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Environmentally degradable polymeric materials (EDPM) in agricultural applications — an overview

Summary — Owing to their low production cost, good physical properties and lightweight, plastic objects have slowly substituted glass, paper and metals in several fields of application including agriculture. At the same time, the current huge global production of plastics (200 million tons/year) has generated an enormous environmental concerns, mainly related to the waste generation by plastic packaging, which are responsible for 35—40% share of annual plastics consumption. Where recovery of plastics is not economically feasible, viable, controllable or attractive, plastics often remain as litter. This is the case in most of agricultural applications of polymeric materials. The market for biodegradable polymers is at this moment focusing on products in which biodegradability provides beneficial effects (*e.g.* waste-disposal, recycling) and a number of biodegradable materials are already being marketed or are close to market introduction and customer acceptance. This overview is meant to provide an outline on the history and recent developments in biodegradable polymeric materials applied in agricultural practices with particular reference to the mulching segment. Special attention has been devoted to material based on renewable resources or utilization of waste products from the agroindustrial sector, thus suggesting cost-effective and environmentally sound solutions to specific social needs.

Key words: environmentally degradable plastics, plastic waste, agricultural applications, mulching.

PLASTICS WASTE MANAGEMENT AND EPDM — GENERAL REMARKS

The characteristics of strength and durability designed into plastics, in order to meet end-use requirements, coupled with the problems associated with their post-consumption disposal, played a significant role in offering new options alternative to plastics recycling and landfilling practice. Particular effort has been devoted to options based on the recovery of plastic waste as raw material or energy source and, whenever applicable (biodegradable materials), *via* a biorecycling [1]. Several technologies have been recognized as viable options along with environmental degradation, such as recycling of plastic materials, including mechanical recycling, recycling to monomeric components followed by repolymerization to the same or new polymeric material, recycling to hydrocarbon feedstocks by pyrolysis, direct incineration and composting. Each of these dis-

posal technologies is playing a role in polymer waste management [2]. The choice among them depends on several factors, including available processing facilities, collection of waste material, cost of new polymers, property requirements, and specific service responses.

Utilization of plastics in agriculture in the form of mulch films, greenhouse components, irrigation tubes and general-purpose containers continue to generate plastic waste in large quantities. Currently, any systematic collection of plastic waste for recycling and/or disposal is rather expensive and limited only to certain communities. Moreover, when plastics are contaminated with soil, foods or other chemicals their recycling is rather difficult and for this reason only 2% of the plastic waste is nowadays recycled in the United States.

In the European Community legislation, directives have been so far issued on wastes [3] on dangerous wastes [4], on waste from packaging applications [5] in which waste has been classified depending on its origin and its potential danger. This new classification has introduced a new category of "special wastes". Waste deriving from agricultural and agrochemical activities has

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been placed in this category with the need of post-consumption reclamation and further treatment in controlled infrastructures, thus leading to substantial increase of disposal costs, which in some cases may be even higher than the cost of the virgin material itself.

The biodegradability and utilization of agricultural polymeric materials is a topic rising in importance over the last few years [6]. Industries have started to develop several products based on environmentally degradable polymeric materials to be applied in agricultural practices such as mulching films, green houses sheets, laminates, containers, seedling pots, and for applications such as soil structurization and controlled release system of chemicals (fertilizers, herbicides, growth stimulants and pesticides).

Globally increased agricultural productivity has promoted the utilization of agricultural products in environmentally acceptable plastic materials. The usefulness of a variety of agricultural coproducts as commodity plastics substitutes is under consideration of researchers in academies and industries [7]. The use of EPDM based on agricultural wastes or crop surplus to be used in agriculture applications or other merceologic commodity segments appears as an extremely promising approach for contributing to the solution of plastic waste management.

APPLICATION OF POLYMERIC MATERIALS IN AGRICULTURE

Polymeric materials started to be applied in agricultural practices from the sixties, mostly in replacing glass as greenhouses and tunnels covering. Thus, plastics made possible the introduction of mulching films, a novel agricultural technology not applied before the production of plastic films started. The polymeric materials used consisted mainly of polyethylene and poly(vinyl chloride).

All main classes of polymeric materials, *i.e.*, plastics, elastomers, fibers, coatings, and water-soluble polymers, are presently utilized in applications including controlled release of pesticides, soil conditioning, plant protection, seed coating, gel planting, water transport and packaging [8]. New technology based on polyethylene had especially a strong impact on the growing of soft fruits and vegetables [9—12].

Although plastics in agriculture comprise less than 2% of total plastic usage in Europe and about 4% in the USA, much more is used in Mediterranean countries (Spain 8%, Israel 12%) and in China (20%) where agriculture is more intensive [10].

The assessment of structure-property-performance relationships in polymer selection for agricultural applications is of vital importance, including parameters such as strength, toughness, weathering, thermal expansion, light and thermal transmission, biodegradability and permeability to oxygen, carbon dioxide, and

water. Table 1 summarizes main agricultural applications of degradable polymeric materials of synthetic origin mainly derived from fossil fuel feedstocks and of natural origin, derived from renewable resources.

Table 1. Applications of degradable polymeric materials in agriculture [13]

Application	Polymeric materials
Plant growing sheets	Polyethylene ^{*)} Poly(lactic acid) Poly(vinyl alcohol) Starch Cellulose Lignin Fruit by-products Soy protein Pectin Chitosan
Soil amendments	Poly(amino acids) Polyesters Poly(vinyl alcohol) Carboxymethylcellulose
Fertilizers and growth stimulants	Proteic eluate from tanning industry Poly(aspartic acid)

^{*)} Photodegradable, thermally degradable.

Since research is aimed at developing polymers for applications in which they offer unique advantages over the competitive alternatives, interest in biodegradable plastics used in agriculture, has grown, as costs may be reduced by using photo-thermally or biologically degradable polymers, thus avoiding the labor intensive and costly step of collection and sorting typical in recycling. With this point in mind degradable polymers based on polyethylene started to be investigated since the 1970s [13—23] and led to the development of degradable materials, as recently reviewed by Scott [23], and listed in Table 2.

Much effort has been focused in recent years to develop environmentally compatible polymeric materials

Table 2. Degradable materials based on polyolefins

Category	Polymeric material	Commercial name
Photolitic polymers	Poly(ethylene-co-carbon monoxide)	E-CO
	Poly(ethylene-co-vinyl ketone)	Ecolyte
Oxodegradable polymers	Polyethylene	Plastor TDPA (EPI)
Polyethylen/starch blends	PE-starch	Coloroll, St Lawrence Starch

by starting from renewable resources as an alternative to petroleum-based synthetic polymers. As an additional advantage, some renewables are comparatively less expensive, environmentally friendly and naturally biodegradable. Particularly, materials such as annual crops, agricultural waste and/or by-products are a good source for the formulation of environmentally compatible polymeric materials.

A more detailed description and categorization of the polymeric materials used in specific segments of agricultural practices is reported below, by their specific applications.

Mulches

In the past, mulch practice has been performed by the use of natural materials such as straw and leaves to provide an insulating layer around the roots of vegetables and soft fruits. Actually, the use of plastic sheets or films in mulching is the largest single application of plastics in agriculture. Mulch controls radiation, soil temperature and humidity, weed growth, insect infestation, soil compaction, and the degree of carbon dioxide retention. In some cases, weed control has been reported because of solar heating plastic films mulches (solarization). Not only do mulch-grown crops mature faster, but also yields are increased and in most cases the product is easy to harvest and cleaner with evident returns on the production costs [23].

Table 3 specifies examples of crop yields obtained with and without mulching as reported by Scott in his recent publication on the environmental impact of polymers [13].

Table 3. The effect of mulching films on crop yields [13]

Crop	Location	Treatment	Yield ^{a)} kg	Increase %
Musk melon	New Brunswick	Bare ground	62.7	47
		Mulched	92.6	
Tomatoes	Oregon	Bare ground	10.5	45
		Mulched	15.2	
Bell pepper	Rio Grande	Bare ground	1356	389
		Mulched	6633	

^{a)} Referred to: 7 plant (mellon), 1 plant (tomatoes), 1 hectare (pepper).

The use of black mulching films with elimination of weeds and avoidance of soil compaction eliminates the need for cultivation, thus preventing root damage and plants stunting or killing. Fertilizer and water requirements are also reduced, the use of plastic mulches results in 50% saving of irrigation water and as much as 30% saving in nitrogenous fertilizers even in temperate climates [13]. Low density polyethylene, poly(vinyl chloride), polybutylene, and copolymers of ethylene with vi-

nyl acetate have been generally used for mulching. Just in 1998 the worldwide yearly consumption for polyethylene mulch film alone was around half million tons [24, 25].

The fact that plastic do not degrade as fast as the previously used natural materials may sound as an advantage because it ensures a coherent protective barrier between the roots of the plants and the environment throughout the growing life of the plant. If left in place, however, conventional plastic films can cause problems during harvesting or during cultivating operations in the following year [26]. Thus, many soft fruit crops are now harvested automatically with a procedure leaving stems and leaves on the ground. The presence of plastic fragments mixed with the crop residue may clog the engines of harvesting machines and turns automatic collection into a difficult task. Removal and disposal are costly and inconvenient. Attempts to promote collection systems, recycling technology and applications for the recycled material deriving from mulching films have shown a series of difficulties. Transportation of the long strips of the films, compaction and washing were found to be the most critical and labor intensive steps in the process, because of the films deterioration and the high level (30—40% by weight) of soil contamination [27]. Moreover many landfills reject mulch films because of pesticide residues for which they must be treated as hazardous waste. Furthermore, nowadays the thickness of mulching films can be as low as 8—10 μm that makes them too fragile to be easily and efficiently collected from the field after cropping.

Interest in the development of biodegradable or photodegradable films with short service lifetimes and eventually controllable has grown. Degradable mulches should break down to small brittle pieces, to pass through harvesting machinery without difficulty and should not interfere with subsequent planting operations. The induction time therefore must be variable, predictable, and reproducible [28]. Crop yields could be considerably reduced if the film degrades before end of the growing season. In addition, toxic residues are unacceptable, processing stability must not be affected by film components and storage must not modify the ultimate mechanical and physical product properties. For these reasons thin photo-biodegradable polyethylene films are presently used for crops, which are supposed to be automatically harvested.

Table 4 presents some examples of biodegradable polymers applied in mulching practices.

Photodegradable films have been proposed as degradable mulching films, such as poly(1-butene) [29]. More recently, interest in the development of new photodegradable films has mounted in mainland China and Taiwan [30—32]. As reported before, in these countries the plastic consumption for agricultural practice is very high (20%) [33]. In such materials a polyolefin is blended with a modified starch as coupling agent, a photode-

grading agent, an oxidation accelerant, a self-oxidant, and a degradation controlling agent. In consequence, debris of the polyolefines tend to accumulate in the soil after degradation and disintegration of the films.

Table 4. Biodegradable polymeric materials used in mulching practices

Synthetic polymers	Natural /artificial polymers
Photodegradable polyethylene	Starch, cellulose, kraft paper
Poly(vinyl alcohol)	Pectin, fruit (pit and seed), chitin
Poly(lactic acid)	Wheat gluten, cereals waste
Poly(hydroxy butyrate)	Wood, sugar beet, bagasse
Poly(hydroxy alcanooates)	Soy protein, gelatin, protein hydrolyzate
Poly(caprolactone)	Cellulose esters Crosslinked amino acid

In another approach, degradable mulching films were prepared by blending synthetic polymers with natural fillers such as starch. Films based on starch blended with: polyethylene [34], poly(vinyl alcohol) [35], poly(ethylene-*co*-acrylic acid) (EAA) [36—38] and poly(vinyl chloride) (PVC) [39] were then developed. Thus, in some of these materials only the starch component was degraded while the continuous matrix represented by the synthetic polymer was accumulating in the environment. In starch-polyethylene films, fragments resulting from film deterioration, may require decades to completely biodegrade; moreover, the effect of long term soil exposure to polyhydrocarbon debris is largely unknown [40]. For these reasons the interest moved toward blends based on starch and synthetic polymers, which are also biodegradable such as poly(vinyl alcohol) [41, 42], polycaprolactone (Materbi) [43] and other synthetic polyesters.

Advantages resulting from the use of material from renewable resources as fillers in blends with synthetic degradable polymers have induced interest in a wide group of natural polymers, such as lignocellulosic materials, pectins, chitin, animal and vegetal sources.

Poly(vinyl alcohol) has been blended with pectin [44, 45], chitin [46, 47], sugar cane bagasse and fruit juice extraction by-products such as apple and orange wastes [48], soy protein [49], gelatin [50, 51].

Use of biodegradable thermoplastic polymers from renewable resources as the continuous matrix is also focusing recent research activity [52—56]. Several patents have been filled for and issued dealing with polyester compounds from renewable resources for agricultural films production, also in blends with natural polymers [57—59].

Up to now, such polyesters were produced biotechnologically from refined raw materials (*e.g.* glucose and sodium propionate). For example, polyhydroxyalkanoates (PHAs) can be produced from saccharides, al-

cohols, and low molecular weight fatty acids. Polyesters can be produced by a much cheaper method starting from agricultural wastes (*e.g.* molasses, maltose, glycerol phase from biodiesel production, whey), as long as these materials have a known composition and are available in appropriate quantities [60].

Mulching practice based on the use of recycled materials has also attracted interest as an alternative to plastic films usage [61]. Therefore, farmers sometimes use organic mulches such as paper, leaves, straw. Kraft paper coated with polymerized vegetable oils has been recently proposed as biodegradable mulch [62, 63].

Films and/or laminated films produced with natural polymers have been also the object of research activity. Thus, films have been claimed as fabricated by chitosan and pectin [64], starch and pectin [65], soy protein and starch [66, 67].

Composite films have been developed in our laboratories based on natural and synthetic degradable polymers blended with waste agricultural materials. Materials such as sugar cane bagasse have been blended with natural polymers such as gelatin waste from pharmaceutical industry. Prepared composites had mechanical properties [68] and degradation times [69] interesting for agricultural applications. Thus, animal and vegetable protein based materials possess an intrinsic agronomic value because of their fairly high nitrogen content (10—12%).

Similarly, interesting properties have been reported for composites films based on poly(vinyl alcohol) and waste products from orange and apple juice extraction [70].

Other applications

Plastic films and sheets have been found suitable for application in greenhouses [8]. Plastics are lightweight, and appreciably durable materials, permitting a number of structural designs to be implemented, including air-supported buildings, which turn to be less expensive and more easily maintained than glass greenhouses.

Greenhouses must allow transmission of solar radiation to soil and plants and must also be able to retain the re-irradiated infrared energy at night. Plastics used for the manufacturing of greenhouse components must be impermeable to radiation between 7 and 55 μm in the infrared region and possibly must have insulating capacity, UV-stability, fungi resistance, and CO₂ and water permeability.

Polymers utilized for greenhouse enclosures can be both rigid as well as flexible including poly(vinyl chloride), polyethylene, ethylene/vinyl acetate copolymers (EVA), poly(ethylene terephthalate), poly(methyl methacrylate), polycarbonate, polystyrene, styrene/acrylonitrile copolymers (SAN), and may include also cellulose and a variety of fiber-reinforced composites, which have been considered for this purpose.

Plastics used in greenhouses must be resistant to the environment, so stabilization is extremely important in the cost competing with glass usage. This constitutes a very active area of research focused on improvement in the durability of polyethylene against deterioration by light and heat.

The capacity of certain polymers to hold water allows for their spraying and blowing alone in slurries with other mulching materials and nutrients for seed coating or soil conditioning.

In seed coatings a hydrophilic polymer is usually coated directly onto the seed surface. After planting, the polymer absorbs water and thereby increases the rate of germination as well as the percentage of germinated seeds. However, depending on the application, the type of polymeric coatings can be varied to delay germination, inhibit root growth, control pests, fertilize, and bind the seed to the soil. Agar, water-soluble cellulose ethers, such as carboxymethyl-, hydroxyethyl-, and hydroxy-

methylcellulose, and hydrolyzed starch-g-polyacrylonitrile copolymers (HSPAN) have been studied to the greatest extent in seed coating. HSPAN coatings have been applied to a variety of seeds, including soybeans, cotton, corn, sorghum, sugar beet, and a number of vegetables [71].

Polymers may also be present as tackifiers to help holding the mulch in place once applied. In some cases, a type of thatch is formed that protects seeds and soil against erosion. Hydrophilic polymers, such as poly(acrylamide), poly(vinyl alcohol), carboxymethylcellulose, and HSPAN have been used as soil conditioners in techniques called hydro-mulching [8, 71, 72].

The effect on the environment deriving from the use of fertilizers is also an issue of global concern. Biodegradable polymers such as thermally synthesized polyaspartate [73] have been proposed for this application.

Kolomaznik *et al.* [74] propose protein hydrolysate from tanning industry for use as an organic nitrogenous

Table 5. Companies involved in the manufacturing of agricultural products using biodegradable polymers

Company	Trademark name(s)	Applications	Materials
Bayer	BAK 1095 [®]	Films and sheets	Polyester amide
Bioplastic, Inc.	Envar [™]	Mulch films	PCL ^{a)} , Starch
Biotec	Bioplast [®]	Films and sheets	TPStarch ^{b)}
	Bioflex [®]	Plant pots.	Cellulose acetate
	Biopur [®]	Trays for cultivating plants	PCL-Starch
Bird-X Inc./Eco Turf Inc.	TurfTaks [®]	Turf and erosion control	Degra-Novon [®]
BSL ^{c)}	Sconacell [®]	Films, flower pots	Starch acetate
Cargill Dow Chemicals	EcoPLA	Mulch films, green houses pots	PLA ^{d)}
Chronopol Inc.	Heplon [™]	Plant growth stimulant, films	PLA ^{d)}
DuPont	Biomax [®]	Mulch containers, plant pots	Polyester resins
Eastman	Eastar Bio	Seed mats, root covers	Copolyesters of diacids and glycols
Idroplast	AgriBag [®]	Chemicals distribution	PVA ^{e)}
	SoilBag [®]	Wrap plant roots	PVA ^{e)}
Kemira Agro Oy	ns ^{f)}	Controlled release	ns
Marshall Plastic Film, Inc	ns	Agricultural films	Degra-Novon [®]
Metabolix, Inc.	ns	Lawn and leaf bags, films	PHA ^{g)}
Monsanto	Biopol [®]	Mulch films, plant pots	PHA
NATCO ^{h)}	E-Z Turf [™]	Biodegradable seeded grass	Wheat-starch
	Sta-Wet [™]	Mats for instant lawns	Super absorbent
Nova Chem Ltd.	Nutri Save [®]	Coating for fruit and vegetables	Carboxymethyl derivatives of chitosan
	Phero Release [®]	Delivery device for pheromones for pest control	Carboxymethyl derivatives of chitosan
Novamont	MaterBi [™]	Mulch films, nurse pots	PCL-starch
Novon	Degra-Novon [®]	Mulch films	Modified starch, other chemicals
	Aqua-Novon [®]	Sanitary applications	Modified PVA
	Poly-Novon [®]	Mulch films	Starch
Poly Expert	ns	Mulch films	Novon Starch based polymer
PPT, Inc. ⁱ⁾	EnviroPlastic [®]	Mulch films	PCL alloys
	EnviroPlastic [®]	Controlled release of fertilizers	Urethane acrylics, styrene, vegetable oils
Solvay Sa	CAPA [®] 600	Controlled release of fertilizers	PCL
TPS, Inc. ^{j)}	Vinex [™]	Packaging for chemicals	PVA
Union Carbide Corp.	TONE [®]	Mulch films, pots, controlled release of chemicals	PCL

^{a)} PCL = Polycaprolactone, ^{b)} TPStarch = Thermoplastic starch, ^{c)} BSL = Buna Sow Leuna Olenfinverbund, ^{d)} PLA = Poly(lactic acid), ^{e)} PVA = Poly(vinyl alcohol), ^{f)} ns = not specified, ^{g)} PHA = Polyhydroxyalkanoates, ^{h)} NATCO = Natural Absorbent Technology Co., ⁱ⁾ PPT, Inc. = Planet Polymer Technologies, Inc., ^{j)} TPS, Inc. = Texas Polymer Services, Inc.

fertilizer or fertilizer component, and use in the manufacturing of biodegradable polymers for agriculture sowing tapes.

Table 5 summarizes some examples of companies involved in the manufacturing of agricultural products using biodegradable polymers and the relative recommended application.

CONCLUSIONS

Modern agricultural technology is ever more demanding for agrochemical materials and manufactures that are ecocompatible and attainable at a reasonably competitive price. In that respect, introduction of biodegradable polymeric materials in a large variety of agricultural applications appears to be a viable solution, provided these materials may be derived from cheap raw materials and eventually from agroindustrial waste or a suitable combination of natural resources and fossil fuel.

The extremely active academic and industrial research on the use of biodegradable polymers for agricultural applications has led to the introduction of several products on the market. These products based on biodegradables are supposed to be applied in agricultural practices such as mulching films, green house sheets, laminates, containers and for application as soil structuring and controlled release of chemicals such as fertilizers, herbicide.

The number of biodegradable items for agricultural application entitled to enter the market is going to increase also in consideration of the role and impact that the so called "biological agriculture and horticulture" are going to assume in the near future.

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