Additives for Controlled Degradation of Agricultural Plastics: ENVIROCARE™

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Summary: ENVIROCARE™ additives are specialty chemicals that can be added to conventional thermoplastic polymers to obtain degradable agricultural plastic articles. Their main benefits are connected with their possible incorporation in "commodity plastics". This allows the production of degradable agriculture plastic articles processable with standard manufacturing machines, without negative effects on the main properties of the plastic article and with evident costs advantages. Furthermore, required outdoor exposure lifetimes for different articles and different environmental conditions can be modulated with the incorporation of the appropriate additive loading in the plastic and with combinations of selected stabilizers. Mulch films, small tunnel films, banana bags and sleeves, direct covers, non-woven, ropes, twines and pots are convenient agricultural applications for this technology. ENVIROCARE™ products induce plastic degradation following a two steps mechanism: first the plastic is photo- and thermo-oxidized during the outdoor exposure; once the degradation process has been activated by light or heat, ENVIROCARE™ acts by increasing the degradation rate and degradation continues until the article is totally degraded. Since degradation is both photolytically and thermally triggered, degradation occurs both at the surface and in the soil. Experimental laboratory results allow the assessment of the contribution of different important parameters – i.e. type of polymer, type of article, presence of other stabilizers/additives or pigments, different environmental conditions- on the control of the article lifetime and degradation. Field exposure in different environments integrates the test results and allows for the design of the additive systems adapted to the specific needs.

Keywords: agricultural film; biodegradation; controlled degradation, ecotoxicity; environmentally friendly; mulch

Introduction

Agricultural films (Ag-films) are widely used to improve crop cultivation and to protect agricultural products after harvesting, in the form of greenhouses, tunnels, mulch, silage films and bale wraps. Approximately 2.8 millions MT of agricultural plastics are annually consumed over

 DOI: 10.1002/masy.200350738

the whole world and they cover more than 5 millions hectares of land [1]. The majority of this surface is covered by mulch film accounting for 4.5 millions hectares.

Mulch films are extensively used to modify soil temperature, limit weed growth, prevent moisture loss, and improve crop yield and precocity. They mostly require a relatively short life span and normally have less contact with critical agrochemicals during their service life compared to e.g. greenhouse films.

Like all polymer articles, polyethylene mulch films also undergo photo-/thermo-oxidation characterized by a steady decline in physical properties. As a result, they will last only a few months without the use of proper pigments or stabilizers. The inherent film parameters and other environmental parameters that affect the actual lifetime of mulch films in the field are detailed in Table 1.

Table 1.

1. Film inherent parameters	
Polymer type	PE-LD, PE-LLD, EVA copolymer
Film type	Monolayer, coestruded multilayer
Film thickness	10-80 micron
Stabilization	Stabilizer system and concentration
Fillers	Kaolin, chalk
Pigments	Carbon black, TiO_2, ect.
Other additives	Antiblocking, antifogging agents, etc.
Film manufacturing	
2. General environmental parameters	
Mechanical stress	
Climate related:	
Solar irradiation	UV intensity, global energy
Temperature	Mean, maximum
Wind, rain, snow	
3. Special environmental parameters	
Crop type	Tall, short
Agrochemicals	Type, frequency and mode of application

Additionally, the required increase in productivity and intensity of agricultural settings, driven especially by labor and fixed cost, leads to down gauging and functionalization of mulch films.

Required functionalities vary from photoselectivity, barrier properties, anti-fogging effect, increased pesticide resistance up to controlled degradation of film [2-4].

The retention of the original properties is clearly important during the service life of both degradable and classical mulch films, so not to interfere with seed development and crop growth. Nevertheless, in the case of degradable films, the target is that these properties will be quickly affected after the useful lifetime. Finally, upon total degradation, the residual plastic should be taken up into the bio-cycle without any negative influence on the environment. Under the above-mentioned conditions, the use of environmentally and controlled degradable agricultural films can be considered as a valid alternative to recollection and traditional waste disposal routes [3].

Designing the best integrated solution including ENVIROCARE™, which is based on proprietary technology from EPI Environmental Products Inc., requires a careful evaluation of the influence of the parameters mentioned in the above table. Results of the work carried out at the Ciba Application Center (Italy) and of field trials will be further discussed in the next section.

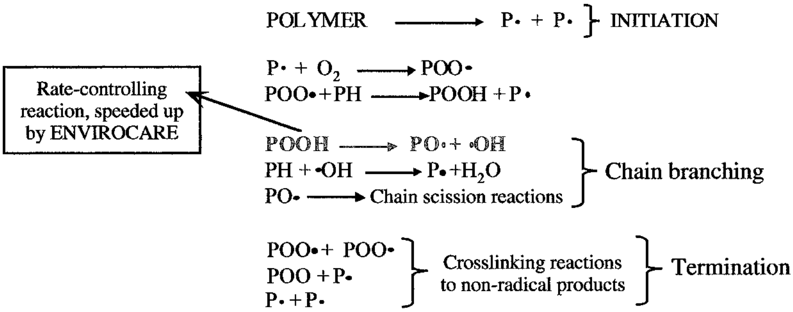
Controlling the Degradation of Agricultural Plastics with ENVIROCARE™

Organic materials undergo oxidation reactions that cause modification of the properties of the material. Polyethylene oxidation by the effect of heat, UV light or mechanical stress is manifested in a loss of mechanical properties and in discoloration of the article. The change of the polymer properties is the consequence of oxidative reactions of PE that finally result in the scission of the carbon-carbon bonds of the PE molecules producing molecular fragments [5, 6]. These fragments are inherently hydrophilic because of the presence of ketones, aldheydes, acids and alcohol groups. Soil microorganisms can then attack these oxidized fragments leading to complete disappearance of the article.

Oxidized polyolefin films containing similar technology from EPI Environmental Products Inc. showed to undergo bio-assimilation by microbes and microflora in the soil (performed at University of Pisa by Prof. Emo Chiellini and at University of Clermont-Ferrand by Prof. Jacques Lemaire). Within the experimental evaluation conditions, a mineralization rate comparable to that obtained with cellulose was reached [7].

In the use conditions, ENVIROCARE™ additives incorporated in PE accelerate the standard oxidative degradation process of the substrate. With an appropriate selection of the ENVIROCARE™ product and its loading, it is possible to control the time to degradation, so that the embrittlement of the plastic article is reached at the time required for the specific agricultural practices.

The standard oxidative degradation process of PE follows the sequence of chemical reactions that are reported in Fig. 1. One of the functions of ENVIROCARE™ additives is to accelerate the rate-controlling reaction of the oxidation scheme, namely the hydroperoxide decomposition reaction.



WHERE:

PH	=	**polymer,**
P•	=	**polymer alkyl radical,**
PO•	=	**polymer oxy radical,**
POO•	=	**polymer peroxy radical,**
POOH	=	**polymer hydroperoxide,**
HO•	=	**hydroxy radical**

Figure 1. Photo-Oxidative Degradation Mechanism

Another important feature of ENVIROCARE™ additives is that they promote degradation both by the action of the UV light and by heat. Thanks to this feature, the degradation of mulch films can occur both on the surface that is exposed to UV light and, due to the thermal effect, on the parts of film that are covered by the soil.

Because of the complexity of the degradation and stabilization processes, a basic understanding is necessary to develop the appropriate ENVIROCARE™ system. Many different films were evaluated in the Application Centre of Ciba SC in Pontecchio Marconi (BO) Italy, where the main variables that can affect the film life-time were simulated. The tests were carried out following different procedures in controlled laboratory conditions in order to be able to differentiate the contribution of the different parameters.

Figure 2 shows how the lifetime of transparent LLDPE blown films exposed in an oven at 50°C can be controlled, by thermal effect, with the addition of ENVIROCARE™.

Figure 3 shows how the lifetime of transparent and black LLDPE blown films exposed in a WeatherOMeter can be reduced, by UV effect, with the addition of ENVIROCARE™.

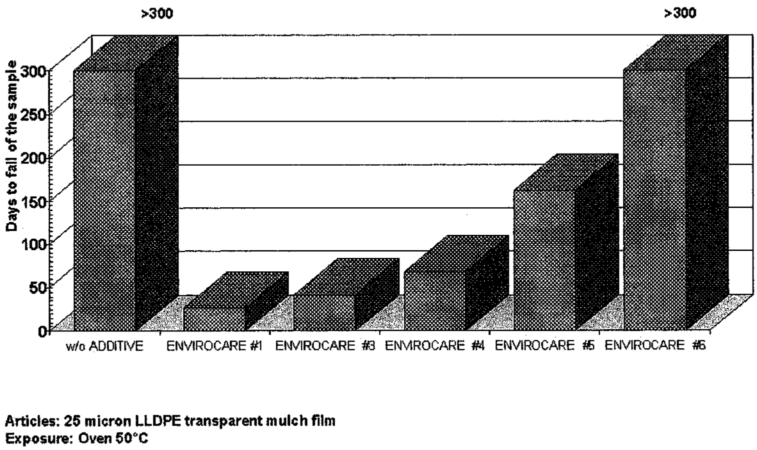
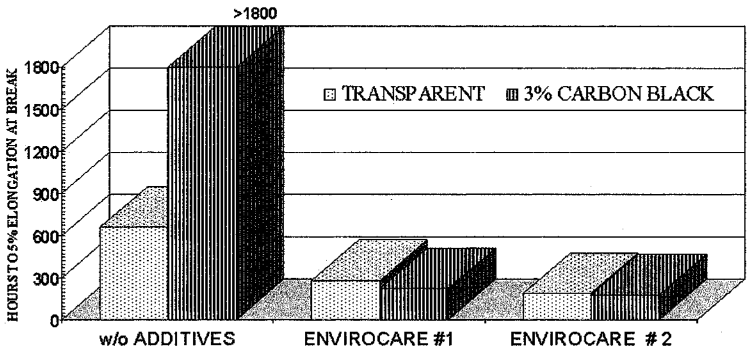


Figure 2. Performance of ENVIROCARE™ systems in long-term heat aging



ARTICLES : 25 micron LLDPE mulch film
EXPOSURE: WOM (BPT : 63 ± 3°C)

Figure 3. Performance of ENVIROCARE™ systems in accelerated UV weathering

In addition to these laboratory tests, other tests were carried out to simulate the complexity of real life conditions. Films were laid on plastic boxes filled with soil, one part of the film being exposed to the light and another part being covered by the soil. The boxes were outdoor exposed in Pontecchio Marconi (BO), Italy. The above set-up, simulating the mulch film application, allows the monitoring of the film degradation process both on the surface and under the soil.

The contribution of different parameters, like different additive systems based on ENVIROCARE™, different pigments and different film thickness were evaluated. As failure criteria, time to cracking, time to embrittlement and time to complete visual disappearance on and under the soil were measured. The mentioned criteria are significant for the estimation respectively of the service life, of the time needed to embrittle the film enough for re-working the soil and of the time needed to get the field 'plastic free'. Figure 4 shows the time of cracking of ENVIROCARE™-containing films. It shows that, by appropriate selection of the additive system, it is possible to achieve film lifetimes from 30 days (or less than 20kLys) upwards.

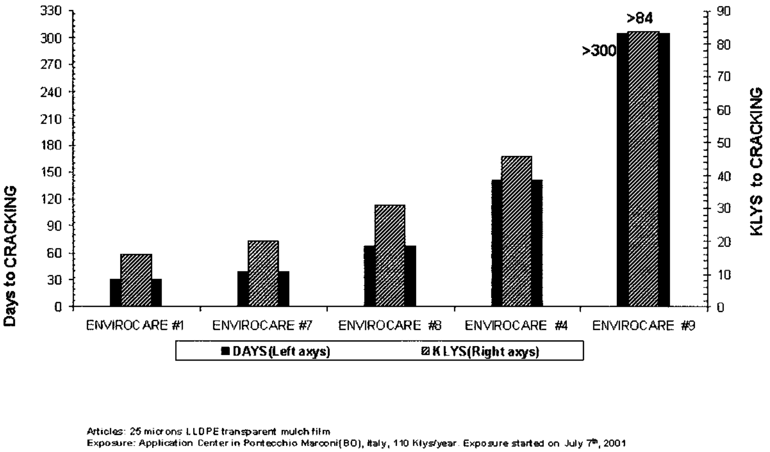


Figure 4. Performance of ENVIROCARE^{TM} systems in outdoor exposure in contact with soil

Figure 5 shows the time of cracking and the time to visual disappearance. The latter ranges between less than two months up to several months, depending on the ENVIROCARE™ formulation and on the film structure.

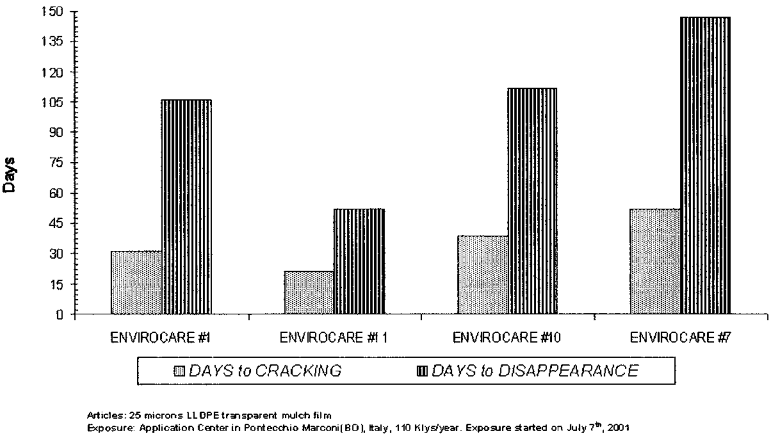
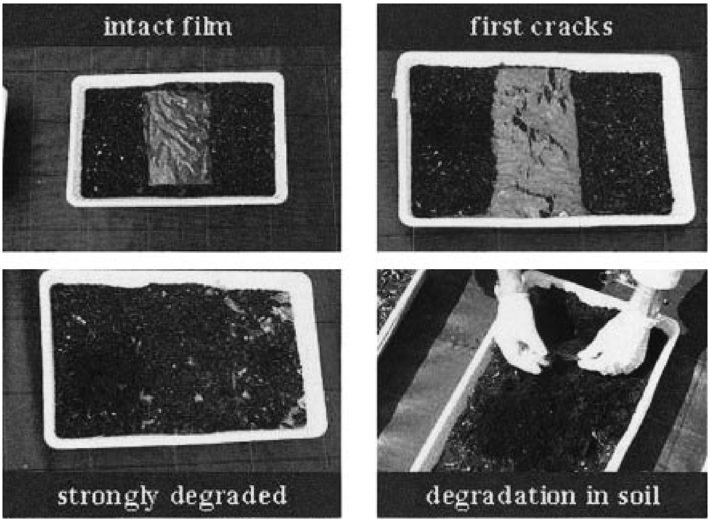


Figure 5. Performance of ENVIROCARE^{TM} systems, cracking and disappearance of LLDPE blown films

The propagation of degradation to the parts of the film covered by the soil is shown in Fig. 6, where the brittleness of the buried film is evident. Although the film could still be detected, it was heavily degraded and friable.

This result confirms ENVIROCARE™ effectiveness by the action of heat and is in line with the previously shown oven aging data. The described set up and the different degradation stages of a film containing ENVIROCARE™ formulation are also shown in Figure 6.



Articles: 25 micron LLDPE mulch film
Exposure: Applicationl Center in Pontecchio, Italy, 110 Klys/year. Exposur started on July 7^{th}, 2001

Figure 6. Visual assessment of the degradation process and degradation under soil

Typical results from IR spectroscopy are presented in Figure 7, which shows the carbonyl region of the spectrum for two film samples based on ENVIROCARE™. One sample is non-exposed and the second one was recollected after 5 months burial. The extensive degradation, after burial, of the additive-containing sample is clear from the growth of the IR bands between 1700 and 1750 cm-1 associated with carbonyl groups of oxidation products.

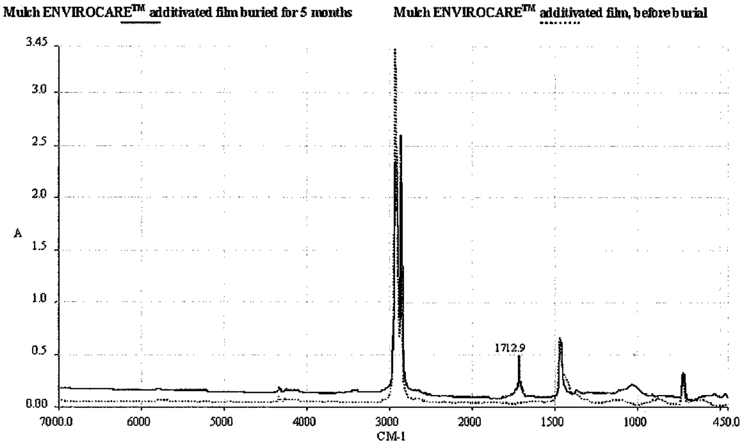


Figure 7. Carbonyl evolution in buried ENVIROCARE™-containing film

Providing Solutions for the Field

Before undergoing controlled degradation, agricultural plastics that will end up in the soil should not have any negative influence on the environment. It was demonstrated that agricultural plastics based on ENVIROCARE™ technology do not contain any hazardous substances following international standards (e.g. norm EC OJL,219,7.8.98 for soil improvers) and are non-ecotoxic for the environment following the below listed tests performed by SGS.

Table 2.

Test
Daphnia magna Immobilization test according to ISO 6341
Earthworm, acute toxicity test, according to ISO 11268-1
Cress test according to ISTA
Oat & lentils test according to ISO 11269-2

Previous trials and the outdoor tests were combined with large-scale field trials. Due to the fact that the conditions and the requirements for mulch films change from region to region, the assessment of the film lifetime is a complex matter. The basic laboratory data can be used to define the appropriate ENVIROCARE™ system, meeting the specific needs. For this, a complete set of information is needed relevant to the plastic article (polymer, thickness, pigment), to the conditions of use (crop, way of application, expected time life) and to the environmental conditions.

Up to now, ENVIROCARE™ containing mulch films have been extensively tested in field trials in different countries and for different crops. This data helped Ciba to recommend additives adapted to the specific conditions and agronomic needs. Successful results were obtained for instance in maize, melon and cotton mulch film applications. Additional field trials are ongoing for longer lifetime films like: strawberries, pineapple, tomato and watermelon.

In addition to mulch films, other agricultural applications, where the use of ENVIROCARE™ additive is beneficial, were selected. Hence field trials are running in solarization films, small tunnel films, twines, bale wrap, seeding bags and banana bags.

The major benefit for the user of ENVIROCARE™-containing films is convenience. After use, the plastic film or thicker part does not need to be recollected, transported to a collection center and disposed of by burial, landfilling or incineration. A second important benefit is that these additives can be used with commodity plastics, with standard processing equipment and, last but not least, with standard processing conditions without affecting the mechanical and the optical properties of the plastic articles. Figure 8 shows some applications of ENVIROCARE™-based agricultural articles used by farmers on an industrial scale.

Melon **Maize** **Cotton**

Figure 8. Degradable mulch containing ENVIROCARE ™

Conclusions

Using agricultural plastics containing ENVIROCARE™ additives, it is possible to meet the degradation requirements of a variety of conditions related to their use in the field. ENVIROCARE™ provides an environmental friendly and cost efficient alternative to recollection and traditional waste disposal routes.

Although studies demonstrated the potential degradation in a biological environment of films based on ENVIROCARE™ technology, a major issue for evaluation of polymer biodegradation is the lack of generally acceptable standards for defining or testing biodegradability. Essentially all organic materials are biodegradable in some timescale, though complete conversion to CO_2 and water (mineralization) may take centuries [3, 6–8]. Concerning biodegradation in the soil, such as is required in agricultural applications, existing standards related to composting conditions do not take into account the substantially differing degradation conditions encountered in a soil medium. However, as environmentally degradable polymers are becoming a more important part of the consumer's life, national and international working groups (like ASTM and CEN) are investing a lot of energy in order to deliver more effective and sustainable test criteria.

Within this context Ciba Specialty Chemicals participates in working groups in order to support a sustainable future for biodegradable plastics in agriculture.

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