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SOME DEVELOPMENTS OF POLYMERIC MATERIALS FOR APPLICATION IN AGRICULTURAL AND FOOD INDUSTRY

by

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I - INTRODUCTION

Since the introduction of plastic film in the 1930s and 1940s for greenhouse covering, fumigation, mulching, etc, agricultural application of polymers have grown at an increasing rate.

Numerous technical breakthroughs in polymerisation and processing techniques resulted in compositions and properties designed for packaging, agricultural and industrial applications.

All principal classes of polymers such as plastics, fibers, coatings, composites, water soluble polymers, barriers polymers, are presently utilized in applications which include greenhouse covering, mulching, windbreaks, nets, silage, farm buildings, tubing, piping, drip irrigation, photodegradable films, controlled release of pesticides, fertilizers, growth regulators, food packaging and many other uses.

II - POLYMERS IN AGRICULTURE

A large number of polymeric materials has been tested for agricultural applications, including celluloses, rigid and flexible polyethylene, polyvinyl chloride, ethylene - vinyl acetate (E V A) copolymers, polyethylene terephtalate, polymethyl methacrylate , polycarbonate, polystyrene, styrene - acrylonitrile copolymers and a variety of fiber - reinforced composites. Plastics can be used through applications such as greenhouses, mulchings, silage, wind protection,etc.

Requirements within the greenhouse are :

Transmission of solar radiation to soil and plants, retention of reirradiated infra red energy at night, insulative capacity, ultra-violet stability, fungus resistance, carbon dioxide and water permeability, weatherability and of course cost.

To meet some of these requirements , special films such as ultra-violet or long-life , anti-mist, thermal, anti-fog films have been developed.

The plastics used for mulch films are generally low density polyethylene, polyvinyl chloride, polybutylene or copolymers of ethylene with vinyl acetate. The mulch controls radiation, soil temperature and humidity , weed growth, pest infestation, and the degree of carbon dioxide retention. Mulch - grown crops mature faster and yield are increased. Fertilizer and water requirements are reduced.

If left in place, conventional films can cause problems during harvesting or during cultivation operations the next year. Removal and disposal are costly and inconvenient. Therefore interest in the development of photodegradable or biodegradable films with short lifetimes has grown.

Most of the synthetic polymers on the market are not biodegradable. Attempts to develop new biodegradable materials have centered mainly on:

- Synthesis of novel biodegradable polymers.
- Modification of natural polymers.
- Synthetic polymers obtained from petrochemical materials.

The most common hydrolysable groups found in natural polymers are the aliphatic, carboxylic, and phosphoric esters, the amide groups and the glycosidic linkages.

The use of biodegradable additives and the modification of synthetic polymers are approaches which have been tried with fair success.

Polyethylene mixed with starch has been used as a biodegradable plastic. Polycaprolactone can be tailored for the slower or faster rates of degredation .

A polyester produced by microorganisms is said (1) to have excellent properties as a plastic with very good biodegradability, biocompatibility and optical activity. At present this plastic is very expensive. Its price is 3 to 5 times the price of general purpose plastics such as polyethylene and polypropylene. At first they are expected to be on the market for relatively expensive products such as stitches for surgical operations or as bone fixing material , and later will be made available into capsules for chemicals.
In spite of important obstacles to the wider commercial use of biodegradable polymers , considerable interest has been focused on the controlled release of pesticides , and nutritients.

POLYMERS FOR CONTROLLED RELEASE OF AGRICULTURAL CHEMICALS

Controlled release concept is a combination of biologically active chemicals and polymeric materials arranged to allow delivery of the agnet to the target at controlled rate over a specified period of time.
During the last decade, the use of polymers for controlled release of agricultural chemicals including pesticides , pheromones, growth regulators and fertilizers has been very important.

Pesticides leaching into drainage waters and subsequent transport into non-target areas and damage of aquatic and life are of growing ecological concern (2, 3).
Very long-life pesticides have been indesirable because their residues enter the food chain (4 , 5) and pesticides with short-lives have been ineffective in controlling pests for a prolonged period.
With some pesticide systems , 60-99 % (6) of the useful chemical activity is lost by various mechanisms including photo-decomposition, evaporation, leaching, microbial metabolism and interaction with non-target organisms.

To compensate for losses , these biocides are commonly applied in amounts far in excess of that required to assure sufficient control of a particular pest for a long period.

When the active agents are delivered by conventionel methods, the level and time of availability of agent to the target cannot be controlled independently , and only the concentration, and frequency of application can be monitored.

Figure (1) compares the behaviour of a polymeric controlled release pesticide (curbe B) with the conventional formulation (curve A).

The area between curve A and B represents the fraction of pesticide without serving any useful purpose and shows clearly how much room exists for improvement in application techniques.

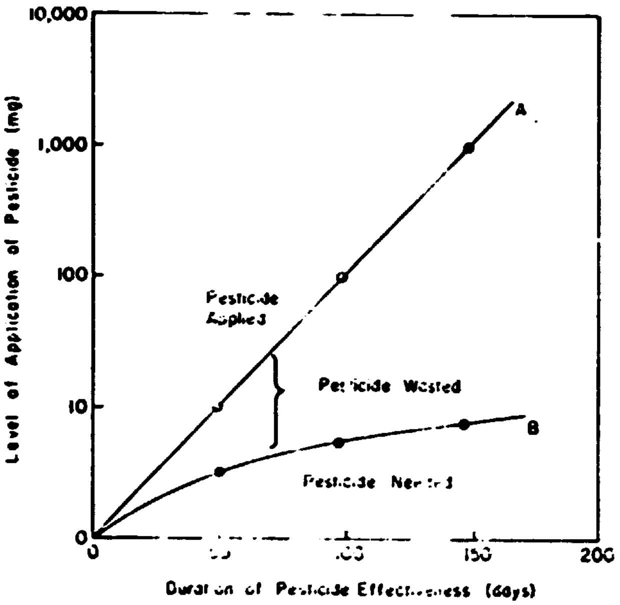

Figure 1. Comparative duration of pesticide effectiveness for practical and ideal application levels.

For many years scientists have dealt with biological problems by designing new biologically active agents.

The use of these agents to produce the desired biological response is often inefficient because of inabilities to deliver the agents to thier target at the prcise time and in the optimum quantities required. With the cost and limitations in the design of new bioacides agents , researchers began to turn to an alternative approach by developping methods to improve the precision and efficiency in delivering the new and old agents. One way to accomplish these objectives is to use controlled release formulations.

Within the last two decades, there has been a remarkable interest in this type of dosage form for substances ranging from drug to chemicals.

This has been due to various factors including several side effects of conventional agents, the high cost of developing new active agent, the expiration of existing patents, and the discovery of novel polymer systems and devices suitable for controlled delivery technolgy.

This technology activated the interest and attention of several professional groups including chemists, biologists, agronomists, entomologists, pharmacologists, veterinarians, dentists and physicians.

The principles of controlled release technology have been applied to several biologically active materials including pesticids,fertilizers, pheromones, growth regulators and pharmacenticals.

Advantages of controlled release systems

The ability of polymers to meter active agents at controlled and reproducible rates for extented time periods provide significant benefits over conventional methods or applications.

Some of these advantages are listed in table 1.

Table 1

Advantages of agricultural controlled release polymeric systems

- Control of the release of active agents
- Extend duration of activity at equal level of active agent
- Reduce phytotoxicity
- Reduce leaching into the earth and transport into streams
- Reduce evaporative losses and flammability of liquids
- Reduce pesticide contamination of the environment
- Economical because less active material is needed
- Reduce the amount of chemical wasted
- Control the pest population more effectively
- Increase chemical and physical stability of active agents in exposure to environment.

Limitations of controlled release systems

The advantages of controlled delivery systems are remarkable, however they must be weighed against their potential disadvantages before large expenditures for development work are committed . Some of these disadvantages include : Cost at preparation and processing , environmental impact of the polymer degradation products , and special equipment may be necessary for application.

Controlled release mechanisms and rates

Controlled release polymeric systems are regulated by the mechanismes and rates of the system used. The mechanisms are divided in : physical, chimical and erodible systems. by the polymer matrix. In physical system, the active agent is dissolved, dispersed, or encapsulated by the polymer matrix. The active agent release is regulated by diffusion processus or by biological or chemical break down of the matrix.

In chemical systems, the active agent is part of the polymer backbone or attached to the side chain of the polymer. Release of the active agent results from biological cleavage of the bond between biocide and polymer.

Erodible systems combine physical and cal methods in which an active agent is uniformaly dissolved or dispersed in a polymer matrix which can erode.

Erosion of the matrix can occur by several mechanisms which include :

a) Water soluble polymers insolubilized by hydrotically unstable crosslinks,

b) Water insoluble polymers solubilized by hydrolysis reactions of pendant side groups ,

c) Water insoluble polymers solubilized by backbone cleavage reactions.

Release by erosion of a polymeric system is a surface area dependant phenomenon.

In Table 2 are listed polymers used in controlled release formulations (7) .

Table 2 : Polymers used in controlled release devices

Naturel polymers

Ethylcellulose
Bark
Methylcellulose
Propylhydroxycellulose
Kraft lignin
Natural rubber

Synthetic elastomers

Polybutadiene
Polyisoprene
Neoprene
Polysiloxane
Styrene-Butadiene rubber
Silicone rubber
Hydrin rubber
Chloroprene
Butyl rubber
Nitrile
Acrylonitrile
Ethylene-propylene-diene

Synthetic polymers

Polyvinyl alcohol
Polyethylene
Polypropylene
Polystyrene
Polyacrylamide
Polyurea
Epoxy
Ethyl vinylacetate copolymer
Polyvinylidene chloride
Polyvinyl chloride
Polyacrylate
Polyacrylonitrile
Chlorinated polyethylene
Acetal copolymer
Polymethylmethacrylate
Polyvinylacetate
Polyhydroxyethyl methacrylate

Table (3) lists veterinary and agricultural applications (7).

Choice of a polymer and the system for release of an agricultural active agent depends on cost , seasonal conditions, desired release rate, duration, formulation, application.etc...

The nature of the polymer, melting and glass transition temperatures, active agent compatibility, stability of the combination processing, shape and site of the final product are very important.

Table 3

Agricultural and veterinary active agents utilizing controlled release

- Algicides
- Analgesics
- Anthelmintics
- Antimicrobials
- Bactericides
- Chemosterilants
- Disinfectants
- Fumigants
- Fungicides
- Germicides
- Growth regulators
- Herbicides
- Insecticides
- Insect diets
- Juvenile hormones
- Minerals
- Nematicides
- Nutrients
- Repellents
- Pheromones
- Viruses
- Vitamins

The ability of polymers to meter active agents at controlled and reproducible rates for extented time periods provide significant benefits over conventional methods of applications. Several controlled release systems have reached commercial production (7).

III - POLYMERS IN FOOD INDUSTRY

The use of plastic films has shown a very important growth during the past three decades.

Food packaging accounts for 35 % in tonnage of all plastics used worldwide.

The traditional materials such as metal, glass, paper and card board are now being subtituted by plastics everywhere.

Forecast of usage of materiels in food and beverage packaging shows gains for plastics (8).

<u>Materiel</u>	<u>Growth rate</u> (1983-93) (% year)
. Steal	- 6
. Glass	[illegible]
. Aluminum	- [illegible]
. Plasticc	+ 8,5

[illegible] (9) suggests that the market share of plastics in the food packaging will rise more than 40 % in the [illegible] years.

Apart of the quantitative growth for plastics, [illegible] qualitative growth is comming into effect.

[illegible]

[illegible] over the traditional [illegible] the food and beverages industries [illegible] of their versatility and broad range of properties.

Barrier polymers are organic polymers displaying the ability to restrict the passage of gases, vapors and organic liquids.

These polymers when used alone or in combination with other polymers or materials, provide an efficient and economical method for the packaging and shelf-life extension of food and beverages.

The barrier polymers are expensive , and by themselves, usually are not strong enough to provide the needed physical, environmental, and thermal protection for packaged foods.

Very thin layers of expensive high-performance materials can be coextruded with other less expensive materials to incorporate specific properties and optimize the contributions of each component.

Speciality films and their coated , coextruded and laminated composites are well suited for meeting the packaging requirements of food items in terms of processing , protection , barrier properties, consumer appeal, and goverment regulations.

The most important properties required for packaging include : transparency, ability to heat seal, moisture proofness, printability, flexibility, chemical resistance, grease and oil resistance, good tear resistance, ease of working on wrapping-machines, resistance to flexibility, chemical resistance, resistance to sunlight , low or high permeability to gases according to the product being packed, plasticiser stability and non-toxicity.

Not all these properties are essential for any particular purpose. Selection of the right materiel for the particular application is necessary.

Several barrier polymers are on the market and they include : poluvinylidene chloride (PVDC) , copolymer of ethylene and vinyl alcohol (EVOH), polyamide (Nylon 6) , polyethylene terephtalate (PET),acrylic imide, modofied polyvinyl alcohol, polyacrylonitrile (PAN) ..

FOOD PROCESSING

Controlled - atmosphere packaging (CAP) and aseptic package have contributed to the revolution in food packaging.

Controlled atmosphere packaging is employed with food products that are sensitive to oxygen or are degraded by bacteria, it thus tends to replace packing of produce preservation systems.

In the C A P process, the container is filled with the food product, and the dead space is then flushed and filled with an optimized mixture of gases (nitrogen, oxygen, and carbon dioxide) designed specifically for the food product so as to kill harmful organisms and to maintian freshness.

A coextruded multilayer film is needed to retain the controlled atmosphere .

For example CAP is used to extend the shelf-life of cooked pasta to nearly a month. Vegetables packed with CAP do not have to be packed in ice. These packages are easy to handle when they are used, less weight is shipped, spoilage is reduced 20 - 30 % .
In the aseptic package, a sterilized containar is filled with a sterilized food under aseptic conditions and is then sealed. This process allows foods to retain their color, texture and nutritients. Foods processed aseptically achieve an unrefrigerated shelf-life of a year or more.

A cost estimate for juice packaging, shows the cost of plastic aseptic packaging to be about one-half that of comparable glass or steel packaging (10).

Several areas of growth opportunity and innovation include : strong increase of PET bottles; new markets for materials for bottles,film, and sheet; multilayer packaging for shelf-stable alternatives to metal and glass containers; dual-ovenable trays of cristallised polyester (CPET); coextrusion technology; extension of coextrusion to blow molding and injection, adaptation of high-temperature resin to containers; and strong marketing pull for plastic packagaging.

Continuing development of coextruded film and sheet structures from combinations of high performance polymers with low cost polymers and improved adhesive resins will expand the market opportunities for plastics [illegible] competition with other materials. Easy combination of many layers and a better understanding of synergistic behavior in multilayer film and sheet will also lead to new applications.

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