caused by a primary phosphate group which is attached at the C-6 position of the AGU whereas the peak at 3.8 ppm can obviously be assigned to the corresponding C-2 and C-3 positions of the AGU due to the correlation with two $^{1}H$ NMR signals at 4.06 and 4.45 ppm. Assigning the peaks in this way would be in accordance with Santacruz et al.[34] and Frigård[35] who found a down-field shift of the C-3

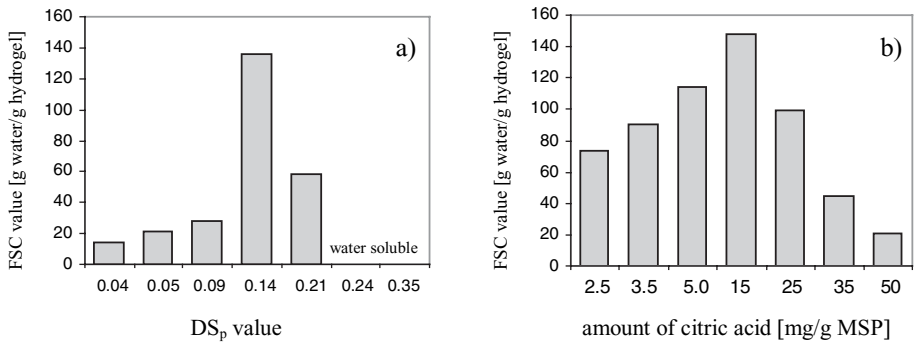
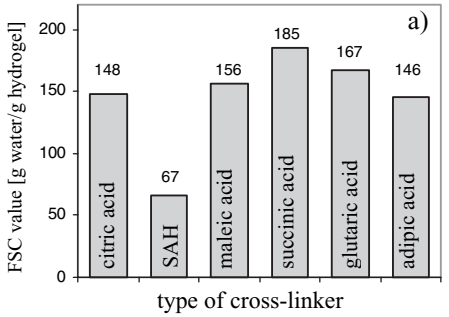



***Figure 3.***
(a) Dependency of free swelling capacity FSC on degree of substitution $DS_p$ for selected citric acid cross-linked mono-starch phosphates; (b) Interrelation between values of free swelling capacity FSC and the amount of cross-linking agent (citric acid) for a mono-starch phosphate with $DS_p$ 0.14.



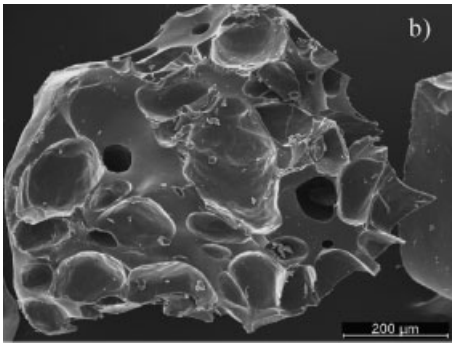




***Figure 4.***
a) Free swelling capacity (FSC) of mono-starch phosphate (MSP) hydrogels cross-linked with different dicarboxylic acids (0.08 mmol/g MSP), citric acid (0.08 mmol/g MSP), and succinic acid anhydride (SAH; 0.015 mmol/g MSP); MSP with degree of substitution, $DS_p$ 0.14; b) SEM picture of the surface of mono-starch phosphate ($DS_p$ 0.14) cross-linked with citric acid at a ratio of 1:0.015 (w/w).

phosphate in partly purified potato tuber amylopectin starch in comparison to C-6. Calculations with SPARTAN[36] using α-methyl glucoside and its 2-*O*-, 3-*O*-, and 6-*O*-phosphates as model compounds may support these findings because the estimated chemical shifts of 4.6 ppm (C-2) and 4.2 ppm (C-3) as well as the shift difference between these two signals correspond reasonably well to the values obtained.

### Influence of Degree of Substitution ($DS_p$) and Mono-Starch Phosphate/Cross-Linker Ratio on the Values of Free Swelling Capacity FSC

All the mono-starch phosphates obtained with $DS_p$ values between 0.04–0.35 were cross-linked with citric acid at a ratio of 0.25 mg of citric acid/g mono-starch phosphate (0.13 mmol/g). It has been found that the FSC of cross-linked mono-starch phosphates reaches a sharp maximum at a comparatively low $DS_p$ value of 0.14 (Figure 3a). Furthermore, $DS_p$ values higher than 0.24 gave water soluble products upon cross-linking which is obviously due to a strongly increasing polarity caused by the phosphate groups. Another reason for solubility of products with $DS_p$ values higher than 0.24 could be hindered cross-linking by phosphate groups.

Similar results were reported by Heinze et al.[20] They found that the swelling power of starch phosphate carbamides strongly depends on the $DS_p$ values of the mono-starch phosphates. They obtained an increase of the swelling ability up to a $DS_p$ of about 0.25 whereas higher $DS_p$ values result in a declining swelling power.

In a next step, the $DS_p$ 0.14 mono starch phosphate which was found to give the highest FSC value upon cross-linking with 25 mg of citric acid/g mono-starch phosphate was cross-linked with different amounts of citric acid i.e. 2.5–50 mg CA/g MSP (0.013–0.26 mmol CA/g MSP) in order to investigate the interrelationship between the amount of employed cross-linking agent and the obtained cross-linking density.

The free swelling capacities of the selected cross-linked mono-starch phosphate (Figure 3b) clearly reveal that the water adsorbing ability of the material studied increases at first with a rising concentration of citric acid. After reaching a FSC optimum of 147.8 g/g at a cross-linker concentration of 15 mg of citric acid per gram mono-starch phosphate (0.08 mmol CS/g MSP), the FSC values decline distinctly with further addition of citric acid. This is obviously due to an increasing agglomeration of the amylose and amylopectin molecules and hence the more hampered penetration of the network by the water molecules. On the other hand, the strengthening of the starch granules through cross-linking restricts their swelling

which also negatively affects the FSC values.

The results are consistent with those of several authors[19,37] where it was found that the swelling power and water-binding capacities of cross-linked starch phosphates usually decline when a certain degree of cross-linking is exceeded.

Generally, the FSC values obtained of our cross-linked mono-starch phosphates i.e. 21.0 to 147.8 g/g are in principle high enough to meet the demands of a soil-water storing material.

### Effect of the Type of Cross-Linking Agent on Free Swelling Capacity FSC

The effect of different cross-linking agents on gel formation and free swelling capacity was investigated by cross-linking a selected mono-starch phosphate with a $DS_p$ of 0.14 with several bifunctional organic compounds having different spacer distances between the two carboxylic groups. The following cross-linkers were studied i.e. maleic acid, succinic acid (C4 spacers), glutaric acid (C5 spacer) and adipic acid (C6 spacer), and succinic anhydride. The same amount of cross-linker (0.08 mmol) per gram mono-starch phosphate was used (except succinic anhydride where 0.015 mmol/g MSP was used) after heaving revealed that the highest FSC values were obtained at this rate when cross-linking the same mono-starch phosphate with citric acid.

Figure 4a shows that the highest FSC value was obtained by cross-linking mono-starch phosphate with succinic acid (185 g/g) whereas the lowest FSC value (146 g/g) amongst the dicarbxylic acids was obtained with adipic acid. The relative low FSC value (66.7 g/g) of the product cross-linked with succinic acid anhydride is caused by a small amount of cross-linking agent which was only 0.015 mmol/g MSP.

Furthermore there is a relationship between chain length of the spacer and the FSC of the resulting hydrogels when succinic, glutaric, and adipic acid are used: The higher the chain length of the spacer, the lower is the FSC of the resulting hydrogel. In that way succinic acid and probably the corresponding anhydride seems to be the most suited cross-linking agents of the studied dicarboxylic acids giving hydrogels with high swelling capacities. Figure 4b shows a SEM picture of the porous structure of a mono-starch phosphate which was cross-linked with citric acid at a MSP/citric acid ratio of 1:0.015 (w/w). The surface shows cavaties which have an average diameter of about 50 to 200 μm. According to Lechner and Lazik[7] gel particle diameters should be in the range of 100 to 500 μm for a fast water adsorption.

### Rheology

#### *Influence of Cross-Linking Density*

Figure 5–7 show the frequency dependence of dynamic viscosity $\eta^*$, storage modulus $G'$, loss modulus $G''$, and loss factor tan $\delta$ for selected hydrogels which were obtained by cross-linking a mono-starch phosphate with a $DS_p$ of 0.14 with different amounts of citric acid (2.5–50 mg CA/g MSP).

As Figure 5 illustrates, the products studied differ for about 2.5 orders of magnitude in their dynamic viscosities $\eta^*$ over the whole frequency range of $\omega = 0.4$ to 20 $s^{-1}$. The gel which was cross-linked with the highest amount of citric acid (50 mg/g MSP) shows the highest values. The lower the amount of the cross-linker, the lower also is the dynamic viscosity $\eta^*$ of the sample. This relationship points to the phenomenon, that with increasing cross-linking density the products become more viscous. In general, the viscosity of all gels shows a linear trend and decreases for about two orders of magnitude over the observed frequency range which is typical for gel structures.

The storage modulus $G'$ of the gels investigated (Figure 6a) is located in the plateau region of the oscillatory curve and is slightly increasing with increasing frequency $\omega$. The loss modulus $G''$ (Figure 6b) was found to be 0.25 to 1 order of magnitude lower than the storage modulus $G'$ which is typical for gel structures.[29]

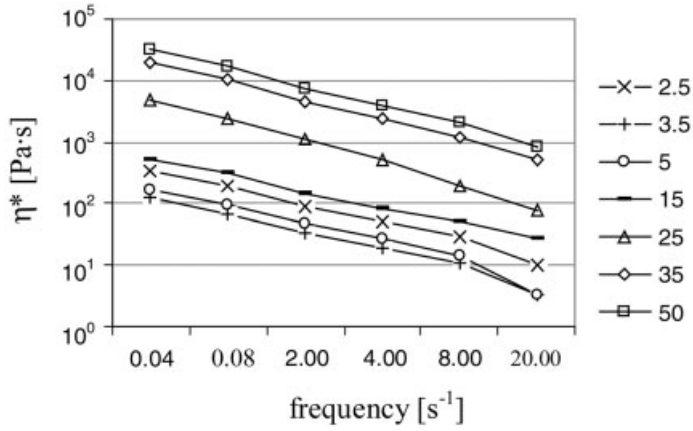



***Figure 5.***
Dynamic viscosity $\eta^*$ of mono-starch phosphate (MSP) hydrogels cross-linked with different amounts of citric acid (CA) in mg CA/g MSP (degree of substitution $DS_p$ 0.14).

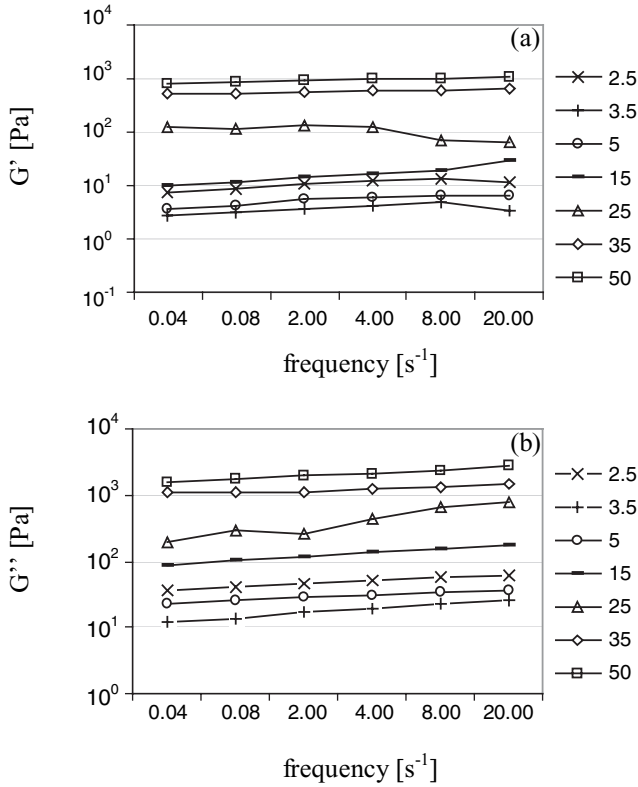



***Figure 6.***
(a) Storage modulus G′ and (b) loss modulus G″ of mono-starch phosphate (MSP) hydrogels cross linked with different amounts of citric acid (CA) in mg CA/g MSP (MSP with degree of substitution 0.14).

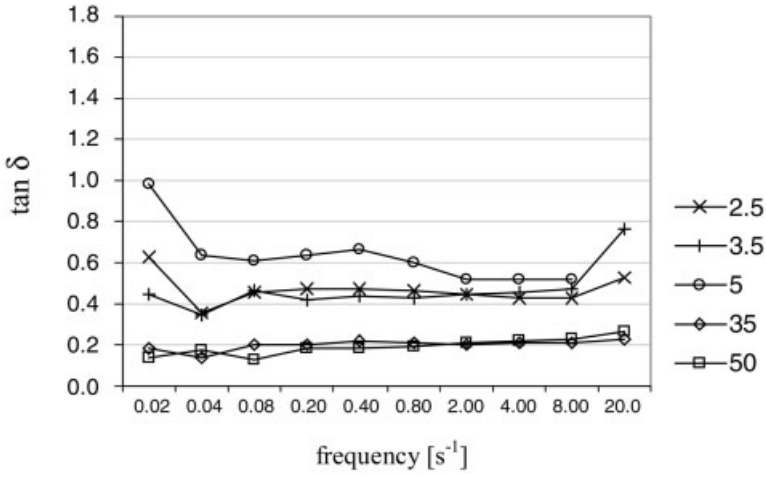



***Figure 7.***
tan δ of mono-starch phosphate (MSP) hydrogel cross-linked with different amounts of citric acid (CA) in mg CA/g MSP (MSP with degree of substitution 0.14).

Similar to the dynamic viscosities, G″ values of the hydrogels studied cover a wide range of about 2.5 orders of magnitude (Figure 6b). The highest G′ and G″ values were estimated for the product which was obtained from cross-linking with the highest amount of citric acid which indicates that elevated cross-linking density increase both viscosity and elasticity. In turn, increasing elasticity results in a higher strength of the gels.

The interrelation between frequency and loss factor tan δ is shown in Figure 7. The latter is calculated from the quotient of the loss modulus G″ and the storage modulus G′ reflecting the proportion between the dissipated and stored energy. The values obtained of tan δ range from 0 to 1 indicating the viscoelastic properties of the materials. The samples with a lower cross-linking density (2.5–5 mg CA/g MSP) were found to give a higher tan δ of about 0.5 than the MSP which were cross-linked with higher amounts of citric acid. On the other hand, the less cross-linked mono-starch phosphates are more sensitive to frequency changes on both sides of the studied range between 0.02 to 20 $s^{-1}$ whereas the tan δ of the hydrogels which have a higher cross-linking density (35–50 mg CA/g MSP) almost do not respond to frequency changes except a slight increase within the applied frequency scale. From the comparatively low tan δ values of about 0.2 corresponding to a more pronounced elastic portion one may conclude that such hydrogels are more stable than the mono-starch phosphates with a very low degree of cross-linking.

A maximum in the material functions dynamic viscosity $\eta^*$, storage modulus G′ and loss modulus G″ can be observed for gels with the highest cross-linking density by varying the cross-linking density and the amount of cross-linking agent respectively. Tan δ values of only about 0.15 indicate a rather small viscous part (G″) and comparatively high sturdiness.

**Influence of the Cross-Linking Agent**

Figures 8–10 show the frequency dependent measurements of dynamic viscosity $\eta^*$, storage modulus G′, loss modulus G″, and loss factor tan δ for starch phosphate based hydrogels which were obtained by cross-linking with different carboxylic acids i.e. citric, adipic-, succinic-, glutaric-, and maleic acid.

The dynamic viscosity $\eta^*$ (Figure 8) of all samples decreases almost linearly for about 2 orders of magnitude within the measured frequency range from 0.08 to

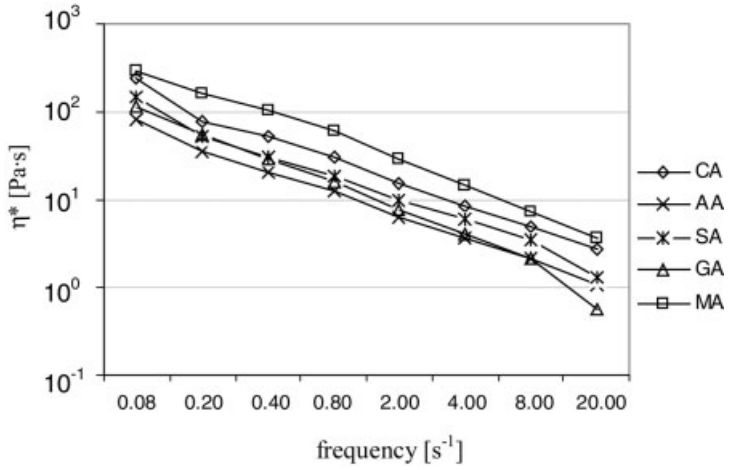



***Figure 8.***
Dynamic viscosity $\eta^*$ of mono-starch phosphate (MSP) hydrogels cross-linked with citric acid (CA), maleic acid (MA), succinic acid (SA), glutaric acid (GA) and adipic acid (AA) (MSP with degree of substitution 0.14).

$20\ s^{-1}$ reflecting the typical behaviour of gel structures as already stated above (compare with Figure 5). Furthermore, a clear relationship between viscosity and the chain length of the spacer which separates the carboxylic groups of the cross-linking agents can be derived. The highest viscosity was observed for maleic acid which is the cross-linker with the shortest spacer, whereas adipic acid with four methylene groups between the carboxylic acid groups gave the lowest viscosity. The gel which was cross-linked with glutaric acid has a lower viscosity than the products which were obtained with citric and succinic acid. All these observations lead to the conclusion that the longer the chain of the spacer, the lower the viscosity of the hydrogel.

However, the effect of the different cross-linking agents and hence the spacer was less pronounced (0.5 to 1 order of magnitude) at the selected cross-linker/mono-starch phosphate ratio of 0.08 mmol/g compared with the effect of cross-linking density and amount of cross-linking agent, respectively (compare with Figure 5).

The storage and loss modules G′ and G″ of all hydrogels are located in the plateau region of the oscillation curve (Figure 9a, b) and show a nearly linear slightly increasing trend within the observed frequency range. The values of the storage modulus G′ are in general about 0.25 to 0.35 orders of magnitude higher than those of the loss modulus G″. These facts signify that with increasing frequency more energy can be dissipated (viscous part) and stored (elastic part) by the system with a slight domination of the elastic part (G′) within the whole frequency range. Highest G′ and G″ values were determined for the mono-starch phosphate which was cross-linked with citric acid, whereas the lowest values were observed for glutaric acid.

The values obtained of tan δ were in the range of 0 to 1 which is typical for viscoelastic materials (Figure 10). Furthermore, the hydrogels which were obtained by cross-linking with succinic-, glutaric-, and adipic acid show a decreasing tendency of tan δ within the frequency region from 0.04 to $20\ s^{-1}$. Parallel to this, the dissipated energy declines with increasing frequency and the elastic part rises. On the other hand, slightly increasing tan δ values were observed for mono-starch phosphates which were cross-linked with citric acid whereas the tan δ of products from maleic acid cross-linking decrease at low frequency between 0.04 and $0.4\ s^{-1}$ before rising from 0.8 to $0.20\ s^{-1}$ (Figure 10). The MSP which was cross-linked with glutaric

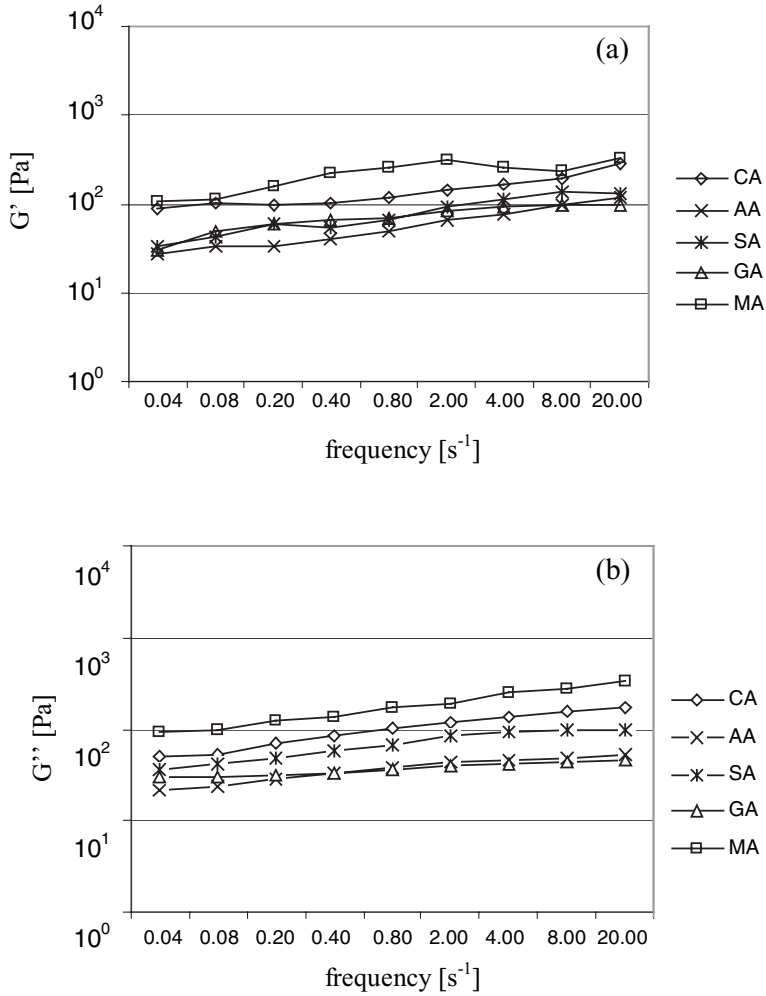



***Figure 9.***
(a) Storage modulus G′ and (b) loss modulus G″ of mono-starch phosphate (MSP) hydrogels cross-linked with citric acid (CA), maleic acid (MA), succinic acid (SA), glutaric acid (GA) and adipic acid (AA) (MSP with degree of substitution 0.14).

acid gave the lowest tan δ of about 0.5 and has therefore most pronounced elastic properties and the highest stability.

## Conclusion

Cross-linking of mono-starch phosphates ($DS_p$ from 0.04 to 0.35) with citric acid reveals that the hydrogels obtained have a sharp maximum of FSC already at a comparatively low $DS_p$ of 0.08. Cross-linking of such low substituted mono-starch phosphates with citric acid, succinic anhydride, and different dicarboxylic acids yields stable hydrogels which are characterized by high swelling capacities. Variation of MSP/cross-linking ratio and cross-linking agent clearly show that both parameters influence the FSC of the products as well as their rheological behaviour. In general, the effect of MSP/cross-linking ratio was more pronounced compared to the effect of the cross-linking agents studied.

A maximum in the material functions dynamic viscosity $\eta^*$, storage modulus G′

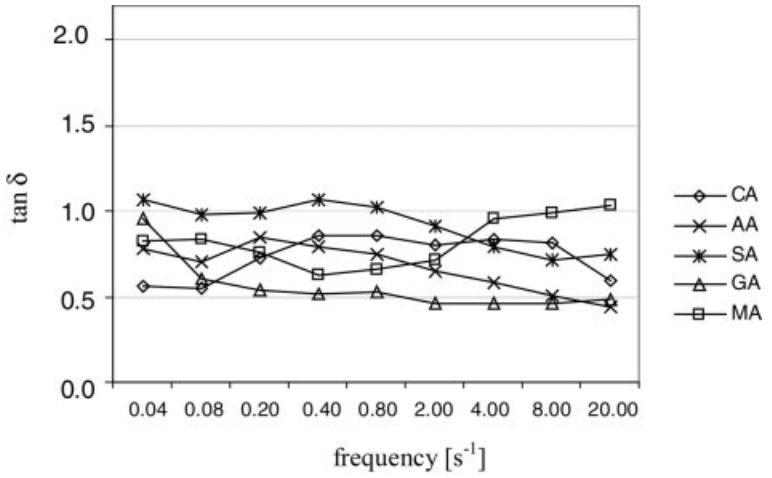



***Figure 10.***
tan δ of mono-starch phosphate (MSP) hydrogels cross-linked with citric acid (CA), maleic acid (MA), succinic acid (SA), glutaric acid (GA) and adipic acid (AA) (MSP with degree of substitution 0.14).

and loss modulus G″ can be observed for gels with the highest cross-linking density by varying the cross-linking density and amount of cross-linking agent respectively. Variation of the spacer length of dicarboxylic acids plays a critical role in the material properties of the hydrogels. In this regard, using a cross-linker with the shortest chain length (maleic acid) leads to a maximum in these material functions of hydrogels. Amongst all obtained products, those mono-starch phosphates which were cross-linked with glutaric- and succinic acid seems to be most promising for the intended utilization as soil improving material. Investigation of the microbiological degradation and persistency of mono-starch phosphate based hydrogels under soil conditions is subject to further research.

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