André Alexandre Lopes Gonçalves

# Biodegradable Hydrogels for Agriculture

Master Degree Thesis in the scientific area of Chemical Engineering,
supervised by PhD Arménio C. Serra and by PhD Jorge F. J. Coelho
submitted to the Faculty of Science and Technology of the University of
Coimbra

**Supervisors:**

PhD Arménio C. Serra

PhD Jorge F. J. Coelho

**Host institutions:**

CEMUC - Centre for Mechanical Engineering, Department of Chemical
Engineering, Faculty of Sciences and Technology of the University of
Coimbra

Coimbra

2014

· U C ·

UNIVERSIDADE DE COIMBRA

*"The roots of education are bitter,*

*but the fruit is sweet."*

*Aristotle (384-322 BC)*

# Acknowledgments

Antes de mais é importante afirmar que esta etapa se apresentou como um dos maiores obstáculos a nível académico e pessoal que alguma vez tive, em muito por ser o culminar de todo um exigente mas gratificante curso de Mestrado em Engenharia Química e que só foi possível realizar graças a todo o sentimento, a todo o apoio, a toda a presença, a todo o ensinamento, a todo o envolvimento, toda a dedicação e a toda a sabedoria de inúmeras pessoas que, consciente ou inconscientemente, participaram e deram o seu essencial contributo. Esta é portanto a oportunidade de agradecer e deixar o meu reconhecimento a essas mesmas pessoas.

A todos os profissionais, que fizeram parte da minha jornada académica, por todo o conhecimento científico, por toda a experiência e por toda a sabedoria partilhada que me permitiram ser a pessoa que sou hoje a nível académico e também pessoal e social.

Aos meus orientadores, Doutor Arménio C. Serra e Doutor Jorge F. J. Coelho, por toda a ajuda, dedicação e motivação fornecida durante o desenvolvimento do projeto, por todos os ensinamentos e sabedoria que me transmitiram e também por me terem dado a oportunidade de fazer um projeto com excelentes condições de trabalho e com pessoal de elevado profissionalismo.

À Mestre Inês G. P. Fabela e à Mestre Bianca F. Barros, por toda a ajuda e apoio dado, tanto a nível de laboratório como a nível de escrita, bem como por toda a simpatia e disponibilidade que foram características desde o primeiro dia de desenvolvimento do projeto até à sua finalização. Um especial agradecimento à Mestre Inês G. P. Fabela pela incansável ajuda e disponibilidade na parte final do trabalho, onde sem ela tudo teria sido mais difícil e moroso.

A todos os membros do grupo de investigação de polímeros, que desde o primeiro dia me fizeram sentir parte do grupo, me proporcionaram um excelente ambiente de trabalho e me ajudaram a desenvolver ainda mais o interesse e o gosto pela área de polímeros.

A todos os meus amigos e familiares, que sempre me apoiaram em todas as minhas decisões e me ajudaram perante qualquer dificuldade. Eles surgem como pessoas essenciais em qualquer etapa da minha vida e neste caso não foi exceção. Um especial obrigado ao Rui Churro, ao Fábio Branco, ao João Santos e ao José Lobo por toda a

ajuda a vários níveis, pela partilha de conhecimento, pela troca de opiniões, pelo cruzar de sabedoria e pelos momentos de alegria e descontração, característicos de grandes amizades e de futuros grandes profissionais.

À minha Carolina (*Dolores*), por ser a pessoa especial e importante que é e por estar sempre a meu lado em todos os momentos. O facto de estares sempre presente, de acreditares sempre em mim e de me motivares para tudo é, e foi de uma importância tremenda. Obrigado por todos os momentos de compreensão, paciência, carinho, motivação, dedicação e apoio que me proporcionaste e que foram tão essenciais para finalizar este projeto e para todos os momentos da minha vida.

Aos meus pais e irmãos, por me permitirem chegar onde cheguei, por me terem sempre apoiado e ajudado, por estarem sempre presentes não só nesta etapa final, mas durante todo o meu curso, por terem lutado a meu lado perante todas as adversidades, por toda a educação e carinho ao longo destes anos, por terem sido essenciais e me permitirem tornar na pessoa e profissional que sou hoje e na pessoa e profissional que serei no futuro.

# Abstract

Hydrogels are 3D networks of hydrophilic polymers that can absorb and retain significant amounts of water or aqueous solutions without dissolution. These compounds can be synthesized by any technique that leads to a crosslinked polymer, using generally three reagents: an initiator, monomers (or polymers) with water affinity and a crosslinking agent.

Hydrogels can be used in several areas, such as hygiene, agriculture, industry, medicine or even in pharmaceutical. In this work the area of interest is agriculture, where the hydrogels can improve and minimize the use of water and the yield in the crop fields without adverse consequences to the environment and the natural resources.

Concerning agriculture, it is important to refer the superabsorbent polymers (SAPs), an evolutionary category similar to hydrogels in almost everything except that they have the capacity to absorb greater amounts of water and other fluids (1000 times its own dry weight) in short periods of time comparing to conventional hydrogels. Most of the SAPs used in agriculture are from synthetic source and their degradation contributes for the accumulation of harmful compounds and for the contamination of soils and possibly groundwater. Thus, it would be motivating to develop more biodegradable SAPs with proprieties good enough for a possible application in agriculture, where high capability of absorption and retention of water are essentials.

This work had, therefore, as the main goal, the development of a more biodegradable SAPs based in compounds of natural source, such as acrylated epoxidized soybean oil (AESO) and cellulose derivatives, carboxymethyl cellulose sodium salt (CMCss) and hydropropyl cellulose (HPC).

In a first stage it was used AESO, comonomers, initiators and crosslinking agents and reaction conditions normally used in SAPs synthesis. It was possible to understand which conditions were the best and which reagents were the most suitable to obtain hydrogels with AESO in their constitution. The most promising and interesting synthesized hydrogels were then evaluated for the capacity of water absorption and it was possible to conclude that those hydrogels had a rather low swelling capacity (3-49 g water/g dry hydrogel).

The second stage of this work, were realized two phases. In the first phase, it was reproduced a SAP with good features of swelling and subsequently it was modified with the aim of obtain new SAPs with improved proprieties compared with the base SAP. Among the several synthesised SAPs, the one which had better maximum capacity of absorption of water was the SAP5 with a maximum swelling of 2700 g water/g dry hydrogel. This material was fully characterized, through which it was possible to understand that even for pHs slightly acid or basic, high values for the swelling capacity were achieved. Also, it was possible to observe improvements in the retention of water in the soil caused by the presence of SAP5 and to understand the ability of this material in load high amounts of urea and thereafter to release this fertilizer in a controlled way for the surrounding medium. However it was also possible to have an idea of the negative influence of the ionic strength of the medium on the swelling properties of the SAP5.

At last, it was performed the second phase, where it was used the knowledge and the methodology developed in the previous phase, to synthesize more biodegradable SAPs using carboxymethyl cellulose sodium salt and hydropropyl celloluse as comonomers. Those derivatives were also functionalized in order to occur incorporation of functional groups that could help in the synthesis and improve the proprieties of the new SAPs. Through the FTIR analysis it was possible to confirm the success of the performed functionalizations. Despite attempts made, it was not possible to obtain a more biodegradable SAP on this phase. This can be due to various reasons, such as the difficulty of ensure dissolution of the cellulose derivatives in water during the reaction and for the temperatures utilized.

# Resumo

Hidrogéis são uma rede tridimensional de polímeros hidrofílicos que podem absorver e reter grandes quantidades de água ou soluções aquosas, sem dissolver. Estes compostos podem ser sintetizados recorrendo a qualquer técnica que origine um polímero reticulado e utilizando normalmente 3 reagentes: iniciador, monómeros (ou polímeros) e agente reticulante.

As áreas de aplicação dos hidrogéis vão desde a higiene até à agricultura, passando pela indústria, medicina e farmacêutica. Neste trabalho em concreto a área de interesse é a agricultura, área onde os hidrogéis podem melhorar e minimizar a utilização de água e a produção nos campos de cultivo sem consequências adversas para o ambiente e para os recursos naturais.

Quando a aplicação se trata da agricultura é importante falar em polímeros superabsorventes, uma categoria evolutiva semelhante em tudo aos hidrogéis mas com capacidade de absorver maiores quantidades de água e outros fluidos (1000 vezes o seu peso seco), em curtos períodos de tempo, do que os hidrogéis convencionais. A maior parte dos polímeros superabsorventes utilizados na agricultura são de origem sintética e a sua degradação contribui para a acumulação de compostos prejudiciais e para a contaminação dos solos e possivelmente das águas subterrâneas. Seria interessante então desenvolver polímeros superabsorventes mais biodegradáveis e com propriedades suficientemente boas para uma possível aplicação na agricultura, onde a elevada capacidade de absorção e de retenção de água são essenciais.

Este trabalho teve portanto como principal objetivo desenvolver polímeros superabsorventes mais biodegradáveis recorrendo a compostos de origem natural, como o óleo de soja acrilatado e epoxidado (AESO) e os derivados da celulose, carboximetil celulose sal de sódio (CMCss) e hidroxipropil celulose (HPC).

Numa primeira etapa recorreu-se ao AESO, a comonómeros, iniciadores e agentes reticulante e a condições de reação normalmente utilizados na síntese de polímeros superabsorventes. Foi possível perceber quais as melhores condições e os reagentes mais apropriados para obter hidrogéis com AESO na sua constituição. Os hidrogéis sintetizados mais promissores e interessantes foram posteriormente avaliados através do cálculo da capacidade máxima de absorção de água e foi possível concluir que esses hidrogéis apresentam uma capacidade de inchamento bastante baixa (3-49 g água/g de hidrogel seco).

Na segunda etapa do trabalho foram realizadas duas fases. Uma primeira fase onde se reproduziu um polímero superabsorvente com boas propriedades de inchamento e posteriormente se fez modificações com o objetivo de obter polímero superabsorvente com propriedades melhoradas em relação ao polímero superabsorvente base. Dos vários polímeros superabsorventes sintetizados, o que apresentou melhor capacidade máxima de absorção de água foi o SAP5 com um inchamento máximo de 2700 g água/g hidrogel seco. O material foi caracterizado de forma exaustiva, sendo possível perceber que mesmo para pHs um pouco ácidos ou um pouco básicos eram atingidos elevados valores para a capacidade de inchamento. Também foi possível observar melhorias na retenção de água no solo provocadas pela presença do SAP5 e perceber a capacidade deste composto em carregar elevadas quantidade de ureia e posteriormente libertar este fertilizante de forma controlada para o meio envolvente. No entanto, também foi possível ter uma ideia da negativa influência da força iónica do meio nas propriedades de inchamento do SAP5.

Por último foi realizada uma segunda fase onde se utilizou o conhecimento e a metodologia desenvolvida na fase anterior para sintetizar polímeros superabsorventes mais biodegradáveis recorrendo à carboximetil celulose sal de sódio e a hidroxipropil celulose como comonómeros. Esses derivados também foram funcionalizados para haver incorporação de grupos funcionais que ajudassem na síntese e melhorassem as propriedades dos possíveis polímeros superabsorventes obtidos. Através da análise FTIR foi possível confirmar o sucesso das funcionalizações realizadas. Apesar de terem sido realizadas várias tentativas não foi possível obter num polímero superabsorvente mais biodegradável. Isto pode ter ocorrido devido a várias razões, tais como a dificuldade de garantir a dissolução dos derivados da celulose em água durante a reação e para as temperaturas utilizadas.

# List of Acronyms

| | |
|---|---|
| AC | Absorption capacity |
| AAm | Acrylamide |
| AESO | Acrylated epoxidized soybean oil |
| AA | Acrylic acid |
| $Al_2(SO_4)_3.18H_2O$ | Aluminum sulfate octadecahydrate |
| AMA | Ammonium acrylate |
| APS | Ammonium persulfate |
| $M_0$ | Amount of urea loaded in SAP |
| BPO | Benzoyl Peroxide |
| BMEP | Bis[2-(methacryloyloxy)ethyl] phosphate |
| BDM | Butandiol Dimethacrylate |
| CMC | Carboxymethylcellulose |
| CMCss | Carboxymethylcellulose sodium salt |
| CAt | Cellulose acetate |
| CAc | Citric acid |
| CA | Crotonic acid |
| DSC | Differential Scanning Calorimetry |
| DMF | Dimethyl formamide |
| DMSO | Dimethyl sulfoxide |
| DVS | Divinyl sulfone |
| EG | Ethyleneglycol |
| EGDE | Ethyleneglycol diglycidyl ether |
| EGD | Ethyleneglycol dimethacrylate |
| FTIR | Fourier Transform Infrared Spectroscopy |
| HEC | Hydroxyethyl cellulose |
| HEMA | Hydroxyethyl methacrylate |
| HPC | Hydroxypropyl cellulose |
| IR | Infrared Irradiation |

| | |
|---|---|
| $W_0$ | Mixture initial weight |
| $W_t$ | Mixture weight at certain time |
| NIPAAm | N-isopropyl acrylamide |
| MBA | N,N’-methylenebisacrylamide |
| VP | N-vinyl-2-pyrrolidone |
| n | Number of urea release measurements at various time intervals |
| Tonset | Onset temperature |
| OM | Optical Microscopy |
| KMA | Potassium methacrylate |
| KA | Potassium acrylate |
| KPS | Potassium persulfate |
| SEM | Scanning Electron Microscopy |
| SAP | Superabsorbent Polymer |
| SMB | Sodium metabisulfite |
| NaPA | Sodium Polyacrylate |
| SPMps | Sulfopropyl methacrylate potassium salt |
| THF | Tetrahydrofuran |
| TGA | Thermogravimetric Analysis |
| 3D | Three-dimensional |
| TMPM | (3-trimethoxysilyl)propyl methacrylate |
| TMPTA | Trimethylolpropane triacrylate |
| WR | Water Retention |
| Mw | Weight average molecular weight |
| $M_l$ | Weight of loaded dry hydrogels |
| $W_d$ | Weight of the dry hydrogel |
| $W_s$ | Weight of the swollen hydrogel |
| $M_0$ | Weight of unloaded hydrogels |
| $(\Delta W)_i$ | Weight of urea released from the 20 mL sample |
| $T_5$% | 5% weight loss temperature |
| $T_{10}$% | 10% weight loss temperature |

**Contents**

# List of Figures

# List of Tables

# Chapter I

# 1. Theoretical Introduction

## 1.1. Polymers

Hermann Staudinger, a German chemist who received the 1953 Nobel Prize in Chemistry, proposed in 1920 that natural compounds such as rubber and cellulose are long chains of short repeating molecular units linked by covalent bonds and posteriorly demonstrated the existence of this macromolecular structure. Staundiger's work and theories were an important step in polymer science and helped the development of this area and future works [1].

Polymers are large molecules made up by the repetition of simple structural units, called monomers, with molar mass clearly above 103 g/mol. The terms polymer and monomer were derived from the Greek roots poly meaning "many", mono meaning "one" and meros meaning "part" or "segment" [2-5].

Polymers can be classified taking into account different features: type, topology, composition and functionality, as displayed in Figure 1.1 [6].

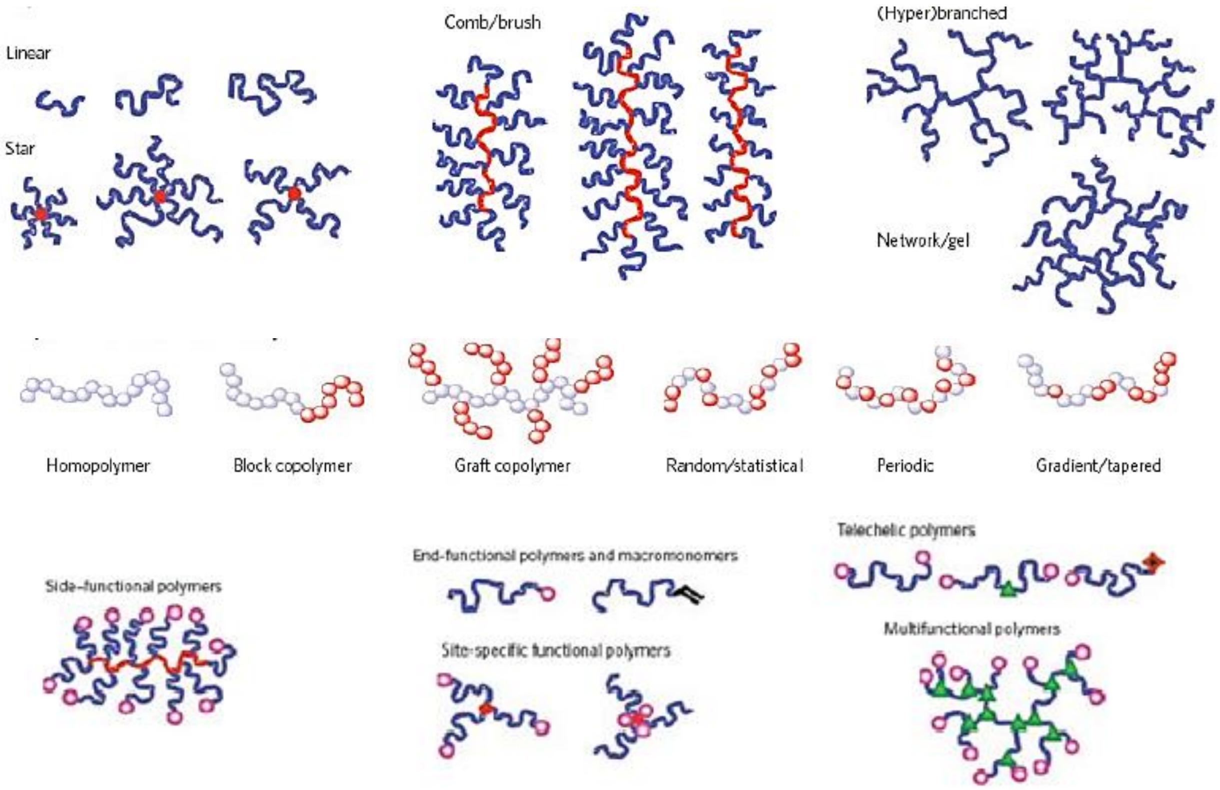


**Figure 1.1 – Polymer classification, adapted from [6].**

Regarding to the origin, polymers can be: natural, such as polysaccharides (cellulose, starch), proteins (wool, silk) or natural rubber; synthetic (man-made polymers) such as polystyrene, polyethers, polyamides or polyurethanes; artificial (modifications of natural polymers) like cellulose acetate (CAt), HPC or carboxymethyl cellulose (CMC). Based on their structure, polymers can be classified as linear, star, comb/brush, branched or network. The composition of a polymer can present only one type of repetition unit (homopolymer) or two or more different types of repetition unit in the polymeric chain (copolymer). In relation to the different copolymer group,block, graft, random, periodic and gradient copolymers stand out. Also, in terms of functionality, there are side-functional, end-functional, site-specific functional, telechelic and multifunctional polymers [2-5].

Polymers can be obtained by two major polymerization processes: step-growth polymerization and addition polymerization, also called chain-reaction polymerization [7].

In the chain-reaction polymerization, different reactions (initiation, propagation and termination) operate at different stages of the polymerization. The initiator, which can be a free radical, a negative or a positive charge, is required to start the reaction. The monomer is activated and the polymerization propagates through the consecutive activation of the succeeding monomers. In this process, chain growth is due to successive addition of the monomer at one end (active end) of the chain, where a rapid increase of the molecular weight as well a very slow consumption of the monomers occurs. Further, the polymerization rate initially increases and then becomes constant until the monomer depleted [3,4,7,8].

In the step-reaction polymerization the same mechanism operates throughout the reaction and no initiator is required to start the reaction. This mechanism comprises a random reaction between two molecules that can result from the combination of a monomer, an oligomer or even a longer-chain molecule. This polymerization is also characterized by a rapid loss of monomers, a slow increase of molecular weight and a decrease of polymerization rate as the number of reactive functional groups decreases [3,4,7,8].

Polymers and derivatives are present everywhere and represent an important part in everyday life. They are used in several different areas, such as medicine, industry and agriculture. There are several reasons that can explain the polymer popularity, such has their low density and thermal conductivity, high electrical and chemical resistance or even their low price. Also, the ability of tailoring the final polymer properties in order to meet specific requirements is a great interest [2,3,4].

The search of new polymers with improved properties is a validation of the significant role of these compounds in our society.

## 1.2. Hydrogels

Hydrogels are a three-dimensional (3D) network of hydrophilic polymers (Figure 1.2) that can absorb and retain significant amounts of water or aqueous solutions (up to thousands of times their dry weight), without dissolution [9-11].

This 3D network structure is insoluble in water or aqueous solution due to polymer chains crosslinking, that can result from covalent, hydrogen bonding, Van der Waals forces or physical entanglements [9,10,12].

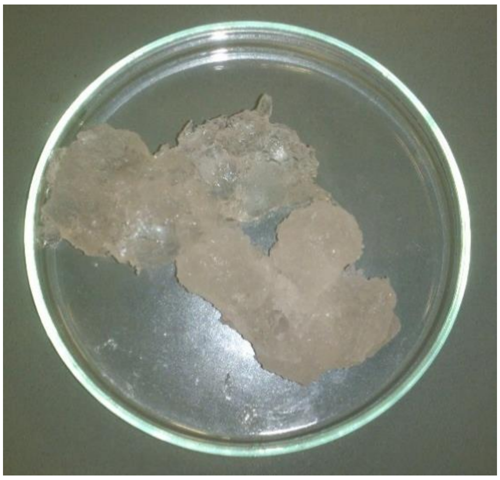


**Figure 1.2 – Synthesized hydrogel.**

The mechanism of physical water absorption of those hygroscopic materials is based on physical entrapment of water via capillary forces in its structure, hydration of functional groups and thermodynamically favoured expansion of the macromolecular chains limited by crosslinking [2,13,14].

In 1938, the first water absorbent hydrogel was synthesized by the polymerization of acrylic acid (AA) and divinylbenzene in aqueous medium. Later, in the late 1950s, a group of hydrogels mainly based on hydroxyalkyl methacrylate and related monomers were studied and reported. They showed a good absorption capacity (40-50%) and were used in ophthalmology area, particularly in the field of contact lenses [9,15].

Due to their commercial potential, in recent years an important research work on water-absorbent polymers has been developed.

Hydrogels have gained preponderance and nowadays a wide range of materials are commercially available. The raw materials and techniques used for their synthesis as well as desired characteristics and properties are different according to the final application and ultimately the development of new hydrogels suitable for new and diverse applications is a reality.

For example, AA and its salts and acrylamide (AAm) are mainly used for preparation of hydrogels that can be employed in hygienic and agriculture applications.

### 1.2.1. Preparation of hydrogels

Basically, for the hydrogels preparation three components are need: initiator, monomers (or polymers) and crosslinker. However to control the final hydrogels properties and/or the heat of polymerization, solvents like water and acetone are frequently used.

The main monomers or polymers used for synthesis and preparation of hydrogels are AA, AAm, methacrylic acid, hydroxyethyl methacrylate (HEMA), ethyleneglycol dimethacrylate (EGD), ethyleneglycol (EG), methoxyethyl methacrylate, N-vinyl-2-pyrrolidone (VP), vinyl acetate, PEG acrylate, N-isopropyl acrylamide (NIPAAm), cellulose, starch, chitosan, gelatin and some of their possible derivatives (e.g. CMC). Usually initiators used are ammonium persulfate (APS), potassium peroxydisulfate ,Irgacure 2959 and 2,2’-azobis. Further, crosslinking agents are divinyl sulfone (DVS), epichlorohydrin, trimethylolpropane triacrylate (TMPTA) and N,N’ methylenebisacrylamide (MBA) [10,17,18,19].

In a simple way, a hydrogel can be produced by any technique that leads to a crosslinked polymer. So, several methods are used to produce hydrogels.

It can be resorted to various forms of crosslinking of water-soluble linear polymers and form hydrogels, such as linking polymer chains *via* chemical reaction, through physical interactions like entanglements, electrostatics and crystallite formations and also by using ionizing radiation to generate main-chain free radicals which can recombine as crosslink junctions [14,16,17,18].

But, usually hydrogels are produced by reacting hydrophilic monomers with multifunctional crosslinkers (copolymerization/crosslinking free-radical polymerization) and using various polymerization techniques. However, hydrophobic monomers can also be used to adjust the properties of the hydrogels. [14,16]

The polymerization techniques most used are the suspension polymerization, the solution polymerization, the polymerization by irradiation, the bulk polymerization and the graft polymerization [16,18,19].

### a) Polymerization by irradiation (or photopolymerization)

Polymerization by irradiation is based on the formation of macro-radicals on different polymer chains in aqueous polymer solution and the subsequent recombination of these macro-radicals results in a crosslinked structure [16,20,21,22].

To obtain macro-radicals on chains an aqueous polymer solution is irradiated with an ionizing high energy radiation (gamma rays or/and electron beans) and radicals are formed. This energy also promotes the formation of hydroxyl radicals through radiolysis of water molecules. Then hydroxyl radicals attack the polymer chains and macro-radicals are formed [16,21].

This technique allows the preparation of hydrogels from unsaturated compounds with the advantage of being a relatively pure and initiator free production. Radiation method is used, for instance, to synthesized poly(vinyl alcohol) and poly(AA) [16,20,21,22].

### b) Bulk polymerization

The production of hydrogels by this simple technique involves the reaction between three compounds: monomers, monomer-soluble initiator and crosslinking agent, without using any solvent [2,16].

Hydrogels obtain by bulk polymerization can be formed with one or more types of monomers and usually only small amounts of crosslinking agent are required. Although several vinyl monomers can be used to produce hydrogels, their choice is depending in the final application.

Further, to initiate the polymerization reaction usually chemical catalysts, radiation or UV light (ultraviolet), are used. This technique allows the production of homogeneous hydrogels with glassy, transparent and hard matrix, having a wide range of forms (from particles to membranes) [2,16].

Bulk polymerization has the advantage of avoiding elimination of traces of volatile solvent before processing the final hydrogel, but with this method, Trommsday-Norrish effect (gel effect) can be a problem. This effect was mainly reflected in the difficulty to control the heat of transfer, with high chances of occurring autoacelerations and runaway reactions and can be avoided by polymerising only to low conversion, adding a chain transfer agent or changing to other polymerization technique [2,4,23].

### c) Solution polymerization

In the case of solution polymerization, the monomers are mixed with the multifunctional crosslinkers in the presence of a solvent and usually a redox initiator system thermally initiated the reaction [16,18].

After the polymerization, the hydrogels are washed in order to remove the soluble and extractable polymer, the unreacted monomers, cross-linking agent, initiator and other impurities. The excess of solvent can be removed by swelling the hydrogels in water or by other processes such as extraction [16,18].

The main advantage of this technique is based on the presence of solvent that acts as a heat sink, which guarantees lower viscosity allowing the prevention of diffusion controlled termination and a quicker removal of polymerization medium heat causer of the gel effect [16,18,24].

Water, methanol, methanol-acetone mixtures, benzyl alcohol, ethanol and water-ethanol mixtures are some of the most used solvents for the preparation of hydrogels by solution polymerization [16].

### d) Suspension polymerization

In suspension polymerization, two immiscible liquid phases are present, an aqueous continuous phase and a non-aqueous discontinuous phase consisting of monomers, initiator and polymers [16,18].

In this technique, the solution with all reactants is dispersed in the continuous phase forming fine monomer droplets. These droplets are thermodynamically unstable and a vigorous continuous stirring and the addition of hydrophilic-lipophilic balance suspending agents are required to stabilize the dispersion [16,18].

The initiator is soluble in the monomer but not in the continuous phase, which implies that in each droplet reside all the reactants and occur reactions similar in all to bulk polymerization. With thermal decomposition of the initiator, radicals that initiate the polymerization are formed [16,18].

At the end of the polymerization, hydrogels are obtained in the form of powder or beads (microspheres). Like the solution polymerization, those hydrogels macro-particles must be washed in order to remove unreacted monomers, initiator, cross-linkers and other impurities [16,18].

A very practical advantage of this technique is that grinding is not required and the shape of particles can be controlled by the viscosity of monomer phase and the type of suspending agent, respectively. However, that the drawback is the need to remove the continuous phase [25,26].

A variation of this technique, inverse suspension technique, has been widely used, for instance, to prepare poly(AAm) hydrogels. In this case, the monomer and initiator are hydrophilic and dispersed in the continuous organic phase (e.g. parafilm oil). Furthermore, heterophase polymerization has been detailed discussed by Watanabe [24,27].

### e) Graft polymerization

Graft polymerization is a slightly different technique compared with the other techniques described above. In this polymerization method for the preparation of hydrogels, free radicals are generated onto a surface of a non soluble material and then monomers are polymerized directly onto it. With the addition of more monomers, chains of monomers are formed and remain covalently bonded to the support [16,28].

Usually, this technique is used to improve certain properties of the hydrogels. The hydrogel is grafted to a stronger support, leading to an improvement in its structural and mechanical properties, when compared to other hydrogels prepared by different polymerization techniques (e.g. bulk polymerization) [16,18].

A wide range of supports have been used for the synthesis of hydrogels by graft polymerization, like medical stone, carbon nanotubes, cellulose nanoparticles and others [29,31].

### 1.2.2. Classification of hydrogels

There are different points of view through which hydrogels can be classified. In Table 1.1, a brief summary of this classification is displayed.

**Table 1.1 – Classification of hydrogels [16,18,32-35].**

| Point of view | Classification | |
|---|---|---|
| Source | Natural origin | |
| | Synthetic origin (petrochemical-based) | |
| Morphology | Particle | |
| | Powder | |
| | Fiber | |
| | Emulsion | |
| | Spherical | |
| | Membrane | |
| Configuration (physical structure and chemical composition) | Amorphous (non-crystalline) | |
| | Semi-crystalline (mixture of amorphous and crystalline phase) | |
| | Crystalline | |
| Polimeric composition | Homopolymeric hydrogels (polymer network derived from a single specie of monomer) | |
| | Copolymeric hydrogels (two or more different monomer species with at least one hydrophilic component) | |
| | Multipolymer Interpenetrating polymeric hydrogel (IPN) (network formed by teo independent cross-linked synthetic and/or natural polymer) | |
| Type of cross-linking | Chemical cross-link junctions (permanent junction) | |
| | Physical cross-link junctions (transient junction) | |
| Environment response | Temperature response (swelling and deswelling behaviour of the hydrogels depend on the surrounding temperature) | Positive |
| | | Negative |
| | | Thermo-reversible |
| | pH response (hydrogels exhibit swelling and deswelling according to pH of the environmental) | Cationic |
| | | Anionic |
| | Electrical signal-sensitive (hydrogels swelling and deswelling depending on the applied electrical field) | |
| | Ionic stregth response (swelling and deswelling of hydrogels varies with changes in ionic stregth of the surrounding environment) | |
| | Others (light response, sound field response and magnetic field response) | |
| Network electrical charge | Nonionic (neutral) | |
| | Ionic (including anionic or cationic) | |
| | Amphoteric electrolyte (ampholytic-containing both acidic and basic groups) | |
| | Zwitterionic (containing both anionic and cationic groups in each structural repeating unit) | |

It is important to mention that hydrogels have an important and useful characteristic which is the capacity to response to environmental change and act like “smart materials”. This capacity of some hydrogels allows their utilization in innovative applications and increase their potential and value. Environmental response hydrogels materials can be synthesized with controllable responses as shrink (deswelling) or expand (swelling) to a variety of physical (electric or magnetic field, temperature, light) and chemical (ionic strength, pH) *stimuli*. However, hydrogels can suffer phenomenon such as phase transition or volume collapse due to drastic response when drastic changes in the external environmental occurs [18,35,36,37,38].

## 1.2.3. Hydrogels Properties

The knowledge of hydrogels properties is very important and the most reliable basis to obtain all necessary information about these materials. Thus, the study of hydrogels properties allows to know more about synthetic process, predict and understand hydrogel’s behaviour in real systems (in physiological media, in contact with plants, in soil, etc.), compare between different types and kinds of hydrogels and optimize them for different end use applications.

The most important features of a hydrogel are their swelling, mechanical and biocompatibility properties. However, the importance and relevance of these properties depends on their final application [39].

### 1.2.3.1. Swelling properties

The most important properties of hydrogels are water absorbing capacity and swelling behaviour. These properties allow the efficient and unique use of crosslinked polymers in a wide range of applications and scientific areas.

There are several ways to measure absorption capacity, such as, by using a microwave method (measures the microwave absorption by energy changes), a gravimetric method (measures the weight changes of hydrogel sample), a spectroscopic method (measures changes of the U.V. spectrum of the hydrogel sample) and a volumetric method (measures absorbed fluid before and after the absorption or the volume changes of hydrogel sample) [14,18,19].

Further, absorption and swelling properties of hydrogels are attributed to the presence of hydrophilic groups such as CONH-, $-SO_3H$, $-CONH_2$- and -OH- in their network [18,39,40].

The swelling process can be easily explained: the hydrogel is placed in solvent and the molecular chains interact with solvent molecules that try to penetrate in the polymer networks. With the entrance of the solvent molecules in the hydrogel network (promoted by relatively good thermodynamic compatibility), the molecule chain between the crosslinked points expands and 3D-molecular network also expands to the solvated state (Figure 1.3). However, there is an elastic contractive force in this network that tries to make it contract. The contraction and expansion reach a balance when these mentioned opposing forces reach equilibrium and at this point the swelling stops [18,41,42].

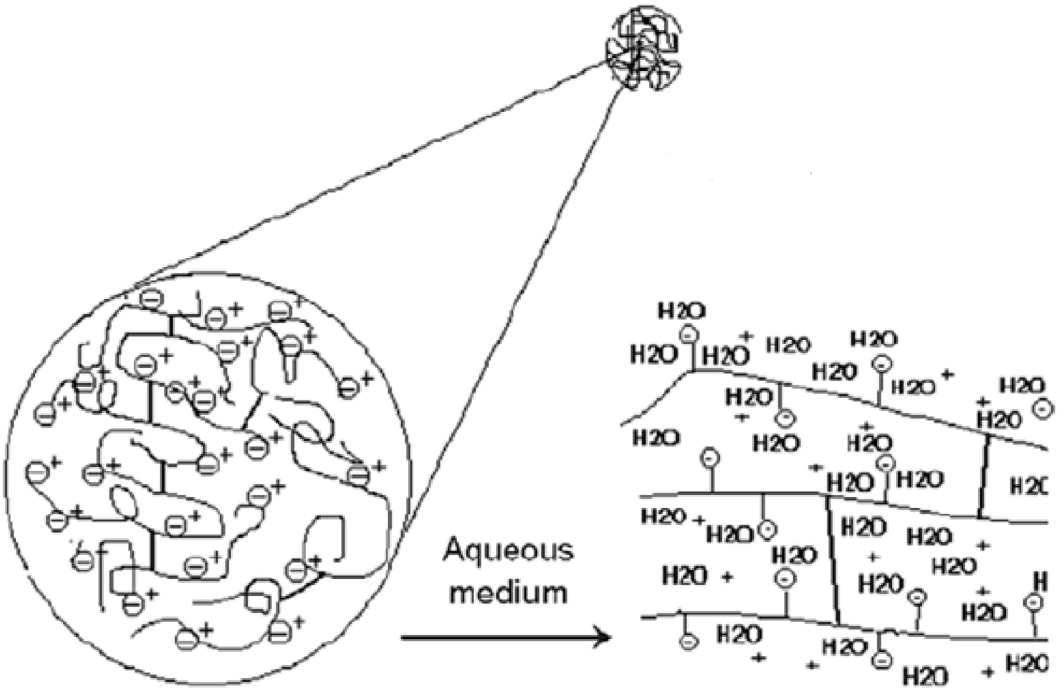


**Figure 1.3 – Schematic presentation of the hydrogel swelling, adapted from [19].**

The swelling process of crosslinked polymer gels was firstly described by Flory and Rehner (1956) who developed a model to represent the equilibrium swelling degree of these materials considering a Gaussian Distribution of polymer chains [18,41,42].

For neutral hydrogels the swelling process can be considered under rubbery state and the degree to which a polymer network swelled was governed by the polymer and solvent interactions such as hydration and the formation of hydrogen bonds (thermodynamic compatibility) and the elastic retractive forces of the polymer chains [41,43].

A large portion of hydrogels presents an ionic character and in this case the swelling behaviour can be mainly described as a result of the balance between the osmotic pressure (the difference in concentration of mobile ions inside the hydrogel relative to external solution) and the elastic energy of the network [14,41,42,43].

Polyelectrolyte gels have chains with charges that repel each other due the presence of negative groups such as carboxylate groups for example. These chains are neutralised and the electrical neutrality is maintained through the balance between these negative groups and positive ions (sodium or potassium). Positive ions hydrate in contact with water and their attraction to negative groups becomes weaker. This enables their free movement within the network and at the same time prevents its “escape” from the hydrogel. These events contribute to the osmotic pressure and allow the obtainment of more highly swollen and hydrophilic networks with the variation of the ionic content in hydrogel or with the variation of the level of ions in swelling agent (outside of the hydrogel). Also, in deionised water the maximum swelling will occur and the hydrogel will show better swelling behaviour due to higher osmotic pressure [41,42,43].

It is important to mention that the osmotic pressure is associated with the Donnan equilibrium (electrical potential developed between inside and outside of the hydrogel) when swelling agent (solvent) is an electrolytic solution [18,41].

Briefly, for ionic hydrogels beyond the interaction between polymer and solvent and the network elasticity, there are ionic contributions influencing the degree of swelling equilibrium [41,42,43].

There are many factors affecting the swelling properties of hydrogels such as the affinity between the solvent (often water) and the polymer, the chemical structure of the repeating unit or chemical compositions, the specific *stimuli* or the surrounding medium, the crosslinking density of the network, the osmotic pressure, the solvent concentration, the porosity and the particle size. Specific influence of the most important factors in this process will be analysed below [18,41,43].

### a) Factors influencing swelling properties

#### Monomer/polymer type

Absorption capacity is affected by the type of monomer or polymer used in the hydrogel synthesis, particularly by the presence of hydrophilic or hydrophobic groups in its constitution [18].

Monomers or polymers with hydrophilic groups lead to hydrogels with higher absorption capacity in comparison to hydrogels produced using polymers or monomers with hydrophobic groups. Hydrophobic groups can collapse to minimising contact to the water and therefore are less exposed to water molecules, resulting in a lower absorption capacity of the hydrogel [18].

#### Initiator content

The initiator content is another parameter that have influence in the swelling properties of hydrogels. For instance, when the content of initiator is low, the network structure may show more space volume due to the low polymerization rate and consequently longer polymer chains, which enhances the absorption capacity [18,44,45].

Moreover, with higher initiator content, the polymerization reaction takes place readily and the network structure may have smaller space size and volume. With these characteristics, the fluid molecules have more difficulty to enter in the network and absorption capacity of hydrogel is lower [18,44,45].

#### Degree of Neutralization

The neutralization of the polymer chains is another important factor to be considered. In hydrogels production, the neutralization process can be carried out on the hydrogel (post-neutralization) or in the monomer solution before the polymerization (pre-neutralization) [43].

Some studies and theories indicate that absorption capacity increases with the degree of neutralization (acid base neutralization) until a certain value of this. So with the increase of degree of neutralization, the ionic content inside of the network ($-CO_2-Na$ groups) and the electrostatic repulsion between the negatively charged groups in polymer chains also increase. This leads to higher osmotic pressure between the outside and the inside of the hydrogel and therefore, the absorption capacity is also higher. However at certain values of degree of neutralization, a decrease in absorption capacity was observed probably due to increase in chains stiffness and the counter ion condensation on the chains that inhibits the electrostatic repulsion (anion-anion repulsion forces) [18,43,46,47].

For most polymerization processes a degree of neutralization between 0-80 % is usually used [48].

**Crossliking density**

Some of the parameters with greater impact in absorption properties are the kind of crosslinker and the crosslinking density. These parameters are related and the crosslinking density can be controlled by the amount of crosslinker used in the polymerization reaction [18,43].

The amount of crosslinking agents have a huge influence in absorption capacity and the concentration used must be well considered and studied in order to allow the best swelling properties [18,43].

At high concentrations of crosslinking agent, a network structure with high crosslinking is obtained due to formation of a large number of growing polymer chains. With these characteristics, the water cannot enter in the network, which leads to a reduction in the absorption capacity of the hydrogel [18,43,49,50].

Further, at low concentration of crosslinking agent, there is no proper and effective formation of the 3D network of the hydrogel and this structure cannot hold the water molecules, which also leads to a decrease in the absorption capacity [18,43,49,50]. Thus, there is an “optimal” concentration of crosslinking agent which gives the maximum or the desired swelling of the hydrogel.

Moreover, the number of functional groups and the presence of hydrophilic groups (NH groups) in composition of crosslinking agent will affect the swelling behaviour of the hydrogel. Using crosslinkers with more functional groups, will increase the crosslinking density mainly due to a higher amount of crosslinking sites and consequently the absorption capacity will decrease. If the crosslinker has hydrophilic groups, new hydrophilic interactions can occur and the increase in absorption capacity is probable [18,49,50].

### Ionic strength of absorbed fluid

As described previously, the majority of hydrogels can have an ionic strength response due to *stimuli* in surrounding medium. This response is more pronounced if the origin of raw materials used to synthesize the hydrogels is a polyelectrolyte [18,41].

The effect of ionic strength of absorbed fluid in swelling properties of hydrogels can be described using Donnan equilibrium theory. In this theory, electrostatic repulsion between polymer chains is responsible for absorption capacity and it depends on the concentration of mobile ions in and out of the network of hydrogels (osmotic pressure) [18,41].

If the different concentration of mobile ions in and out the network structure is low, the electrostatic repulsion is weaker and the equilibrium between the different charges and consequently the equilibrium swelling will be reached quickly [18,41,51]. However, if the osmotic pressure is high, the electrostatic repulsion is more intense and the hydrogels will show higher absorption capacity and better swelling properties [18,41,51].

Hydrogels have shown better swelling properties in distilled water than those in saline solutions (NaCl and $CaCl_2$) as extensively describe in the literature. This demonstrates that the effect of ionic strength of absorbed fluid is important and essential in the ability of hydrogels to incorporate more or less water [18,52].

### Morphology properties

The absorption capacity of hydrogels can also be affect by morphological properties like particle size and porosity.

In terms of particle size, with a small average grain size of hydrogel it is possible to obtain higher absorption capacity. However, if the average grain size of hydrogel is higher, for the same amount of product, the contact area between solvent and particles is smaller and the absorption capacity is reduced [31,54].

In hydrogels, the pores allow and promote the solvent diffusion into the network. When the hydrogel has many and large pores, the molecules of solvent can more easily enter in the structure and the contact between these and hydrophilic groups is more efficient, which facilitates the absorption process. Thus, if the hydrogel shows high porosity and pore size, the absorption capacity is enhanced and swelling equilibrium is reached more quickly. Though, these characteristics may be undesirable, for instance, in the case of controlled release of fertilizers or drugs [55,56].

#### 1.2.3.2. Other Properties

##### a) Mechanical properties

Other important properties of hydrogels are the mechanical properties, especially if they are used at pharmaceutical and/or biomedical applications. However, in applications such as agriculture or horticulture, mechanical properties of hydrogels are no longer as relevant.

Hydrogels must present such mechanical properties that ensure its proper and adequate implementation. For instance, hydrogels must be able to maintain its physical texture during the delivery of therapeutic moieties for the predetermined period of time [39,58].

Typically, in many applications the purpose is the production of relatively strong hydrogels, having also some elastic capacity. This is achieved and the mechanical properties of the hydrogels can be manipulated mainly through the changes in degree of crosslinking and/or using comonomers, which results in different mechanical characteristics [14,39].

It is possible to obtain hydrogels with a stronger and brittle structure and low percentage of elongation by increasing the degree of crosslinking. The opposite also occurs: for lower values of crosslinking degree, hydrogels typically exhibit a more pronounced elastic behaviour. Therefore, the desired mechanical property of the hydrogel can be achieved by adjusting the crosslinking degrees [39].

Furthermore, the use of different types of comonomers also allows the synthesis of hydrogels with different mechanical properties. Comonomers characteristics, like size of the chains and capacity to create hydrogen bonding within the hydrogel can determine a lower or higher elastic capacity of the hydrogel [39].

The mechanical characterization of the hydrogel can be made by the determination of hydrogel linear viscoelastic range, using relaxation experiments (normal stress relaxation at constant deformation) and subsequent determination of Young modulus and relaxation spectra. The determination of hydrogel crosslinking density and estimation of the average polymeric mesh size is also important [14,39,57].

**b) Biocompatible properties**

Mainly for hydrogels to be applied in the biomedical field, biocompatible and nontoxic assume a very important role. In this field, hydrogels must present bio-functionality and no cytotoxic, carcinogenic and/or mutagenic character, allowing an appropriate host response (bio-safety) [39,58].

Hydrogels can be hazardous if a 100% conversion of toxic chemicals (initiators, unreacted monomers, crosslinkers) used in their synthesis is not observed. Several purification techniques and processes should be used to remove toxic chemicals. This compounds may be toxic to host cells, and in-vivo application of hydrogels can lead to several problems if they present low biocompatibility [39,58].

The evaluation of toxicity of hydrogels can be made by in-vivo toxicity and citotoxicity tests. More recently, utilization of natural compounds and synthesis of natural polymers with higher biocompatibility resulted in a minor concern about toxicity, but this is a property that should always be considered if the material has to interact with a living system [39].

## 1.2.4. Application of hydrogels

Hydrogels can be applied in a wide range of products and areas (hygiene, industry, biomedical, pharmaceutical, agriculture) due to their unique properties such as hydrophilicity, biocompatibility and especially high absorption capacity and swelling/de-swelling behaviour [18,19,35].

Another factor that increases the range of applications of hydrogels is the fact that they can provide a fast response to environmental *stimuli* and/or variations. This characteristic allows the use of hydrogels in applications insusceptible to perform only by environmental sensitive polymers.

### 1.2.4.1. Hygiene field

Hydrogels, are extensively used in personal hygiene products, like disposable diapers and napkins, to absorb fluids. Furthermore, disposable diapers containing SAP are used both in hospitals and in care centers. SAP materials also can be used in training pants or other adult incontinence products [19,35].

The purpose of using hydrogels in these materials is to promote skin health and consumer comfort, keeping wetness and moisture away from the skin. The use of hydrogels in hygienic field allows the development and improvement of diapers while reduced environmental hazards and brought benefits in terms of economy [19,35].

### 1.2.4.2. Industry field

In the industry field, hydrogels are also applied with several purposes. Its application extends from oil industry up to textile industry. In oil industry, hydrogels have been used as controllers of mobility of fluid in formation allowing an improvement in enhanced oil recovery applications. In pulp and paper industry, temperature-sensitive hydrogels are used in a simpler water-removal process which reduces the used amount of water via recycling process and brings economic and energetic advantages [18,60,61].

Furthermore, hydrogels are used in other waste treatment, in removal of heavy metals from aqueous solutions and in textile industry by grafting or adsorbed onto the surface of polymer fibers [18,62-65].

### 1.2.4.3. Biomedical and pharmaceutical fields

Hydrogels are widely used in the biomedical and pharmaceutical fields. These materials have allowed great advances and improvements in many biomedical and pharmaceutical applications and have become very important and influential at this level.

Hydrogels, namely pH-sensitive hydrogels, can serve as actuators or artificial muscles due to their capacity to convert chemical energy into mechanical energy. Photo-response artificial muscles, memory devices and switches were also developed based on light-sensitive hydrogels [18,62,67].

In addition, pH, electro and thermo-sensitive hydrogels have been applied and studied as drug delivery systems. They can be mainly used in solid tablets where the contact with physiological fluids allows a swelling controlled release of the drug, or can be used for a controlled release through their matrix, directly at the site of interest [18,66,68,69].

Furthermore, hydrogels are often used in therapeutic, diagnostic and implantable devices (artificial skin, biosensors and tissue engineering). For example, hydrogels are ideal platforms for tissue regeneration in regenerative medicine, allowing the design of biomimetic scaffolds due to their highly biocompatible, rubbery mechanical properties close to soft tissues, large water absorption and specially the possibility to incorporate bioactive molecules and cells during the gelling process [18,70-73].

Another interesting biomedical applications of hydrogels is their capability to act as body water retainers in the treatment of some pathological conditions (diuretic-resistant edemas and renal failure) where they are used for removal of excess water from the body. For instance, in the case of stomach bulking agents, the ability of the hydrogels to swell is used to reduce the available space in the stomach and consequently to reduce the amount of food intake and promoting weight loss [66].

The possible application of hydrogels as ocular lenses and at the same time as drug delivery system has gained relevance in the last years. The purpose is to apply lenses which have the capacity to release drugs similarly to a drug delivery system, during the time of the treatment or for the desired time. Recently, ocular lenses made of hydrogels (soft contact lenses) was developed and commercialized [18,74].

Moreover, hydrogels have been used in wound care, as dental materials, in separation of various molecules including proteins and as injectable polymeric system [35].

#### 1.2.4.4. Agriculture field

In agricultural field, the presence of water is essential and the research for ways to reduce the water losses and also to obtain better living conditions for vegetation increased significantly in the past few years.

Hydrogels, namely SAPs, have unique characteristics, like ultrahigh absorption and control-release capacity that allows its application in agricultural area and contribution to alleviate certain agricultural problems.

The most important functions of hydrogels in agricultural area are related with the reducing of irrigation water consumption, with the increasing of water-holding capacity of the soil and with the capacity of acting as a fertilizer controlled release system [18,19,66,75-78].

**Figure 1.4 – Faba bean plants in soil 9 weeks afeter planting: untreated soil (left); treated with hydrogel soil (right), adapted from [18].**

During and after irrigation and/or raining, the SAPs particles will be swollen (absorb water) and may be taken as “water reservoirs” in soil. Water inside the particles will be removed by a more controlled way, upon the root demand through osmotic pressure difference. This process allows a more efficient water utilization, reduction of irrigation necessities, improve water holding capacity of the soil and promote the growth and quality of plants [18,19,78-80].

Further, hydrogels can uptake some nutrients (fertilizers) like urea, holding them tightly and then releasing their dissolution to the soil by a controlled way. This enables a continuous and more prolonged access to fertilizers by the plant that results in improved performance rates, growth, quality and quantity of plants or/and fruits (Figure 1.4) and improved fertilizers retention in soil [18,19,75,76,81].

Moreover, hydrogels can be applied to increase soil aeration and microbial activity, reducing environmental pollution and compaction tendency, diminishes soil density and eliminates the leaching of nutrients and stops erosion and water run-off [18,19,78,80].

#### 1.2.4.5. Other areas and applications

In addition to preview discussed areas, hydrogels are used or can be used in many other areas and applications, such as, food/meat packaging (yogurt dewatering for example), building internal decoration, fire extinguishing/retarding gels, artificial snow, turf of sport fields (football and golf for example) and others [19,35,66].

### 1.2.5. Superabsorbent polymers (SAPs)

A new class of hydrogels, known as SAP, were discovered and reported in the 1970s by the U.S. Department of Agriculture. Although being similar in production, preparation and classification, this class of hydrogels can absorb larger amounts of water or other fluids in relatively short periods of time comparing with conventional hydrogels. For instance, in deionized water these materials can exhibit an ultrahigh absorption capacity and swell 1000 times than of their dried weight [16,19,24].

Viewed as an evolution of common hydrogels, the characteristics of SAPs materials allow to extend the application of hydrogels to areas where high absorbency is needed, such as hygienic and agricultural areas.

#### 1.2.5.1. Market and History

The alkaline hydrolysis of starch-graft-polyacrylonitrile allows the production of the first commercial SAP in the 70s, however this product has shown disadvantages such as they are quite expensive and have weak structural properties, which caused his precocious market defeat [19,82].

Nevertheless, in 1978, with advances in technology and industry, SAPs synthesis was improved and these materials began to be produced for commercial purposes with a focus on hygiene market, particularly for use in feminine napkins. Later, in 80s, SAPs were used in baby diapers, low-fluff diapers and other personal health care materials [10,19].

In late 1990, the world production of SAPs was very high, more than one million tons, due to their extensive use in various fields [19,82].

European Disposables and Nonwovens Association (EDANA) estimates that in 2005, the total production of SAPs was approximately 1,483,000 tons, and the greatest SAP manufacturers are the Degussa, Nippon Shokubai, BASF, San-Dia Polymers, Sumitimo Seika Chemicals and Dow Chemicals [19,83,84].

The present work is focus on the SAPs materials, mainly due to its impact in agriculture areas.

#### 1.2.5.2. Motivation to use SAPs in agriculture

As is known, water is an essential and indispensable resource for the existence and support of life on Earth [85-87].

The largest consumer of fresh water is the agricultural sector, specifically irrigated agriculture, which currently consumes over 85% of the available water due to the intensification of agriculture and the fact that a large percentage of world’s food comes from irrigated land. [88,90]To get a more concrete idea of what was mentioned, since 1975 up until 2005 there was an increase of 70% in global irrigated land and by 2050, was projected that this increase will be 140% [91,92].

With the increasing of the demand of water in several sectors like industry, domestic, among others, climatic and environmental changes, population growth and utilization of some inefficient methods and technologies of irrigation, arises the need to rationalize and use less water in agriculture sector. It is important to look for possible paths and strategies to mitigate and optimize consumption of water through environment-friendly and efficient technologies and combination of good management practices.

Nowadays, the dominant method of irrigation applied in the fields is surface irrigation. With this method, one half of the water released is lost in surface runoffs, evaporation and conveyance. So, enhance the efficiency of irrigation is one possibility for improved water management in agriculture and this improvement can be achieved by changing the water retention properties of the soils. Further, the hydraulic conductivity of the soil is an important characteristic that affects the surface runoffs and the infiltration rates. These characteristic can be changed by modifications in soil properties [90,93].

In this case, the main gold is to maintain sustainability of water resources while the use of irrigation water for agricultural operations and others activities (like golf courses) is optimized.

SAPs appear as materials with promising characteristics and the ability to change and improve the water retention and water holding capacity in soils. Consequently, these materials can maximize water utilization and production in croplands without adverse consequences for the available natural resources and environment.

#### 1.2.5.3. SAPs in agriculture

The application method of SAPs in lands includes mixing the dry hydrogel, in form of granules or powder, with soil in the area near the roots of the plant. Later, when the culture is watered or rains, water is absorbed by the hydrogel that turns from a glassy to a rubber-like state (Figure 1.5). Subsequently, water and possible nutrients are released from hydrogel to the soil as needed, which allows the availability of these resources by a longer period of time and prevents a rapid loss of water by evaporation or drainage, making the irrigation process more efficient and productive [9,94].

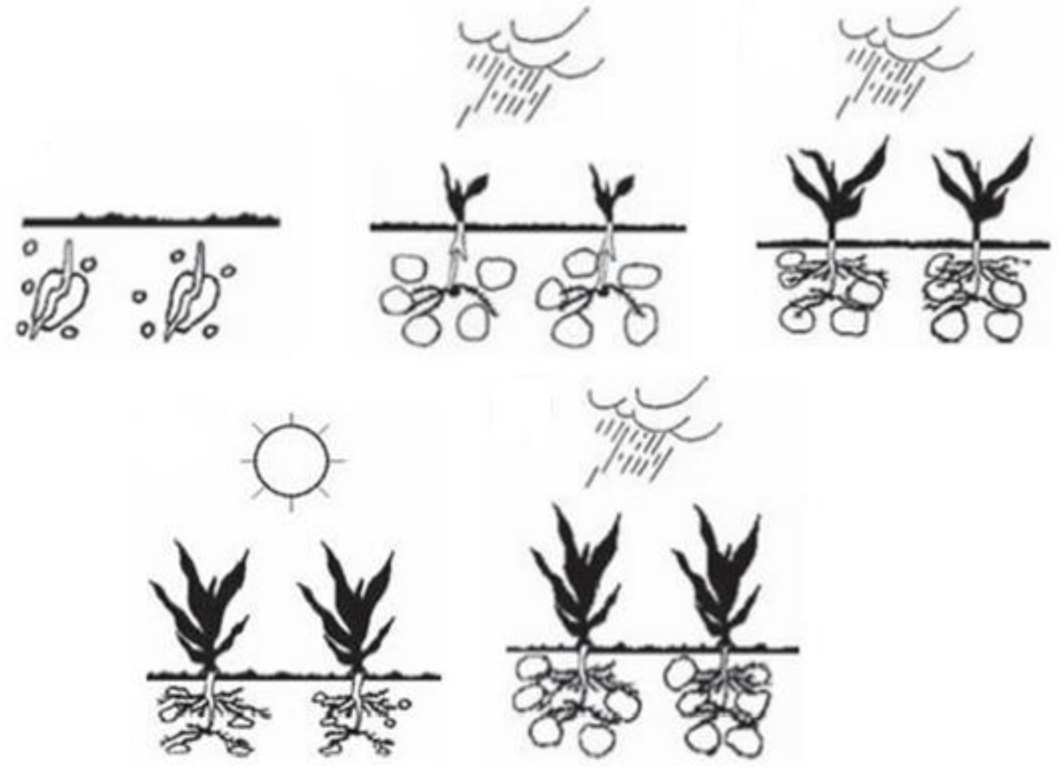


**Figure 1.5 – Operation of SAPs in agriculture, adapted from [94].**

Further, the dry hydrogel might also be loaded with fertilizers/nutrients and plant pharmaceuticals, which can be released in a controlled manner to soil and consequently promote the plants growth and quality.

It is important to note that use of SAPs is not favourable and suitable for all type of soils, being the most indicate the dry soils, available in arid and desert regions. For instance, when the soil is too moist or soaked, plant growth is hampered because of lack of oxygen. In this case, the utilization of SAPs could prolong this unfavourable condition, so their use is not recommended [95].

Moreover, the amount of SAP used in the soil should be the appropriate to ensure that the above mentioned benefits are achieved. At the same time it is crucial to ensure that the soil do not becomes spongy and saturated with water. A few studies have been performed, at different environmental conditions and with different plant species, to determine the appropriate hydrogel amounts and application rates for each specific case.

To sum up, the utilization of SAPs in the agricultural field brings benefits, such as reduce irrigation frequency and compaction tendency, stop water runoff and erosion, increase water use efficiency, soils water holding capacity and plant performance, enhance soil permeability, infiltration rates and biological activity, enable use of desertified areas and abandoned or slightly fertile croplands, and others [78,79,80,90].

However, there are some limitations to SAPs application in soil. The water absorption capacity of SAPs decreases when they are in contact with certain ions like $Ca^{2+}$ and $Al^{3+}$ that are often present in the soil or when the irrigation water shows high salinity. Further, swelling properties of SAPs are negatively influenced by the pressure caused by soil weight and their ability to absorb water is greatly reduced. SAPs can also lose their water retention capacity due to its fragile structure and tendency to break out or even due to abrupt variations in environmental and soil conditions like temperature rises. Furthermore, a study reported in literature, demonstrated that the effectiveness of SAPs decreases with the rewetting and that alterations in hydraulic properties of soil only are achieved using high application rates. Also some authors reported that high application rates of SAPs can affect negatively the economic value of crops and sometimes be harmful to plants or even cause their death [54,96-100].

#### 1.2.5.4. Environmentally-friend SAPs

Currently, most of these commercial products are acrylate-based and not biodegradable due to their superior price-to-efficiency balance [19,66,101].

However, intensive use of these products associated with non-degradability and the fact that they are mainly made by synthetic compounds, may cause over-dosage with presence of some undesired components in harmful amounts in soil and croplands. This over-dosage can be potentially dangerous to cultivations and can cause other problems like contamination of groundwater or other essential water reservoirs [66,101,102].

Moreover, in several domains like agricultural area, where normally synthetic polymers are used for a limited period of time, there is a need to reduce the resistance of these materials to the action of living systems and also reduce polymeric wastes and possible environmental contaminations and hazards [66,101].

It is very important to protect and reduce negative impacts on the environment. Also the use of more natural compounds instead of compounds obtained from classical sources like petroleum is more adequate. Thus, there is the current trend to develop environmentally friendly alternatives to synthetic SAPs normally applied in agricultural fields.

It would be interesting to develop SAPs that when disposed in bioactive environments can degrade by the enzymatic action of microorganisms such as fungi and bacteria and/or their polymer chains may also be broken down by non-enzymatic processes such chemical hydrolysis [101,102].

This can be achieved through partial/total replacement of synthetic compounds used to synthesize SAPs by “greener” alternatives or natural compounds such as polysaccharides (cellulose, natural gums, chitin, starch), poly(amino acids), vegetable oils and others [101,102].

However, must be taken into account that natural compounds are often unable to provide the desired properties and characteristics in SAPs. In this cases, it is necessary to use combinations and junctions of natural and synthetic compounds to obtain desired product [66].

Polysaccharides and vegetable oils are materials with huge potential for use in synthesis of hydrogels more biodegradable and environmentally friendly [66].

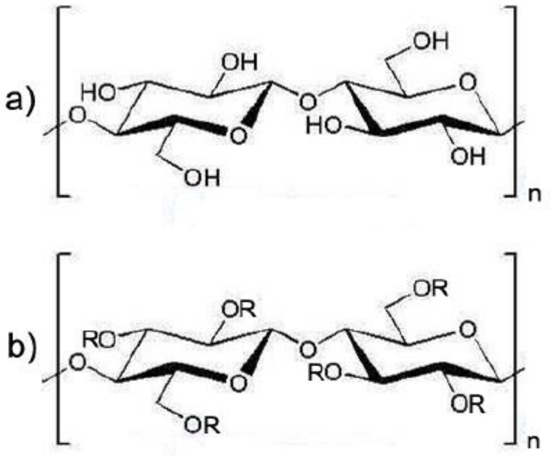
The use of these materials in production of hydrogels brings numerous advantages due to its abundance, low price, high availability, low or non-toxicity, inherent biodegradability and not cause negative consequences on the environment [66,101].

### a) Cellulose-based SAPs

Cellulose is the most abundant polysaccharide, it is a natural polymer constituted by glucose monomers, present in plants and natural fibers that can also be synthesize by a bacterial pathway (e.g. Acetobacter xylinum) [66,103].

Cellulose is a material with considerable interest and potential for use in polymeric synthesis, but it is also a very difficult material to process and apply in certain types of polymerization and mechanisms. For example, it is very difficult to solubilize cellulose in water, which is a huge disadvantage in the production of hydrogels which involves that uses water as polymerization solvent [104,105].

However, there are many cellulose-derivatives, named cellulosics, which can be produced from cellulose by esterification or etherification of its hydroxyl groups with organic species, which are more easily processable, water-soluble, and can be used in more applications in the industry. In Figure 1.5, repeating unit of cellulose and some of their derivatives are displayed [66,103].



| | |
|---|---|
| MC | R= H, $CH_3$ |
| HPMC | R= H, $CH_3$, $CH_2CH(OH)CH_3$ |
| EC | R= H, $CH_2CH_3$ |
| HEC | R= H, $CH_2CH_2OH$ |
| NaCMC | R= H, $CH_2COONa$ |

**Figure 1.6 – Repeating unit of cellulose (a) and repeating unit of cellulose derivatives (b), adapted from [66].**

Carboxymethylcellulose sodium Salt (CMCss), ethyl cellulose, methylcellulose, hydroxypropyl methylcellulose, HPC and hydroxyethyl cellulose are examples of cellulose-derivatives widely used nowadays [66,103].

In terms of production of SAPs, the cellulose-derivative that shows most promise and suitable is CMCss due to its polyelectrolyte character. This cellulosic is sensitivity to pH and to ionic strength variations and its presence in the constitution of hydrogel allows the electrostatic charges anchored to the network, which causes a great improvement on water absorption capacity and confers a smart behaviour to hydrogel. However other cellulose-derivatives, such as HPC may also be promising for the synthesis of SAPs [66].

Mainly through chemical or physical stabilization of aqueous solutions of cellulose-derivatives, using chemical agents or physical treatments (i.e., high-energy radiation), respectively, it is possible to synthesize stable cellulose-based hydrogels. To this synthesis are often added other natural and/or synthetic compounds (polymers) that allow to obtain improved hydrogels with specific properties [66,103].

### b) Vegetable oil-based SAPs

The vegetable oils are natural compounds composed predominantly of triglyceride molecules, a glycerol central structure attached to three fatty acids [106].

The fact that the triglycerides present several double bonds (C=C) and can s various degrees of unsaturation allows the functionalization of vegetable oils with polymerizable or functional chemical groups [106].

Some important examples of these possible functionalizations are epoxidation, convert unsaturated groups into epoxy groups, and insertion of acrylate functional groups by reacting epoxidized vegetable oils with acrylic acid [106,107].

These modifications in vegetable oils allow to obtain derived compounds that are more easily polymerizable (e.g., by free radical polymerization), more reactive and show improved properties and less limitations.

Vegetable oils and their derivatives are used in several production processes such as production of coatings, lubricants, agrochemicals and other similar materials [106].

However, in the area of hydrogels for agricultural applications, these materials weren’t much explored or even used. Despite this, derived vegetable oils compounds are materials that have promising properties and characteristics and it would be of great interest and also a challenge to study its possible application in synthesis of SAPs [107].

An important derivative of vegetable oils, namely of soybean oil, is the acrylated epoxidized soybean oil (AESO), compound widely used to produce polymers and/or polymer composites very useful in several applications and areas and that has been gaining relevance these days [106,107].

This compound is produced from soybean oil through two steps, the first corresponding to epoxidation of the oil and the second corresponding to the reaction of epoxy intermediate with AA in favourable conditions [106].

The great interest in AESO (Figure 1.7) arises largely due to its easy polymerization/copolymerization via free radicals reaction under several initiator systems as UV radiation, high energy radiations, photo initiators or thermal initiator decomposition. The polymerization/copolymerization is greatly facilitated because of the presence and possibility to use the double bonds from acrylate functional group [107].

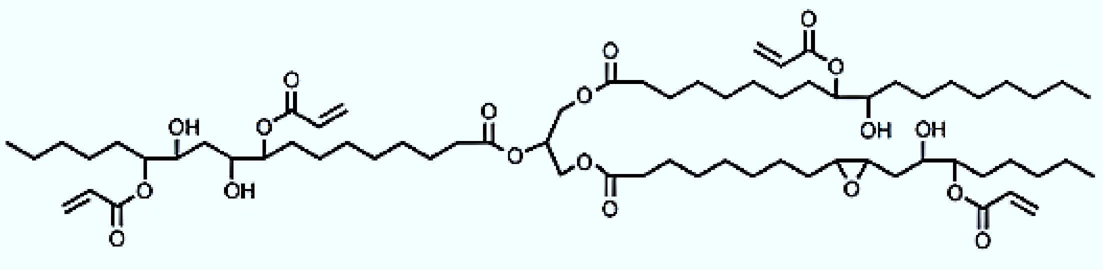


**Figure 1.7 – Representative structure of AESO, adapted from [108].**

The type of polymerization/copolymerization mentioned above is quite interesting from the viewpoint of SAPs synthesis and the presence of acrylate functional groups in AESO may promote the properties of the hydrogel (SAP) possibly synthesized resorting to this material.

The use of AESO as monomer or as crosslinking agent appears like an alternative to the production of SAPs for agriculture.

## 1.3. Literature review

This topic consists in a brief summary of the studies developed about SAPs and their practical application in agriculture field. It will be also consider works about different biodegradable hydrogels, such as cellulose-based and AESO-based materials.

Several papers and books have been developed and published over the years to review hydrogel materials and to study its applications and consequences for soils and cultivations.

In terms of broader reviews, in 1989, Kulicke and Nottelman made a brief review of synthetic, semi-synthetic and biopolymeric hydrogels [13].

More later, in 1996, Mathur conducted a review about methods for synthesis of hydrogels networks, giving emphasis to the synthetic methods and discussing properties of the hydrogel networks [17].

Recently, Waham reviewed definitions, classifications, main properties and applications of polymer hydrogels. In this review, raw materials, preparation tecnhiques of the polymer hydrogels and factors that can affect swelling properties were also described and discussed [18].

Another similar work, was perfomed by Ahmed in 2013. However, in this case a more extensive review on technologies adopted for hydrogel production was made, highlighting process design implications, block diagrams and optimized conditions of the preparation process. Further, SAPs were also discussed in more details [16].

SAP materials were extensively reviewed by Zohuriaan-Mehr and Kabiri. They made a short introduction about these materials, showing their different classifications and types, discussing its properties, production processes, application and finally approached environmental concerns and safety issues related with SAP materials.[19]

Taking into account the use of hydrogels in agriculture, the review performed by Kazanskii and Dubrevskii, in 1992, appears to be an important study. Here is described the chemistry and physics of hydrogels for agriculture with emphasis on the methods of SAPs synthesis, measurements and treatment of its key physical properties as well as its behaviour and the effects of hydrogels in soil and on plant growth [14].

Later, in 1995, the utilization of synthetic polymers as soil conditioners were reviewed by Bouranis [109].

Pouci have made a review related with the utilization of polymers in agriculture, where considered the SAPs used in agricultural applications. The main goals and advantages of using SAPs in agriculture were approached and were also mentioned various types of synthesized and reported SAPs, highlighting SAPs produced using biodegradable compounds and composite SAPs [102].

Another review about polymers applications in agriculture was made by Ekebafe where the utilization of SAPs and composites in agriculture were discussed [101].

An important review about SAPs and its pratical application in croplands, was perfomed in 2013 by Dabhi. In this study, a relevant literature review has been conducted to understand different properties of SAPs used in agriculture. Irrigation efficiency, effects of SAPs over the morphological features of the plant, application rates of SAPs under different conditions, biodegradability and optimum use of fertilizers with SAPs are some features considered and analized [90].

In terms of reviews about hydrogels synthesized from biodegradable compounds, stand out the review conducted by Sannino, in 2009. In this review, theoretical references about cellulose and its derivatives were made and the design and application of cellulose-based hydrogels was discussed, with reference to applications in agriculture [66].

Cellulose-based hydrogels were also reviewed by Chang and Zhang in 2010. They reported extensively the recent progress in methods of design and fabrication of hydrogels and composite hydrogels from cellulose. A small approach to the applications of these hydrogels was also perfomed [103].

Since AESO only recently appears as a possible compound for the production of hydrogels, there are no studies reported about this type of materials. However, it is important to consider the article published by Pelletier about photocrosslinking of acrylated vegetable oils, where was discussed UV-induced free radical polymerization of acrylate soybean oil and the final properties of the crosslinked material obtained [107].

Another reviews about SAPs were made in the last few years. In 1994, Buchholz studied the uses and recent advances in superabsorbent polyacrylates, namely superabsorbents based on crosslinked, partially neutralized poly(acrylic acid) and graft copolymers of starch and acrylic acid. Later in 1996, superabsorptive materials based on the polysaccharides and proteins, were reviewed by Ichikawa and Nakajima. In another review, Dayal prepared crosslinked acrylic acid-co-sodium/potassium acrylate through suspension and solution polymerization techniques. More recently, in 2002, Dutkiewicz reviewed superabsorbent materials obtained from shellfish waste [15,110-112].

Beyond the reviews mentioned above, it also important to note that there are two important books, *Absorbent Polymer Technology* and *Modern Superabsorbent Polymer Technology*, which focus on SAPs and help to better understand the technology related with production of these compounds and also its properties, applications and potential.[9,10] It important to mention some other relevant papers related to the development of new SAPs and their application in soil and culture of some plants showed in Table 1.2.

**Table 1.2 – Relevant papers related to the development of new SAPs. [113-124]**

| Reference | Hydrogel reactants | | | Type of polymerization | Swelling in distilled water (g water/ g dry SAP) | Properties studied |
|---|---|---|---|---|---|---|
| | Monomers | Cross-linking agents | Initiators | | | |
| [113] | AAm; CMC | MBA | | Photografting polymerization | | Swelling behaviour (influence of various parameters). |
| [114] | CMCss; HEC | DVS | | Ionizing radiation polymerization | 450 | Swelling behaviour. |
| [115] | AAm; CA | EGD; BDM | | Ionizing radiation polymerization | 6,90-20,45 | Swelling behaviour, network and some parameters about diffusion. |
| [116] | AAm; KMA; HEMA | MBA | APS | Solution polymerization | 450 | Swelling behaviour and water retention capacity in soil. |
| [117] | AA; AAm; Starch | PEG | | Grafting polymerization | | Swelling behaviour, effect of different drying methods on water absorbency, water retention capacity in soil and influence in germination and growth of plants. |
| [118] | NaPA | MBA; EGDE | | | 55 (in 0,9 wt% NaCl) | Swelling behaviour (influence of various parameters) in water and 0,9% NaCl solutions. |
| [119] | AA; Ammonia; Urea | MBA | APS | Inverse suspension polymerization | 965 | Swelling behaviour, slow release (urea) property in water and water retention capacity in soil. |
| [120] | AA; AAm; CMC | MBA | KPS/SMB | Graft solution polymerization | 920 | Swelling behaviour and water retention capacity in soil. |
| [121] | CMCss; HEC | CA | | Solution polymerization | 1100 | Swelling behaviour and water retention capacity in soil. |
| [122] | CMCss; four starches types | Al2(SO4)3.18H2O | | | | Water retention capacity in soil and influence in plant growth. |
| [123] | CMCss; PVP | | | Irradiation polymerization | 144 | Swelling behaviour, moisture retention capability and urea loading and release studies. |
| [124] | AA; KA/AMA; NIPAAm | TMPTA | KPS | Solution polymerization | 1130 | Swelling behaviour, fertilizer uptake and release studies and swellability of SAP under soil. |

## 1.4. Characterization of SAPs

After the synthesis of the SAPs it was essencial to proceed with their characterization. Considering SAP materials and their application in agricultural field, the focus will be the study of their swelling properties.

The knowledge of the swelling properties is essential to infer about the potential of the hydrogel to be used in agriculture. These types of hydrogels must have high water absorption and retention capacities in order to ensure all the previously mentioned advantages and benefits.

However, it is also relevant to consider another methods of characterization such as structural, thermal and morphological (pore and particle size), which provide important and essencial information for better understanding the material and their characteristics.

### 1.4.1. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared Spectroscopy is an analytical technique very used for the identification and characterization of the functional groups present in a given sample. This analysis is based on the detection of the vibrations caused by the interaction between the atoms of the sample and the incident infrared (IR) radiation [125,126].

With the incidence of IR radiation on the sample, it is obtained a spectrum that shows the fraction of radiation absorbed in a particular energy range, compared to a reference spectrum recorded previously without a sample. Each functional group shows a specific vibration frequency that corresponds to a particular energy peak, allowing the identification of the funcional group. The spectrum obtained represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. As a fingerprint, two molecular structures do not have the same infreared spectrum [125,126].

### 1.4.2. Thermogravimetric Analysis (TGA)

TGA is a thermal characerization technique that allows the analysis of the thermal stability of the SAPs sample. This technique studies the weight variation/loss of sample as a function of temperature and/or time, when the sample is submitted to a significant temperature variation. Its main advantages are related to the ability to analyzed a wide range of temperatures using a small amount of sample and the possibility of changing the surrounding atmosphere [127,128].

Besides the study of the sample weight loss, this thermal technique also allows the study of the sample's degradation. To help this analysis it is possible to represent the TGA derivative's known as Derivative Thermogravimetric (DTG) curve. The DTG curve shows different peaks associated to each TGA steps, which represents the maximum rate of mass loss [127,128].

### 1.4.3. Scanning Electron Miscroscopy (SEM) and Optical Microscopy (OM)

The SAP samples were analyzed in Scanning Electron Microscope (SEM) and in Optical Microscope (OM) to study its morphological features (pores and particles size).

**a) Pores**

The SEM technique was used to study the porosity of the SAP. With this technique, the sample is scan with a focused beam of electrons. This electrons interact with the atoms present in the sample, producing different signals that can be detected and that contain information about the sample's composition, surface and topography [129,131].

For conventional imaging in the SEM, samples must be electrically conductive and electrically grounded (prevent the accumulation of electrostatic charge at the surface). Taking this into account, usually the samples are coated with an electrically conducting material, throught high-vacuum evaporation or low-vacuum sputter coating. Resolutions better than 1 nanometer can be achieve with SEM analysis [129,131].

**b) Particle size (Feret diameter, area and perimeter)**

For the analysis of particle size, was used optical microscopy and SAP samples in powder form. The optical microscopy is a kind of microscopy which uses a system of lenses and visible light to magnify images of small samples [132,133].

To determine the average diameter, area and perimeter of the particles of SAP was used a method of image analysis which involves the utilization of an optical microscope to obtain multiple images of SAP powder previously dispersed on a flat surface. With these images and the right software it was possible to count and calculate the characteristics of the various particles present in different images. Treating the results obtained through image analysis on an appropriate platform (Microsoft Excel), it was then possible to determine the average diameter, average area and average perimeter of particles of SAP [132,133].

The diameter of particules calculates in this case corresponds to the Feret diameter which consists in the average distance between two parallel lines tangent to the projection of the particle and allows to get values even for irregular particles [132,133].

# Chapter II

# 2. Experimental Methods

## 2.1. Materials

The materials used to prepare the various hydrogels in the present work include monomers acrylated epoxidized soybean oil, acrylic acid (99%), potassium hydroxide (90%) and 3-sulfopropyl methacrylate potasium salt (98%), initiators benzoyl peroxide (99%) and 2,2-dimethoxy-1,2-diphenyleethan-1-one (Irgacure 651, 99%), crosslinking agent bis[2-(methacryloyloxy)ethyl] phosphate (99.9%) and hydrochloric acid (37%) were purchased from Sigma-Aldrich; Monomers acrylamide (98,5%) and carboxymethyl cellulose sodium salt (Mw=90.000), crosslinking agent N,N'-Methylenebis(acrylamide) (96%) and functionalizing agent 3-(trimethoxysilylpropyl methacrylate) (98%) were obtained from ACROS Organics; Monomer N-Isopropyl acrylamide (98%) was purchased from TOKYO Chemical; Polymer hydroxypropyl cellulose was obtained from Alfa Aesar; Solvents tetrahydrofurane (99,99%), dimethyl formamide (99,9%), acetone (99,99%), methanol (99,99%), toluene (99,99%) and ethanol (99,8%) were obtained from Fisher Chemicals. Initiator potassium persulfate (99%) was acquired from Riedel-deHaën. Crosslinking agent trimethylolpropane triacrylate (98%) was purchased from UCB Chemicals. Sodium hydroxide (97%) was obtained from Panreac Química. Urea was acquired from ANALAR Trademark.

All the reagents, solvents, functionalizing agent and other materials were used as received without further purification.

## 2.2. Procedures

### 2.2.1. 1st stage – Synthesis of SAPs with AESO

As the foundation and the starting point to perform these stage, it was considered the procedure held by Carlos Castro, making the necessary adaptations to this concrete case [134].

Initially, the reactions were conducted in a 150 mL reactor with 3 entries with mechanical agitation. However, to reduce the amount of reagents spend in each reaction, the synthesis became to be held in vials (20 mL) with magnetic stirring.

Basically, the synthesis involves mixing all the reactants, passing this mixture to a reactor/vial and the subsequent placement of this reactor/vial in a water bath at the temperature considered and with stirring (mechanical or magnetic) to occur reaction.

It it important to highlight, that after the polymerization occurence, the polymer was washed with acetone, to remove unreacted monomers, cut into small pieces and then dried (usually on an dryer oven at a temperature of 30ºC). In the cases where solution polymerzation was carried out, dialysis, for the polymers purification and for having no influence of the solvents on the properties subsequently calculated, was also performed. After one day of dialysis the polymers were placed again on the dried oven.

The amouts of reactants and reaction conditions used for each reaction are described in the Results and Discussion section.

#### 2.2.1.1. AAm/AESO reactions

The reactions in the case of AAm/AESO were performed according to the following steps:

- ✓ Initially AAm (2-15 grams) and AESO (0.075-2 grams) were dissolved in the solvent (4-155 mL);
- ✓ Thereafter, the initiator (0.04-0.15 grams) was added to the mixture;
- ✓ The mixture was placed in a reactor/vial with appropriate stirring and at the desired temperature (30-70ºC);
- ✓ Allowed to react until formation of the polymer;
- ✓ The obtained polymer was washed with acetone, cut into small pieces and dried in an oven at 30ºC overnight;
- ✓ Subsequently dialysis was performed to the dry polymer and during 24 hours;
- ✓ Finally and after dialysis, the polymer was again dried in an oven at 30ºC and stored when presenting constant weight.

#### 2.2.1.2. AA/AESO reactions

In AA/AESO case, reactions were performed according to the follow methodology:

- ✓ Initially AESO (0.2-3 grams) was dissolve in the AA (2-4 grams);
- ✓ Thereafter, the initiator (0.04-0.08 grams) was added to the mixture;

- ✓ The mixture was placed in a reactor/vial with appropriate stirring and temperature (30-80ºC);
- ✓ Allowed to react until formation of the polymer;
- ✓ The obtained polymer was washed with acetone, cut into small pieces and dried in an oven at 30ºC and stored when presenting constant weight.

### 2.2.2. 2nd stage – Synthesis of SAPs based on the literature and using cellulose derivatives

The SAP taken as the basis to realize the second stage of this work, was synthesized by free radical copolymerization using as comonomers NIPAAm, AA and potassium acrylate (KA), as crosslinking agent TMPTA, the as initiator potassium persulfate (KPS), at 70ºC in aqueous solution. [124]

#### 2.2.2.1. 1st phase of the 2nd stage – Synthesis of base SAP and new SAPs

To perform phase 1 of this stage was used a similar methodology and the synthesis of different polymers was performed in a 150 mL glass reactor. One head of the reactor served to introduce all of the reagents. In a second head was placed a condenser and in the central part of the reactor a mechanical agitator was installed to ensure that a homogeneous sample was obtained. The reagents were added to the reactor in the following molar percentages: AA 62%, KA or Sulfopropyl methacrylate potassium salt (SPMps) 35%, NIPAAm 2.44%, TMPTA or H232 0.44% and KPS 0.12%. The mixture was heated, reacting during a specific period of time and stopping when gelification (formation of gel) occurred. After the polymerization the SAP samples were washed with ice cold methanol to remove unreacted monomers. The SAP samples were cut into small pieces and oven dried to constant weight at 50ºC. The dry SAPs were purified by Soxhlet extraction using acetone-methanol (1:1 v/v), at 50ºC for one day, powdered, dried again in the oven and stored.

#### 2.2.2.2. 2nd phase of the 2nd stage – Synthesis of SAPs with cellulose derivatives

In the phase 2 of 2nd stage was also considered based methodology and the attempts to synthesize the polymers were also performed in a 150 mL glass reactor. Once again, one head of the reactor served to introduce all the reagents. A second head served to put a condenser and the central part of the reactor to put a mechanical agitator. To perform the reactions described in the table 3.6, the reactants were mixed with water (30-40 mL) in the following mass quantities: AA (0.7-2 grams), SPMps (1.3-2 grams), NIPAAm (0.11-0.23 grams), CMCss (1 gram), HPC (1 gram), KPS (0.07-0.05 grams) and BMEP (0.006-0.015 grams). Must be considered the not always all reactants participated in the reaction as is noticeable in the table 3.6. The obtained mixture was the placed in the reactor, heated to desire temperature (70ºC) and allowed to react. If polymerization occurs, the polymer should be washed with ice cold methanol, cut into small pieces, purified by Soxhlet extraction using acetone-methanol (1:1 v/v) and dried in the oven.

### 2.2.2.3. Functionalization of cellulose derivatives

The functionalization of cellulose derivatives, CMCss and HPC was performed according to the method reported by Yang and using the compound (3-trimethoxysilyl)propyl methacrylate (TMPM) that have in its structure interesting functional groups (carboxyl groups). [135]

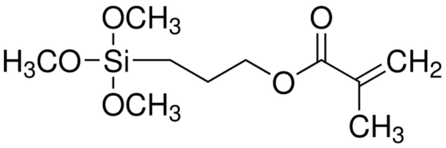


**Figure 2.1 – Representative structure of TMPM, obtained from [136].**

This functionalization steps were as follows:

- ✓ Make a suspension of CMCss or HPC in toluene (CMCss or HPC 1.5g in 100ml of toluene);
- ✓ Place the suspension in a rector equipped with mechanical stirring, condenser and under nitrogen stream;
- ✓ Put the reactor in an oil bath and heat the bath to 100ºC;
- ✓ Add to reactor the TMPM previously dissolved in hot toluene (1.5 mL of TMPM to 5 mL of toluene);
- ✓ Allow to react for 6 hours, filter and dry under vacuum at 110ºC for 2 hours (to ensure the formation of covalent bonds between CMCss or HPC and H349).

## 2.3. Methods of Characterization

### 2.3.2. Characterization Techniques

**a) FTIR**

Fourier Transform Infrared (FTIR) spectra were carried out in a FTIR-4200 spectophotometer by Jasco recorded at a wavelength comprised between 500 and 4000 $cm^{-1}$ and with 4 $cm^{-1}$ resolution. Attenuated Total Reflection (ATR) mode was used.

**b) SEM and OM**

Scanning electron microscope (SEM) (MEV)/EDS, JEOL, model JSM-5310, at an accelerating voltage of 10 kV was used for SEM analysis. In this especific case, for the analysis of porosity, the SAP sample were first immersed in distilled water until reaching equilibrium swelling, then freeze dried and finally submitted to SEM analysis. In SEM analysis, as the SAP samples are non-conductors, before analysis is performed a sample preparation step which consists in coating the samples by sputtering with gold to make them conductive [131].

Optical microscope 3D IFM, model Alicona EO was used for OM analysis (particle size analysis) and for the image treatment and calculus of Feret diameter, area and perimeter of the particles quantification was used ImageJ 1.48v software.

**c) TGA**

TGA were perfomed in a SDT Q600 equipment (TA instruments), at a heating rate of 10ºC/min, for the temperatures ranging from room temperature to 600ºC, under a constant nitrogen flow.

### 2.3.3. Swelling Properties

The absorption capacity of synthesized SAPs were measured both in distilled water and in salt solutions at various pHs using the tea bag method [19,124]. The tea bag method is the most suitable, conventional and fast method for calculating the degree of swelling in SAPs [19].

**Figure 2.2 – Tea bag method performed.**

To carry out the tea bag method, an accurately weighted powdered SAP sample is placed into a tea-bag (acrylic/polyester gauze with fine meshes) and the bag is immersed in an excess amount of water or other solutions at room temperature. Then, after a certain period of time, the bag is taken out from the solution, the excessive water adhering is removed superficially with tissue paper and the bag is weighted [19,124].

This process is repeated several times until the swelling equilibrium is reached, i.e. until the bag present a constant weight. It is possible to define the swelling profiles and calculate the absorption capacity (AC) of the hydrogel in units of amount (g) of water absorbed per gram of SAP, using the equation (2.1):

$$AC = {(W_s - W_d)}/{W_d} \tag{2.1}$$

Where $W_s$ and $W_d$ are the weights of the swollen hydrogel and the dry sample,respectively.

The weight of the swollen hydrogel ($W_s$) can be obtained by subtracting the weight of the tea bag without hydrogel to the weight of the tea bag with the swollen hydrogel. Thus, also were conducted similar tests, where several empty bags were immersed in water, taken out from the water, weighted and then performed an average of obtained weights for the empty and wet bags, which will be used in the calculations.

The tea bag method’s precision has been determined to be around ± 3,5% [19].

### i. Free-absorbency capacity

The free-absorbency capacity of water is related to the amount of distilled water that a SAP sample can uptake while swells freely.

More specifically, to calculate the free-absorbency capacity were placed in tea bags dry SAP samples with a weight between 0.005 and 0.01 grams and these bags were immersed in 1 liter of distilled water. The rest of the test was performed as previously mentioned and the absorption capacity was calculated by taking an average of three measurements (three bags with SAP samples) and using eq (2.1).

### ii. Swelling in salt solutions

The swelling equilibrium of synthesized SAP was also determined in various saline solutions (NaCl). The salt NaCl solutions were prepared with different ionic strength, concretely with 0,3 wt%, 0,6 wt%, 0,9 wt% and 1,5 wt% concentrations and maximum absorption capacity was determined according to the above method described in section 2.3.2. and using dry SAP samples with a weight between 0,005 and 0,01 grams [31,123].

### iii. Swelling at various pHs

The water absorption capacity of the developed SAPs was also determined at various pHs, using individual solutions with specific pH values ( 3, 5, 7, 9 and 11).

Individual solutions with acidic and basic pHs were prepared by diluting 0.1M HCl or NaOH solutions with distilled water in sufficient quantities to obtain the desired pH. The pH value of each solution was precisely checked using a pH meter. In this case, was also used dry SAP samples with weights comprised between 0,005 and 0,01 grams and the methodology of tea bag method previously mentioned [30,31].

### 2.3.4. Water retention capacity of the soil with SAP

To study the water retention capacity of the soil treated with the SAP and compare it with the water retention capacity of the soil without SAP, diffetent amounts of hydrogel (0,5 wt%, 1 wt% and 2wt% relative to the soil weight) were mixed with fixed amounts of sandy soil (40 g). Subsequently, the mixtures were uniformly irrigated with a certain amount of distilled water (20 g) and exposed at a room temperature. For each mixture were performed three assays. It was also performed a control experiment using soil without hydrogel for comparison [137,138].

These mixtures were weighted at certain intervals of time and the weight loss by evaporation of water registered. To determine the water retention (WR) percentage of the treated soil with the hydrogel or without hydrogel (relative to the initial weight of the mixture) was used the equation (2.2) [137].

$$WR = \left[{}^{(W_0 - W_t)}/_{W_0}\right] \times 100 \tag{2.2}$$

Where WR, $W_0$ and $W_t$ are the (%) water retention of the treated soil (at certain time), the mixture initial weight and the mixture weight at certain time,respectively.

### 2.3.5. Urea loading and release

To perform the loading of urea test, samples of dry hydrogel previously weighed (0,05 g) were immersed in urea solutions with different concentrations (5 g/L, 10 g/L, 15 g/L and 20 g/L) for approximately 24 hours (until reaching the maximum swelling). [123,124]

Subsequently, the swollen and loaded hydrogels were oven dried at 50ºC to constant weight. Knowing the weights of unloaded ($M_0$) and loaded dry hydrogels ($M_l$) was possible to calculate the percentage of loading of urea using equation (2.3) [123].

$$Loading\ (\%) = \left[{}^{(M_l - M_0)}/_{M_0}\right] \times 100 \tag{2.3}$$

For each concentration of urea were performed three trials, and an average of these was used to perform the calculations.

Furthermore, using the loaded and dried hydrogels, obtained for the case was used the solution with higher urea concentration (20 g/L), was possible to investigate their ability to release of urea. So, each of these hydrogels (three samples with weights between 0,120 and 0,170 grams) was placed in 500 ml of distilled water at room temperature. At various times, 20 ml from this solution was pipetted out for a glass and its urea content was determined gravimetrically by freeze drying the glass and comparing the weight before and after this process. The percentage of urea released was calculated using the following equation (2.4) [124].

$$\% \, of \; urea \; released = \left. (\Delta W)_n \times [500 - (n-1) \times 20]/20 + \sum_{i=1}^{n-1} (\Delta W)_i \middle/ W_u \right. \tag{2.4}$$

Where $(\Delta W)_i$ , is the weight of urea released from the 20 mL sample, $W_u$ is the amount of urea loaded in SAP and n indicates the number of urea release measurements at various time intervals in a single experiment.

# Chapter III

# 3. Results and discussion

In this section, the methodologies followed and results obtained in the SAPs synthesis reactions, functionalization reaction and methods of characterizations will be discussed.

## 3.1. Methodology Adopted

The main purpose of this work was the development of a more biodegradable SAP, with properties (mainly swelling properties) that would allow its application in agriculture field. The work was divided into two specific and distinct stages.

In the first stage, attempts were made to develop a SAP using the most common reagents (monomers, crosslinkers and initiators) from a natural source and more biodegradable compound, in this case, the AESO.

In the second stage, the recent synthesis of a SAP with excellent properties for agricultural applications, reported by Venkatachalam, was taken as the starting point. This paper was chosen as the basis for this work stage because it is a recent study which report the synthesis of promising SAPs with some of the best properties for agricultural applications found in the literature (see Table 1.2) [124].

Initially attempts were made to reproduce the reported SAPs and to understand the synthesis methodology in question. Subsequently, some modifications were made at the level of crosslinking agent and comonomers used in order to obtain improvements in SAP’s properties and a novel and not reported formulation.

Posteriorly in the final phase, the acquired knowledge and the optimized methodology was used to synthesize a more biodegradable SAP through the utilization of natural origin monomers, namely some derivatives of cellulose (CMCss and HPC).

## 3.2. 1st stage – Synthesis of SAPs with AESO

On a first stage, it was suggested to begin with the free radical polymerization of AAm or AA and AESO. The AESO is a compound from a natural source with biodegradable characteristics and theoretically capable to serve as a crosslinking agent (see Figure 1.7).

In this case, it is also intended that the AESO act as crosslinking agent or as a comonomer in the synthesis of SAPs. Being the AESO a compound with more biodegradable characteristics, its presence would be an advantageous for SAP constitution. The biological degradation of SAPs would be facilitated and the production of harmful compounds to agricultural lands and environment could be decreased.

The choice of AA and AAm is due to their extensive utilization in the synthesis of SAPs, also because they provide an "easier" polymerization, owed to the high reactivity of the double bounds, showing high aptitude to water (hydrofilicity) and functional groups of interest that can improve swelling properties (see Figure 3.1). Furthermore, AA and AAm are generally used to develop hydrogels with good features in terms of capacity of absorption and retention of water, normally considered as a target on agriculture [16,19].

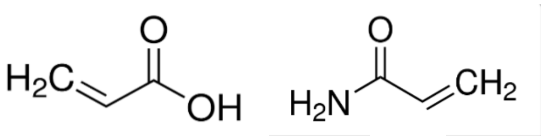


**Figure 3.1 – Representative structure of AA (a) and AAm (b), obtained from [139,140].**

The compounds chosen as initiators in this stage of experimentation were the potassium persulfate and the benzoyl peroxide. These compounds are also widely used in the synthesis of hydrogels as well in these type of polymerizations considered [18,19]. According to the synthesis procedure/ parameters, solvents as water, acetone, Tetrahydrofuran(THF) and Dimethylformamide (DMF) were used.

This stage comprises the implementation of the reactions presented on the Tables 3.1, 3.2 and 3.3 with the main purpose of knowing which formulations are the most favorable for the incorporation of AESO. It is posible to analyse which monomers were used and which conditions enhance the development of a crosslinking polymeric structure that allows to obtain hydrogels with the desired characteristics.

The Tables 3.1, 3.2 and 3.3 concerning the reactions are divided in three sections, corresponding to the reactions involving AAm/AESO, AA/AESO and other necessary reactions.

### 3.2.1. AAm/AESO reactions

In Table 3.1 are displayed the reactions between AAm and AESO, as well as the reaction conditions.

**Table 3.1 - Reactions performed between AAm and AESO.**

| Designation | Reactants | | | | | | | | Temperature (ºC) | Reaction time (h) | Type of polymerization | Conclusions |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Monomers (g) | | Initiators (g) | | Solvents (mL) | | | | | | | |
| | AAm | AESO | KPS | BPO | $H_2O$ | Acetone | THF | DMF | | | | |
| AH1 | 15 | 0.075 (0.5% wt) | 0.1507 (1% wt) | | 150 | 5 | | | 30 | 3 | Solution polymerization | Polymerization ocurred. |
| AH2 | 7 | 0.35 (5% wt) | 0.0735 (1% wt) | | 35 | 35 | | | 30 | 24 | Solution polymerization | No polymerization ocurred. |
| AH3 | 7 | 0.35 (5% wt) | 0.0735 (1% wt) | | | | | 70 | 30 | 12 | Solution polymerization | Polymerization ocurred. |
| AH4 | 7 (progressive addition) | 0.35 (5% wt) | 0.0735 (1% wt) | | | | | 70 | 30 | 20 | Solution polymerization | Polymerization ocurred. |
| AH5 | 4 | 0.2 (5% wt) | | 0.042 (1% wt) | | | 18 | | 70 | 5 | Solution polymerization | Polymerization ocurred. |
| AH15 | 2 | 2 (50% wt) | | 0.04 (1% wt) | | | 4 | | 70 | 6 | Solution polymerization | Polymerization ocurred. |

Regarding the reactions between AESO and the AAm displayed on Table 3.1, it can be concluded, except in the reaction AH2, that gelification occurred and hence a crosslinked polymer formation. In AH2 reaction, the polymerization did not occur probably due to the insufficient dissolution of the initiator and/or the monomers in the solvent mixture.

The characterization of the polymers obtained during the reactions in the case of AAm with AESO, was carried out through FTIR technique.

Basically this characterization was made to understand if the reaction between the AESO and AAm occurred, namely, to understand if the AESO - compound that would “confer” a higher biodegradability to the hydrogel - had been incorporated in the different obtained polymers. If the AESO is present in the obtained polymer, the polymer is crosslinked and has a polymeric matrix that permits to function as an hydrogel.

The FTIR analysis was also carried out in the main monomers, AESO and AAm and the transmittance spectra obtained are represented in Figure A.1 in Appendix A.

The absorption band that seems more proper to identify, to distinguish the presence of AESO in the obtained polymers, was the one corresponding to the C=O bond of the carboxylic group (ester), located approximately at a frequency of 1722 $cm^{-1}$ [141]. After perform the FTIR in the obtained polymers and analyse their transmittance spectra represented in the Figures of the Appendix B, it was possible to observe that only in the spectrum of the polymer of the reaction AH15, also represented in Figure 3.2, was present the band considered characteristic of AESO, at a frequency of approximately 1722 cm$^{-1}$. The presence of the characteristic band of the carboxylic group (ester) of AESO, suggests that this compound is present in the polymer of the reaction AH15 and thus there was incorporation of AESO in the AAm and consequent crosslinking.

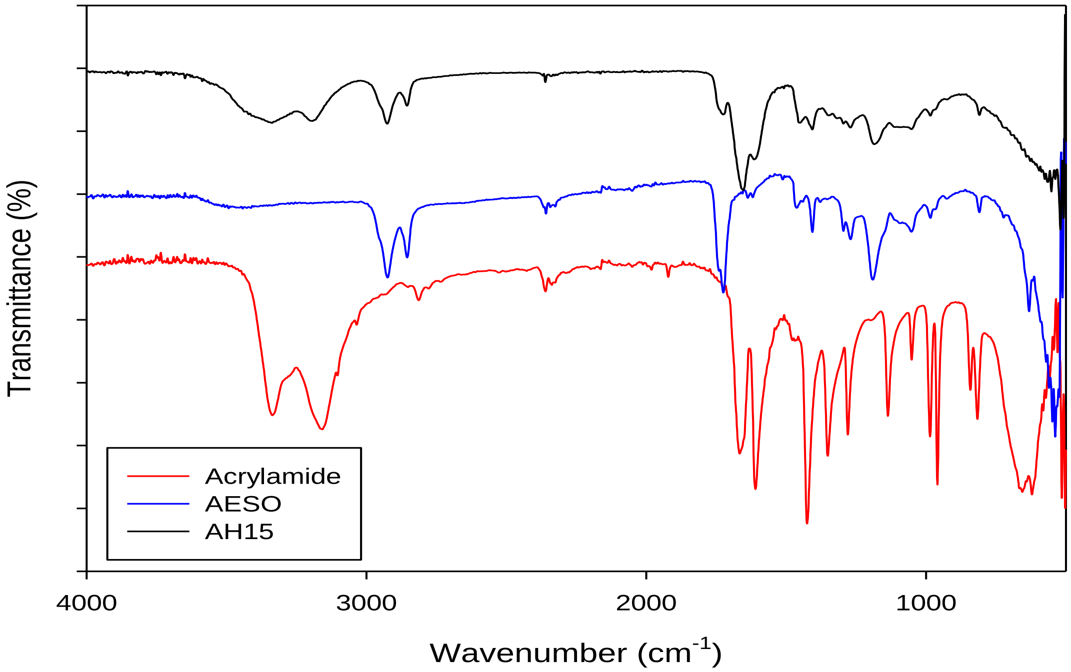


**Figure 3.2 – Transmittance spectra obtained for AAm, AESO and AH15 polymer.**

Since the FTIR spectra didn´t show the AESO’s characteristic band in the polymers obtained in the other reactions, it is possible to see that the AESO was not successfully incorporated in the polymer structure, occurring in theses cases only the AAm’s homopolymerization.

However to confirm that we have a reticulated material, the obtained polymers in the different reactions between AAm and AESO, were placed in vials with a certain solvent and then left in the shaker during 24 hours at 37ºC, checking after that time if had occurred dissolution or not. The polymer obtained in the reaction AH5 didn’t suffer dissolution in the solvents used (water, chloroform, THF and DMF), suggesting that this material is crosslinking and that it isn’t only based on AAm. This suggests that the polymer of the reaction AH5 can present in its composition AESO, which acts as crosslinkig agent and prevents the dissolution of this material in several solvents.

Briefly, in the work developed with AAm and AESO, it can be concluded that the results confirmed the incorporation of AESO and the crosslinking of the AAm for some experiments, when was used a considerable amount in percentage (wt%) of this biodegradable monomer (AH5 and AH15). The possible fact that AAm homopolymerizes so easily, probably hampered the incorporation of the AESO and when it happened complicates the AESO characterization and identification.

### 3.2.2. AA/AESO reactions

In Table 3.2 are presented the reactions between AA and AESO, as well as the conditions under which synthesis were held.

**Table 3.2 - Reactions performed between AA and AESO.**

| Designation | Reactants | | | | | Temperature (ºC) | Reaction time (h) | Type of polymerization | Conclusions |
|---|---|---|---|---|---|---|---|---|---|
| | Monomers (g) | | Initiators (g) | | | | | | |
| | AA | AESO | KPS | Irgacure | BPO | | | | |
| AH6 | 4 | 0.2 (5% wt) | | | 0.04 (1% wt) | 70 | 20 | Bulk polymerization | Polymerization ocurred. |
| AH7 | 4 | 0.2 (5% wt) | 0.04 (1% wt) | | | 30 | 20 | Bulk polymerization | No polymerization ocurred. |
| AH10 | 3 | 3 (50% wt) | | | 0.06 (1% wt) | 80 | 4 | Bulk polymerization | Polymerization ocurred. |
| AH12 | 2 | 2 (50% wt) | | 0.08 (2% wt) | | 70 | 2 | Photopolymerization | Polymerization ocurred. |
| AH13 | 2 | 2 (50% wt) | | 0.04 (1% wt) | | 70 | 2 | Photopolymerization | Polymerization ocurred. |

In AA/AESO case it is prominent that the polymerization is conducted on the bulk, since the AESO is soluble on AA and it is not necessary to use solvent.

In almost every reaction performed between AA and AESO, had occurred a polymerization and thus formation of the polymer, excepting in the reaction AH7. In this reaction didn’t occurred polymerization probably because the KPS does not have enough solubility in AA to remain dissolved and initialize the reaction.

The polymer characterization based on AA was also done with the main target of knowing if the reaction between the AESO and the AA occurred and if the obtained polymers were crosslinked.

As characterization techniques were used the FTIR, TGA and tests of solubility in commonly solvents.

The FTIR analysis was carried out following the same logic as the AESO with AAm, nevertheless to AA, emerged a problem related with overlapping bands of the transmittance spectrum with the AESO bands. This overlapping could lead to an inaccurate and incoherent analysis of the results, thereby making impossible to apply this technique in order to conclude if the goals were achieved.

As has been evidenced, the obtained transmittance spectrum of each reaction performed between the AA and the AESO, are inconclusive, since there was overlapping of the bands of these two compounds, with no characteristic bands enabling to conclude that the AESO was present in the final polymer and had been incorporated with the AA. A clear example is represented in Figure 3.3, where the transmittance spectrum of the polymer obtained in the reaction AH6, AESO and AA, are represented. The transmittance spectra from other reactions performed at this stage are represented in the Figures from Appendix C.

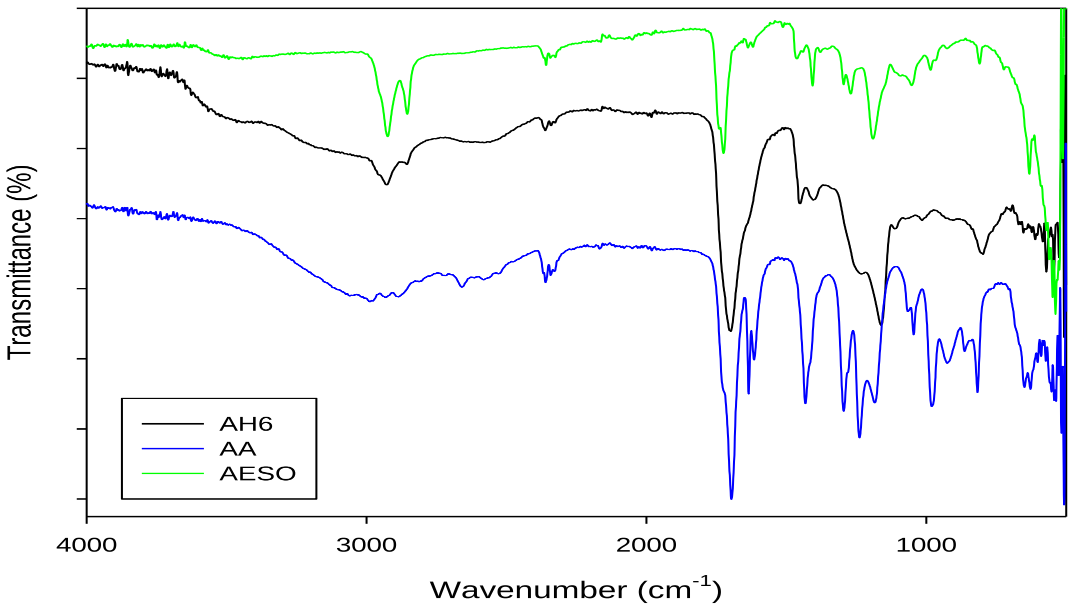


**Figure 3.3 – Transmittance spectra obtained for AA, AESO and AH6 polymer.**

Due to this limitation and the impossibility to exploit the FTIR technique, it was resorted to solubility tests in solvents such as water, chloroform, THF, ethanol, DMF and dimethyl sulfoxide (DMSO) to verify if the obtained polymers were crosslinked.

In this case, the solubility tests were performed to the obtained polymers in the different reactions between the AA and the AESO in the same manner as in the previous case (AAm/AESO). In the cases that not occurred the total dissolution in the solvents tested it was assumed that the samples were crosslinked.

So the solubility tests were performed to the most promising polymers synthesized in the reactions AH6 and AH10. After accomplish the tests it was verified that the dissolution of those polymers in the solvents did not occur and can be concluded that they were crosslinked and had occurred incorporation of AESO.

To make the results of the solubility tests more reliable, it was carried out a test of solubility in the obtained polymer from the reaction AH8, that is P(AA), in THF and the result was compared with the ones of the previous tests.

The P(AA) dissolved on THF unlike the polymers related to the reactions AH6 and AH10. This suggests that those polymers are not only constituted by P(AA) but can have in their structure others compounds, namely AESO, which in this case worked as a crosslinking agent.

Another way of knowing if the polymers of these reactions were crosslinked, and if the AESO had reacted with AA, thermogravimetric analysis was performed. TGA was made to the most important and promising polymers obtained (reactions AH6 and AH10), also to the polymerized AESO (reaction AH9) and to the P(AA) (reaction AH8). Then, the decomposition curves were compared in an attempt of finding similarities that provided evidence of incorporation of the AESO in the polymers, as well as they were crosslinked.

It was possible to observe the TGA's results, in the Figure 3.4.

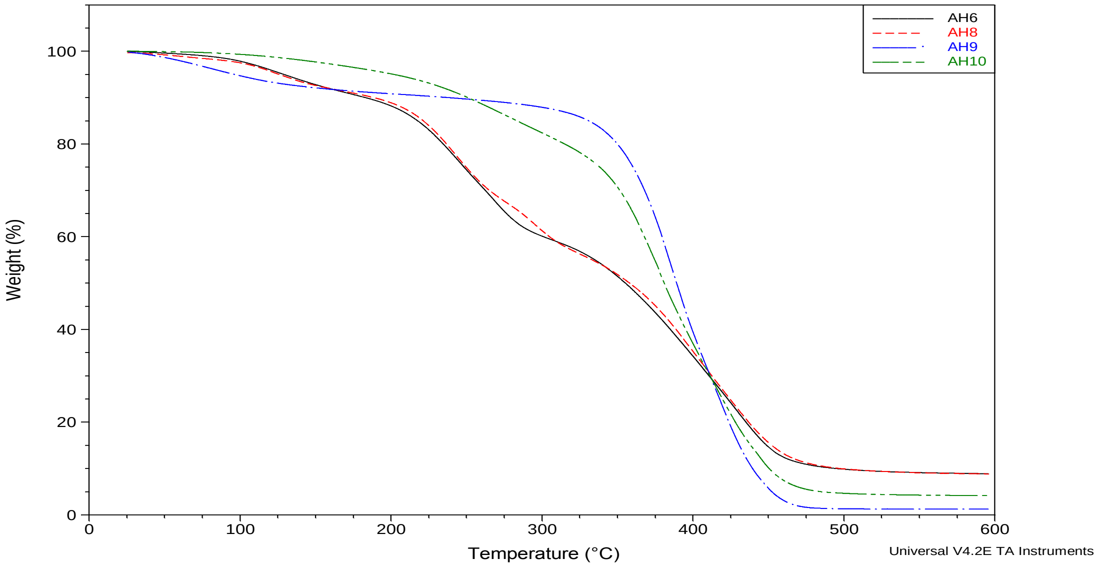


**Figure 3.4 - curves of mass loss in function of the temperature in different polymers (AH6, AH8, AH9, AH10).**

Accordingly to this data, it is possible to state that the curve of the polymer from the reaction AH10, with 50% wt of AESO, is rather similar with the curve regarding the polymerized AESO (AH9) and those two compounds enter in thermal decomposition later than the other ones analysed. This similarity between the curves of mass loss suggests that the polymer of the reaction AH10 has in its constitution AESO, which means that it only starts to decompose at higher temperatures, up to 300ºC. Basically in this case it can be stated that there was incorporation of AESO in AA structure and crosslinking of the same one.

In the other hand, the polymer of the reaction AH6, with 5% wt of AESO, presents a curve of mass loss very similar to the curve of the P(AA) (AH8) and a more pronounced thermal decomposition at lower temperatures (up to 200ºC), suggesting that this polymer has a constitution more akin to the P(AA) than to the polymerized AESO. In this case, the results indicate that there was no incorporation of AESO in the AA structure, or if this incorporation occurred was minimal and this polymer has a greatly reduced quantity of AESO, that it is not sufficient to alter the weight loss curves but however was enough to occur crosslinking.

### Photopolymerization

It was consulted literature related with the AESO, where was performed photopolymerization between this compound and the AA. Based on this article and being the photopolymerization a reaction much softer than the thermal polymerization, emerged an alternative way to obtain a hydrogel based in AESO and AA [107].

This photopolymerization was performed using Irgacure 651 as the photoinitiator, one of the photoinitiator available in the laboratory and that was also utilized in the article of reference.

After performing the photopolymerization, were obtained polymers similar to that obtained in the reaction AH8. These polymers are also insoluble in the solvents used in the solubility tests, which imply that, in this case, the AESO also reacted with the AA and that, resorting to this polymerization technique, is also possible to obtain polymers crosslinked.

A promising alternative is left open to follow and use in future works related with the development of gels and hydrogels of this nature and/or with the utilization of AESO and AA to produce other polymers to different areas.

## 3.2.3. Supplementary reactions

In Table 3.3 are presented supplementary reactions, as well as the reaction conditions.

**Table 3.3 - Supplementary reactions performed.**

| Designation | Reactants | | | | | | Temperature (ºC) | Reaction time (h) | Type of polymerization | Conclusions |
|---|---|---|---|---|---|---|---|---|---|---|
| | Monomers (g) | | | Initiators (g) | | Solvent (mL) | | | | |
| | AA | MBA | AESO | Irgacure | BPO | THF | | | | |
| AH8 | 4 | | | | 0.04 (1% wt) | | 70 | 2 | Bulk polymerization | Polymerization ocurred. |
| AH9 | | | 4 | | 0.04 (1% wt) | 4 | 70 | 20 | Solution polymeriation | Polymerization ocurred. |
| AH11 | | 0.04 (1% wt) | 4 | | 0.04 (1% wt) | 4 | 70 | 20 | Solution polymeriation | No polymerization ocurred. |
| AH14 | | | 4 | 0.04 (1% wt) | | | 70 | 2 | Photopolymerization | No polymerization ocurred. |

It is important to be mentioned that some reactions, such as AH9, AH11 and AH14, were conducted with goals slightly more specific, since the use of the obtained polymer, namely polymerized AESO, as a term of comparison in some techniques of characterization (TGA e FTIR), until the attempt to obtain a hydrogel only based in AESO, in other words, 100% natural.

The polymerization of AESO only occurred in the reactions AH8 and AH9, with no satisfactory results for the reactions AH11 and AH14.

Although in the reaction AH9 it was possible to obtain the hydrogel, the polymerization of AESO in THF was very slow, approximately 20 hours, probably because this solvent behaves as a chain transfer agent, forming small chains with low molecular weights and therefore, is not the most suitable solvent to use in the AESO polymerization.

### 3.2.4. Water absorption capacity of promising hydrogels

The water absorption capacity is one of the most important properties of hydrogels and that allows us to evaluate our products compared with hydrogels already developed and reported in literature. [18]

Hereupon, the tests to calculate the water absorption capacity were performed only in the most promising polymers and that supposedly would serve better the objectives of this work. Accordingly with the previous results, the polymers used in these tests were basically those who appeared to incorporate completely or minimally the AESO in their composition. In the case of AAm with AESO, those polymers were obtained through the reactions AH5 and AH15 and in the case of AA with AESO, were the polymers obtained through the reactions AH6 and AH10.

The tests to calculate the water absorption capacity were then realized accordingly with the tea bag method already described.

Regarding the obtained values, observed in the Figure 3.5, the maximum water absorption capacity in distilled water to the different synthesized polymers, it is noteworthy at the outset that in general, the values of absorption capacity for every polymers are very reduced and lower compared with hydrogels described in literature (see Table 1.2), existing in fact a significant discrepancy between them. In literature it can be found values for the absorption of water, developed for the same application with a biodegradable feature, of 140 [31], 304 [123] and 680 [142] g water/g dry polymer, values much higher than the values obtained in these case.

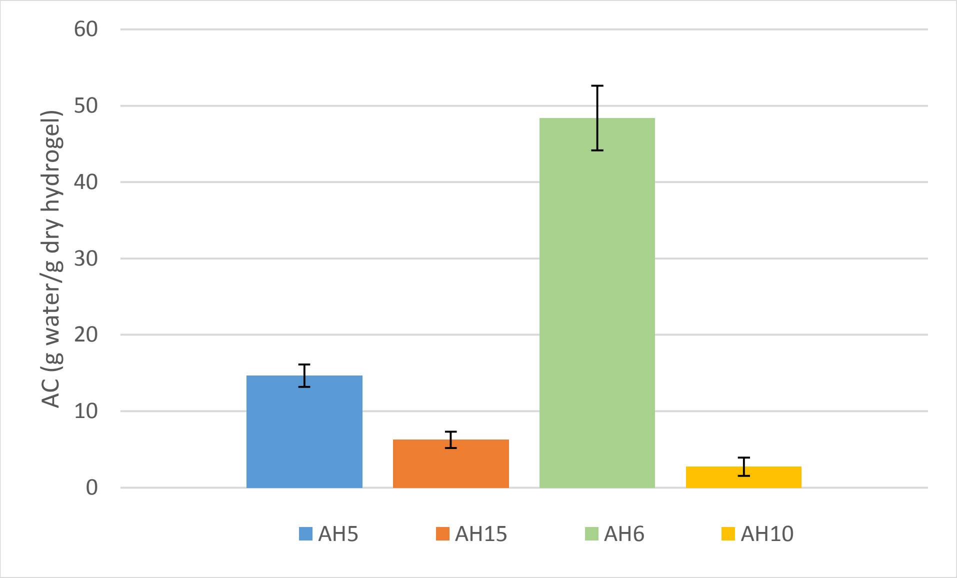


**Figure 3.5 - Maximum water absorption capacities of the most promising hydrogels (AH5, AH15, AH6 and AH10 polymers; after 24 hours).**

It is also important to refer that the worst results for the absorption capacity, both in the case of AAm and AA, were obtained in the polymers where there was incorporation of AESO (AH15 e AH10). This can be justified for the reason that AESO, although working as a crosslinking agent, may have a certain hydrophobicity, also it could have been used in big quantities and probably the obtained hydrogel matrix could be very crosslinked, which confined the capacity of network expansion and hence the water absorption capacity.

In summary, both polymers synthesized based in AAm as polymers synthesized based in AA, have a very low capacity of absorption of water, which can compromises immediately their utilization as a hydrogel for agriculture. The main objective of this work would be to develop a hydrogel that would incorporate the AESO and would have a water absorption capacity near from the reported hydrogels in literature or even the commercialized ones, something that, based on the previous results did not happened. In the case of the polymers that certainly incorporated the AESO, the obtained results are even worst and therefore it can be concluded that the aim of this work was not achieved.

Hereupon, were not performed further characterization tests about the developed hydrogels, such as the calculus of the water absorption capacity in different pHs or in saline solutions. The fact of the developed polymers have very unfavourable results in the main property regarding the goals of the work, leads to the abandonment of this idea and to the delineation of another methodology/approach that allows the achievement of better results.

## 3.3. 2nd stage – Synthesis of SAPs based on the literature and using cellulose derivatives

On a second stage, was performed free radical polymerization, according to the synthesis basis, primarily using the reactants reported and after optimization of synthesis, using novel compounds (some of natural origin).

The various reactions performed to achieve the objectives at this stage are shown in Table 3.4.

**Table 3.4 – Various reactions performed at 2$^{nd}$ stage.**

| Reaction | Reactants | | | Solvent | Reaction Conditions | Conclusions |
|---|---|---|---|---|---|---|
| | Monomers | Initiator | Crosslinker | | | |
| AH30 | AA; KA; NIPAAm | KPS | TMPTA | $H_2O$ | 70ºC; 10 min | Polymerization occured |
| AH44 | AA; KA; SPM; NIPAAm | KPS | TMPTA | $H_2O$ | 70ºC; 60 min | Polymerization occured |
| AH46 | AA; KA; SPM; NIPAAm | KPS | TMPTA | $H_2O$ | 70ºC; 50 min | Polymerization occured |
| AH50 | AA; KA; SPM; NIPAAm | KPS | BMEP | $H_2O$ | 70ºC; 60 min | Polymerization occured |
| AH53 | AA; SPM; NIPAAm | KPS | BMEP | $H_2O$ | 70ºC; 60 min | Polymerization occured |
| AH54 | AA; KA; SPM; NIPAAm | KPS | BMEP | $H_2O$ | 70ºC; 60 min | Polymerization occured |
| AH57 | CMCss*; SPM; NIPAAm | KPS | BMEP | $H_2O$ | 70ºC; 4 horas | No Polymerization occured |
| AH58 | HPC; SPM; NIPAAm | KPS | BMEP | $H_2O$ | 70ºC; 6 horas | No Polymerization occured |
| AH62 | HPC*; AA; SPM; NIPAAm | KPS | BMEP | $H_2O$ | 70ºC; 8 horas | No Polymerization occured |
| AH63 | CMCss; AA; NIPAAm | KPS | BMEP | $H_2O$ | 70ºC; 8 horas | No Polymerization occured |

*functionalized cellulosics

### 3.3.1. 1st phase of the 2nd stage – Base SAP and new SAPs

#### 3.3.1.1. Synthesis of base SAP and new SAPs

Initially was performed the base reaction (AH34), corresponding to the reproduction of the SAP reported by Venkatachalam [124]. As has been said, this reaction served as the starting point for better understands the polymerization method.

Subsequently some modifications and improvements in this method were made, namely at the level of the compounds used as crosslinking agent and comonomers and at the level of the amount of crosslinking agent used in the reaction.

The main purpose of these modifications was to obtain a new SAP material with improved swelling properties and a higher capacity to absorb water compared with other SAPs reported in the literature (see Table 1.2).

### i. Modification in the amount of crosslinker

The amount of crosslinking agent was one of the variables selected to modify, since it appears as a variable that can greatly influence the swelling properties and consequently increase the maximum capacity of absorption of the SAPs to interesting levels for use of this material in agriculture.

The reproduction of the experiment of SAP gives at final a structure somewhat rigid which suggest a polymeric matrix with a high degree of crosslinking (see Figure 3.6). It was then decided to reduce by half the amount of crosslinking agent used in the synthesis. This change was intended to obtain a matrix with lower degree of crosslinking and greater ability to expand, making possible to achieve higher levels of maximum swelling. (Table 3.5)

**Figure 3.6 – Base SAP synthesized in the swollen state.**

### ii. Modification of the compound used as crosslinking agent

Another modification was performed at the level of the compound used as crosslinking agent, replacing the TMPTA used in base reaction by bis[2-(methacryloyloxy)ethyl] phosphate (BMEP).

The selection of this crosslinking agent was due to various factors, such as:

- ✓ The fact of being a crosslinking agent with little or none reported applications in the area of SAPs for agriculture;
- ✓ Have a similar price to TMPTA and other crosslinking agents normally used in SAP synthesis, such as the MBA; [143-145]
- ✓ Be a compound with a longer main chain that TMPTA (see Figure 3.7), which would enable the synthesis of SAPs with a matrix with more available space between crosslinked chains, greater expansion capacity, more flexibility and consequently with a greater water absorption capacity;
- ✓ Have fewer points of crosslinking (two instead of three of TMPTA), which may allow the synthesis of SAPs with a less crosslinked structure than the structure obtained when using the TMPTA and thus with improved swelling capacity.

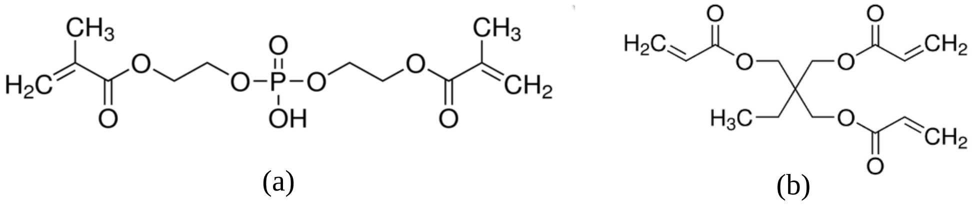


**Figure 3.7 – Representative structure of BMEP (a) and TMPTA (b), obtained from [143,144].**

BMEP is a compound with the phosphate group in its composition (see Figure 3.7 (a)) which may also be advantageous. The biological degradation of the SAPs can become easier and the nutrient phosphorus may be released to the soil. To be present in the soil, this nutrient can be used by plants, favoring its growth or even help the development and growth of beneficial microorganisms to agriculture.

### iii. Modification of comonomers

Finally was also performed a modification at the level of comonomers used in the synthesis of base SAPs, where KA was substituted to sulfopropyl methacrylate potassium salt (SPMps) (see Figure 3.8).

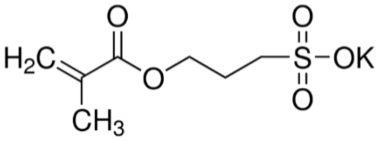


**Figure 3.8 – Representative structure of SPMps, obtained from [146].**

AA is one of the most used compounds in SAP's synthesis and the most essential component to synthesize and ensure a SAP with good swelling properties, due to the ability to confer a more hydrophilic character and the existence of carboxyl groups in its constitution. [16,19,139] So, it was decided to maintain this compound, continue using it in the synthesis of SAPs and substitute another comonomer.

NIPAAm also appears as an essential compound in this synthesis, since it acts as a reaction accelerator, i.e. as a kind of catalyst in the decomposition of persulfate (KPS) and its use allows the occurrence of much more rapid reactions and the obtaining of high levels of polymerization [124].

Thus, the modification fell on the comonomer KA, a component less important in the performed base synthesis. One of the main functions of KA in the synthesis is participate in the neutralization of the SAPs (acid base neutralization) and to ensure that there is a greater osmotic pressure between the inside and the outside of SAPs due to presence of $K^+$ ions in the network. This function can be also accomplished by SPMps since it would use its salt form and the presence of $K^+$ ions in network would be guaranteed.

In addition to participate in the neutralization of the SAPs, the choice of SPMps as comonomer was also due to:

- The fact that it presents carboxyl groups (methacrylate) in its composition that can provide improvements in swelling properties [146];
- Be a compound of more long main chain that KA (more free space on the network of the SAPs and possibilities for improvement of maximum swelling);
- Be a compound not much reported in the synthesis of SAPs for agricultural applications.

It is important to mention that the substitution of KA by SPMs was performed gradually through various reactions, i.e. through a substitution of 25%, 50% and 100% (complete substitution).

The Table 3.5 is concerned about the reactions performed in the 1st phase of the 2nd stage of this thesis and about the modifications carried out in each reaction relative to the base synthesis (AH30).

**Table 3.5 – Reactions and modifications performed in the 1st phase of the 2nd stage.**

| Reaction | SAP | Modification realtive to the base reaction |
|---|---|---|
| AH30 | SAP1 | None (Base reaction) |
| AH44 | SAP2 | Substitution of 50% of KA by SPM |
| AH46 | SAP3 | Substitution of 50% of KA by SPM; Half amount of crosslinker |
| AH50 | SAP4 | Substitution of 50% of KA by SPM; Half amount of crosslinker; Substitution of crosslinker TMPTA by H232 |
| AH53 | SAP5 | Substitution of 100% of KA by SPM; Half amount of crosslinker; Substitution of crosslinker TMPTA by H232 |
| AH54 | SAP6 | Substitution of 25% of KA by SPM; Half amount of crosslinker; Substitution of crosslinker TMPTA by H232 |

In every reaction performed on this stage it was possible to observe formation of the gel, not being necessary to use any other technique to validate these results.

### 3.3.1.2. Water absorption capacity of base and new SAPs

It was also important to understand if the performed modifications in the procedure and in the synthesis of the base SAP had any positive influence in the most essential properties (swelling properties) of the remaining synthesized SAPs.

To understand which one of the synthesized SAPs, was more promising to agricultural applications was also relevant. These evaluations and conclusions were performed using once more the maximum water absorption capacity of distilled water for the different SAPs, because this property translates, in a certain way, the potential of the SAP and is entirely related with many other relevant properties of this material.[18]

The greater the water absorption capacity of the SAP, the better will be the other properties and characteristics, including the maximum swelling in different conditions (pH and salt solutions), the loading and the release of fertilizers, the water retention capacity by the mixture soil/SAP, among other. Consequently SAP with higher maximum water absorption capacity should also be the most promising and the one with higher potential to be used in agricultural applications, where high absorption capacity and water retention are essential for these materials.[19]

Thus, the most promising SAP, with greater maximum water absorption capacity, was chosen to be used in a more complete and detailed study and characterization in terms of properties and characteristics which allow validating in a more practical and reliable way the possibility of agriculture applications.

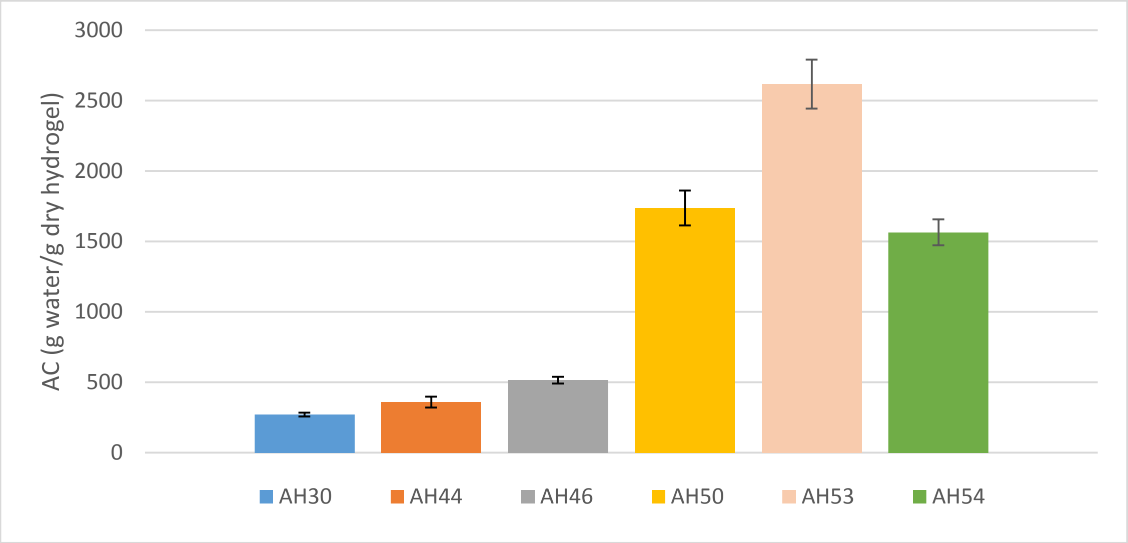


**Figure 3.9 – Maximum water absorption capacity for the synthesized SAPs in the 1st phase of the 2st stage (after 24 hours).**

The graph in the Figure 3.9 shows the maximum water absorption capacity (after 24 hours) for the synthesized SAPs in this stage, calculated through the tea bag method as previously described.

By the observation of the graph, it is possible to infer that all the modifications performed on the base synthesis were positive and brought many advantages regarding the swelling properties allowing relevant improvements in the maximum swelling of the synthesized SAPs compared with base SAP (AH30).

Despite the substitution of comonomers, the change in the amount of crosslinking agent and the substitution of the compound used as a crosslinking agent, had contributed for the increase of the maximum swelling. It should be highlighted that the modification which more positively influenced this feature was the substitution of the crosslinking agent to the BMEP (AH50-AH53).

As referred, this behaviour may be due to the fact that the new crosslinking agent, due to its structure and composition, allows the formation of a matrix with high availability interior space with a lesser crosslinked degree between chains, prompting relevant improvements in the swelling properties.

It is important to refer that the substitution of the KA comonomer for the SPMps, was performed in 25%, 50% and 100% and by the results the total substitution presented to be the most advantageous and the one which provided more relevant improvements in the maximum swelling.

From the obtained results it is possible to assert that the SAPs maximum water absorption capacity showed the highest value, rising from 270 g water/g dry polymer to 2617 g water/g dry polymer, when the three proposed modifications were performed simultaneously, i.e., when in the base synthesis simultaneously substituted the crosslinking agent to BMEP, when the amount of the crosslinking agent was decreased to half and when the KA comonomer were replaced by the SPMps in 100% (total substitution).

The best results happened when the AH53 reaction were carried out and thus the SAP5 provides the best properties of swelling, in particular a maximum water absorption capacity very high (2617 g water/g dry polymer).

Therefore this SAP was the material that allows a more complete characterization and a more concrete assessment of the properties of great interest to the application of these materials in agriculture.

The methodology and reaction conditions for the synthesis of the SAP5 were also considered in the 2nd phase of this stage and used in the attempted synthesis of more biodegradable SAPs resorting to natural based compounds as alreadymentioned.

Another important observation that can be drawn from the 1st phase of the 2nd stage is that with the performed modifications, the needed reaction time to synthesize the SAP increased from 10 minutes to approximately 60 minutes, that can be explained by the fact that in these cases methacrylate compounds were used instead of acrylate compounds (more reactives) used in the base synthesis [2,3].

#### 3.3.1.3. Complete Characterization of SAP5

**FTIR**

FTIR analysis proves to be very important in identifying the key functional groups and chemical bonds in the compound. This technique allows, in a certain way, also to know if all of the reagents took part in the reaction and often it is enough to evaluate if the main work goals have been achieved.

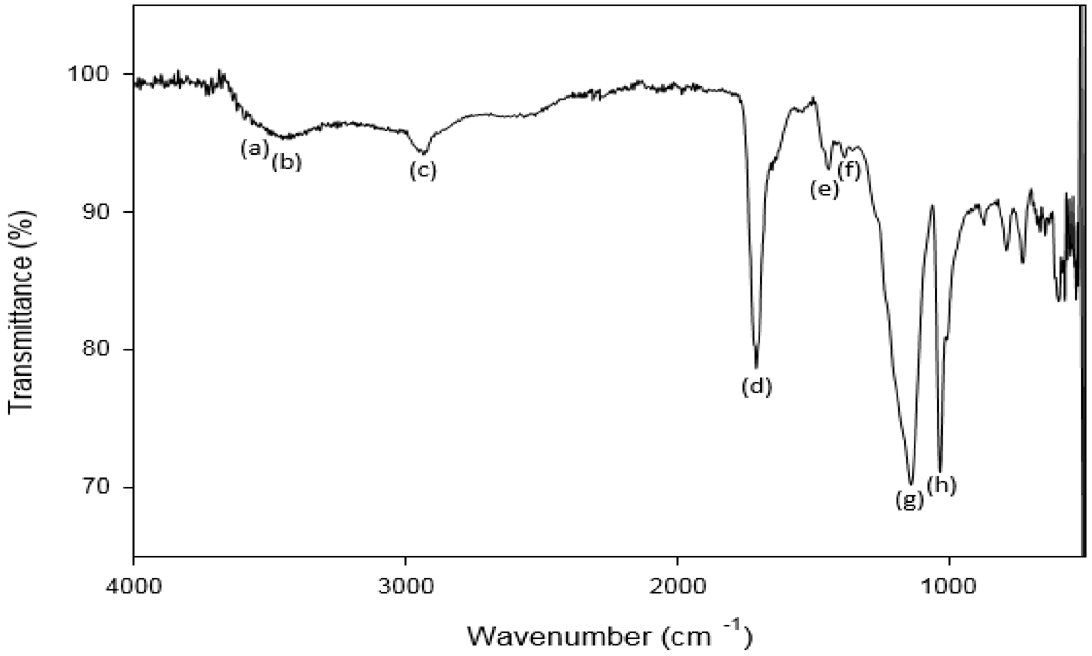


**Figure 3.10 – Transmittance spectrum of SAP5.**

Having regard to the transmittance spectrum obtained by FTIR analysis performed at SAP5 (see Figure 3.10) can be distinguished bands with typical frequencies corresponding to various functional groups and chemical bonds such as: [124,126,147,148]

- ✓ (a) Hydroxyl free –OH stretching (3650-3590) at wavenumber of 3560 $cm^{-1}$;
- ✓ (b) Amide >NH stretching (3500-3400) at wavenumber of 3445 $cm^{-1}$;
- ✓ (c) Aliphatic –CH2 stretching (2926-2853) at wavenumber of 2928 $cm^{-1}$;
- ✓ (d) Ester >C=O stretching (1750-1735) at wavenumber of 1725 $cm^{-1}$;
- ✓ (e) -COOH >C=O bending (1420) at wavenumber of 1452 $cm^{-1}$;
- ✓ (f) Sulfane S=O stretching (1325) at wavenumber of 1326 $cm^{-1}$;
- ✓ (g) Phosphate P=O (1200-1100) at wavenumber of 1145 $cm^{-1}$;
- ✓ (h) >C-O stretching (1300-1000) at wavenumber of 1033 $cm^{-1}$.

The bands mentioned above may serve to conclude about the presence or absence of the reagents in the composition of the synthesized SAP. With the aid of the transmittance spectra obtained by FTIR analysis of the reactants present in Figure D.1 in Appendix D and of the observed results in Figure 3.10 is then possible to confirm the presence in the SAP5 of:

- ✓ NIPAAm, mainly due to band related to the Amide > NH stretching, characteristic of this compound;
- ✓ AA, due to the bands related to the – COOH >C=O bending, hydroxyl free –OH stretching, ester >C=O stretching and >C-O stretching also observed in this compound;
- ✓ SPMs due to the bands related to the ester >C=O stretching, >C-O stretching and mainly to the bond sulfane S=O stretching feature of this compound;
- ✓ BMEP due to the bands related to the ester >C=O stretching, >C-O stretching and mainly to the bond phosphate P=O feature of this compound;

The FTIR analysis can also be used to confirm the occurrence of crosslinking, particularly through the disappearance of bands corresponding to C = C (1680-1600 cm$^{-1}$ and 3095-3000 cm$^{-1}$) after reaction, and the occurrence of crosslinking is validated by placing the SAP in water and checking the formation of a gelled material. [126,147,148]

**TGA**

TGA analysis is a very important characterization technique since it allows the study of the thermal stability of polymeric materials, in this case the SAP5.

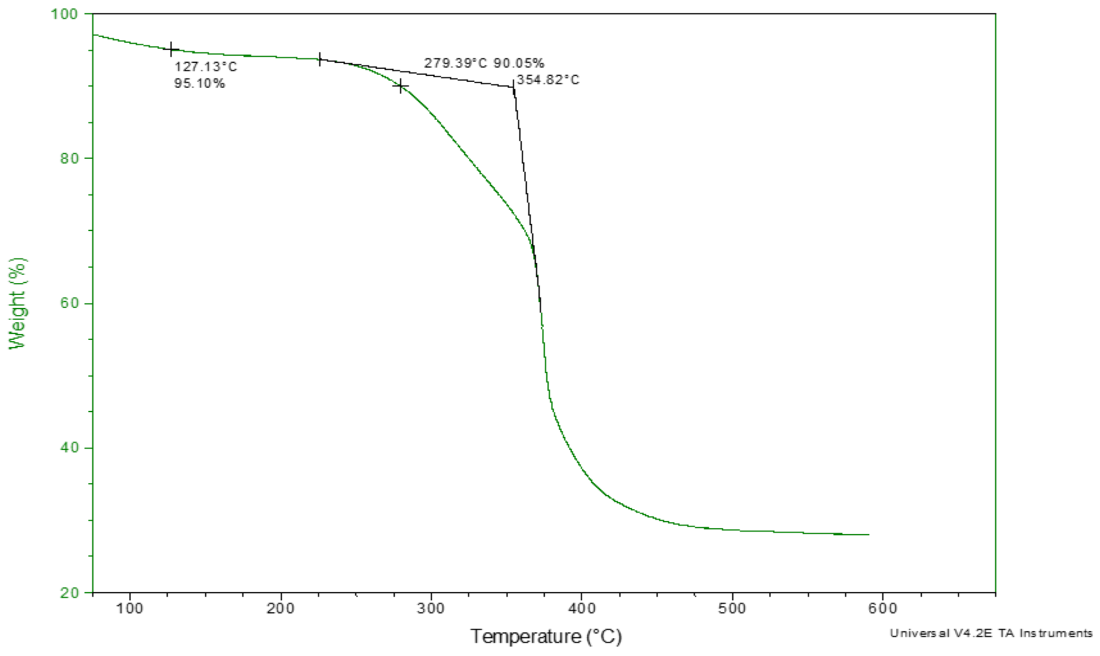


**Figure 3.11 – SAP5 mass loss with temperature (TGA analysis: T5% = 130.94ºC; T10% = 279.74ºC; Tonset = 354.82ºC).**

The graphic shown in Figure 3.11 represents the polymer mass loss with increasing temperature, where it can be observed that the SAP undergoes an initial mass loss (close to 100ºC),probably due to the existence of residual water or non-reacted monomer in the sample. [124]

Around 250 ° C, the polymer experiences a new mass loss, this time more relevant and sharp. At this temperature the mass loss may be is due to a degradation started in the saturated terminal ends, in the olefinic bonds, due to the scission of crosslinks, among others.[124,149]

Finally, the greatest weight loss (approximately 40% of the total mass) by the SAP5 is close to 350 °. The main cause for the occurrence of this mass loss can be attributed to the degradation experienced by decarboxylation of the carboxylate anions. [124,149]

By the results obtained it is possible to say that the SAP5 shows a good thermal stability until temperatures of 250ºC (temperatures much higher than those achieved in agricultural applications).

SAP5 also shows high values for T5%, for T10% and for Tonset (see Figure 3.11), which suggests again a good thermal stability of the material.

### SEM and OM analysis

#### i. Pore size

Considering Figure 3.12, regarding the SAP5, previously swelled and freeze dried, images (cross section) obtained by the SEM analysis at a magnification of 750x (left) and 1000x (right) it is possible to assert that this material shows an homogeneous deeply high porous with honey-comb like structure.

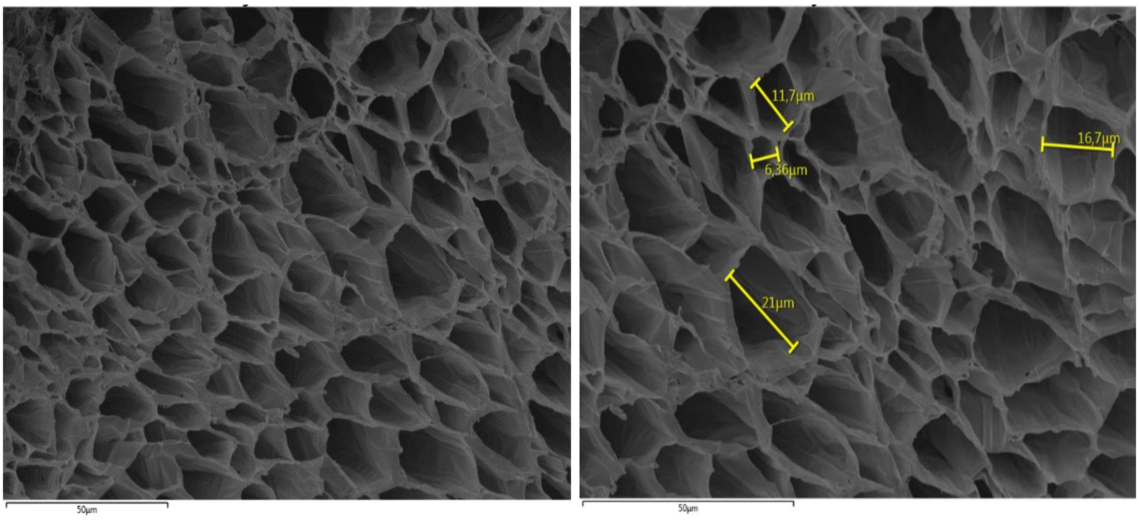


**Figure 3.12 – SEM analysis of SAP5 (swelled and freeze dried).**

The existence of this kind of structure may positively affect the swelling properties, since there is a greater accessibility of water to the SAP amorphous regions. The contact between the water and the interior of the network is therefore facilitated, promoting a more efficient and vigorous absorption and consequently higher maximum swellings values. [123,137]

By the Figure 3.12 it is also possible to notice that the SAP5 structure shows many pore widths, from approximately 6 micrometers to 21 micrometers. Despite this wide distribution of pore widths, it is easily notice that all or almost all of the pores have a width larger than 50 nanometers and are therefore classified as macropores. [150]

The presence of macropores in the SAP5 might once again improve the swelling properties and the water absorption rate, since the larger pores provide an easier diffusion of the water molecules between the outside and the inside of the SAP. However, this feature may be also a drawback because the existence of pores with these characteristics, difficulting the water retention by the SAP, something unwanted for the agricultural applications.[30,123,137]

### ii. Particles sizes

The size of the SAP particles is also an important feature to define because it directly affects the contact area between the SAP and the water molecules.[31]

Therefore with smaller particles probably there will be better swelling properties associated with the fact that there is a greater contact area between the SAP and the water than with the larger SAP particles.[31]

It is important when in the determination of the maximum water absorption capacity and other swelling properties of a certain SAP, to have as well, the knowledge about the particles sizes (diameter, area and perimeter) of the SAP used in the tests.

In the SAP5 case, through the analysis of five microscopic images and 1893 particles of the powder from this material (see Figures E.1, E.1 and E.3 in Appendix E) used in the remaining tests it was possible to have an idea of the average Feret diameter and average perimeter which were around 204 and 618 micrometers, respectively and the average area which was around 57778 micrometers$^2$.

It is relevant, however, to point out that there was a great particle sizes distribution in the analysed SAP powder. In our case there is a very broad size dispersion with Feret diameter sizes from 2.5 to 1894 micrometers. This wide distribution is due to the milling method used that is not very perfect (ice chopper).

The particle sizes of the SAP5 powder are also one of the properties that can be adjustable in order to achieve higher or lower swelling capacity.

In terms of practical application of SAP in the soils, the particle sizes may also be relevant, since for a given amount of SAP applied, an even distribution of this material on the soil can be ensured varying the particle sizes.

**Swelling in distilled water**

The free-absorbency capacity of water is related to the amount of distilled water that a SAP sample can uptake while swells freely.

Figure 3.13 is refer to the measurements of swelling kinetics, which supplies information about the SAP5 water absorption capacity over time when immersed in distilled water, allowings to conclude if the material shows a substantially fast water absorption capacity. It can be observed that, after 120 minutes, about half of its maximum absorption capacity has been reached and at the end of 360 minutes had been reached a value very close to a capacity corresponding to the final swelling (when it reaches equilibrium). However it is important to refer that the period between 360 and

1440 minutes (24 hours) in which the SAP was immersed in distilled water there was still a small increase in the water absorption capacity.

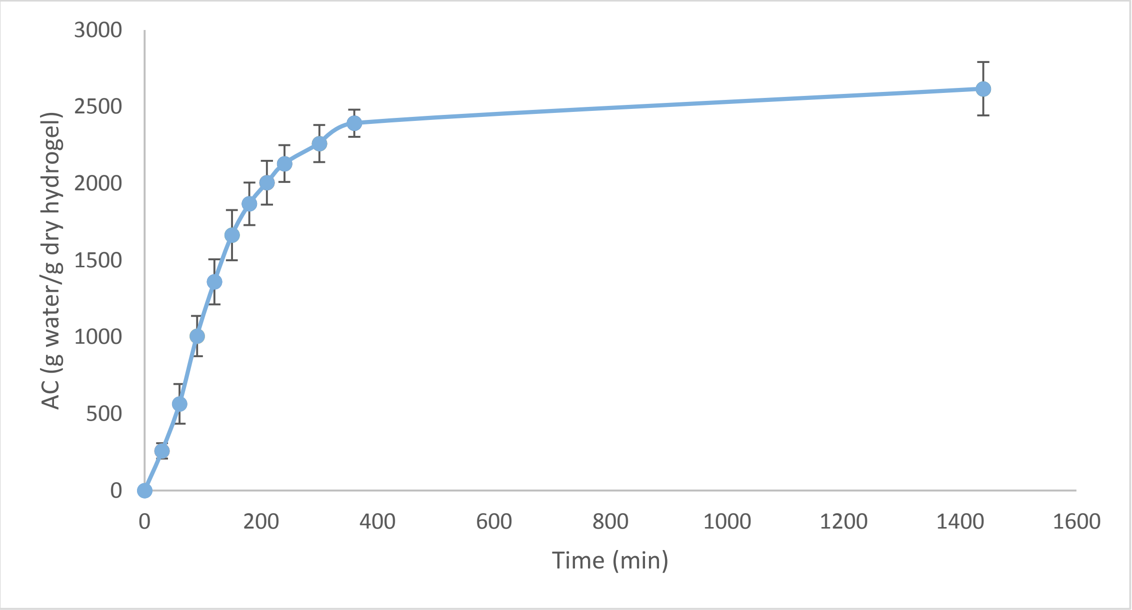


**Figure 3.13 – Water absorption capacity of SAP5 (AH53) in distilled water.**

After 24h of the polymer immerse in distilled water, the last registered absorption capacity corresponding to the swelling equilibrium was approximately 2617 g water/g dry polymer.

SAP5 shows therefore a swelling equilibrium in distilled water much higher comparing with the obtained SAP base (SAP1) and higher than the reported for another SAPs in the literature (see Table 1.2).

This remarkable water absorption capacity associated to the fact of the absorption take place in a considerable fast way suggests the enormous potential of the SAP5 to be used in agriculture field. With the SAP5 application in agriculture it can be possible to ensure a complete swelling and therefore obtaining “reservoirs” in the soil in order to provide a continuous release of water during longer periods of time.

However these are conclusions that can be better scrutinized and validated through the water retention in soil tests with SAPs considered further.

### Swelling in salt solutions

The medium where synthesized SAPs could be applied may have different ionic stregth (salt concentrations) and different pH values, thus it is important to study the water absorption capacity in these different environmental conditions. This allows to obtain more realistic results and a better knowledge of the behaviour of the SAP in practical applications.

Analysing the Figure 3.14 it is possible to check that the obtained values for the SAP5 maximum swelling in different salt solutions are much lower than the obtained for this property in distilled water, with a reduction in two orders of magnitude, from 2600 g water/g dry polymer to 60 g water/g dry polymer (1.5 wt% NaCl).

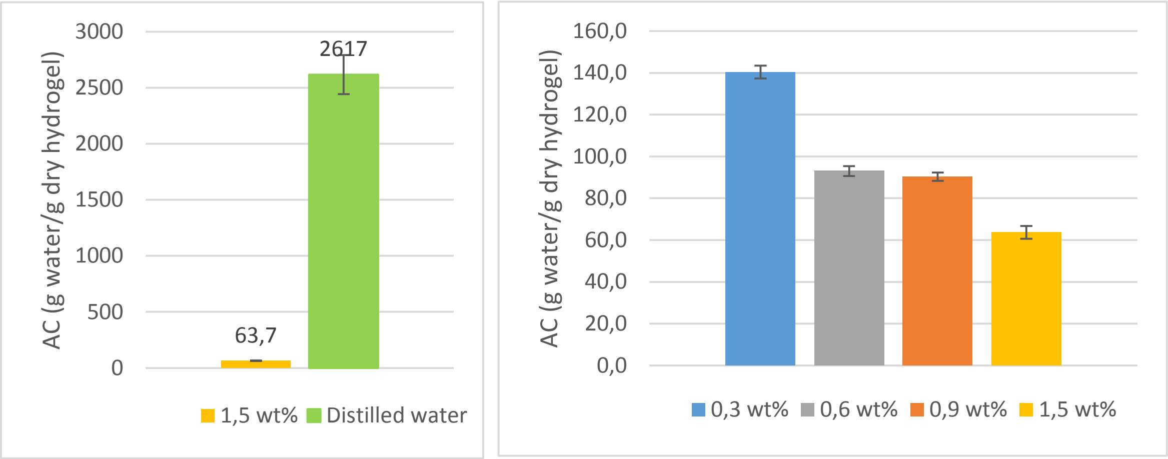


**Figure 3.14 – Maximum water absorption capacity of SAP5 in distilled water and in 1,5 wt% NaCl solution (left) and Maximum water absorption capacity of SAP5 in different concentration NaCl solution (right) (after 24 hours).**

This suggests that the developed SAP is highly sensitive to the salt presence in the swelling medium, in this case NaCl, and that its swelling properties strongly decrease with this condition. The phenomena is easily explained by the Donnan equilibrium theory, since the increase of the ionic strength causes a reduction in the distribution of concentration of mobile ions between the gel and the solution thereby reducing the osmotic pressure. This osmotic pressure decrease (the driving forces for swelling between the gel and the aqueous solution phases of the solution) leads to a significant loss in the SAP maximum water absorption capacity [31,123,124].

This behaviour is also observed for other SAP i.e. the higher the salt concentration of the solutions used as the swelling medium, the smaller will be the maximum absorption capacity of the SAP [31,123,124].

This characteristic behaviour often results from the occurrence of the charged screening effect of the additional cations from the salt which reduces and causes “imperfections” in the anion-anion electrostatic repulsion and consequently induces a decrease in the SAPs swelling capacity [31,123,124].

This reduced capacity of water absorption in salt solutions underlines the inherent disadvantage of the synthesized SAPs, since in practical applications, usually the medium (irrigation or rain water and soil) has a certain ionic strength and in these conditions the SAPs maximum water absorption capacity will be tremendously smaller than the one observed if there was no presence of ions.

So here arises a problem concerning the SAPs properties that should be eliminated and enhanced in order to be possible to ensure a good performance from the material in a practical level in agriculture when the maximum swelling of the material would be maintained even under conditions of expressed ion strength.

It is well-known that is difficult to synthesize SAPs non-sensitive to the ionic strength at the same time showing a fairly high maximum swelling (similar to that obtained in this case), due to the fundamental role of the ionic groups in the SAP’s maximum absorption capacity as well as in the expansion of the network. Moreover, it is possible to verify that usually the reported SAPs in the literature (see Table 1.2) present as “drawbacks” the fact that their swelling properties are too sensitive and negatively influenced by the medium ionic strength.

### Swelling at different pHs

In order to investigate the SAP5 sensibility to the pH, swelling equilibrium experiments were performed to study absorption capacity (after 24 hours), using different pH solutions, namely 3, 5, 7, 9 and 11.

Since the absorption capacity is strongly influenced by the ionic strength, ions were not added (through buffers) to the medium to adjust the pH. Therefore, the NaOH (0,1M) and the HCl (0,1M) solutions were diluted with distilled water to obtain the desired basic and acidic pH, respectively.

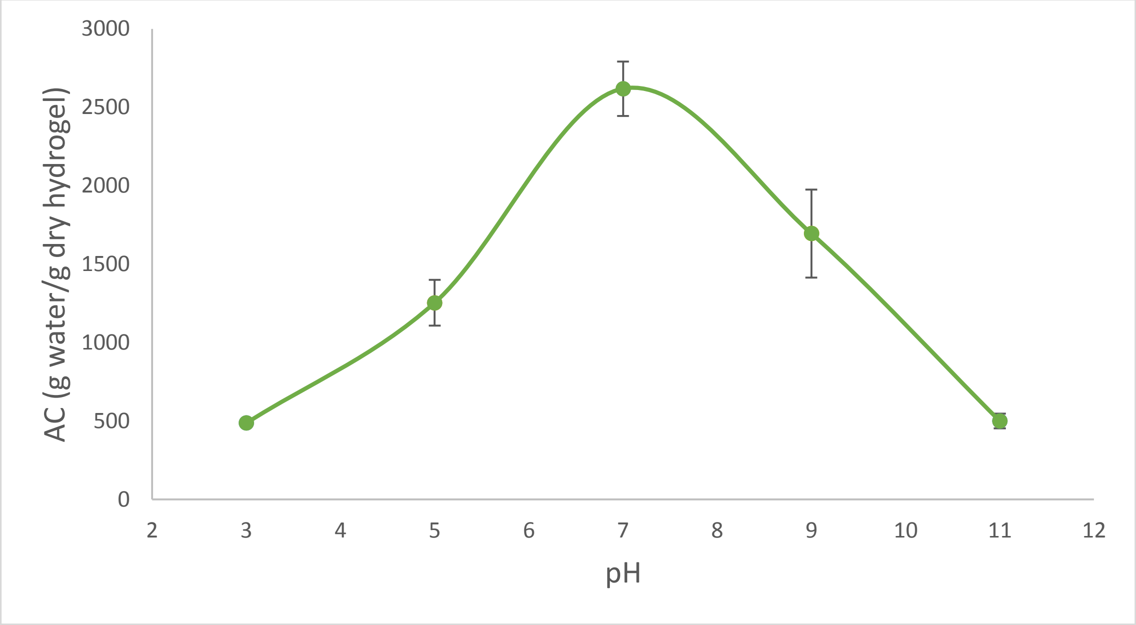


**Figure 3.15 – Water absorption capacity of SAP5 at different pHs (after 24 hours).**

Figure 3.15 is refered to the maximum water absorption capacity of the SAP5 at different pHs, this material exhibits different swelling behaviours depending on the pH of the medium where it is inserted.

The better maximum water absorption capacity of approximately 2600 g water/g dry polymer was achieved in neutral medium, i.e. when the solution had a pH near to 7.

It is possible to see, that for the lower pH values (acidic) and higher than 7 (basic) the maximum absorption capacity of the SAP is significantly reduced.

When the SAP sample is in acidic pH (3 and 5) the major part of the carboxylate groups are protonated. In this condition the electrostatic repulsion between the carboxylate groups can be restricted and the main anion-anion repulsive forces may be even eliminated. This can lead to the hydrogel collapse, which consequently causes a decrease in the maximum swelling, in this case to values between 500 and 1200 g water/g dry polymer [30,31,124].

For neutral conditions (pH 7), most of the carboxylate groups are ionized and the electrostatic repulsive force between the charged sites (-COO- groups) causes a significant increase in the maximum water absorption capacity by the SAP sample [30,31,124].

When the medium has a basic pH (9, 11) it was also observed a significant decrease in the swelling maximum values between 1700 and 500 g water / g dry polymer. This can be explained by the fact that with these pH values, there is a charged screening effect of the counter ions ($Na^+$) due to the $Na^+$ excess in the swelling media, which shields the carboxylate anions and prevents effective anion-anion repulsion.[30,31,124]

Despite the observed sensitivity of the SAP swelling maximum to the pH conditions of the media, it is relevant to refer that this hydrogel can ensure a high capacity (with value of 1200 g water/g dry polymer and similar to the capacities reported to other SAPs in the literature) in a pH ranging from 5 to 9.

This guarantee of high capacity for absorbing water between pH 5 to 9 has become quite useful and advantageous in terms of use of SAP in agricultural applications.

Considering the “soil pH map of the world”, based on the HWSD (Harmonized World Soil Database), in Figure F.1 in Appendix F, it is easy to understand that in the world the majority of the soils does not present neither a very acidic pH (< 4-4,5) neither a very basic value (> 9-10), which suggest that taking only the pH factor into account, the SAP5 would ensure good absorption capacities in every agricultural soils and dry places where it would be applied [151]. However, it is important to refer that the pH is not the only factor that influences the SAP maximum swelling and therefore the previous analysis is a bit simplistic.

### Water retention in mixture soil/SAP5

All crops depend directly on the ability to retain water in the soil where they are inserted. So it is of great importance to verify the SAP practical application if it is beneficial and allows improvements in its capacity.

Tests were performed which allowed to calculate the amount of water in the soil for several days after an initial irrigation in soils with different amounts of SAP5, namely one control soil without any SAP and three soils with increasing amount of SAP (0.5 wt%, 1 wt% e 2 wt% relative to the soil weight).

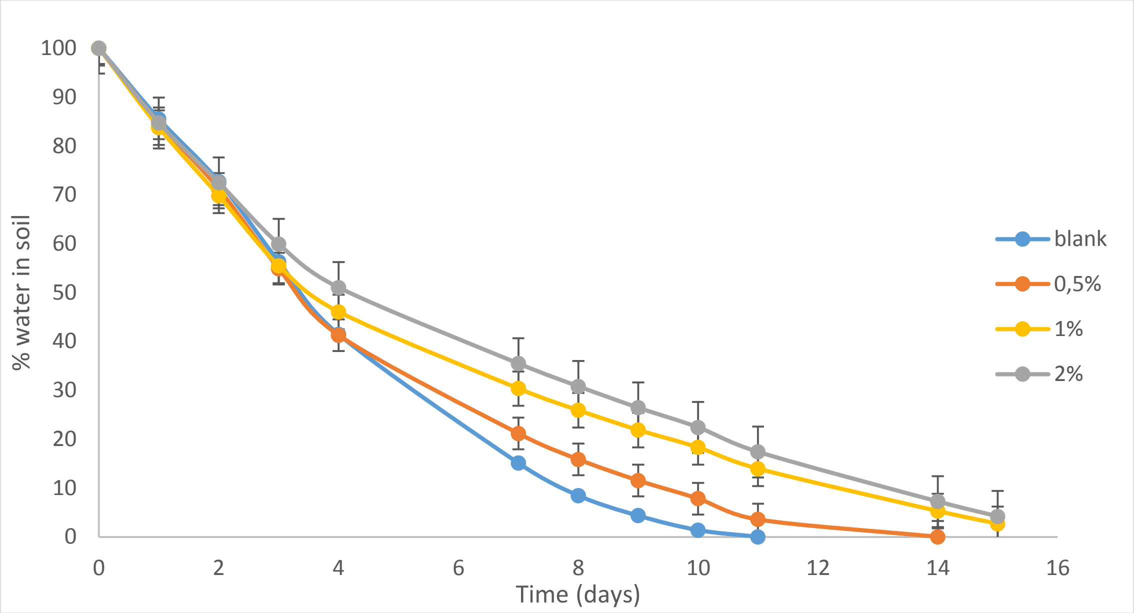


**Figure 3.16 – Water retention in soil and in mixtures soil/SAP5.**

By the results of the water retention tests, as shown in Figure 3.16, it can be seen that the amount of water in the control soil (without SAP) reaches zero after 11 days. Moreover, in the soil with 0.5wt% SAP the amount of water only reaches 0% between 12 and 14 days and in the soils with 1wt% and 2%wt of SAP there is still water present in the soil even after 15 days.

This suggests that the amount of water in the soil over time and therefore its retention is significantly improved by the presence of the SAP, because there is no longer water available earlier in the control soil (without SAP) than in the soils with SAP.

Moreover, the greater the amount of SAP mixed in the soil, the greater will be the improvements in retention capacity and better will be the lifetime of available water in the soil.

The results also confirm the SAP's good storage capacity and control release of water and its relative fast swelling allows a more efficient use and retention of water in the soil, avoiding the natural losses (immediately after the irrigation) which can happen by evaporation and/or draining [137,138].

It should be noticed that the obtained results can be explained by the fact that the SAP absorbs water and the release of that water occurs in a controlled and slow way through a diffusion driven mechanism, according to the humidity content of the surrounding soil decreases. [137,138]

The water evaporation, when it is inside the SAP sample is also significantly slower than the free water evaporation present in the soil exposed to the atmosphere. The interaction between polymer molecules and water favour the water retention and hinder evaporation.[137,138]

The controlled and sustained release of water and consequently the greater capacity of water retention in the soil / SAP mixture are quite important in terms of practical application of SAP in agriculture and in the actual reality about water availability and consumption.

The results suggest that the SAPs application in the soil would allow a better utilization and consequently less waste of water, as well as allows the plants to be supplied with water without the need of a new irrigation (reducing the frequency of watering/irrigation).

These advantages would be of great relevance and would fill the current need to reduce and rationalize the consumption of water and could also provide improvements in agriculture and enable a better response from this sector to the growth of global population and food needs.

### Urea loading and release

Another important feature that SAPs present, is their possible utilization as reservoirs and their capacity to release fertilizers in a more controlled way. This ability proves to be quite useful and advantageous because is thus possible to guarantee a more adequate and controlled supply of nutrients to plants (essential in the plant growth, especially in the initial stage of growth) and avoid aditional costs and waste in fertilizers [152].

The nitrogen appears as one of the most influential and important nutrients for agricultural development. The urea is a low cost compound and shows high nitrogen concentration, being therefore largely used in agriculture as a fertilizer. [153,154] It would be relevant to understand the behaviour of the SAP5 in terms of loading and release of this compound.

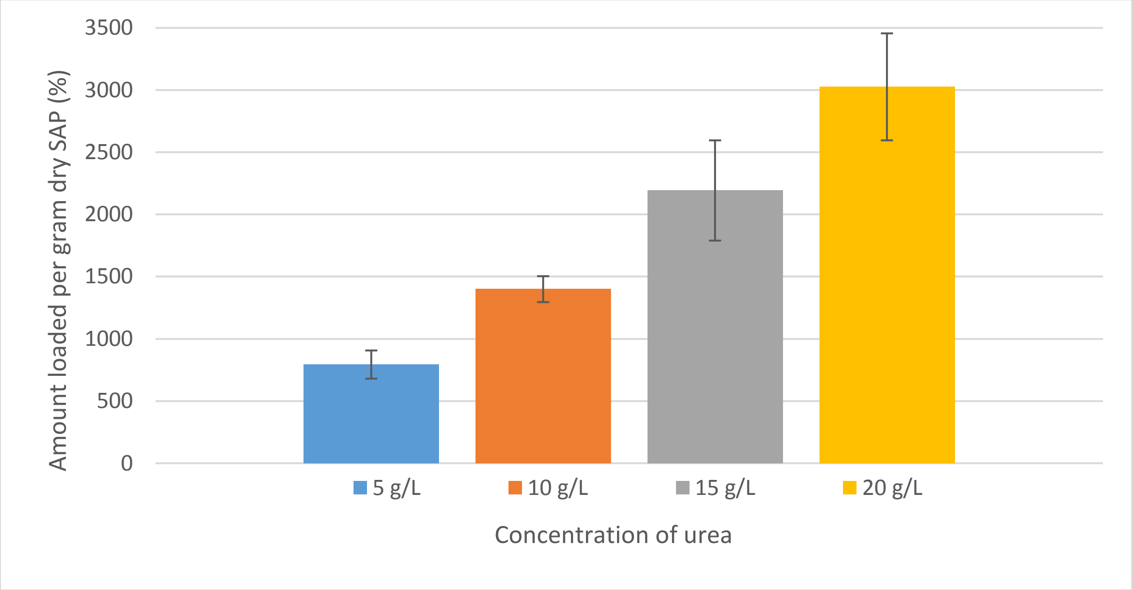


**Figure 3.17 – Effect of urea solution on the loading (%) of SAP5.**

By the analysis of the graph in Figure 3.17 it is possible to say that the SAP shows a great urea loading capacity, reaching values such as 3000% of loading (0.005 grams of dry SAP5 incorporated 0,151 grams of urea), when the concentration of urea was 20 g/L for example.

These values for the loading of urea are very high when compared to other found in the literature for other SAPs, which adhere 250% for a urea's concentration of 20g/L [123].

This may be due to the tremendous capacity for absorption that can be achieved with SAP5, which thus also allows a greater uptake of urea dissolved in the swelling medium [123,124].

The results also support the conclusion that, higher the concentration of urea in the loading solution, much higher will be the percentage loading achieved by the SAP sample. This is probably because having a higher concentration of urea there will also be a higher diffusion of this compound into the SAPs matrix achieving a greater loading [123,124].

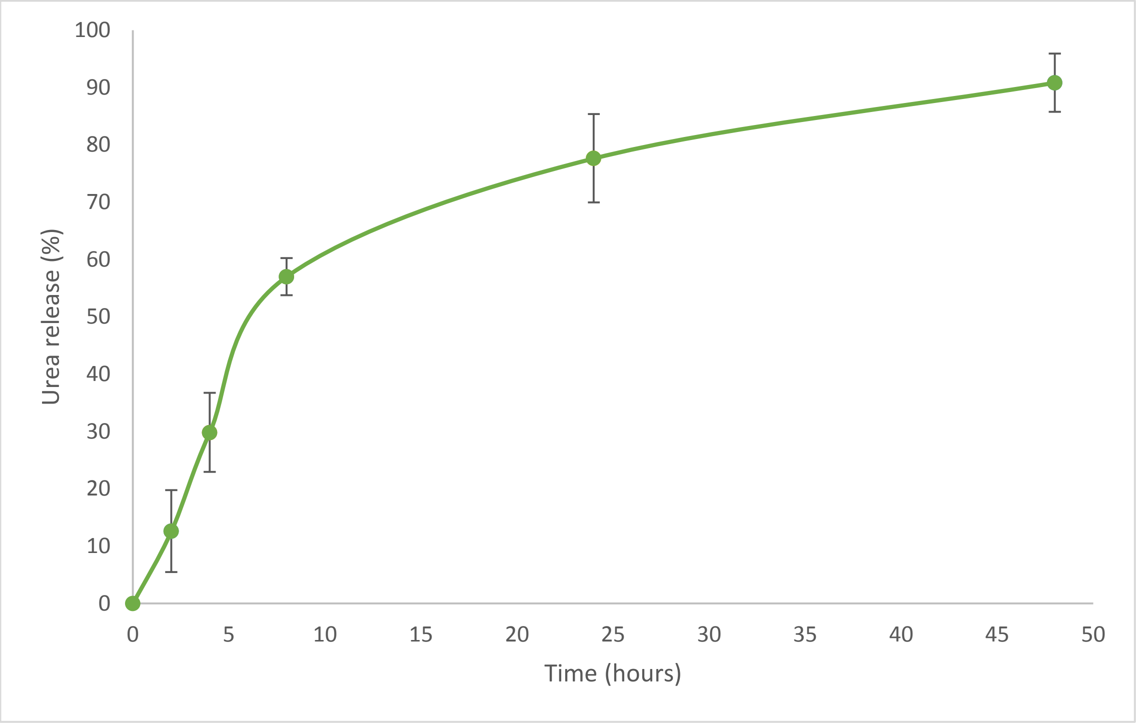


**Figure 3.18 – The release profile of urea loaded SAP5.**

In terms of urea release, graphically shown in Figure 3.18, where the test was only performed with the SAP5 samples which had been loaded in the solution with a concentration of 20 g/L, it can be seen that in the first 8 hours occurs a more pronounced urea release to the swelling medium, probably due to a rapid increase penetration of the solvent on the surface of the loaded SAP with that phase [155,156].

Subsequently it is verified that the release rate will be more attenuated up to 48 hours, in which time virtually all the urea has been released into the swelling medium, particularly 90.8% of urea originally present in the SAP.

It is important to note that the process of "controlled" release of urea by the SAP occurs after the penetration of water into the SAP matrix. This water will dissolve the urea and subsequently allowing its release to the outside of the matrix. This whole process is possible mainly due to the interaction between water, urea and polymer [123,124].

The fact that most fertilizers are water soluble and can evaporate at room temperature, associated with the surface runoff, leaching and vaporization, leads to a poor and reduced use of these compounds by plants and also to the possible release into the environment [157,158].

Therefore, the existence of a controlled release system of fertilizer as the one provided by the SAP5, proves its importance, since beyond ensuring a more prolonged and systematic supply of fertilizers to the plants, avoiding economic and resources losses and still reducing the environmental pollution caused by the fertilizers [157,158].

Although the SAPs allow a more controlled release of urea, it would be interesting to further develop the capability to release the fertilizer over a longer period of time with this SAP system, namely during the initial stage of the plants growing (2 to 3 weeks), where the nutrients needs are larger and more essential [152].

### 3.3.2. 2nd phase of the 2nd stage – SAPs with cellulose derivatives

In the 2nd phase of the 2nd stage of this work several reactions were performed, where the knowledge and the methodology optimized in the previous phase was used to synthesize a SAP with a comonomer of natural source in its constitution and thus with more biodegradable characteristics.

The idea would be to substitute directly a comonomer used in the aforementioned synthesis of SAPs by a cellulose derivative, in this case by CMC sodium salt or by HPC.

Our intention was to perform reactions to functionalize the cellulose derivatives with the incorporation on its surface by taking advantage of the cellulose functionality. If these functionalizations were successfully achieved, these modified cellulose derivatives would also be used as comonomers in the synthesis of more biodegradable SAPs.

The modification of cellulose derivatives serves to incorporate carboxyl groups in these compounds to get a greater contribution to maximum swelling of SAPs.

Thus, the considered substitution of comonomers would be less disadvantageous in terms of swelling properties of the SAPs, and likely could be obtained SAPs which besides being more biodegradable had a high water absorption capacity.

Much of the reported SAPs in the literature (see Table 1.2) using more biodegradable compounds, typically exhibit lower swelling capacity compared to the synthetic ones. The reactions carried out in this phase are detailed in the Table 3.6. In this case it was intended to find out the more favorable and adequate substitutions to obtain the best results. The quantities of reagents used in relation to phase 1 were also changed, in order to adjust the quantities to the availability of modified CMCss or modified HPC, to spare reagents and avoid waste, since this phase of experimentation was not based in reported and studied synthesis and was uncertain the achievement of good results..

**Table 3.6 – Reactions carried out in the 2nd phase of the 2nd stage.**

| Designation | Reagents | | | | | | | | Temperature (ºC) | Type of polymerization | Conclusions |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Monomers (g) | | | | | Initiator (g) | Crosslinker (g) | Solvent (mL) | | | |
| | AA | SPM | NIPAAm | CMCss | HPC | KPS | H232 | $H_2O$ | | | |
| AH57 | | 2 | 0,23 | 1* | | 0,1 | 0,015 | 30 | 70 | Solution polymerization | No polymerization ocurred |
| AH58 | | 2 | 0,16 | | 1 | 0,07 | 0,009 | 30 | 70 | Solution polymerization | No polymerization ocurred |
| AH62 | 0,7 | 1,3 | 0,16 | | 1* | 0,05 | 0,007 | 30 | 70 | Solution polymerization | No polymerization ocurred |
| AH63 | 2 | | 0,11 | 1 | | 0,05 | 0,006 | 40 | 70 | Solution polymerization | No polymerization ocurred |

*functionalized cellulosics.

### 3.3.2.1. Functionalization of cellulose derivatives

In the 2nd phase of the 2nd stage it was initially attempted to perform modifications in natural compounds (CMCss and HPC) that would be used in SAPs' synthesis. These modifications would undergo an attempt to functionalize the compounds in order to improve the synthesis of SAPs and allowing to obtain SAPs with good swelling properties.

After the reactions of functionalization of CMCss and HPC using the TMPM, it was necessary to determine whether this functionalization was successfully achieved and whether there was incorporation on the cellulose surface.

To assess whether or not the functionalization of the CMCss and HPC occurred the FTIR technique was used. Then FTIR analysis was performed for the compound TMPM and also the cellulose derivatives before and after the applied functionalization reaction. Then, through the transmittance spectra obtained and compared among these, was possible to observe if there were new bands (characteristics of the compound TMPM) in the HPC and CMCss spectra obtained after modification. The transmittance spectrum of the TMPM was then used to verify if the new existing bands in the spectra of the cellulose derivatives corresponded to existing features bands in this compound and thus conclude whether or not the functionalization was successful.

Figure 3.19 is related to the transmittance spectra obtained for TMPM and the CMCss before and after the functionalization reaction.

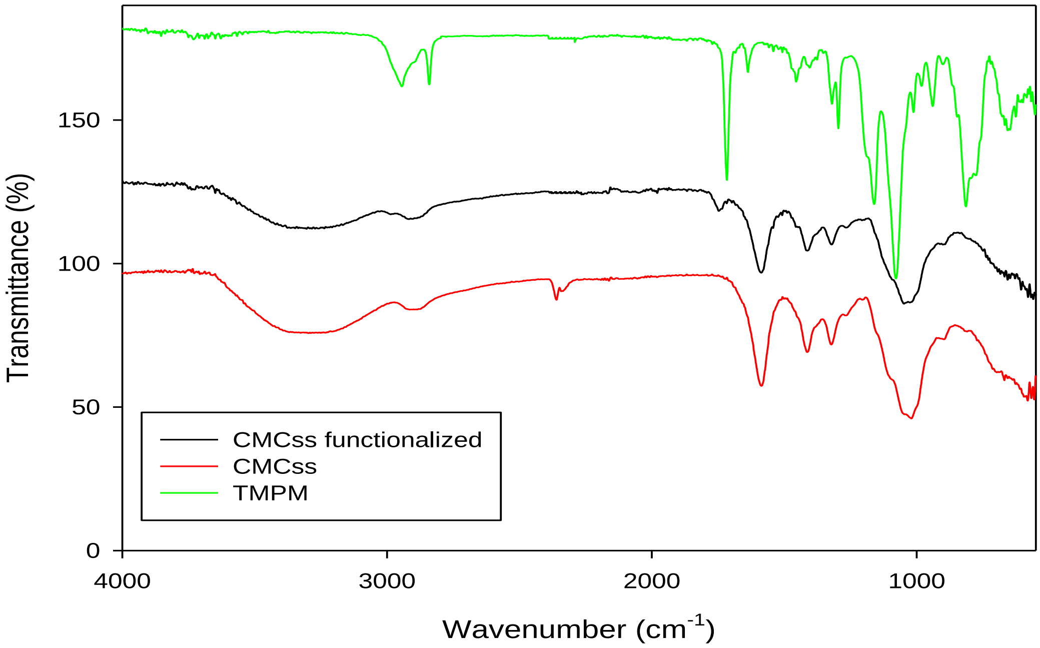


**Figure 3.19 – Transmittance spectra obtained for CMCss, CMCss functionalized and TMPM.**

By observation and comparison of the spectrum in Figure 3.19, it can be concluded that despite the bands are almost all coincident among the CMCss spectra before and after the functionalization reaction, the spectrum of functionalized CMCss shows a new band at a frequency of 1720 cm$^{-1}$ probably due to the presence of the compound TMPM. Observing the TMPM spectrum it is possible to verify the existence of a band in the same frequency and similar to the one obtained in the functionalized CMCss, corresponding to the stretching C=O from ester group present in the TMPM composition.[141]

However, it is also possible to see that the bands of intense expression and characteristics of TMPM, namely in the frequencies 1270 cm$^{-1}$ e 780-760 cm$^{-1}$ referring to the Si-$OCH_3$ groups, are not seen in the functionalized CMCss. [159] Nevertheless, it may happen that these bands are implied and camouflaged by the bands of CMCss also present in this region of the spectrum. Thus it is possible to state that incorporation of the TMPM compound and consequently of the interest groups in the CMCss occurred, being the functionalization of this compound successfully.

Figure 3.20 in turn is related to the transmittance spectra obtained for TMPM and HPC before and after the functionalization reaction.

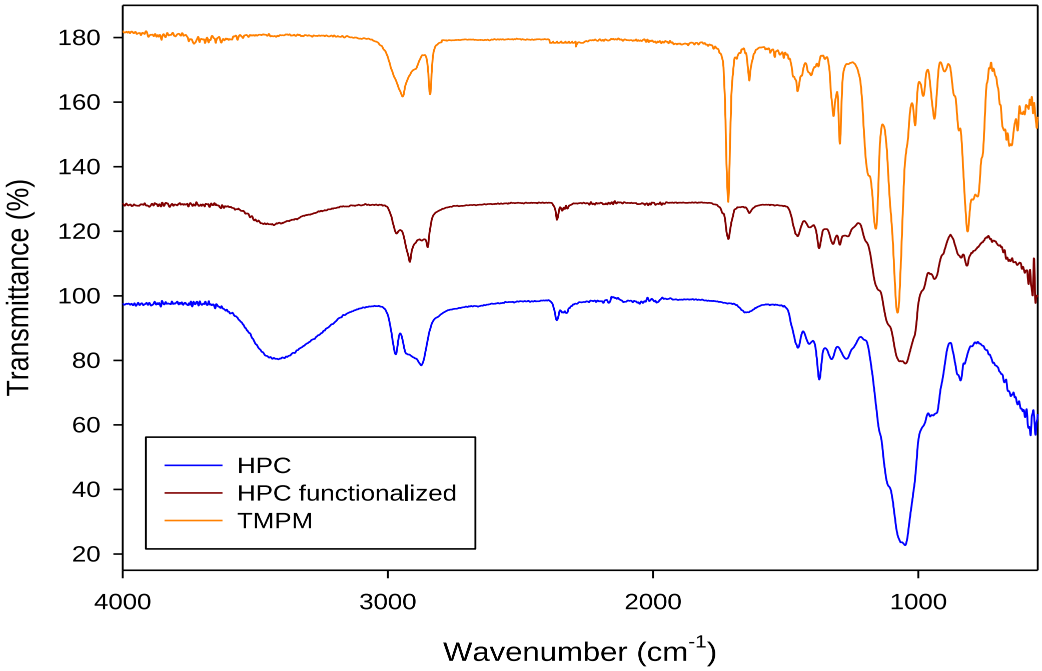


**Figure 3.20 – Transmittance spectra obtained for HPC, HPC functionalized and TMPM.**

In the case of HPC spectrum after passing through this functionalization reaction, and following the same logic of analysis, it is also observed the presence of band at frequency 1720 cm$^{-1}$, that is not present in the spectrum of this compound prior to functionalization.

Back through the TMPM spectrum, it is possible to notice, once more, that the band mentioned above are TMPM characteristic bands corresponding to the stretching C = O of the ester group (1722 cm$^{-1}$). [141] Again it appears that the characteristic bands of the Si-$OCH_3$ groups are not present in the functionalized HPC spectrum but as in the case of CMCss these can be camouflaged. However, it is thus possible admit that there were also functionalization of the HPC occurs with the incorporation of the TMPM.

After the completion of the CMCss and HPC functionalization the next step was to use these functionalized compounds and also the non-functionalized CMCss and HPC as comonomers in the synthesis of more biodegradable SAPs, by the methodology of synthesis, the reaction conditions and the reagents which presented the better results in the 1st phase of the 2nd stage, i.e., corresponding to the AH53 reaction and to SAP5.

#### 3.3.2.2. Synthesis of more biodegradable SAPs using cellulosics

From all the reactions performed in this phase and described in the Table 3.6 in no one was possible to obtain a polymer, even after several hours of reaction.

Although several substitutions and combinations of comonomers have been made, in the attempt to synthesize more biodegradable SAPs, either by replacement of AA by comonomers of natural origin, either by replacing the standard SPMps to CMC or even by combining AA and SPMps with functionalized HPC, it has never been possible to obtain a polymer and none of the various reactions was successful.

This may be due to several reasons such as:

- ✓ The amounts of reagents and reactions conditions; In this case they might not have been the most appropriated or the optimal in order to the reaction take place (the SAP5 synthesis methodology might not be the most appropriate when these natural compounds are used);
- ✓ The more complex and fibrous structure as well as the high molecular weight (Mw to 100000 for HPC and 90000 for CMCss) of the used cellulose derivatives can difficult the polymerization and does not allow these compounds to be used as comonomers or in such high quantities;[66,103]
- ✓ The difficulty of ensuring that the cellulose derivative dissolved in water and remained for the time necessary for the reaction to occur and with the used temperatures. If this dissolution is not guaranteed, copolymerization does not occur; [66,103]
- ✓ The fact that the cellulose derivative, even the functionalized ones, may be of smaller reactivity than the others comonomers usually used, such as AA and AAm for instance.

Given that there was none positive results, nor even was possible to synthesize any more biodegradable SAP, further attempts and changes should have been done in the synthesis methodology and in the reaction conditions (for instance vary the reaction temperature) until any positive outcome. From this positive result new optimizations could have been done in order to reach the objective and synthesize an SAP with more biodegradable characteristics and with good properties for its application in agriculture. However such work was not developed due to the lack of time and due the fact that labour would exceed deadlines, getting well as work to develop in the future.

# Chapter IV

# 4. Conclusions and Outlook

## 4.2. Conclusions

In the present work, different pathways were used to synthesize more biodegradable SAPs that presented good swelling features and could be used in agricultural applications. Through the synthesis of these more biodegradable materials and their application in agriculture, it would be possible to ensure big advantages for this sector, meaning the decrease in the consumption of water, the need of watering/irrigation, leaching of fertilizers, monetary losses in water and fertilizers not used by the crops, among others and also avoid negative impacts in the environment, resulting from the accumulation of undesirable compounds (fertilizers, compounds based in acrylates, etc.) in soils, groundwater, among others.

In a first stage for the attempt of synthesis of more biodegradable SAPs it was recurred to a derivate of vegetal oil (AESO), to AAm and AA and the conditions of reaction normally used and reported in literature. Several hydrogels were synthesized on this stage, being the most interesting and promising the ones obtained through polymerization in solution at 70ºC regarding to AAm or AA and to AESO as monomers, to BPO as initiator and to THF as solvent.

Through the FTIR analysis, TGA and the solubility tests, it was possible to confirm the crosslinking of the synthesized polymers and to infer that incorporation of AESO on the hydrogels occurred when it was used 50 wt% and 5% of AESO.

To the most promising and interesting hydrogels (AH5, AH15, AH6 and AH10) swelling experiments were performed, and the obtained results showed a maximum capacity of absorption of water after 24 hours. It was possible to verify a low capacity for all the synthesized hydrogels (3-49 g water/g dry hydrogel), much lower than the reported values in literature. For this reason this broader approach was renounced and was outlined a more concrete approach that allowed the achievement of better results on the second stage of the work.

The second stage comprehended two main phases. One phase in which initially was reproduced the basic synthesis of a SAP with good swelling properties. Though the reported and considered synthesis, it was possible to synthesize the base SAP, recurring to free radical copolymerization. The changes introduced by us in the synthesis and in the used reagents highly improved the swelling properties. The modifications implied the changes in comonomers, and in the quantity and type of crosslinking agent.

The best material obtained, SAP5, presents a maximum capacity of absorption of water of 2617 g water/g dry polymer. The SAP5 was characterized in a more complete way and it was possible to observe, that this compound presented good heat stability, had a macroporous structure, a good maximum capacity of absorption of water for a pH range between 5 and 9. When mixed with the soil it allowed improvements in water retention (more days without the need of watering/irrigation) and also had the capacity of being loaded with high amounts of urea and thereafter make a controlled liberation of this fertilizer. Although having these desirable features to be applied in agriculture, on the other hand, SAP5 was rather sensitive to the ionic force of swelling medium and had a fast liberation of urea for the intended application.

Other phase involved then the attempt of synthesis of more biodegradable SAPs recurring to knowledge and methodology of synthesis that had been developed and optimized (phase 1) and using compounds of natural source, namely, cellulose derivatives (CMCss and HPC) as comonomers. it was also carried out the cellulose derivatives funcionalizations, with the aim of aid the incorporation of functional groups and not decrease capacities of swelling of the SAPs that would be obtained. These modified derivatives were also used as comonomers on this last phase.

Regarding the methodology, the reagents and the reaction conditions used in the synthesis of SAP5 were then performed to attempt of synthesize more biodegradable SAPs replacing the synthetic comonomers by cellulose derivatives (functionalized and no functionalized). Through the FTIR analysis, it was possible to observe that the funcionalizations were successfully performed. Although the the synthesis of more biodegradable SAPs did not occurred and the polymer was not obtained even after a few hours of reaction. This can be due to the structure of the cellulose derivatives, to the difficulty of dissolution in water of these materials or even the fact that the methodology and the conditions used were not the most suitable for this case.

## 4.3. Future Work

The main purpose of this work was the development of more biodegradable SAPs with good swelling proprieties, which could enable their application in agriculture. Even though there are some interesting and important results, it is significant to note that this work was a first approach to the theme of biodegradable hydrogels for agriculture and this area is fairly wide, with numerous possibilities.

About the first stage, where we recurred to AESO and reaction conditions typical of the synthesis of SAPs, other derivatives of vegetal oils may be tested mainly in order to bring more hydrophilic characteristics to molecules.

Another important remark is regarding the hydrogels developed in the first stage, which despite not having enough properties to be used in agriculture, can be used in other applications where a high maximum capacity of absorption of water is not essential.

In the case of the second stage and its first step there is also future work that could be done. Besides SAP5 presents excellent features, these can be yet improved and optimized to the maximum through a more meticulous study about the conditions of reaction (temperature of reaction, solvent used, etc.), regarding the quantities of the initiator, crosslinking agent and solvent utilized, neutralization degree of SAP, among other factors. In terms of the possible application of SAP5 in agriculture, this can be better studied and substantiated, through the realization of more tests, namely for the properties determination under load swelling, through which it would be easier to understand the influence of the weight of soil upon the capacity of swelling of the SAP. Also field tests could be carried out, where it would be used a mixture soil/SAP in the cultivation of a certain plant, having posterior comparison with a control plant (cultivated only with soil) to understand the influence of the SAP utilization on the growth and in the features of that plant. Proceeding with the possible tests to SAP5, it would be interesting to perform loading and release tests with other fertilizers/agrochemicals than urea.

In terms of properties of this SAP, it was pertinent if there was improvements at the level of controlled liberation of fertilizers, so as to achieve a more prolonged and benefit liberation to the plant and at the level of the influence of the ionic force, with the purpose of reduce the drastic loss of capacity of absorption of water in mediums with dissolved ions, since this feature confines the potential of the SAP in agriculture.

In the case of the second stage, it would be fairly significant to achieve the preparation of the polymer using the methodology of synthesis and the involved reagents, by varying for example, the temperature of reaction, quantity of reagents, reagents used, among others. From the moment it should be done a new optimization concerning those results, in order to obtain the best properties as possible for the synthesized SAPs and according with the needs in agriculture. Another strategy would be to change the used polymerization type, by passing, for example, to graft polymerization, attempting to use cellulose or its derivatives as a support to perform the polymerization at their surface.

Also to consider is trying to modify or hydrolyse the cellulose and its derivatives, in order to obtain a material easier to use, that would give greater assurance in terms of reaction and that allowed an easier obtaining of the polymer.

The previously mentioned proposals are only some few options which could be followed to make this present work more enriching, complete and geared to the accomplishment of better results. This polymerization area emerge as an area rather interesting and with increasing importance and capacity to solve problems and ameliorate situations whether in agriculture or in medicine. There is, therefore, future work that can be developed and enough potentiality aiming the attainment of materials capable of making the difference. This thesis can serve as starting point to developments and studies more meticulous and relevant.

# References

1. The foudation of polymer science by Hermann Staundinger (1881-1965) [Em PDF]. Freiburg, Baden-Württemberg, Germany: International Historic Chemical Landmark, 1999. [Accessed in 07 August 2014]. Available from: http://www.acs.org/content/dam/acsorg/education/whatischemistry/landmarks/staudingerpolymerscience/foundation-of-polymer-science-by-herman-staudinger-commemorative-booklet.pdf
2. Ebewele, R.O., *Polymer Science and Technology*. 2000: Copyright, CRC Press LLC.
3. Stevens, M.P., *Polymer Chemistry: An Introduction*. 3rd ed. 1999:: Oxford University Press.
4. Billmeyer, F.W.J., *Textbook of Polymer Science*. 3rd ed. 1984: Copyright, Jonh Wiley & Sons, Inc.
5. Chang, R., *Química*. 5th ed. 1994: McGraw-Hill.
6. Braunecker, W.A., Matyjaszewski, K., *Controlled/ Living radical polymerization features, developments, and perspectives.* Progress in Polymer Science, 2007. 32: p. 93-146.
7. Ullmann, F., Yamamotoo, Y.S., Gerhartz, W., *Ullmann's Encyclopedia of Industrial Chemistry*. 5th ed. 1995: Wiley-VCH.
8. Fried, J.R., *Polymer Science and Techonology*. 2nd ed. 1995: Prentice Hall.
9. Buchholz, F.L., Graham, A.T., *Modern Superabsorbent Polymer Technology*, 1998: Wiley-VCH.
10. Brannon-Peppas, L., Harland, R.S., *Absorbent Polymer Technology*. 1990: Elsevier.
11. Zhang, J., Wang, A., *Study on superabsorbent composites. IX: Synthesis, characterization and swelling behaviors of polyacrylamide/clay composites based on various clays.* Reactive Functional Polymers, 2007. Vol. 67: p. 737–745.
12. Qiu, Y., Park, K., *Environment-sensitive hydrogels for drug delivery*. Advanced Drug Delivery Reviews, 2001. Vol. 53: p. 321–339.

13. Kulicke, W-M., Nottelmann, H., *Structure and swelling of some synthetic, semisynthetic, and biopolymer hydrogels*. Advanced Chemical, 1989. Vol. 223: p. 15-44.

14. Kazanskii, K.S., Dubrovskii, S.A., *Chemistry and physics of “agricultural” hydrogels*. Advanced Polymer Science, 1992. Vol. 104: p. 97-140.

15. Dayal, U., Mehta, S.K., Choudhari, M.S., Jain R., *Synthesis of acrylic superabsorbents*, Journal of Macromolecular Science-Reviews in Macromolcular Chemistry and Physics, 1999. Vol. C39: p. 507-525.

16. Ahmed, E.M., Hydrogel: Preparation, characterization, and applications. Journal of Advanced Research, 2013. In press (DOI: 10.1016/j.jare.2013.07.006.)

17. Mathur, A.M., Moorjani, S.K., Scranton, A.B., *Methods for synthesis of hydrogel networks: A review*, Journal of Macromolecular Science-Reviews in Macromolcular Chemistry and Physics, 1996. Vol. C36: p. 405-430.

18. Laftah, W.A., Hashim, S., Ibrahim, A.N., *Polymer Hydrogels: A Review*. Polymer-Plastics Technology and Engineering, 2011. Vol. 50: p. 1475-1486.

19. Zohuriaan-Mehr, M.J., Kabiri, K., *Superabsorbent Polymer Materials: A Review*. Iranian Polymer Journal, 2008. Vol. 17: p. 451-477.

20. Luo, W.; Zhang, W.; Chen, P.; Fang, Y. *Synthesis and properties of starch grafted poly[acrylamide-co-(acrylic acid)]/montmorillonite nanosuperabsorbent via Î*$^3$ *-ray irradiation technique*. Journal of Applied Polymer Science, 2005. Vol. 96: p. 1341–1346.

21. Nho, Y.C., Mook Lim, Y., Moo Lee, Y., *Preparation, properties and biological application of pH-sensitive poly(ethylene oxide) (PEO) hydrogels grafted with acrylic acid(AAc) using gamma-ray irradiation*. Radiation Physics and Chemistry, 2004. Vol. 71: p. 239–242.

22. Karadað, E., Saraydin, D., Güven, O., *Radiation induced superabsorbent hydrogels. acrylamide/itaconic acid copolymers*. Macromolecular Materials and Engineering, 2001. Vol. 286: p. 34–42.

23. Kiatkamjornwong, S., *Superabsorbent polymers and superabsorbent polymer composites*. Science Asia,2007. Vol. 33: p. 39–43.

24. Kabiri, K., Omidian, H., Zohutiaan-Mehr, M., Doroudiani, S., *Superabsorbent Hydrogel Composites and Nanocomposites: A Review*. Polymer Composites, 2011. Vol. 32: p. 277-289.

25. Li, Y., Huang, G., Zhang, X., Li, B., Chen, Y., Lu, T., Lu, T. J., Xu, F., *Magnetic hydrogels and their potential biomedical applications*. Advanced Functional Materials, 2013. Vol. 23: p. 660–72.

26. Zhang, J.T., Cheng, S.X., Huang, S.W., Zhuo, R.X., *Temperature sensitive poly(N-isopropylacrylamide) hydrogels with macroporous structure and fast response rate*. Macromolecular Rapid Community, 2003. Vol. 24: p. 447–451.

27. Watanabe, N., Hosoya, Y., Tamura, A., Kosuge, H., *Characteristics of water-absorbent polymer emulsions*. Polymer International, 1993. Vol. 30: p. 525–531.

28. Qunyi, T., Ganwei, Z., *Rapid synthesis of a superabsorbent from a saponified starch and acrylonitrile/AMPS graft copolymers*. Carbohydrate Polymers, 2005. Vol. 62: p. 74–79.

29. Wang, W.B., Xu, J.X., Wang, A.Q., A pH-,salt- and solvent-responsive carboxymethylcellulose-g-poly(sodium acrylate)/medical stone superabsorbent composite with enhanced swelling and responsive properties. eXPRESS Polymer Letters, 2011. Vol. 5: p. 385-400.

30. Mahdavinia, G.R., Pourjavadi, A., Hosseinzadeh, H., Zohuriaan, M.J., Modified chitosan 4. Superabsorbent hydrogels from poly(acrylic acid-co-acrylamide) grafted chitosan with salt- and pH-responsivenedd properties. European Polymer Journal, 2004. Vol. 40: p. 1399-1407.

31. Bao, Y., Ma, J., Li, N., Synthesis and swelling behaviors of sodium carboxymethyl cellulose-g-poly(AA-co-AM-co-AMPS)/MMT superabsorbent hydrogel. Carbohydrate Polymers, 2011. Vol. 84: p. 76-82.

32. Singh, B., Sharma, D.K., Gupta, A., *In vitro release dynamics of thiram fungicide from starch and poly(methacrylic acid)-based hydrogels*. Journal of Hazardous Materials, 2008. Vol. 154: p. 278–286.

33. Wen, Z., Xing, J., Yang, C., Yuying, L., Jun, F., *Degradable natural polymer hydrogels for articular cartilage tissue engineering*. Journal of Chemical Technology and Biotechnology, 2013. Vol. 88: p.327–39.

34. Takashi, L., Hatsumi, T., Makoto, M., Takashi, I., Takehiko, G., Shuji, S., *Synthesis of porous poly(N-isopropylacrylamide) gel beads by sedimentation polymerization and their morphology*. Journal of Applied Polymer Science, 2007. Vol. 104: p. 842.

35. Gulrez, S.K.H., Al-Assaf, S., Phillips, G.O., *Hydrogels: Methods of Preparation, Characterisation and Applications*. Progress in Molecular and Environmental Bioengineering – From Analysis and Modeling to Technology Applications, Prof. Angelo Carpi (Ed.), ISBN: 978-953-307-268-5, InTech, Available from: http://www.intechopen.com/books/progress-in-molecular-and-environmental-bioengineeringfrom-analysis-and-modeling-to-technology-applications/hydrogels-methods-of-preparation-characterisationand-applications

36. Peppas, N.A., Bures, P., Leobandung, W., Ichikawa, H., *Hydrogels in pharmaceutical formulations*. European Journal of Pharmaceutics Biopharmaceutics, 2000. Vol. 50: p. 27–46.

37. Shin, J., Braun, P., Lee, W., *Fast response photonic crystal pH sensor based on templated photopolymerized hydrogel inverse opal*. Sensors and Actuators B: Chemical, 2010. Vol. 150: p. 183–90.

38. Richter, A., Wenzel, J., Kretschmer, K., *Mechanically adjustable chemostats based on stimuli-responsive polymers*. Sensors and Actuators B: Chemical, 2007. Vol. 125: p. 569–573.

39. Nilimankadas, *Preparation Methods and Properties of Hydrogel: A Review*. International Journal of Pharmacy and Pharmaceutical Sciences, 2013. Vol. 5: p. 112-117.

40. Hamidi, M., Azadi, A., Rafiei, P., *Hydrogel nanoparticles in drug delivery*. Advanced Drug Delivery Reviews, 2008. Vol. 60: p. 1638–1649.

41. N.A. Peppas, “Kinetics of Smart Hydrogels”, in “Reflexive Polymers and Hydrogels: Understanding and Designing Fast-responsive Polymeric Systems”, Yui, N., Mrsny, R., Park, K. 2004: CRC Press.

42. Peppas, .A., Hoffman, A.S., “*2.5 Hydrogels*”, in “*Biomaterials Science: An introduction to materials in Medicine*”, Ratner, B.D., Hoffman, A.S., Schoem, F.J., Lemons, J.E. 3rd ed. 2012: Academic Press.

43. Elliot, Mark., "Superabsorbent Polymers" BASF - THE CHEMICAL COMPANY. [Accessed in 5 August 2014]. Available from: http://chimianet.zefat.ac.il/download/Super-absorbant_polymers.pdf

44. Li, A., Wang, A.Q., Chen, J.M., *Studies on poly (acrylic acid)/attapulgite superabsorbent composite. I. Synthesis and characterization*. Journal of Applied Polymer Science, 2004. Vol. 92: p. 1596–1603.

45. Lin, J., Tang, Q., Wu, J., *The synthesis and electrical conductivity of a polyacrylamide/Cu conducting hydrogel*. Reactive and Functional Polymers, 2007. Vol. 67: p. 489–494.

46. Chen, Y., Tan, H.M., *Crosslinked carboxymethylchitosan-g-poly(acrylic acid) copolymer as a novel superabsorbent polymer*. Carbohydrate Research, 2006. Vol. 341: p. 887–896.

47. Liang, R., Liu, M.Z., *Preparation of poly(acrylic acid-coacrylamide)/kaolin and release kinetics of urea from it*. Journal of Applied Polymer Science, 2007. Vol. 106: p. 3007–3015.

48. Chen, X.P., Shan, G.R., Huang, J., Huang, Z.M., Weng, Z.X., *Synthesis and properties of acrylic-based superabsorbent*. Journal of Applied Polymer Science, 2004. Vol. 92: p. 619–624.

49. Xie, J.J., Liu, X.R., Liang, J.F., Luo, Y.S., *Swelling properties of superabsorbent poly(acrylic acid-co-acrylamide) with different crosslinkers*. Journal of Applied Polymer Science, 2009. Vol. 112: p. 602–608.

50. Karadag, E., Saraydin, D., *Swelling of superabsorbent acrylamide/sodium acrylate hydrogels prepared using multifunctional crosslinkers*. Turkish Journal of Chemistry, 2002. Vol. 26: p. 863–875.

51. Sadeghi, M., Koutchakzadeh, G., *Swelling kinetics study of hydrolyzed carboxymethylcellulose – poly (sodium acrylate-co-acrylamide) superabsorbent hydrogel with salt-sensitivity properties*. Science Islamic Azad University, 2007. Vol. 17: p. 19–26.

52. Yoshimura, T., Matsuo, K., Fujioka, R., *Novel biodegradable superabsorbent hydrogels derived from cotton cellulose and succinic anhydride: Synthesis and characterization*. Journal of Applies Polymer Science, 2006. Vol. 99: p. 3251–3256.

53. Guilherme, Marcos Rogério – Desenvolvimento de hidrogéis superabsorventes para o uso eficiente de água. Maringá: 2006. Tese de Pós-Graduação em Química.

54. Bhardwaj, A. K., Shainberg, I., Goldstein, D., Warrington, D.N., and Levy, G.J., *Water Retention and Hydraulic Conductivity of Cross-Linked Polyacrylamides in Sandy Soils*. Soil Science Society of America Journal, 2007. Vol. 71: p. 406 - 412.

55. Isık, B., Kıs, M., *Preparation and determination of swelling behavior of poly(acrylamide-co-acrylic acid) hydrogels in water*. Journal of Applied Polymer Science, 2004. Vol. 94: p. 1526-1531.

56. Turan, E., Çaykara, T., *Swelling and Network Parameters of pH-Sensitive Poly (acrylamide-co-acrylic acid ) Hydrogels*. Journal of Applied Polymer Science, 2007. Vol. 106: p. 2000-2007.

57. Grassi M., Sandolo C., Perin D., Coviello T., Lapasin R., Grassi G., *Structural characterization of calcium alginate matrices by means of mechanical and release tests*. Molecules, 2009. Vol. 14: p. 3003-3017.

58. Hoffman, A.S., *Hydrogels for biomedical applications*. Advanced Drug Delivery Reviews, 2002. Vol. 54: p. 3–12.

59. Das A., Kothari V.K., Makhija S., Avyaya K., *Development of high-absorbent light-weight sanitary napkin*. Journal of Applied Polymer Science, 2008. Vol. 107: p. 1466-1470.

60. Al-Manasir, N., Kjoniksen, A.L., Nystrom, B., *Preparation and characterization of cross-linked polymeric nanoparticles for enhanced oil recovery applications*. Journal of Applied Polymer Science, 2009. Vol. 113: p. 1916–1924.

61. Office of Industrial Technologies, Energy Efficiency and Renewable Energy, U.S, Department of Energy, Water recycle/removal using temperature-sensitive hydrogels. Washington, DC; 1998.

62. Seko, N., Tamada, M., Yoshii, F., *Current status of adsorbent for metal ions with radiation grafting and crosslinking techniques*. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 2005. Vol. 236: p. 21–29.

63. Guilherme, M.R., Reis, A.V., Paulino, A.T., Fajardo, A.R., Muniz, E.C., Tambourgi, E.B., *Superabsorbent hydrogel based on modified polysaccharide for removal of* $Pb^{2+}$ *and* $Cu^{2+}$ *from water with excellent performance*. Journal of Applied Polymer Science, 2007. Vol. 105: p. 2903–2909.

64. El-Hag Ali, A., Shawky, H.A., Abd El Rehim, H.A., Hegazy, E.A., *Synthesis and characterization of PVP/AAc copolymer hydrogel and its applications in the removal of heavy metals from aqueous solution*. European Polymer Journal, 2003. Vol. 39: p. 2337–2344.

65. Liu, B.H., Hu, J.L., *The application of temperature-sensitive hydrogels to textiles: A review of chinese and Japanese investigations*. Fibres and Textiles in Eastern Europe, 2005. Vol. 13: p. 45–49.

66. Sannino, A., Demitri, C., Madaghiele, M., Biodegradable Cellulose-based Hydrogels: Design and Applications. Materials, 2009. Vol. 2: p. 353-373.

67. Wu, J., Wei, Y., Lin, J., Lin, S., *Study on starch-graft-acrylamide/mineral powder superabsorbent composite*. Polymer, 2003. Vol. 44: p. 6513–6520.

68. Katime, I., Novoa, R., Zuluaga, F., *Swelling kinetics and release studies of theophylline and aminophylline from acrylic acid/n-alkyl methacrylate hydrogels*. European Polymer Journal, 2001. Vol. 37: p. 1465–1471.

69. Kang, G.D., Cheon, S.H., Khang, G., Song, S.-C., *Thermosensitive poly(organophosphazene) hydrogels for a controlled drug delivery*. European Journal of Pharmaceutics and Biopharmaceutics, 2006. Vol. 63: p. 340–346.

70. Devine, D.M., Devery, S.M., Lyons, J.G., Geever, L.M., Kennedy, J.E., Higginbotham, C.L., *Multifunctional polyvinylpyrrolidinonepolyacrylic acid copolymer hydrogels for biomedical applications*. International Journal of Pharmaceutics, 2006. Vol. 326: p. 50–59.

71. Landers, R., Hui `bner, U., Schmelzeisen, R., Mui `lhaupt, R., *Rapid prototyping of scaffolds derived from thermo reversible hydrogels and tailored for applications in tissue engineering*. Biomaterials, 2002. Vol. 23: p. 4437–4447.

72. Kim, J., Lee, K.W., Hefferan, T.E., Currier, B.L., Yaszemski, M.J., Lu, L., *Synthesis and evaluation of novel biodegradable hydrogels based on poly(ethylene glycol) and sebacic acid as tissue engineering scaffolds*. Biomacromolecules, 2008. Vol. 9: p. 149–157.

73. Adhikari, B., Majumdar, S., *Polymers in sensor applications*. Progress in Polymer Science, 2004. Vol. 29: p. 699–766.

74. Uchida, R., Sato, T., Tanigawa, H., Uno, K., *Azulene incorporation and release by hydrogel containing methacrylamide propyltrimenthylammonium chloride, and its application to soft contact lens*. Journal of Controlled Release, 2003. Vol. 92: p. 259–264.

75. Wu, L., Liu, M., Rui, L., *Preparation and properties of a doublecoated slow-release NPK compound fertilizer with superabsorbent and water-retention*. Bioresource Technology, 2008. Vol. 99: p. 547–554.

76. Liang, R., Yuan, H., Xi, G., Zhou, Q., *Synthesis of wheat straw-g-poly(acrylic acid) superabsorbent composites and release of urea from it*. Carbohydrate Polymers, 2009. Vol. 77: p. 181–187.

77. Wack, H., Ulbricht, M., *Effect of synthesis composition on the swelling pressure of polymeric hydrogels*. Polymer, 2009. Vol. 50: p. 2075–2080.

78. Abd El-Rehim H.A., Hegazy E.S.A., Abd El-Mohdy H.L., *Radiation synthesis of hydrogels to enhance sandy soils water retention and increase plant performance*. Journal of Applied Polymer Science, 2004. Vol. 93: p. 1360-1371.

79. Bakass M., Mokhlisse A., Lallemant M., *Absorption and desorption of liquid water by a superabsorbent polymer: Effect of polymer in the drying of the soil and the quality of certain plants*, Journal Applied Polymer Science, 2002. Vol. 83: p. 234-243.

80. Wu L., Liu M., *Preparation and characterization of cellulose acetate-coated compound fertilizer with controlled-release and water-retention*. Polymers for Advanced Technologies, 2008. Vol. 19: p. 785-792.

81. Zhan, F., Liu, M., Guo, M., Wu, L., *Preparation of superabsorbent polymer with slow-release phosphate fertilizer*. Journal of Applied Polymer Science, 2004. Vol. 92: p. 3417–3421.

82. Buchholz F.L., Peppas N.A., *Superabsorbent Polymers Science and Technology*. 1994: Copyright, American Chemical Society.

83. Superabsorbents, Website of the European Disposables and Nonwovens Association (EDANA). [Accessed 20 August 2014]. Available from: www.edana.org.

84. Zohuriaan-Mehr M.J., *Super-Absorbents*. Tehran: Iran Polymer Society, 2006.

85. Brown, T.C., *Projecting U. S. freshwater withdrawals*. Journal of Water Resources Research, 2000. Vol. 36: p. 769-780.

86. Gleick, P.H., *Water Use*. Annual Review of Environment and Resources, 2003. Vol. 28: p. 275-314.

87. Arnell, N.W., *Climate change and global water resources: SRES emissions and socio-economic scenarios*. Global Environmental Change, 2004. Vol. 14: p. 31-52.

88. Döll, P., *Impact of Climate Change and Variability on Irrigation Requirements: A Global Perspective*. Climatic Change, 2002. Vol. 54: p. 269–293.

89. Fereres, E., Soriano, M.A., *Deficit irrigation for reducing agricultural water use*. Journal of Experimental Botany, 2007. Vol. 58: p. 147 - 159.

90. Dabhi, R., Bhatt, N., Pandit, B., *Super absorbent polymers – An innovative water saving technique for optimizing crop yield*. International Journal of Innovative Research in Science, Engineering and Technology, 2013. Vol. 2: p. 5333-5340.

91. Foley, J.A., DeFries, R., Asner, G.P., Barford, C., Bonan, G., Carpenter, S.R., Chapin, F.S., Coe, M.T., Daily, G.C., Gibbs, H.K., Helkowski, J.H., Holloway, T., Howard, E.A., Kucharik, C.J., Monfreda, C., Patz, J.A., Prentice, I.C., Ramankutty N., Snyder, P.K., *Global Consequences of Land Use*. Science, 2005. Vol. 309: p. 570-574.

92. Tilman, D., Cassman, K.G., Matson, P.A., Naylor, R., Polasky, S., *Agricultural sustainability and intensive production practices*. Nature, 2002. Vol. 418: p. 671 - 677.

93. Van Genuchten, M.T., *A closed-form equation for predicting the hydraulic conductivity of unsaturated soils*. Soil Science Society of America Journal, 1980. Vol. 44: p. 892-898.

94. Hussain, G., Algosaibi, A.M., Badawi, M.H., *Effect of single salt solution on water-absorption by gel-forming soil conditioners*. Arid Soil Research and Rehabilitation, 1992. Vol. 6: p. 83-89.

95. El-Rehim, H.A.A., Hegazy, El-S.A., Abd El-Mohdy, H.L., *Radiation synthesis of hydrogels to enhance sandy soils water retention and increase plant performance*. Journal of Applied Polymer Science, 2004. Vol. 93: p. 1360-1371.

96. Kim, S., *The Development and Characterization of Double Layer Hydrogel for Agricultural and Horticultural Applications*. 2011: ProQuest, UMI Dissertation Publishing.

97. Taban, M., Naeini, S.A.R.M., *Effect of Aquasorb and Organic Compost Amendments on Soil Water Retention and Evaporation with Different Evaporation Potentials and Soil Textures*. Communications in Soil Science and Plant Analysis, 2006. Vol. 37: p. 2031-2055.

98. Geesing, D., Schmidhalter, U., *Influence of sodium polyacrylate on the water-holding capacity of three different soils and effects on growth of wheat*. Soil Use and Management, 2004. Vol. 20: p. 207-209.

99. Chatzoudis, G. K., Rigas, F., *Soil Salts Reduce Hydration of Polymeric Gels and Affect Moisture Characteristics of Soil*. Communications in Soil Science and Plant Analysis, 1999. Vol. 30: p. 2465-2474.

100. Sarvaš, M., Pavlenda, P., Takáovcá, E., *Effect of hydrogel application on survival and growth of pine seedlings in reclamations*. Journal of Forest Science, 2007. Vol. 53: p. 204-209.

101. Ekebafe, L.O., Ogbeifun, D.E., Okieimen, F.E., Polymer Applications in Agriculture. Biokemistri, 2011. Vol. 23: p. 81-89.

102. Puoci, F., Iemma, F., Spizzirri, U.G., Cirillo, G., Curcio, M., Picci, N., Polymer in Agriculture: a Review. American Journal of Agricultural and Biological Sciences, 2008. Vol. 3: p. 299-314.

103. Chang, C., Zhang , L., Cellulose-based hydrogels: Present status and applications prospects. Carbohydrate Polymers, 2011. Vol. 84: p. 40-53.

104. Sannino, A., Esposito, A., Nicolais, L., Del Nobile, M.A., Giovane, A., Balestrieri, C., Esposito, R., Agresti, M., *Cellulose-based hydrogels as body water retainers*. Journal of Materials Science – Materials in Medicine, 2000. Vol. 11: p. 247-253.

105. Sannino, A., Mensitieri, G., Nicolais, L., *Water and synthetic urine sorption capacity of cellulosebased hydrogels under a compressive stress field*. Journal of Applied Polymer Science, 2004. Vol. 91: p. 3791-3796.

106. López, S.H., Santiago, E.V., *Acrylated-Epoxidized Soybean Oil-Based Polymers and Their Use in the Generation of Electrically Conductive Polymer Composites*. Soybean – Bio-Active Compouds, Prof. Hany El-Shemy. 2013: InTech. [Accessed in 7 August 2014]. Available from: http://www.intechopen.com/books/soybean-bio-active-compounds/acrylated-epoxidized-soybean-oil-based-polymers-and-their-use-in-the-generation-of-electrically-cond

107. Pelletier, H., Belgacem, N., Gandini, A., *Acrylated Vegetable Oil as Photocrosslinkable Materials*. Journal of Applied Polymer Science, 2005. Vol. 99: p. 3218-3221.

108. Shibata, M., Kaneko, K., Kakihara, T., Supramolecular composites of photocured acrylated epoxidized soybean oil and fibers formed by the self-assembly of low molecular weight organic gelators. Polymer Journal, 2011. Vol. 43: p. 552-558.

109. Bouranis, D.L., Theodoropoulos, A.G., Drossopoulos, J.B., *Designing synthetic polymers as soil conditioners*. Communications in Soil Science and Plant Analysis, 1995. Vol. 26: p. 1455-1480.

110. Buchholz, F.L., *Recent advances in superabsorbent polyacrylates*. Trends in Polymer Science, 1994. Vol. 2: p. 277-281.

111. Ichikawa T., Nakajima T., *Superabsorptive Polymers (from natural polysaccharides and polypeptides),* in *Polymeric Materials Encyclopedia,* Salamone, J.C. 1996: CRC Press.

112. Dutkiewicz J.K., *Superabsorbent materials from shellfish waste-A review*. Journal of Biomedical Materials Research Part B: Applied Biomaterials, 2002. Vol. 63: p. 373-381.

113. Kubota, H., Kuwabara, S., *Cellulosic absorbents for water synthesized by grafting of hydrophilic vinyl monomers on carboxymethyl cellulose*. Journal of Applied Polymer Science, 1997. Vol. 64: p. 2259-2263.

114. Esposito, F., Del Nobile, M.A., Mensitier, G., Nicolais, L., Water Sorption in Cellulose-Based Hydrogels. Journal of Applied Polymer Science, 1996. Vol. 60: p. 2403-2407.

115. Karadag, E., Saraydin, D., Çaldiran, Y., Güven, O., Swelling Studies of Copolymeric Acrylamide/Crotonic Acid Hydrogels as Carriers for Agricultural Uses. Polymers for advanced technologies, 2000. Vol. 11: p. 59-68.

116. Raju, K.M., Raju, M.P., Mohan, Y.M., Synthesis and Water Absorbency of Crosslinked Superabsorbent Polymers. Journal of Applied Polymer Science, 2002. Vol. 85: p. 1795-1801.

117. Chen, P., Zhang, W., Luo, W., Fang, Y., *Synthesis of superabsorbent polymers by irradiation and their applications in agriculture*. -, Journal of Applied Polymer Science, 2004. Vol. 93: p. 1748-1755.

118. Ma, S., Liu, M., Chen, Z., *Preparation and Properties of a Salt-Resistant Superabsorbent Polymer*. Journal of Applied Polymer Science, 2004. Vol. 93: p. 2532–2540.

119. Liu, M., Liang, R., Zhan, F., Liu, Z., Niu, A., Preparation of superabsorbent slow release nitrogen fertilizer by inverse suspension polymerization. Polymer International, 2007. Vol. 56: p. 729-737.

120. Suo, A., Qian, J., Yao, Y., Zhang, W., *Synthesis and Properties of Carboxymethyl Cellulose-graft-Poly(acrylic acid-co-acrylamide) as a Novel Cellulose-Based Superabsorbent*. Journal of Applied Polymer Science, 2007. Vol. 103: p. 1382–1388.

121. Demitri, C., Del Sole, R., Scalera, F., Sannino, A., Vasapollo, G., Maffezzoli, A., Ambrosio, L., Nicolais, L., *Novel superabsorbent celulose-based hydrogels crosslinked with citric acid.* Journal of Applied Polymer Science, 2008. Vol. 110: p. 2453-2460.

122. Nnadi, F., Brave, C., *Environmentally friendly superabsorbent polymers for water conservation in agricultural lands*. Journal of Soil Science and Environmental Management, 2011. Vol. 2: p. 206-211.

123. Raafat, A.I., Eid, M., El-Arnaouty, M.B., *Radiation synthesis of superabsorbent CMC based hydrogels for agriculture applications*. Nuclear Instruments and Methods in Physics Research B, 2012. Vol. 283: p. 71-76.

124. Venkatachalam, D., Vediappan, V., Gounder, S.K., Synthesis and Evaluation of Trimethylolpropane Triacrylate Crosslinked Superabsorbent Polymers for Conserving Water and Fertilizers. Journal of Applied Polyme Science, 2013. Vol. 129: p. 1350-1361.

125. Larkin, P., Infrared and Raman Spectroscopy: Principles and Spectral Interpretation. 2011: Elsevier.

126. Stuart, B.H., *Polymer analysis.* Vol. 30. 2008: Wiley. com.

127. Morrison, R. and Boyd, R., *Organic Chemistry.* 14 ed. 1992: Prentice- Hall.

128. Gabbott, P., *Principles and Applications of Thermal Analysis.* 1 ed. 2008, UK: Blackwell Publishing.

129. Stoney, D.A., Stoney, P.L.- *Use of scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS) Methods for the analysis of small particles adhering to carpet fiber surfaces as a means to test associations of trace evidence in a way that is independent of manufactured characteristics*. [PDF]. Chantilly, VA: National Criminal Justice Reference Service, July 2012. [Accessed in 8 September 2014]. Available from: https://www.ncjrs.gov/pdffiles1/nij/grants/239051.pdf

130. Seal Laboratories (Evans Analytical Group), How SEM Works. [Accessed in 8 September 2014]. Available from: http://www.seallabs.com/how-sem-works.html

131. Wikipedia, Scanning electron microscope. [Acessed in 8 September 2014]. Available from: http://en.wikipedia.org/wiki/Scanning_electron_microscope

132. Wikipedia, Optical microscope. [Acessed in 8 September 2014]. Available from: http://en.wikipedia.org/wiki/Optical_microscope

133. Rack, P.D., Optical Microscopy. [PDF]. Tennesse: University of Tennesse. [Accessed in 8 September 2014]. Available from: http://web.utk.edu/~prack/MSE%20300/Lightmicroscopyhandout.pdf

134. Castro, Carlos, et al. (2010). Phase Behaviour of Hydroxypropyl Cellulose/Polyacrylamide Gels. *Macromol. Symp.* Vo. 296. p. 429-435.

135. Yang, J., Han, C.R., Duan, J.F., Ma, M.G., Zhang, X.M., Xu, F., Sun, R.C., Synthesis and characterization of mechanically flexible and tough cellulose nanocrystals-polyacrylamide nanocomposite hydrogels. Cellulose, 2013. Vol. 20: p. 227-237.

136. Sigma-Aldrich, 3-(Trimethoxysilylpropyl methacrylate. [Acessed in 10 September 2014]. Available from: http://www.sigmaaldrich.com/catalog/product/aldrich/440159?lang=pt&region=PT

137. El-Rehim, H.A.A., Characterization and Possible Agricultural Application of Polyacrylamide/Sodium Alginate Crosslinked Hydrogels Prepared by Ionizing Radiation. Journal of Applied Polymer Science, 2006. Vol. 101: p. 3572-3580.

138. Demitri, C., Scalera, F., Madaghiele, M., Sannino, A., Maffezzoli, A., Potential of Cellulose-Based Superabsorbent Hydrogels as Water Reservoir in Agriculture. International Journal of Polymer Science, 2013. Vol. 2013.

139. Sigma-Aldrich, Acrylic Acid. [Acessed in 10 September 2014]. Available from: http://www.sigmaaldrich.com/catalog/product/aldrich/147230?lang=pt&region=PT

140. Sigma-Aldrich, Acrylamide. [Acessed in 10 September 2014]. Available from: http://www.sigmaaldrich.com/catalog/product/sigma/a9099?lang=pt&region=PT

141. Cal Poly Pomona University, Spectroscopy Data Tables. [Acessed in 27 August 2014]. Available from: http://www.csupomona.edu/~psbeauchamp/pdf/424_spectra_tables.pdf

142. Silva, D.P., Pozza, A.A.A., Leite, B.S., Leite, S.A.F., Investigation of Hydrogel Application on the Culture of Beans to Optimie Water Resource and Productivity. Chemical Engineering Transactions, 2012. Vol. 19: p. 511-516.

143. Sigma-Aldrich, Trimethylolpropane triacrylate. [Acessed in 10 September 2014]. Available from: http://www.sigmaaldrich.com/catalog/product/aldrich/246808?lang=pt&region=PT

144. Sigma-Aldrich, Bis[2-(methacryloyloxy)ethyl] phosphate. [Acessed in 10 September 2014]. Available from: http://www.sigmaaldrich.com/catalog/product/aldrich/496758?lang=pt&region=PT

145. Sigma-Aldrich, N,N’-Methylenebisacrylamide. [Acessed in 10 September 2014]. Available from: http://www.sigmaaldrich.com/catalog/product/sigma/m7279?lang=pt&region=PT

146. Sigma-Aldrich, 3-Sulfopropyl methacrylate potassium salt. [Acessed in 10 September 2014]. Available from: http://www.sigmaaldrich.com/catalog/product/aldrich/251658?lang=pt&region=PT

147. Coates, J., *Interpretation of Infrared Spectra, A Practical Approach.* 1 ed. 2000, USA: John Wiley & Sons.

148. UCLA Chemistry and Biochemistry, Table of IR Absorptions. [Acessed in 28 August 2014]. Available from: http://www.chem.ucla.edu/~webspectra/irtable.html

149. Chen, Y., Tan, H-M., *Crosslinked Carboxymethylchitosan-g-poly(acrylic acid) copolymer as a novel superabsorbent polymer*. Carbohydrate Research, 2006. Vol. 341: p. 887-896.

150. Rouquerol, J., Avnir, D., Fairbridge, C.W., Everett, D.H., Haynes, J.H., Pernicone, N., Ramsay, J.D.F., Sing, K.S.W., Unger, K.K., Recommendations for the characterization of porous solids. Pure and Applied Chemistry, 1994. Vol. 66: p. 1739-1758.

151. GlobalSoilMap, Soil pH map of the world based on the HWSD. [Accessed 9 September 2014]. Available from: http://www.globalsoilmap.net/content/soil-ph-map-world-based-hwsd

152. Curtis, N., Childs, C., *Plant Nutrition and Soils*. [PDF]. Victoria: Heather Wansbrough. [Accessed in 29 August 2014]. Avalaible from: http://nzic.org.nz/ChemProcesses/soils/2A.pdf

153. University of Minnesota, Nutrient Management – *Fertilizer Urea*. [Accessed in 30 August 2014]. Available from: http://www.extension.umn.edu/agriculture/nutrient-management/nitrogen/fertilizer-urea/

154. World Bank Group, Pollution Prevention and Abatement Handbook – *Nitrogenous Fertilizer Plants*, July 1998. [Accessed in 30 August 2014]. Available from: http://www.ifc.org/wps/wcm/connect/250cdd8048865857b57ef76a6515bb18/nitrofert_PPAH.pdf?MOD=AJPERES

155. Kim, S.W., Bae, Y.H., Okano, T., *Hydrogels: Swelling, Drug Loading and Release*. Pharmaceutical Research, 1992. Vol. 9: p. 283-290.

156. Eid, M., In Vitro Release Studies of Vitamin B12 from Poly N-vinyl pyrrolidone/starch Hydrogels Grafted with Acrylic Acid Synthesized by Gamma

Radiation. Nuclear Instruments and Methods in Physics Research Section B, 2008. Vol. 266: p. 5020-5026

157. Chen, L., Qiu, X., Deng, M., Hong, Z., Luo, R., Chen, X., Jing, X., *The Starch Grafted Poly(L-lactide) and the Physical Properties of its Blending Composites*. Polymer, 2005. Vol. 46: 5723-5729.

158. Chen, L., Qiu, X., Xie, Z., Hong, Z., Sun, J., Chen, X., Jing, X., *Poly(L-lactide)/starch blends compatibilized with poly(L-lactide)-gstarch copolymer*. Carbohydrate Polymers, 2006. Vol. 65: p. 75-80.

159. Launer, P.J., Infrared Analysis of Organosilicon Compounds: Spectra-structure Correlations. [PDF]. New York: B. Arkles et al. Petraarch Systems, 1987. [Acessed in 7 September 2014]. Available from: http://gelest.com/goods/pdf/Library/11Infra.pdf

# Appendices

# A. FTIR analysis (monomers AESO and AAm)

Figure A.1 show the FTIR spectra of AESO and AAm monomers.

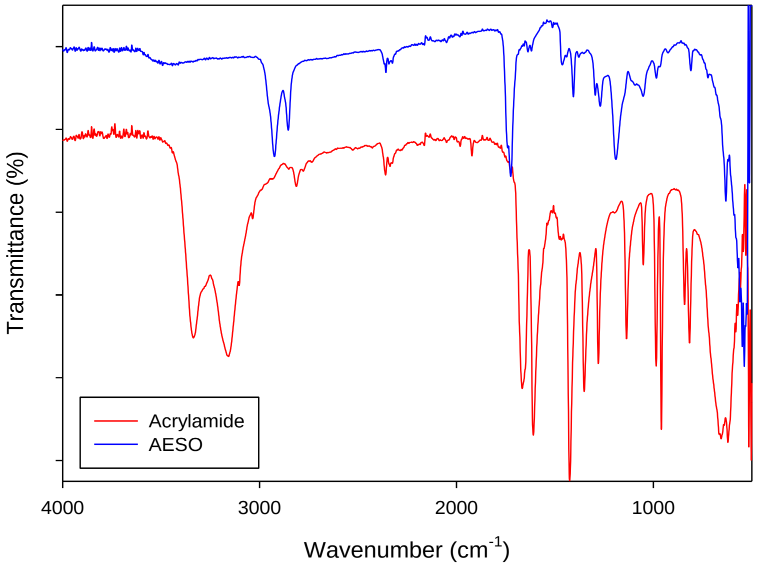


**Figure A.1 – Transmittance spectra obtained for AAm and AESO.**

# B. FTIR Analysis (AAm/AESO reactions)

Figure B.1 to Figure B.5 show the FTIR spectra of all the reactions AAm/AESO polymers.

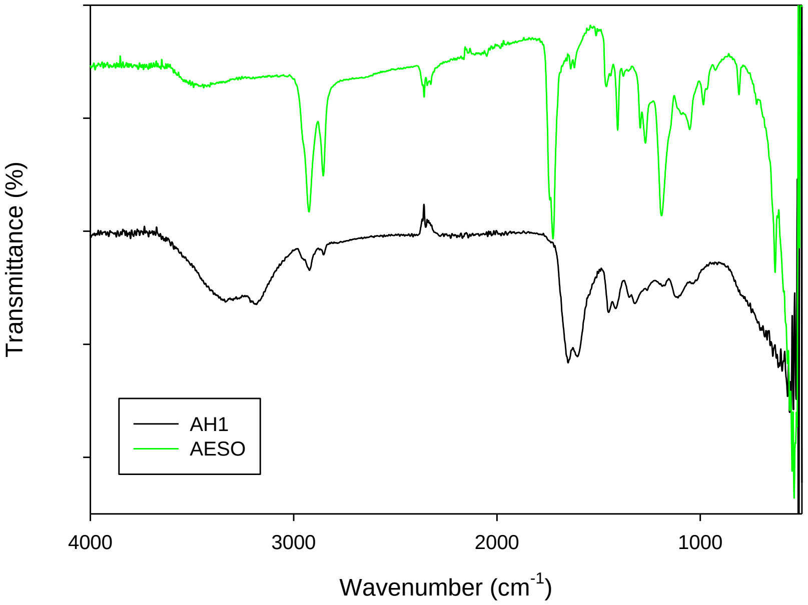


**Figure B.1 – Transmittance spectra obtained for AESO and AH1 polymer.**

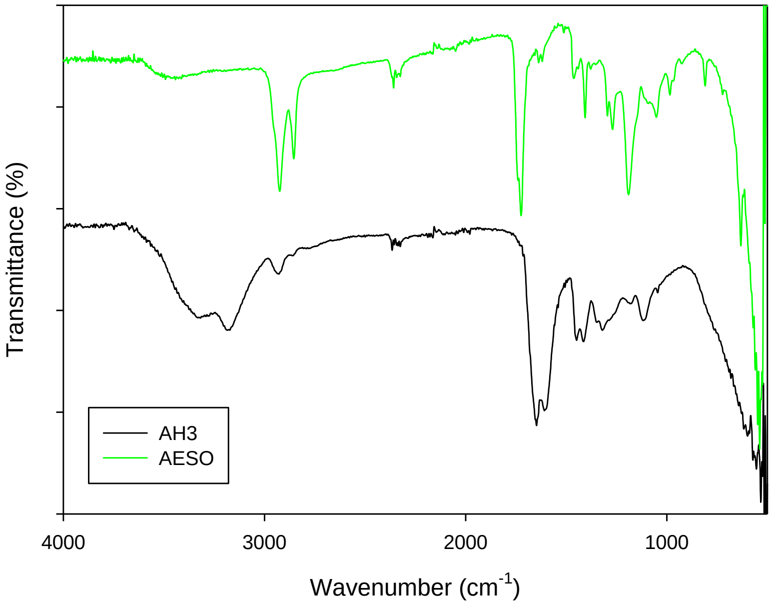


**Figure B.2 – Transmittance spectra obtained for AESO and AH3 polymer.**

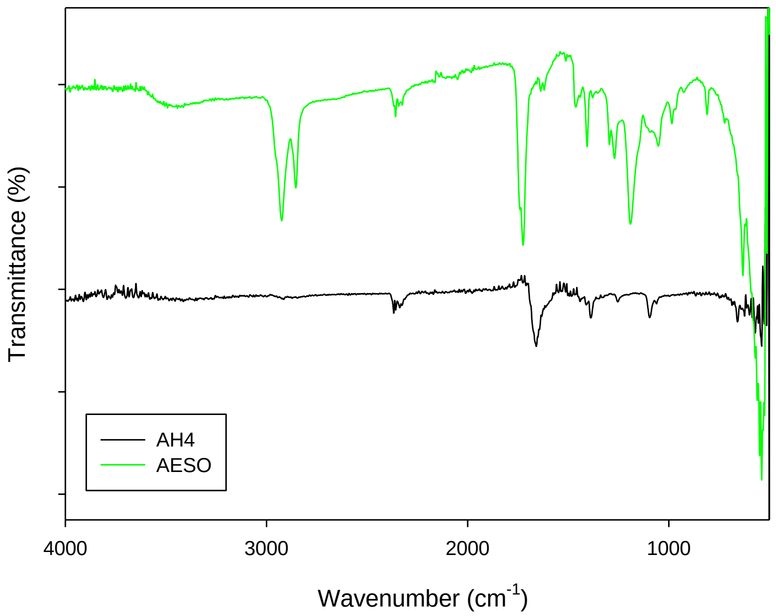


**Figure B.3 – Transmittance spectra obtained for AESO and AH4 polymer.**

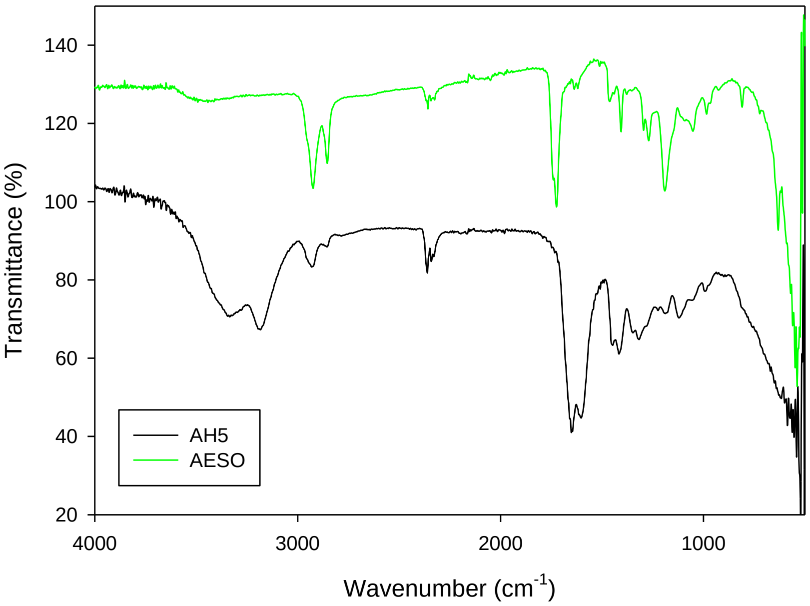


**Figure B.4 – Transmittance spectra obtained for AESO and AH5 polymer.**

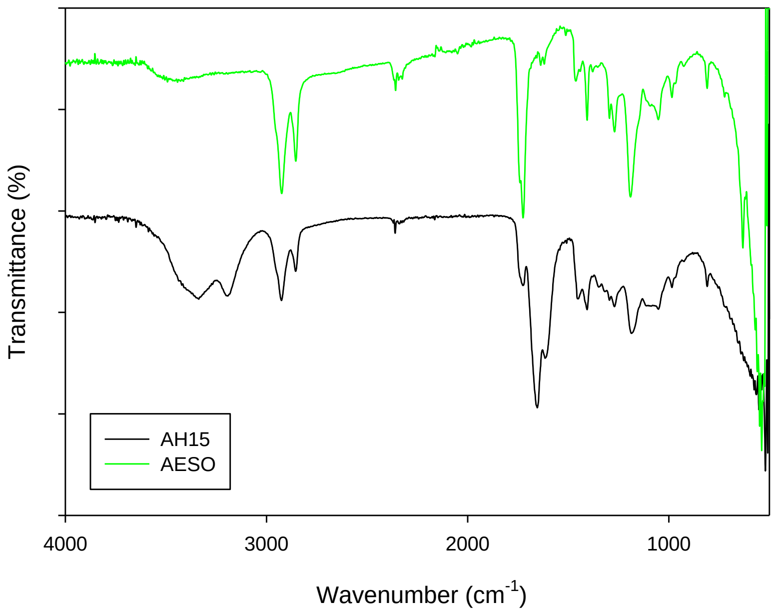


**Figure B.5 – Transmittance spectra obtained for AESO and AH15 polymer.**

# C. FTIR Analysis (AA/AESO reactions)

Figure C.1 and C.2 show the FTIR spectra of all the reactions AA/AESO polymers.

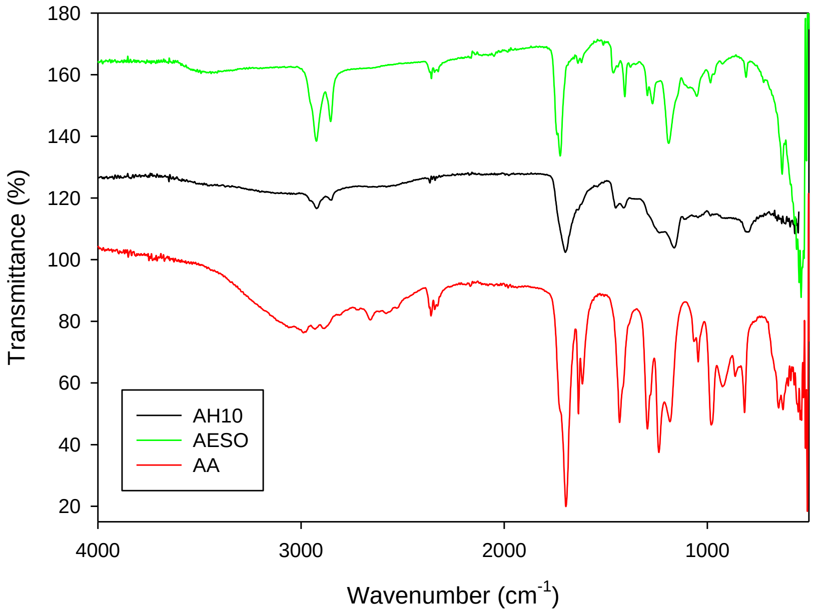


**Figure C.1 – Transmittance spectra obtained for AESO, AA and AH10 polymer.**

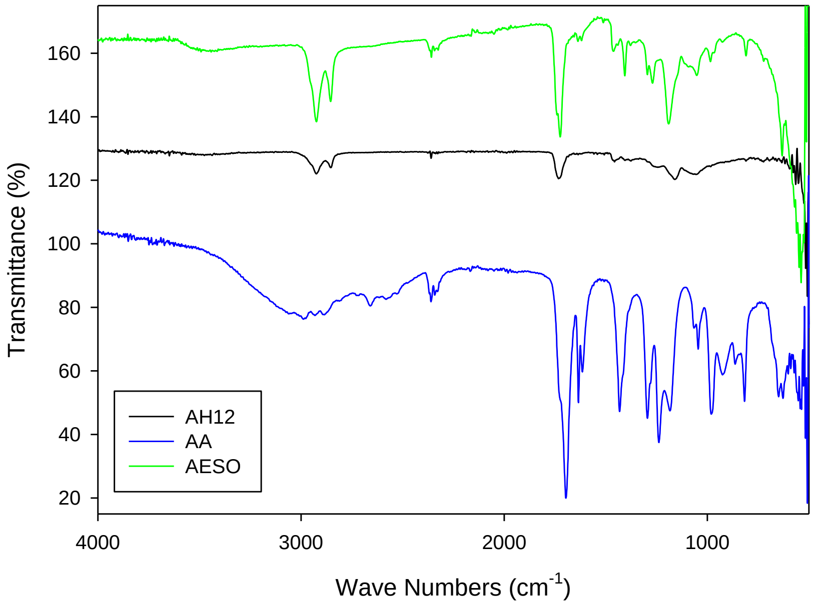


**Figure C.2 – Transmittance spectra obtained for AESO, AA and AH12 polymer (similar to AH13 polymer).**

# D. FTIR Analysis (all reactants of AH53/SAP5 reaction)

Figure D.1 show the FTIR spectra of all the reactants of AH53 reaction (SAP5).

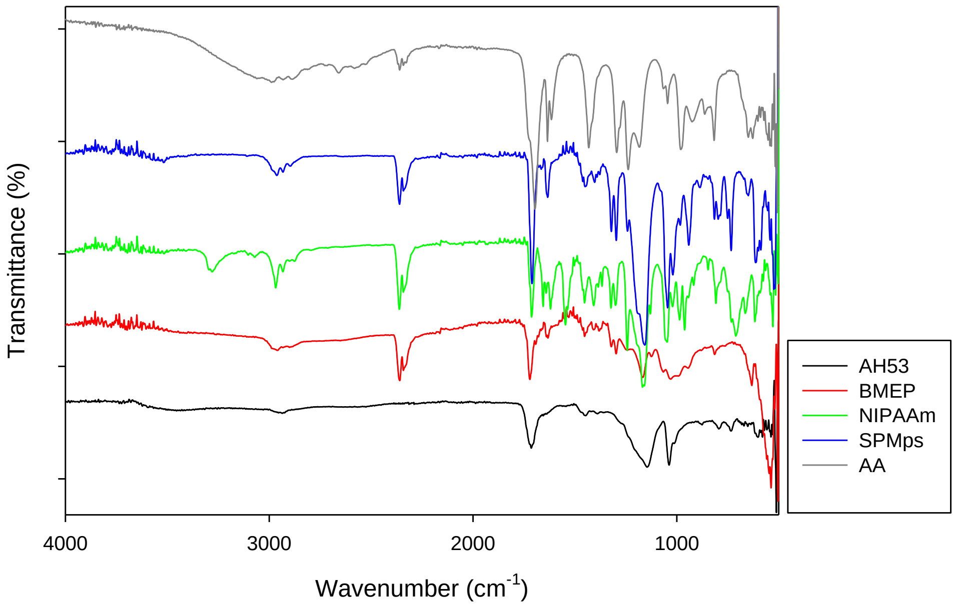


**Figure D.1 – Transmittance spectra obtained for SAP5 and all Ah53 reactants (BMEP,NIPAAm, SPMps and AA).**

# E. Analysis of particle size

Figure E.1 to E.3 show the areas of powder used for analysis of particle size.

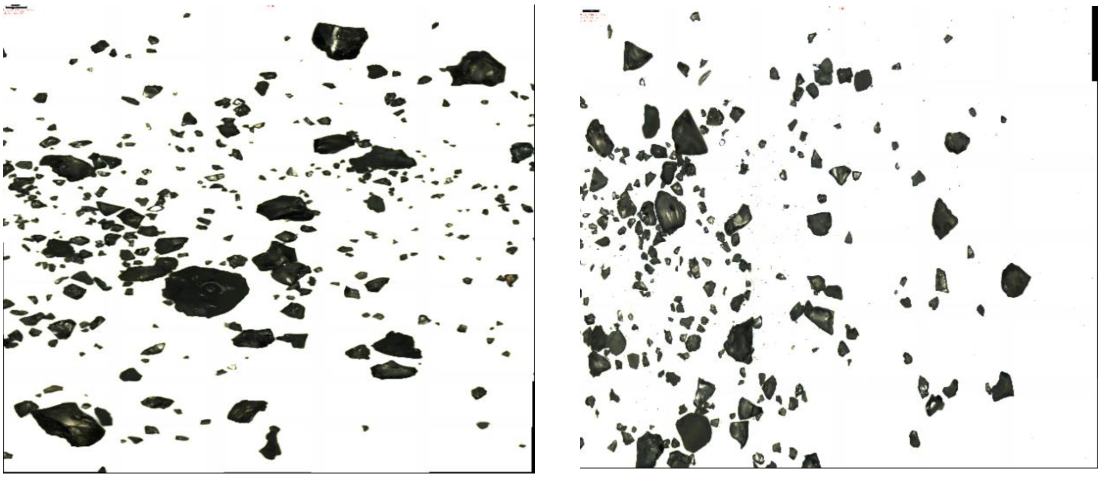


**Figure E.1 – Area 1 (left) and 2 (right) used for the analysis of particle size.**

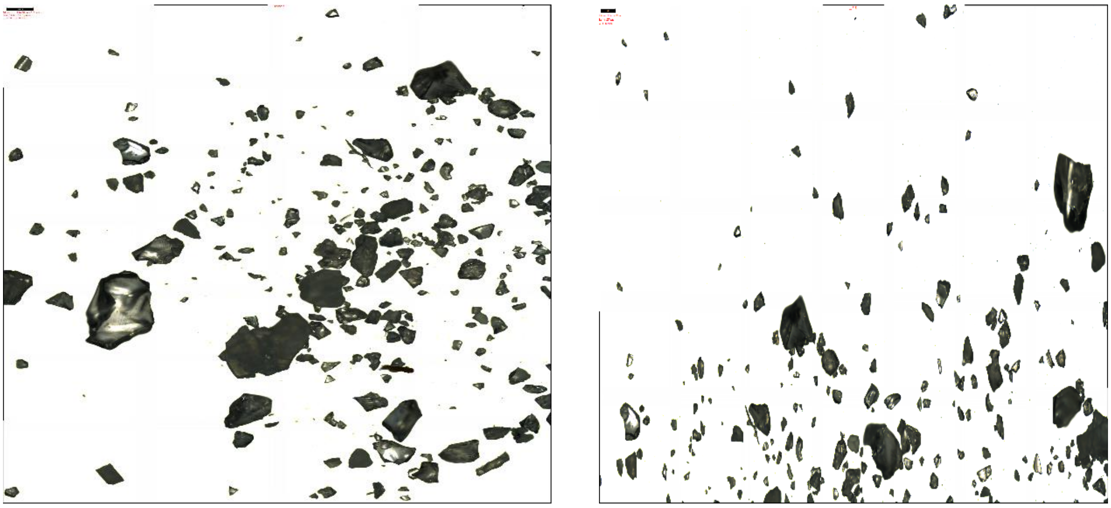


**Figure E.2 – Area 3 (left) and 4 (right) used for the analysis of particle size.**

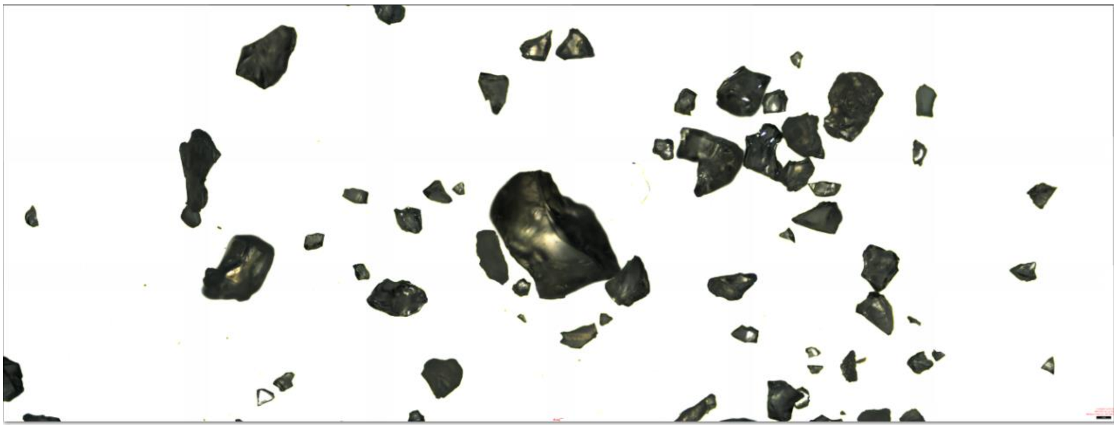


**Figure E.3 – Area 5 used for the analysis of particle size.**

# F. Soil pH

Figure F.1 show the soil pH map of the world based on the HWSD. [151]

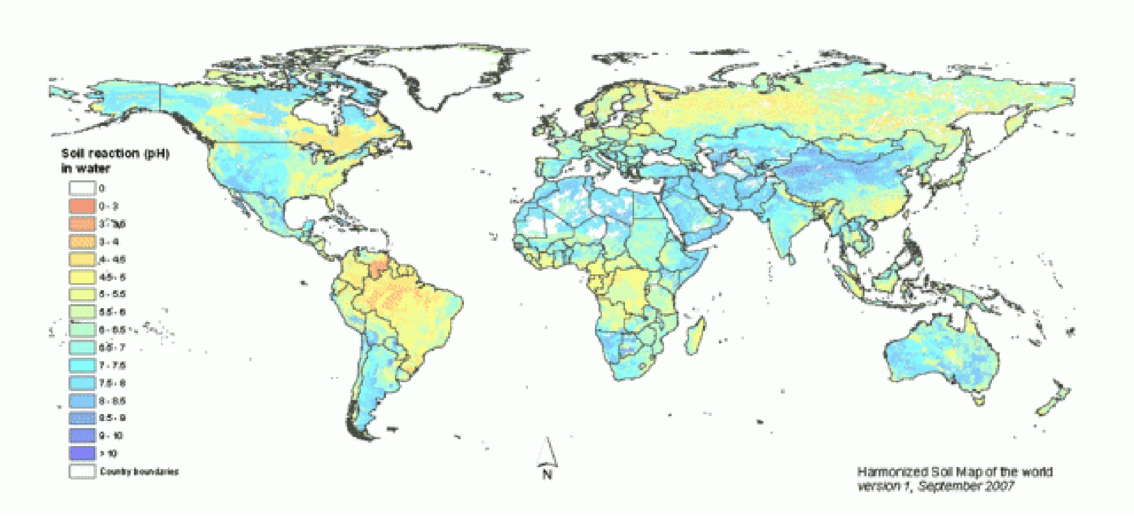


**Figure F.1 – Soil pH map of the world based on the HWSD, adapted from [151].**