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Combined effect of UVA radiation and agrochemicals on the durability of agricultural multilayer films

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New generation agricultural films combine multilayer technologies, with the latest developments in chemicals resistant UV stabilisers and possibly the incorporation of barrier layers against agrochemicals. The photo-degradation behaviour of a series of experimental multilayer (ML) films exposed to accelerated ageing in combination with agrochemicals, was analysed. It has been shown that the presence of a barrier layer (EVOH or PA) adversely affects the mechanical behaviour of ML films, because of the low ductility of these barrier layers, whose failure is propagating to the other layers leading to premature failure of ML film structures. ML films with barrier layer have shorter lifespan due to the rapid photo-degradation of the barrier layer. It was confirmed that these layers absorb the main part of the agrochemicals load, acting as effective barriers. Agrochemicals were shown to accelerate the detrimental effect of the UVA radiation on PA and EVOH layers causing premature failure of the barrier layers, compromising evenmore the mechanical strength and durability of the entire film. The presence of barrier layers such as PA (mainly) and EVOH in agricultural ML films is not recommended, as both their mechanical properties and photodegradation behaviour are adversely affected by the presence of low ductility barrier layers, deteriorated by the combination of UVA radiation and agrochemicals.

1. Introduction

1.1. Agricultural films

Agricultural plastic films, including greenhouse, tunnel and low tunnel films, direct coverings, mulching films, disinfection and solarisation films and silage films, represent the dominant category of agricultural plastics. They secure and increase the production yields, under various climatic and environmental conditions, reducing inputs (water, agrochemicals, energy) and enhancing the food quality and safety [1,2].

The main polymers used for agricultural films are: Low Density Polyethylene (LDPE), Linear Low Density Polyethylene (LLDPE), High Density Polyethylene (HDPE), Ethyl Vinyl Acetate (EVA)/Ethylene Butyl Acrylate (EBA) and recycled PE. Other polymers used to a much lower degree include Poly Vinyl Chloride (PVC), Ethylene Vinyl Alcohol (EVOH), Polyamide (PA), etc. The agricultural plastics production at international level was estimated at 6.5 mt in 2011 [3] with almost half of this amount been used in the sector of protected cultivations. The global demand for agricultural films in 2012 was 4.4 mt, while their Compound Annual Growth Rate (CAGR) from 2013 to 2019 is estimated to 5.7% [4]. Greenhouse and mulching films, account for almost 75% of the total agricultural films market [5]. The dominant polymer accounting for more than 55% of the total market of agricultural plastics in 2012 is the LLDPE with the global consumption estimated at 1,5 mt by 2019 [4].

1.2. Degradation and stabilisation of agricultural films

Degradation of agricultural films is the result of complex and, in many cases, inter-related processes such as photo-degradation, chemical degradation due to gaseous contaminants, agrochemicals, and soil disinfectants as well as mechanical degradation [1,6]. Photo-degradation, induced under the action of UVA radiation (315–400 nm) in the presence of internal or external impurities, possibly containing chromophoric groups (e.g. Hydroperoxides, Carbonyls), is considered as the most destructive degradation process of agricultural plastics [7]. Photo-degradation, accelerated by high temperatures and chemical contaminants, is leading to reactions of chain scissoring and cross-linking of the polymeric

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chains and oxidation. Among the main byproducts of photo-degradation are carbonyls (C=O), hydroxyl (OH) groups, and vinyl groups [6]. Several research works have correlated the increase of carbonyls concentration with the degradation of the mechanical properties, the molecular weight decrease and increase of crystallinity [7].

A wide range of specialty UV-stabilisation additives have been developed to control polymers photo-degradation, by reducing oxidation reactions [5,6,8,9]. Hindered Amine Light Stabilisers (HALS) and Nickel Quenchers, combined with selected UV absorbers, represent the main stabilisation additivation schemes used with agricultural plastics.

The UV absorbers compete with the impurities (chromophores) present in the polymer to absorb UV radiation and convert it into harmless infrared radiation or heat that is dissipated into the polymer matrix. Among the most important UV absorbers included are: 2-(2-hydroxyphenyl)-benzotriazoles, 2-hydroxy-benzophenones, hydroxyphenyl-s-triazines and oxalanilides [10,11].

Nickel Quenchers, organic complexes e.g. nickel dibutyldithiocarbamate [12], disable the chromophoric groups responsible for the launch of photo-degradation by deactivating the excited polymer states and dissipating the energy in other harmless forms. Nickel quenchers are not used widely anymore, replaced by the more effective and environmentally friendly HALS, because Ni is classified as class I carcinogenetic [13].

The HALS stabilisers, used commercially since the 1970s [10], are mainly synthesised of 2,2,6,6-Tetramethylpiperidine Derivatives (TMP) [55]. HALS do not absorb radiation, but instead they protect the polymer resin from chemical degradation chain reactions by neutralising the "free radicals" produced through the photo-chemical reactions (highly reactive molecules of high energy with unstable configuration) [14]. Eventually, HALS are regenerated during the free radicals neutralisation process offering protection throughout the life-time of the plastic [10]. They improve the mechanical, thermal and chemical properties of polymers under conditions of photo-and thermal degradation [15,16].

1.3. The effect of agrochemicals on agricultural films

The life time of agricultural plastics stabilised with HALS is greatly influenced by the use of agrochemicals containing iron, sulphur (S) and active halogens, such as chlorine (Cl) or bromide, and elemental sulphur (powder, wettable or burnt). Pesticides and fumigants containing sulphur or halogen, as well as their derivatives, may interact with the UV-stabilisers and "block" their action resulting in premature photo-degradation of the film [17–20]. Sulphur reacts with HALS molecules exactly at their active site where HALS neutralise free radicals preventing them from performing their function. The effect of sulphur applied by burning or sublimating or by dusting has been shown to be especially detrimental for greenhouse films not stabilised with chemicals resistant HALS. The extensive use of sulphur based agrochemicals with organic farming and Integrated Pest management (IPM) explains the recorded increase of premature failures of agricultural films over the last years. Taken into consideration that the use of nickel quenchers is gradually abandoned, the development of a new generation of pesticide resistant stabilisers has become a first priority for the additives industries. Already, agricultural films producers warn the farmers that the detection in films of S, Cl or other halogens at cumulative concentrations exceeding a given threshold (e.g. up to a maximum 150 ppm of Cl and up to 1500 ppm of S) invalidate the warranty offered.

The detrimental action of agrochemicals depends on their active ingredients, the method of implementation and frequency, the environmental conditions, the applied stress and also on the synthesis and the thickness of the plastic product, the type of chemical bonds, the presence of catalysts etc. [7,8,21,22].

The permeability of a gas or liquid through a polymer is a function of several factors, including [23]: chain packing described by the fractional free volume (FFV) [24]; temperature [24,25]; chemical structure of the polymer (presence of polar or bulky side groups or rigid linkages increases chain rigidity, reducing penetrant diffusion coefficient) [24]; additivation systems (e.g. plasticisers and special modifiers may increase permeation), fillers (depending on adhesion and compatibility to polymer),co-polymerisation (depending on barrier properties of co-monomer) [25]; crystallinity (increased crystallinity decreases gas permeability) [24,25]; orientation of polymer chains (orientation decreases permeation especially in polymers of high crystallinity), substance concentration (depends on solubility, diffusivity; permeability depends on the substance–polymer system) [24] and the molecular structure of gas or liquid substance (depending on size of the liquid molecule, molecular shape and polarity) [25].

Efforts to protect stabilised agricultural plastics against agrochemicals follow three main lines: a) improving the UV stabilisers (HALS) resistance to agrochemicals; b) reducing the agrochemicals use; c) reducing the agrochemicals permeability through the polymer.

Films stabilised with hindered amine light stabiliser series (NOR-HALS) with very low basicity show good chemical resistance to agrochemicals (pesticides, insecticides, soil disinfectants) containing iron, sulphur and active halogens [5,17]. NOR-HALS combined with specific UV absorbers (e.g. Tinuvin 326) act synergistically [55]. An example is "Tinuvin XT-200" and "Tinuvin NOR-371" [5].

A service life of 24 months has been reported for greenhouse films stabilised with Tinuvin XT-200 [5]. According to [26], a 200 μm greenhouse film stabilised with sulphur resistant HALS, can withstand up to 3 years if exposed to maximum concentrations of 150 ppm Cl and 1500 ppm S. In the study of [26], mechanical degradation of PE greenhouse films occurred with combined concentrations of 1600 ppm S, 70 ppm Cl and 100 ppm of iron (Fe). EBA films stabilised with HALS exposed to accelerated ageing in the presence of pesticides exhibited low carbonyl index [27]. EBA films with Tinuvin NOR-371 retained their original mechanical properties after 3150 h exposure to accelerated ageing.

The effect of agrochemicals on the mechanical strength of EVA films and EVA with thermoplastic polyurethane (TPU) films, stabilised with HALS and NOR-HALS and UV absorbers, showed that UV stabilisers react with different agrochemicals in different ways, as it was reflected in the measured mechanical properties [28]. Better mechanical performance was displayed by EVA films contained NOR-HALS and triazine UV absorbers, while EVA with thermoplastic polyurethane (TPU) films, stabilised with NOR-HALS, also retained their mechanical properties at satisfactory levels. The radiometric characteristics of the same agricultural films [8] suggested major changes, only in the spectrum of the far infrared radiation (LWIR 7500–12.500 nm).

Plastika kritis S.A. [29], showed that the stabilised greenhouse films (180–200 μm) exposed to agrochemicals in different Mediterranean countries failed at an average S content of 1820 ppm,while co-stabilised greenhouse films with an average Cl level of 223 ppm did not fail prematurely.

1.4. Multilayer agricultural films

Conventional greenhouse films were usually manufactured by three layers coextrusion structures made of LDPE and EVA polymers and various additivation schemes in each layer. The new generation greenhouse films combine the latest developments of