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Polymer Applications in Agriculture

L. O. Ekebafe[1], D. E. Ogbeifun[2]* and F. E. Okieimen[2]

[1]Department of Polymer Technology, Auchi Polytechnic, Auchi, Nigeria
[2]University of Benin, Centre for Biomaterials Research, Benin City, Nigeria

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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, evaporation and infiltration rates of water through the soils.

Functionalized polymers were used to increase the efficiency of pesticides and herbicides, allowing lower doses to be used and to indirectly protect the environment by reducing pollution and clean-up existing pollutants. This account; a detailed review study, has been put together as an expose on the myriad application of polymer in the field of agriculture, highlighting present research trend , impact on food security and future outlook.

Keywords: Agriculture, soil, plants, polymeric materials.

1 Introduction

World population is increasing at an alarming rate and is expected to reach seven billion by the end of year 2050. Population growth and the resultant development of large high-density urban populations, together with parallel global industrialization, have placed major pressures on our environment, potentially threatening environmental sustainability and food security. This has resulted in global warming and the buildup of chemical and biological contaminants throughout the biosphere, but most notably in soils and sediments [1].

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 [2]. 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.

*Author to whom correspondence should be addressed.
E- mail address:daveogbe@yahoo.com

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 [3].

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.

2 Functionalized Polymers in Agriculture.

Synthetic polymers play important role in agricultural uses as structural materials for creating a climate beneficial to plant growth e.g. mulches, shelters or green houses; for fumigation and irrigation, in transporting and controlling water distribution. However, the principal requirement in the polymers used in these applications is concerned with their physical properties; such as transmission, stability, permeability or weatherability; as inert materials rather than as active molecules. During the last few years, the science and technology of reactive functionalized polymers [4] have received considerable interest as one of the most exciting areas of polymer chemistry for the production of improved materials. They have found widespread applications as reactive materials based on the potential advantages of the specific active functional groups and the characteristic properties of the polymeric molecules. Their successful utilizations are quite broad including a variety of fields, such as solid-phase synthesis, biologically active systems and other various technological uses [4].

2.1 Polymeric Biocides and Herbicides.

New technique has recently emerged for the controlled release formulations designed to avoid or reduced the possible side effects accompanying the use of biologically active agents. The purpose of this technique include; to protect the supply of the agent, to allow the automatic release of the agent to the target at controlled rates, and to maintain its concentration within the optimum limits over a specified period of time, thereby producing a great specificity and persistence. There are two different approaches in combining the biological agents with the polymeric materials. Either by physical combination (encapsulation or heterogeneous dispersion) to acts as a rate controlling device, or by chemical combination to act as carrier for the agent [4].

The polymeric biocide has many advantages and its potential benefits include: it allows lower amounts than conventional biocides to be used as it releases the required amount of active agent over a long period, number of applications is reduced because of long period of activity by a single application, it eliminates the time and cost of repeated over applications because less active materials is needed, reduction of toxicity, it eliminates the need for widespread distribution of large amount of biocide levels in the surrounding environment, reduction of evaporation and degradation loses by environmental forces or leaching by rain into the soil or waterways due to the macromolecular nature, it extends the duration of activity of less or non-persistent biocides which are unstable under an aquatic environment by protecting them from environmental degradation and hence , enhances the practical applicability of these materials, reduction of phytotoxicity by lowering the high mobility of the biocides in the soil and hence reduces its residue in the food web, extension of herbicide selectivity to additional crops by providing a continuous amount of herbicide at a level sufficient to control weeds but without injury to the crop.

The rate of release of active group from the polymer matrix and the consequent duration of the effective action is influenced by: chemical characteristics of the active agents structure, nature of the active - agent - polymer bond (such as esters, amides, ureas, urethanes, acetals), the distance of the active agent from the polymer backbone; for achieving an enhanced rate of release; a permanent spacer group may be necessary to prevent steric hindrance , rate of breakdown of the bond between the active material and the polymer by chemical, biological or environmental agents such as UV, moisture and microorganisms, chemical nature of the polymer backbone, chemical nature of the groups surrounding the active moieties , dimension and structure of the polymer molecule as governed by the degree of polymerization, comonomers, solubility, degree of crosslinking and the stereochemistry.

The main problem with the use of less persistent conventional herbicides that have greater specificity is the use of excess amounts than that actually required to control the herb because they are unstable in an aquatic environment and of the need to compensate the amount wasted by the environmental forces of photodecomposition, leaching and washing away by rai. They are also highly toxic to farm workers and expensive on multiple applications which are required because of their lower persistence. On the other hand, the applications of large amounts of persistent herbicides are undesirable because of their frequent incorporation into the food chain.

In an attempt to make connection with the problems encountered in using conventional herbicides. Some functionalized polymers containing pesticide moieties as pendandt groups have been prepared by free radical polymerization of vinyl monomer type and their hydrolysis rates were studied under different conditions. As active pesticide group, pentachlorophenol (PCP) a major industrial chemical, represents one of the most widely used biocides in a variety of agrochemical applications, such as herbicide, molluscide, fungicide, insecticide, algicide and bactericide. In addition its hydroxyl group provides also a suitable mean for covalent bonding to a variety of polymerizable units.

A series of vinyl monomers containing PCP via an ester linkage have been prepared [5]. These monomers have been homo- and co-polymerized with styrene and 4-vinylpridine to induce hydrophobic and hydrophilic nature to the polymers. The rates of release of PCP from the polymers have been studied at four different media (water, pH=4 pH= 10, and dioxane-water) and all at 30°C. A comparison between the rates of release from these polymers indicate that the rates increase with increasing the degree of hydrophilicity, that is, copolymer hydrolyzes faster than the homopolymer which has higher rate than the hydrophobic copolymer.

Polymer herbicides containing active moieties ionically bound to ammonium salt groups have been investigated [4] to demonstrate the reactivity displayed by the polymers through changing the chemical nature of linkage bond and the chemical characteristics of the active agent structure. In addition to PCP the herbicides of general use that contain functional group for bonding to the polymer matrix have also been used, such as 2,4-dichlorophenoxyacetic acid, 2-methyl-4-chlorophenoxyacetic acid and 2,4-dinitro-6-methyl phenol.

The major drawback to the economic use of these polymeric herbicides is the large amount of inert control that must be employed as a carrier for the herbicides and the disposal of the herbicide residual materials which may be harmful for the soil and the plant. Some attempts have been made to reduce this problem, which mainly based on the concept of attaching the pesticides to biodegradable carriers of similar structures to agricultural residues consisting of polysaccharides such as bark, sawdust, cellulose and other cellulosic wastes. However, the main disadvantages with the use of such naturally occurring polymers are the difficulties encountered with their chemical modification. Hence the use of excessive amounts of such bioactive polymers usually necessary for herb control is inevitable.The hydrophilic and cross linking nature of these polymers lead to a faster rate of hydrolytic cleavage of the pendant pesticide. Another factor is their rapid deterioration in soil by biodegradation and the subsequent destroying of the polymeric matrix within a short period of time, which leads to shorter period of effectiveness of the herbicide.

In order to eliminate or at least to reduce the disadvantage of using excessive amounts of inert polymers as carriers, in addition to the drawbacks of using soluble nitrogen fertilizers. The principle of a duel application of controlled release herbicide-fertilizer have recently been used. This principle is based on the use of appropriate polymers as carriers in which the residual products after the degradation of the polymer become beneficial to the plant growth and the soil by acting as fertilizer. For example, herbicide derivatives of bifunctional compounds have been prepared and polymerized under condensation polymerization conditions. The second attempt is based on the concept of attaching the herbicides to polymeric hydrogels in order to alter the basic character of sandy soil. In addition to the primary function of these polymers to control the rate of delivery of herbicides, they can also play an important role to increase the water retention by sandy soil through avoiding its rapid leaching. Hence, the use of such dual combination of controlled release herbicide-water conservation can contribute positively to change the conventional agricultural irrigation especially for sandy soil[5].

2.2 Polymeric Molluscicides

Bilharzia is one of the most widespread trematode endermic diseases in tropical countries where the spreading of cultivated areas increases, Since the use of molluscicides is responsible to combat various mollusks, the applications of large quantities of these chemicals are required for combating bilharzias disease through the control and eradication of the schistosoma snails. As active molluscicide, Niclosamide

(5,2-dichloro-4'- nitrosalicylanilide) has been introduced by Bayer Co., under the trademark Bayer 73 and is applied for combating the bilharzias disease. However, the use of great amounts of this compound has offered some economic and environmental toxicity problems.
The chemical combination of molluscicides with the functionalized polymers has been use in an attempt for enhancing the eradication of the snails with the elimination of the side effects associated with the use of a relatively massive Niclosamide dosage. Accordingly, molluscicide polymers containing Niclosamide via covalent and ionic bonds have been prepared by chemical modifications of polymers [6].

3. Super absorbents polymers and composites for agriculture

Polymeric soil conditioners were known since the 1950s [7]. 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 [8,9]. 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 [10]. 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 run off, and increase the soil aeration and microbial activity [11].

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 [12]. 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 favouring 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 [13-15].

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 [11]. 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 [16].

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. [17] encouraging results were obtained. The turf density, colour intensity and coverage percentage was increased, while it's wilting level was substantially decreased when SAP was used [18].

SAP materials have shown excellent influence on decreasing damages (up to 30%) in the productive process of the olive sapling [19]. 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 [20]

The preparation of polymer/clay superabsorbent composites [21] 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 [22]. 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.

Water - insoluble polymers

This second class of polymers often referred to as gel-forming polymers or insoluble water-absorbing polymers were first introduced for agricultural use in the early 1980's. These polymers do not possess linear chain structures as described previously but the chains are rather cross-linked to form a three-dimensional network. Cross-linking occurs when polymerization is carried out in the presence of a small amount of a divinyl compound. Depending on synthetic conditions, type and density of covalent bonds that form cross-links, these polymers can absorb up to 1000 times their weight in pure water and form gels. Three main types of hydrogels (water absorbing) have so far been developed as agricultural polymers: (1) starch-graft copolymers obtained by graft polymerization of polyacrylonitrile onto starch followed by saponification of the acrylonitrile units (2) cross-linked polyacrylates (3) cross-linked polyacrylamides and cross-linked acrylamide-acrylate copolymers containing a major percentage of acrylamide units. Most of the hydrogels marketed for agriculture come from the latter group as they are claimed to remain active for a much longer time.

Gel-forming polymers are small dry crystals that absorb water similar to sponges. Contact between the polymer granule and water results in absorption until equilibrium is reached. When polymers are incorporated into a soil or soilless medium, it is presumed that they retain large quantities of water and nutrients. These stored water and nutrients are released as required by the plant. Thus, plant growth could be improved, and/or water supplies conserved. It has been reported that a 171% to 402% increase in the water retention capacity is recorded when polymers were incorporated in coarse sand [23]. It has been reported that increased water retention capacity attributed to polymer addition significantly reduced irrigation frequency [24] and the total amount of irrigation water required.

Researchers [25] have reported that the use of hydrogels increases the amount of available moisture in the root zone, thus implying longer intervals between irrigations. It must be pointed out that the polymers do not reduce the amount of water used by plants. The water-holding capacity depends on the texture of the soil, the type of hydrogel and particle size (powder or granules), the salinity of the soil solution and the presence of ions. Cross-linked polyacrylamides hold up to 400 times their weight in water and release 95% of the water retained within the granule to growing plants. In general, a high degree of cross-linkage results in the material having a relatively low water-retention capacity. However, the water-holding capacity drops significantly at sites where the source of irrigation water contains high levels of dissolved salts (e.g effluent water) or in the presence of fertilizer salts [26]. The amount of water retained is also adversely affected by chemicals or ions (Mg^{2+}, Ca^{2+}, Fe^{2+}) present in the water [49]. It has been suggested that these divalent cations develop strong interactions with the polymer gels and are able to displace water molecules trapped within the polymer [27]. Even though monovalent cations (Na^{+}) can also replace water molecules, the effect is not as pronounced as with the divalent counterparts as the process is fully reversible by repeated soaking with deionised water.

Moreover, the use of hydrogels leads to increased water use efficiency since water that would have otherwise leached beyond the root zone is captured. During hot days, the hair root system of a plant pulls out and depletes most of the water from the area close to the root system, thus causing the plant to go into stress. While increasing the amount of available moisture, hydrogels help reduce water stress of plants resulting in increased growth and plant performance [28]. The performance of the gel on plant growth depends on the method of application as well. It was shown that spraying the hydrogels as dry granules or mixing them with the entire root zone is not effective [24]. Better results seem to be obtained when the hydrogels are layered, preferably a few inches below soil surface. However, generalizations should be avoided when interpreting results as a number of factors such as type of hydrogel, particle size, rate of application and type of plant has to be taken into consideration. Hydrogels are also claimed to reduce fertilizer (NPK) leaching. This seems to occur through interaction of the fertilizer with the polymer. Cross-linked polyacrylamide is also being considered as a potential carrier for insecticides, fungicides and herbicides[29].

Polymers for soil remediation.

Contamination of soils with toxic metal elements is of great concern to scientists and the general public. Long-term intake of contaminant metals by humans may lead to chronic effects, although maximum acceptable limits in food were already established for several toxic elements by the National agency for food, drugs and administration and control, European Food Service Authority and the U.S. Food and Drug Administration. [30,31]

Effects of metals on ecosystems and biological resources are also increasingly recognized [32]. Metals do not degrade as organic compounds do, and have long residence times in soils. They can however exist in different forms, which include water-soluble (ionic and chelated with soluble compounds), adsorbed on soil surfaces, chelated by insoluble organic matter, precipitated, occluded by soil oxides and hydroxides, present in living organisms or residues, and as part of primary and secondary minerals [33]. Ideally, a contaminated soil should be restored to regain its original potential, but this can be a very expensive process, and thus depends not only on the expected benefit of the cleanup and future value of the soil, but also on political and public awareness of the problem. Conventional remedial approaches to severely metal-contaminated soils involve removal and replacement of soil with clean materials or capping the soil with an impermeable layer to reduce exposure to contaminants [34], chelating agent ethylenediaminetetraacetic acid (EDTA) has been used extensively for heavy metals extraction from soil [35-37]. Much work has been done on the recovery of metal-loaded EDTA by electrochemical [38,39]] or chemical processes [40,41]. Another chelating agent, pyridine-2, 6-dicarboxylic acid has also been shown to be effective in heavy metals although these are not considered the most economically or environmentally sound solutions available. Only through the establishment of a vegetation cover to stabilize metal-contaminated soils will a successful long-term rehabilitation be achieved [42].

Water-soluble polymers (WSP) have been used extensively for the removal or recovery of metal ions from aqueous solutions. There are now reviews on the use of this technology for metal ion separations [43]. However, this technology has only recently been used to remove metals such as lead from solid surfaces. Three distinct advantages of using WSP are: 1) The metal bound to the polymer in solution can be easily concentrated by ultrafiltration (UF) 2) the metal subsequently released from the WSP can be easily segregated by UF to allow for recycle of the extraction agent and disposal of the metal; and 3) commercially available polymers can be modified to selectively bind the target metal ions. Polyethylenimine (PEI), a highly branched aliphatic polyamine, was chosen as the backbone polymer for the studies on lead extraction from soil. PEI is readily functionalized with chloroacetic acid to give aminocarboxylate groups which are known to chelate lead effectively.

2.3 Biodegradable polymer in agriculture

Biodegradable polymers have increasingly been used as plastics substitutes for several applications in agriculture. 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 70s', a new approach called solarization, 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 green house 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 made of synthetic polymers should be treated as waste with additional costs. Moreover, there are several problems related to environmental pollution for all films that, in violation of the law, are burned after their use. A biodegradable film made of natural polymers, for solarization offers advantage that it does not have to be removed from the soil after they are used. Polymer films for solarization containing alginates, polyvinyl alcohol and glycerol has been reported [44,45]. Alginates are water soluble linear copolymer, containing a-gluronic and P- mannuronic acid units, present in seaweed [46].

2.4 Drag-reducing polymers in agriculture.

Extremely minute concentrations of large polymer molecules, fibres or particles when present in a fluid cause reduction in the friction resistance in a turbulent flow compared to that of the fluid alone.
Drag-reducing polymers reduce the drag in a turbulent flow (by a mechanism not yet fully understood) while increasing the drag in a laminar flow, due to an increase in the shear viscosity [93]. This feature of drag-reducing polymers has been utilized in reducing the energy requirements of sprinkler irrigation system. The water containing drag-reducing polymers percolates losses of water. Utilizing this aspect, a slow-release urea has been developed by blending urea with guargum.[47]
The list of possible areas of applications has increased enormously to include oil well fracturing, crude oil and refined petroleum product transport, fire fighting, irrigation, sewage and flood water disposal, hydrotransport of solids, water heating circuits, jet cutting, hydraulic machinery, marine applications and biomedical applications.

3. 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 behaviour, 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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