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# SUPER ABSORBENT POLYMERS AND COMPOSITES FOR AGRICULTURE-A SHORT REVIEW

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## Abstract

The use of polymer in agriculture is gaining popularity in science, particularly in the field of polymer chemistry. This has provided solutions to the problems of the present day agriculture which is to maximize land and water productivity without threatening the environment and the natural resources. Superabsorbent polymer hydrogels potentially influence soil permeability, density, structure, texture, and evaporation and infiltration rates of water through the soils.

**Keywords**: Agriculture, soil, plants, polymeric materials

## Introduction

During the 20th century, the main emphasis of agricultural development all over the world was the increasing productivity per unit area of land used for crop production to feed the ever-increasing population. This was substantially accomplished through over exploitation of natural resources such as water and plant resources and excessive use of fertilizers and pesticides [1]. Although this practice resulted in considerable increase in crop yields in the short-tem, it was not sustainable in the long-run. The productive capacity of the arable land was impaired; the natural water resources were depleted and also polluted with hazardous pesticides and chemical fertilizers which threatened the survival and well being of all life forms on earth. Therefore, the emphasis on agricultural development in the present century has shifted to the sustainable use of land, water and plant resources in agriculture. The major goal of the present day agriculture is to maximize land and water productivity without threatening the environment and the natural resources.

As a matter of priority, one major role of agriculture is in the provision of food supply and security. However, emerging trends indicate an increasing role with respect to soil and water management and conservation. With reference to global climatic anomalies, drought due to protracted absence, deficient or poor distribution of precipitation has occurred over many parts of the globe in varying scales of severity and duration throughout human history. Many nations have experienced considerable distress arising out of drought occurrences -mass starvation (even famines), cessation of economic activity particularly within the developing world where economies are inextricably and intrinsically tied to agriculture [2]. Within the sciences, the study of polymers has helped to foster the emergence of agricultural polymers through focus on natural/synthetic macromolecular substances such as proteins, polyacrylates, polyacrylamides, and polysaccharides. Through the concerted efforts of polymer chemists, a series of commercially natural/synthetic polymers have been successfully used in many applications in the field of agriculture. In this regard, this account; a detailed review study, has been put together as an exposé on the myriad applications of polymer in the field of agriculture, highlighting present research trends , impact on food security and what the future holds.

## Superabsorbent Polymers

The water lack and the desertification are very serious problems for many regions of the world because, first of all, they compromise agriculture development. Desertification is the degradation of land in arid, semi arid and dry areas resulting from various factors including climatic variations, but primarly human activities. A valid aim to these problems could come from the use of synthetic materials with good water absorption and retention capacities even under high pressure or temperature. Systems of this type are the Superabsorbent polymers (SAPs). Because of their excellent properties, these SAPs were already well established in various applications such as disposable diapers, hygienic napkins, cement, drug delivery systems, sensors, and agriculture. In such applications, water absorbency and water retention are essentials. Their use for agricultural applications has shown encouraging results; they have been observed to help reduce irrigation water consumption and the death rate of plants, improve fertilizer retention in the soil, and increase plant growth rate. Recent articles reported the modification of these superabsorbent copolymers with a view to enhance their absorbency, gel strength, and absorption rate. Raju et al. [3] prepared a series of superabsorbent copolymers by using acrylamide (Am), potassium methacrylate (KMA) and 2- hydroxyethilmethacrylate (HEMA) as monomers, and N,N-methylenebisacrylamide (MNBA) as a cross- linking agent. The influence of various synthetic parameters such as the monomer concentration, crosslinker concentration, and initiator concentration were studied. The experimental results showed that these superabsorbents polymers have a good absorbency both in water and NaCl solutions and a fast swelling capacity. Furthermore, it was observed that SAPs determine a considerable increase of the water retention of the soil; in their presence, besides, the germination energy of groundnut seeds and growth of young plants enhanced enormously. In order to obtain more easily biodegradable

SAPs and reduce the product cost, Chen and al.[4] prepared novel polymers by grafting copolymerization of acrylic acid and acrylamide onto starch by using -ray radiation technique and poly(ethilene glycole) (PEG) as a crosslinker. Also in this case, the effect of various synthetic parameters (irradiation dose, irradiation dose rate, monomer concentration, monomer/starch ratio, and PEG content) and the effects of different drying methods on water absorbency of the SAPs were studied. From this study turned out that, with increasing of the monomer concentration, the water absorbency decreases rapidly. This happen because high monomer concentration increase the polymer density and, consequently, also its capacity of retaining the heat produced by polymerization. As a consequence, an increase of the system temperature accelerate the chain termination and transfer speeds. On the contrary, the water absorbency increases rapidly when the PEG concentration in the polymer increases, but reaches saturation at about 0.65 wt % PEG. Furthermore, this SAPs show good water retention at high temperature and this property makes them suitables for a potential application in agriculture, especially in arid and desert regions. By adding a small percentage of SAPs (0.1 wt %) to sand and soil samples, in fact, the water retention of sand and soil was considerably enhanced. Finally, the effects of the SAPs on the germination of corn seeds and growth of young plants were investigated, showing that not only the germination energy of the seeds with SAPs is higher than that of the seeds without SAPs, but the superabsorbent polymers also promote the seeds growth and have a favorable effects on the weights of leafages and roots of the plants. Polyacrylate superabsorbents generally exhibit a very high absorbency in deionized water; they, however, have the problem of poor resistance to salts as evinced by their notable low absorbency exhibited to electrolytic solutions such as an aqueous common salt solution. In order to enhance the water absorbency properties of SAPs in such electrolytic solutions, Ma et al.[5] prepared salt-resistant superabsorbent as follows. At first, they prepared crosslinked sodium polyacrylate; then, they used ethylene glycol diglycidyl ether (EGDE) to crosslink the molecular chains existing at least in the vicinity of the surfaces of the crosslinked sodium polyacrylate; last, the surface-crosslinked superabsorbent was mixed with inorganic salt powders.

The experimental data showed that the water absorbency first increased with increasing reaction temperature, neutralization degree of acrylic acid, amount of initiator, crosslinking agent, and surface- crosslinking agent. In recent years, superabsorbent polymers prepared from natural polymers such as starch[6], chitosan[7], a high molecular weight polysaccharide from chitin, and poly(amino acid)s[8] have received increasing interest because they are environmentally friendly, biodegradable, and independent of soil resources. Zhang et al.[9] prepared a novel superabsorbent composite through graft polymerization with chitosan, acrylic acid and attapulgite in aqueous solution, using N,N- methylenebisacrylamide (MNBA) as a crosslinker and ammonium persulfate as an initiator. Cellulose and its derivatives are also attracting a great deal of interest again for preparing superabsorbent polymers because of their biodegradable characteristics[10,11], their natural abundance, and potentially high absorption properties[12]. Many efforts have been made to synthesize cellulose-based superabsorbents and to improve the swelling capacity. For example, Kuwabara and Kubota[13] synthesized highly water-absorbing acrylamide (AA) grafted carboxymethylcellulose (CMC) by photografting in the presence of N,N1 methylenebisacrylamide (MNBA) as a crosslinker. Yoshinobu et al.[14] reported partially hydrolyzed graft copolymers of crosslinked polyacrylamide on cellulose and its derivatives synthesized by a ceric salt initiation method. Kubota and Kuwabara[15] prepared AA-grafted and methacrylic acid grafted CMC superabsorbents by photo initiation, ceric salt initiation, and radiation initiation, and the highest water absorbency obtained was less than 250 g/g. Lionetto et al. prepared a superabsorbent cellulose-based hydrogel by crosslinking a sodium salt of CMC and hydroxyethyl cellulose with divinyl sulfone as a crosslinker. Suo et al.[16], instead, attempted to synthesize a new cellulose-based superabsorbent by simultaneously grafting two kinds of hydrophilic monomers, acrylic acid and acrylamide (Am), onto CMC in the presence of the crosslinker NMBA and potassium persulfate and sodium metabisulfite (PPS/SMB) as a redox couple of the initiator. The initiator and crosslinker contents, and bath temperature mainly affect the molecular weight and crosslinking density of the copolymer and the polymerization rate. The greater the weight percentage of the AA monomer in the starting stock is, the more numerous the ionic carboxylate groups are, and this greatly improves the water absorbency. The preparation of polymer/clay superabsorbent composites has also received great attention because of their relative low production costs and high water absorbency. This excellent water absorbency and water retention may prove especially practical in agricultural and horticultural applications.

# Biodegradable Polymers in the Agricultural Field

In the last decade, one of the problems affecting the environment has been the increased use of plastic materials and their subsequent disposal. Plastics have been used in innumerable applications with little consideration for their ultimate disposability. Conventional polymers, such as polyethylene and polypropylene persist for many years after disposal. Built for the long haul, these polymers seem inappropriate for applications in which plastics are used for short time periods and then disposed. Furthermore, plastics are often soiled by food and other biological substances. In other words, the resistance of synthetic polymers to the action of living systems is becoming more and more problematic in

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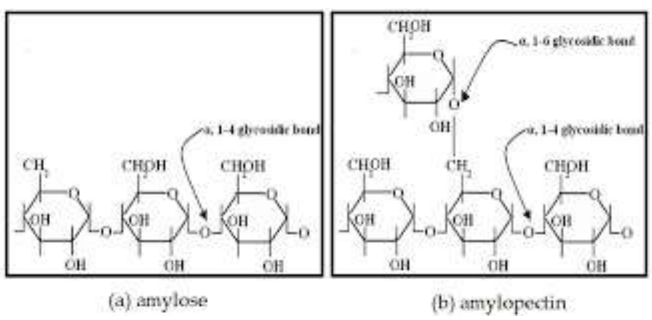
several domains where are used for a limited period of time before becoming waste. Among the various possible routes to eliminate polymeric wastes, biodegradation and biorecycling via bioassimilation are regarded as attractive solutions for environmental protection, when incineration is not feasible because it is a source of unacceptable pollution. Biodegradable polymers (BPs) have increasingly been used such as plastics substitutes for several applications in the agriculture field[17-19]. BPs, disposed in bioactive environments, degrade by the enzymatic action of microorganisms such as bacteria, fungi, and algae and their polymer chains may also be broken down by non enzymatic processes such as chemical hydrolysis. Unfortunately, in the majority of cases, the properties of natural polymers do not fit the needs of specific applications, and blending with synthetic polymers is a route largely used to gain the desired properties[20,21]. Convenient candidates for those applications are natural polymers such as agar, starches, alginates, pectins and cellulose derivatives, along with synthetic biodegradable polymers, such as polycaprolactone, polylactide and poly (vinyl alcohol).[22-25]



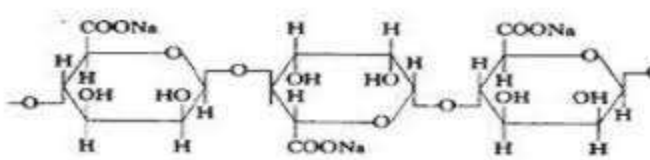
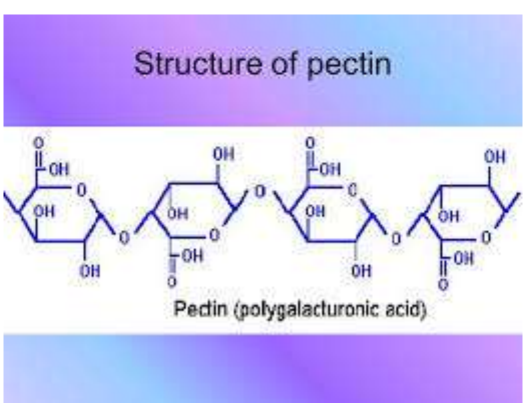
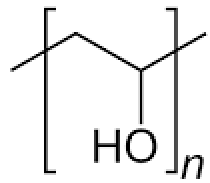



FIG. 3. Structure of sodium alginate.



Poly Vinyl alcohol

Fig. 1: Natural and synthetic biodegradable polymers

Starch is an inexpensive, annually renewable material derived from corn and other crops. All starches contain amylose and amylopectin, at ratios that vary with the starch source. This variation provides a natural mechanism for regulating starch material properties. Starch-based biodegradable polymers can be produced by blending or mixing them with synthetic polymers.

By varying the synthetic blend component and its miscibility with starch, the morphology and hence the properties can be regulated easily and efficiently.[26] Blends containing thermoplastic starch (non crystalline starch) may be blended or grafted with biodegradable polyesters, such as polycaprolactone, to increase flexibility and resistance to moisture. Blends, mainly formed into films and sheets, with more than 85% starch are used for foaming and injection molding[27]. By mixing thermoplastic starch with cellulose derivatives, rigid and dimensionally stable injection- molded articles result. Chemically modified plant cellulose is used in a remarkably diverse set of applications. For example, cellulose acetate is used in many common applications, including toothbrush handles and adhesive tape backing. Studies in simulated compost environments revealed that cellulose acetates with degrees of substitution of up to 2.5 are biodegradable. A decrease in the degree of substitution of cellulose acetate from 2.5 to 1.7 results in a large increase in the rate of their biodegradation[28]. An important application of these biodegradable polymers is their employment in solarization process. Indeed, one of the problems afflicting agricultural production is the presence of parasites in the soil that, along with spontaneous weeds, take away nourishment from the soil. In the past, the elimination of parasites and seeds of undesirable plants, before a new sowing, was performed through fumigation with methyl bromide, which has been indefinitely banned for its toxicity. In the 1970s, a new approach, solarization,[29,30] which involves covering the soil to be reconditioned with polymeric films, was introduced. The polymeric films for this application have to be mechanically resistant, transparent to visible light, and opaque to infrared radiation. The optical properties are important because, during the day, visible radiation, which passes through the film, warms the soil. During the night, when the soil cools by emitting infrared radiation, the film, which is impermeable to infrared radiation, traps it and thus prevents heat loss. Actually, a film with these optical properties has a micro greenhouse effect on the soil. This technique is largely used today, particularly at those latitudes with temperate climate. It makes use of low-density polyethylene with fillers, such as phosphates, that increase the opacity to infrared radiation. Solarization guarantees the decontamination of soils assigned to insemination within 4–6 weeks. At the end of the treatment, the problem of the removal and disposal of films has to be resolved. Films based on synthetic polymers have to be treated as special waste with additional costs. Moreover, there are severalproblems related to environmental pollution for all films that, in violation of the law, are burned after their use. A biodegradable films, made of natural polymers, for solarization offers the advantage that it does not have to be removed from the soil after they are used. In literature film for solarization containing alginates, poly(vinyl alcohol) and glycerol are reported.[31,32] Alginates are water-soluble linear copolymer, containing -gluronic acid and -mannuronic acid units, present in seaweed.[33,34] The proposed materials were characterized in terms of the mechanical parameters and optical properties. The films were transparent in the visible region and opaque in the infrared region to ensure a micro greenhouse effect on the soil.

# Super absorbents polymers and composites for agriculture

Polymeric soil conditioners were known since the 1950s. These polymers were developed to improve the physical properties of soil in view of:

(i) Increasing their water-holding capacity,
(ii) Increasing water use efficiency
(iii) Enhancing soil permeability and infiltration rates
(iv) Reducing irrigation frequency
(v) Reducing compaction tendency
(vi) Stopping erosion and water run-off
(vii) Increasing plant performance (especially in structure -less soils in areas subject to drought).

The presence of water in soil is essential to vegetation. Liquid water ensures the feeding of plants with nutritive elements, which makes it possible for the plants to obtain a better growth rate. It seems to be interesting to exploit the existing water potential by reducing the losses of water and also ensuring better living conditions for vegetation. Taking into account the water imbibing characteristics of SAP materials, the possibilities of its application in the agricultural field has increasingly been investigated to alleviate certain agricultural problems. Super absorbent polymers (SAPs) are compounds that absorb water and swell to many times their original size and weight. They are lightly cross-linked networks of hydrophilic polymer chains. The network can swell in water and hold a large amount of water while maintaining the physical dimension structure [35,36]. It was known that commercially used water-absorbent polymeric materials employed are partial neutralization products of cross-linked polyacrylic acids, partial hydrolysis products of starch– acrylonitrile copolymers and starch–acrylic acid graft copolymers. At present, the material's biodegradability is an important focus of the research in this field because of the renewed attention towards environmental protection issues [37]. The half life is in general in the range 5 - 7 years, and they degrade into ammonium, carbon dioxide and water. SAP hydrogels potentially influence soil permeability, density, structure, texture, evaporation, and infiltration rates of water through the soils. Particularly, the hydrogels reduce irrigation frequency and compaction tendency, stop erosion and water runoff, and increase the soil aeration and microbial activity [38]. In arid areas, the use of SAP in the sandy soil (macroporous medium), to increase its water-holding capacity seems to be one of the most significant means to improve the quality of plants [39]. The SAP particles may be taken as "miniature water reservoirs" in soil. Water will be removed from these reservoirs upon the root demand through osmotic pressure difference. The hydrogels also act as a controlled release system by favoring the uptake of some nutrient elements, holding them tightly, and delaying their dissolution. Consequently, the plant can still access some of the fertilizers, resulting in improved growth and performance rates [40-42]. SAPs can also be used as retaining materials in the form of seed additives (to aid in germination and seedling establishment), seed coatings, root dips, and for immobilizing plant growth regulator or protecting agents for controlled release . A distinctive instance for the agricultural application of SAP has been recently practiced. The SAP effect on the growth indices of an ornamental plant (Cupressus arizonica) under reduced irrigation regimes in the field and on the soil water retention curve in a laboratory was investigated [43]. Additional interesting instance is a research recently conducted on the effect of SAP materials on the characteristics of sport turf. Turf is of significant importance as an inseparable part of all kinds of green spaces. Irrigation water consumption of turf is very huge, especially in the hot and dry climates due to surface evaporation and infiltration. In the research conducted by Mousavinia et al. [44]

were obtained. The turf density, colour intensity and coverage percentage was increased, while it's wilting level was substantially decreased when SAP was used [45]. SAP materials have shown excellent influence on decreasing damages (up to 30%) in the productive process of the olive sapling [46]. Meanwhile, non-cross-linked anionic polyacrylamides (PAM, containing <0.05% AM) having very high molecular weight (12-15x106 g.mol-1), have also been used to reduce irrigation-induced erosion and enhance infiltration. Its soil stabilizing and flocculating properties improve runoff water quality by reducing sediments, N-dissolved reactive phosphorus (DRP), chemical oxygen demand (COD), pesticides, weed seeds, and microorganisms in runoff. In a series of field studies, PAM eliminated 80-99% (94% avg.) of sediment in runoff from furrow irrigation, with a 15-50% infiltration increase compared to controls on medium to fine-textured soils [47] The preparation of polymer/clay superabsorbent composites [48] has also received great attention because of their relative low production costs and high water absorbency. superabsorbent composites by graft copolymerization reaction of acylic acid (AA) and acrylamide (Am) on attapulgite micropowder using N,N-methylene bisacrylamide (MBA) as a crosslinker and ammonium persulphate (APS) as an initiator in an aqueous solution has been prepared [49]. Acrylamide is a kind of nonionic monomer and has great advantage on its good salt resistant performance as a raw material for superabsorbent. Attapulgite, as a good substrate for superabsorbent composite materials, is a layered aluminium silicate with reactive groups –OH on the surface.

# Conclusion

Throughout human history, agriculture has been a source of food, fuel and fiber. Opportunities have arisen through external events and trends that impacted patterns of production and utilization. Numerous publications describe the increase in yield of various plants as a result of better soil conditions. SAPs have created a very attractive area in the viewpoint of super-swelling behavior, chemistry, and designing the variety of final applications. When working in this field, we always deal with water, aqueous media and bio-related systems. Thus, we increasingly walk in a green area becoming greener via replacing the synthetics with the bio-based materials, e.g., polysaccharides and polypeptides. Considering the high- cost and increasing prices of crude oil, the necessity of preparing natural based SAPs seems more obvious. This paves the way for further developments in this area in the mid and far future ahead. Key opportunities exist to build biodegradable polymers from annually renewable crops and agro industrial waste-streams. The production of monomers and polymers with enzymes, microbes, or plants represents a cleaner and safer way of doing chemistry. However, polymers have provided solution for the need to develop cost-effective techniques that would contribute to phytostabilization of severely metal contaminated soils.

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