



REVIEW PAPER

Degradation and Stabilization of Low-density Polyethylene Films used as Greenhouse Covering Materials

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A large quantity of plastics is used annually world-wide in the agricultural sector, of which a significant amount is intended for protected cultivation, in greenhouses and low tunnels. For this specific application, thin films of low-density polyethylene is the most widespread material used. As expected, due to the harsh conditions met during their use, from ultraviolet irradiation, heat, agrochemicals, as well as due to their limited thickness, such films degrade in a short time and often unexpectedly, creating both environmental problems and economic difficulties. In this paper, the most important mechanisms of degradation of low-density polyethylene agricultural films are described, giving emphasis on the special conditions and degradation parameters met during their use as greenhouse covering material. The methods of stabilizing such films, thus extending their service life, are also briefly discussed.

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1. Introduction

The quantities of plastic materials annually used all over the world in the agricultural sector amount to two million tonnes (Table 1, Garnaud 1994). Almost half of this amount is used in protected cultivation (greenhouses, mulching, small tunnels, temporary coverings of structures for fruit trees, *etc.*). Of extreme importance is the financial impact of products originating from protected cultivation to the agricultural income in many less favoured regions of southern European Union (EU) countries. For example, the consumption of plastics intended for agricultural use in Italy increased from 116 000 t/yr in 1977 to 250 000 t/yr in 1993, 40% being used in protected cultivation (Pacini, 1993). In these areas, where the climate is generally favourable, plastic-covered greenhouses represent one of the most competitive and productive sectors of agriculture. It is easily realized, therefore, that the reliability of the agricultural plastic films is an important factor in the positive economic development of these

areas. Losses due to premature failure of the protective covering material can have devastating consequences to the competitiveness and the productivity.

Contrary to other agricultural applications of plastics, as irrigation pipes or containers for agricultural products, plastic films used for plant protection have a limited service life and quickly degrade when subjected to a combination of factors, such as solar irradiation, heat, oxygen and agrochemicals. Among other reasons, this rapid degradation (also called ageing) is due to the reduced thickness of these plastic films when compared to other agricultural applications.

The durability of the most widely used polyethylene plastic films used for protected cultivation varies from a minimum of one cultivating season to a maximum of 2–3 yr, and at the end of their useful life, they are classified as waste. Most of this waste is currently disposed of in unauthorized dumping sites or burned uncontrollably in the fields. Management of the huge quantities of waste produced in this way represents a problem with great environmental implications. In order to minimize the environmental impact of this plastic waste stream, it is desirable that the films used in protected cultivation have an increased life, thus producing less waste per annum.

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Table 1
Amounts of plastic material used in agriculture in the world

Use	Area, ha	Quantity, t/yr
Mulching	3 500 000–4 000 000	550 000–750 000
Low structures	250 000	100 000
Greenhouses	220 000	250 000–350 000
<i>Total protected cultivation</i>		900 000–1 200 000
Irrigation piping	—	> 500 000
Micro-irrigation (drip)	1 500 000–2 000 000	150 000–200 000
Drainage	400 000	120 000–150 000
Silage	—	200 000
Total		1 870 000–2 250 000

As a consequence, in recent years, both the scientific community, as well as all the major plastic film producers have concentrated their efforts towards improving the formulation of the plastic films used in protected cultivation, while at the same time tailoring their products for the demands of the specific application.

Overall, the vast majority of the greenhouse area covered by plastic materials is dominated by the use of plastic films made out of polyethylene (PE) (Briassoulis *et al.*, 1997a). In particular, low-density polyethylene (LDPE) is the most widely used polyethylene grade, due to its relatively good mechanical and optical properties, combined with a competitive market price. However, this material is easily affected by the harsh environmental conditions during its use. Various factors, such as the solar radiation, temperature, agrochemical use, humidity and others can alter the chemical structure of the polymer and eventually compromise both its mechanical as well as its optical properties. Thus, the most commonly used LDPE film is expected to last for only one year. For this reason, special additives are generally added to the formulation of the film in order to provide improved resistance and durability.

The maximum useful life advertised by film producers, and obtained through the use of the more sophisticated and expensive technology available, is four seasons (four winters, three summers). Even this expected life is significantly affected by the particular environmental conditions the film will face during its use. Thus, a film, whose life is estimated to be four seasons in northern to central Europe, will only last two to three seasons in the Mediterranean region.

2. Material characteristics and properties of polyethylene films for greenhouses

As mentioned, low-density polyethylene (LDPE) is a widely used polyethylene, accounting for almost half of

the global PE production. Its chemical structure is shown in *Fig 1*. It is mainly produced by the original ICI process for polymerizing ethylene. This process involves compressing ethylene to very high pressures (1400–2400 bar) and polymerizing at high temperature (200–250°C) with the use of free radical catalysts (Ziegler–Natta catalysts). Other polyethylene materials are produced by low-pressure processes resulting in high-density polyethylene (HDPE) and co-polymerization with butene and hexene which introduce ethyl and butyl short-chain branching, resulting in medium-density polyethylene (MDPE) and linear low-density polyethylene (LLDPE) (Table 2). However, these grades are not normally used for protected cultivation due to undesirable properties or prohibitive prices. On the other hand, low-density polyethylene is the polymer most commonly used, especially in the Mediterranean region, as greenhouse covering material and has a density of between 910 and 935 kg/m³ (Briassoulis *et al.*, 1997a; Mills, 1993) possesses good toughness, flexibility, low temperature resistance, clarity in film, and relatively low heat resistance (Briassoulis *et al.*, 1997a, 1997b). The range of some of its characteristic properties as a function of the material density is shown in Table 3.

Low-density polyethylene is a material with semi-crystalline character, where regions of crystalline polymer, called spherulites due to their spherical shape, are

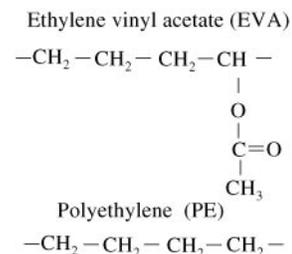


Fig. 1. Chemical structures of ethylene vinyl acetate and polyethylene

Table 2
Densities of various polyethylene (PE) grades

<i>Polyethylene grade</i>	<i>Density, kg/m³</i>
Linear low density (LLDPE)	920–930
Low density (LDPE)	910–935
Medium density (MDPE)	940
High density (HDPE)	955–977

separated by regions of amorphous material. As a result, the film exhibits properties that fall in between those of a crystalline and a purely amorphous material. For example, since crystalline areas are typically more densely packed than amorphous areas, polyethylene with high crystallinity is inherently denser than its less crystalline analogue. As its crystallinity and therefore density is increased, increases also occur in stiffness, shrinkage, brittleness temperature, and chemical resistance and decreases in its impact resistance, cold flow, tear strength and environmental stress-crack resistance. These effects are shown in Tables 4 and 5. Moreover, most of the degradation processes takes place in the amorphous phase of the material (see Section 3.2).

Another significant effect of the extrusion processing of thin films of PE for agricultural purposes is the orientation of the long polymer chain, due to the applied shear forces in the machine direction. In this oriented state, the spherulites take the appearance of ellipsoids, regularly also called lamellae. In general, this orientation imparts changes in the mechanical properties of the plastics. In Table 6, for example, the mechanical properties of LDPE films have different values in the extrusion machine (or longitudinal) direction and in the transverse direction (Briassoulis *et al.*, 1997b; Patel *et al.*, 1994). Furthermore, different mechanisms of degradation apply than those which occur in unoriented material (Igarashi and DeVries, 1983).

Most LDPE greenhouse films on the market today comprise co-extruded multi-layered films with 4–10% ethylene vinyl acetate (EVA). The addition of EVA imparts superior elasticity, mechanical strength, resistance

Table 3
Properties of low density polyethylene (LDPE)

<i>Characteristic property</i>	<i>LDPE</i>
Density, kg/m ³	910–925
Crystal melt temperature, °C	95–130
Tensile strength, MPa	4.1–15.9
Tensile modulus, MPa	96.5–262
Elongation at break, %	90.0–800.0
Hardness, shore D	41–50

to ultra-violet (UV) radiation and thermic effect to the films as can be seen in Table 6 and should always be reported (Briassoulis *et al.*, 1997b).

This change of properties with EVA content can be partly explained by considering the chemical structure of the two polymers. The differences in the chemical structure of the repeat units which form the two polymer chains are seen in Fig. 1. The bulky side branch of EVA cannot easily be accommodated within the ordered polyethylene polymer crystals. This leads to a decrease in the percentage of crystallinity with increasing amount of EVA copolymer.

In general, it is accepted that the material characteristics of the polymer films do dictate its characteristics and behaviour under the various environmental conditions. By improving the formulation of the polymer films, or even the structure of the polymer molecules, the critical film properties should also improve. In 1960, high-activity Ziegler–Natta catalysts made possible the inexpensive and easily controlled production of polyethylene. Currently, with metallocene catalysts discovered in the 1980s, producers can refine, or even design at will, the structure of the polymers (Thayer, 1995). Although based on transition metals such as titanium and zirconium (as are Ziegler–Natta catalysts), metallocenes differ in that they have well-defined single catalytic sites and well-understood molecular structures. Typically, they consist of a transition-metal atom sandwiched between ring structures to form a sterically hindered site. Thus, polymer molecular weight and molecular weight distribution, co-monomer distribution and content, and tacticity can be independently controlled. With well-characterized molecular structures, catalyst composition and geometry can be varied systematically to produce extremely uniform homo- or copolymers ‘programmed’ with the desired physical properties. At the same time, new industrial processes, such as the supercondensed mode (SCM) process developed by Exxon, can lead to a marked increase in the productivity (60–200% for the SCM process) (Thayer, 1995).

Metallocene-based PE has been available commercially since about 1991. The new process imparts onto such polymers features such as increased impact strength and toughness, better melt characteristics and improved clarity in films. Most early applications have been in speciality markets where value-added and higher priced polymers can compete. However, as the technology develops and catalyst costs decrease, metallocene-based polymers are expected to compete in the broader plastics market, and therefore to be available for use in the agricultural field. In the future, the improved clarity, high strength and stability of metallocene-based PE will prove a significant advantage, especially for its use as a greenhouse covering material. It is easily realized, therefore,

Table 4
The effect on polyethylene of increasing density, melt index and molecular weight

<i>Property</i>	<i>Increase in density</i>	<i>Increase in melt index</i>	<i>Increase in molecular weight</i>
Tensile strength (at yield)	Higher	Lower	
Stiffness	Higher	Slightly lower	Slightly lower
Impact strength	Lower	Lower	Lower
Low-temperature brittleness	Higher	Higher	Lower
Abrasion resistance	Higher	Lower	
Hardness	Higher	Slightly lower	
Softening point	Higher		Higher
Stress-crack resistance	Lower	Lower	
Permeability	Lower	Slightly higher	
Chemical resistance	Higher	Lower	
Melt strength		Lower	Higher
Gloss	Higher	Higher	Lower
Haze	Lower	Lower	
Shrinkage	Lower	Lower	Higher

that developments in the field of catalysis, process engineering and material science can lead to the production of new and improved materials which will be more resistant to the various factors affecting the degradation of these materials in the field.

In the following, the mechanisms of degradation which affect polyethylene in general are discussed, with emphasis given to the degradation factors for greenhouse LDPE films. Finally, the mechanisms of stabilization of such films are briefly presented.

3. Mechanisms of degradation

Degradation is a complicated non-linear time-dependent process which affects directly, or indirectly, several

properties of the material related to its functional characteristics. In its final stage of degradation, a material does not meet its functional requirements and is easily prone to mechanical failure. As a practical rule, the useful life of a material is considered to be reached when its initial mechanical strength is reduced by 50% (Henninger & Pedrazetti, 1988). There are several factors to monitor and criteria to define the degree of degradation (Randy & Rabek, 1983). Not all properties are affected by degradation in the same way though. Thus, the elongation at break (expressed as a %) appears to be a more sensitive 'index' of degradation than the tensile strength, the stress at yield or the modulus of elasticity. Actually, the material becomes more brittle with degradation and so it cannot retain its initial elongation at break. There is a suggestion that two widely used criteria describing the

Table 5
The effect on polyethylene of increasing density, melt index and broadening of molecular weight distribution

<i>Properties</i>	<i>Increase in density</i>	<i>Increase in melt index</i>	<i>Broadening of molecular weight distribution</i>
Melt viscosity	Higher	Lower	
Vicat softening point	Much higher	Lower	Lower
Surface hardness	Higher	Slightly lower	Lower
Tensile strength			
Yield	Much higher	Slightly lower	Lower
Break	Slightly higher	Lower	Lower
Elongation	Lower	Lower	Higher
Creep resistance	Higher	Slightly lower	Higher
Flexural stiffness	Much higher	Slightly lower	
Flexibility	Lower		
Toughness	Lower	Lower	Lower
Low-T brittleness	Lower	Lower	Higher
Stress crack resistance	Lower	Lower	Higher

Table 6
Mechanical properties of low-density polyethylene with and without ethylene vinyl acetate in the longitudinal (L) and transverse (T) directions

Film	Elongation at break (L/T), %		Strength at break (L/T), kg/mm ²		Creep, %
	L	T	L	T	
Without EVA	500	550	1.80	1.80	8
With EVA	600	650	2.50	2.55	24

evolution of degradation are inter-related: the decrease of the final elongation at break and the increase of the number of carbonyl groups (Henninger & Pedrazzetti, 1988; Ram, 1978). Several researchers, however, are cautious against generalising a direct relationship between the number of carbonyls and mechanical properties (Henninger & Pedrazzetti, 1988; Rull *et al.*, 1995).

Degradation of polymers is induced by different external factors and mechanisms. Briefly, the various degradation types for polymers are the following:

- (1) *thermal*—occurs due to use or processing at high temperatures;
- (2) *photo-induced*—on exposure to the energetic part of the sunlight, *i.e.* the UV radiation, or other high-energy radiation, the polymer, or impurities within the polymer absorb the radiation and induce chemical reactions;
- (3) *mechanical*—occurs due to the influence of mechanical stress-strain;
- (4) *ultrasonic*—the application of sound at certain frequencies may induce vibration and eventually breaking of the chains;
- (5) *hydrolytic*—for polymers containing functional groups which are sensitive to the effects of water;
- (6) *chemical*—corrosive chemicals, such as ozone or the sulphur in agrochemicals, may attack the polymer chain causing bond breaking or oxidation; and
- (7) *Biological*—specific to polymer with functional groups that can be attacked by micro-organisms.

Depending on the use of the particular polymer, as well as its identity, some mechanisms may be prominent, while others might not act at all. The degradation of LDPE films used as covering material is governed mainly by thermal, radiation, mechanical and chemical mechanisms. Ultrasonic, hydrolytic and biological degradation do not regularly affect this polymer due to absence of ultrasonic waves in agricultural applications, and the absence of functional groups which might make the polymer liable to hydrolytic or biological attack. The degradation mechanisms which do take part in the degradation of agricultural LDPE films are discussed in the following sections.

3.1. Thermal degradation

Polymeric molecules are only stable below a certain temperature around 100 to 200°C, which is rather low compared to their low-molecular weight counterparts. At temperatures above some critical temperature, bond scission may occur with high frequency leading to quick deterioration of the polymer structure and properties. However, this critical temperature is usually higher than 400–600°C, in order to provide sufficient energy for the breaking of bonds which have a dissociation energy around 150–400 kJ per mole at 25°C. Thus, bond breaking due to thermal dissociation is not important for applications at ambient temperature, such as in the agricultural field where the temperatures at locations where the film is in contact with elements of the greenhouse do not exceed 80°C in the worst case (von Elsner, 1997). Indeed, polyethylene is practically stable up to 100°C in inert atmosphere (Schnabel, 1981) with a glass transition temperature of 155°C. Depolymerization due to thermal treatment of polyethylene occurs only to a negligible effect; a monomer fraction of only 1% was detected after heat treatment in an inert atmosphere (Schnabel, 1981). However, elevated temperatures can significantly increase the rate of various chemical reactions, such as oxidation, and therefore lead in an indirect way to degradation of the polymer. This effect is discussed further in the following section on photo-degradation.

3.2. Photo-degradation

There exists a direct relationship between the degradation of the mechanical properties of many plastic materials and their exposure to solar radiation (with wavelengths of 290–1400 nm) (Amin *et al.*, 1995; Hamid *et al.*, 1992). The most energetic part of the solar spectrum, the UV radiation in the range between 290 and 400 nm (Khan & Hamid, 1995), can be absorbed by the plastic and lead to bond cleavage and depolymerization, causing photo-degradation. The free radicals produced in this way may then react with the atmospheric oxygen and lead to further degradation of the plastic, which is called photo-oxidation. While photo-degradation affects

the whole of the plastic film, when such film is transparent, photo-oxidation can only take place in the near-surface region. This is because the oxidation process is limited by the diffusion of oxygen inside the material (Yanai *et al.*, 1995; Hawkins, 1984).

Pure polyethylene, based on its basically inert chemical structure (see *Fig. 1*), should not in principle be affected by photo-oxidation, since it contains no groups (such as double bonds) capable of absorbing in the near UV spectrum. However, commercial polyethylene films contain various internal or external impurities, usually photo-absorbing chromophores, which impart photosensitivity to the films (Rabek, 1995; Gugumus, 1979). Due to the presence of these groups, the activation spectra maximum for photo-oxidation of polyethylene has been observed to be at 300 nm.

Initiators of photo-degradation can be introduced to the polymer: (a) during manufacture (i.e. polymerisation); and (b) during processing (i.e. extrusion) and use. The distinction is made because the polymerization process cannot be closely controlled and different batches may contain different level of catalyst residues, while the processing and use usually follow a pre-set pattern.

In general, the groups introduced during manufacture (Schnabel, 1981) are:

- (a) *catalyst residues* containing Ti, Al and Cl;
- (b) *unsaturated groups* formed during polymerization by chain transfer, or disproportionation of growing chain ends; and
- (c) *carbonyl groups*, introduced by carbon monoxide impurities in the monomer and through oxidation.

Other photosensitive groups introduced during processing and use are

- (a) hydroperoxides and peroxides which are primary products of thermal oxidation during processing, are extremely photochemically active and are initiators of photo-reactions;
- (b) carbonyl groups produced by thermal oxidation during processing and storage and from photo-oxidation during use which are also well-known key initiators of the Norish I and II type photo-reactions; and
- (c) reactive forms of oxygen such as ozone (O_3) which is present in the atmosphere and singlet oxygen (1O_2) which can be produced inside the polymer by quenching of UV excited species by ground-state oxygen (3O_2).

All these impurities lead to enhancement of photo-degradation by either absorbing energy of the UV spectrum, or by being initiators of photo-oxidation reactions (in the case of carbonyl and hydroperoxide groups). Of course, the presence of these impurities depends strongly on the manufacture and processing conditions, which can

in principle be altered in order to minimize them (such as metallocene-based PE). However, the associated costs may make such alterations neither practical nor desirable for the industry.

Once these impurities are present in the LDPE films, the photo-degradation proceeds, in two distinct parts:

- (a) photo-oxidation of the outer layers which can come in direct contact with the atmospheric oxygen, and proceeds rapidly mainly through radical chain oxidation reactions, while
- (b) the inner layers, which cannot under usual circumstances be reached by the atmospheric oxygen, degrade more slowly through photo-reactions of peroxy radicals or reaction of radical pairs.

Usual products of these reactions are carbonyl ($C=O$), hydroxyl (OH) and vinyl groups, while trans-vinylene groups are produced in trace amounts. Due to the existence of two distinct modes of degradation, the effects of photo-degradation are concentrated in the surface layers of the films. It has been shown with the use of infrared spectroscopy (IR) that the carbonyl content falls sharply just below the surface, in the first 0.8 mm (Hawkins, 1984). Furthermore, the thickness of the surface layer in which the diffusion of the oxygen is not the limiting step was estimated to be of the order of 20 μm (Popov *et al.*, 1983). On the other hand, electron spectroscopy for chemical analysis (ESCA) reveals that the oxidation of LDPE irradiated for 1334 h, extends to at least the first 130 \AA (Rabek, 1995) and possibly even more. As a result, the material becomes more brittle and degraded near the exposed surface. More detailed investigations (Yanai *et al.*, 1995), using multilayer slabs of LDPE revealed that the carbonyl content showed a parabolic symmetry around the centre layer which was the least affected. Use of oxygen barriers on one or both surfaces significantly reduced the photo-oxidation. It was concluded therefore that photo-oxidation is autocatalytic and affected primarily by oxygen diffusion.

Furthermore, researchers in the past (Amin *et al.*, 1995; Liu *et al.*, 1995; Qureshi *et al.*, 1990) have shown that an increase in the carbonyl content coincides with a decrease in mechanical properties, lower values of molecular weight and a substantial increase in the crystallinity of the exposed greenhouse film as seen by Fourier-transform Raman (Rull *et al.*, 1995) and X-ray diffraction (XRD) (Ram *et al.*, 1980), possibly due to crystallite formation in the amorphous region of the polymer matrix (secondary crystallization). These results were also confirmed by a drop in oxygen permeability, which is characteristic of increased crystallinity (Ram *et al.*, 1980). However, other researchers using calorimetric analysis have not observed such an increase in crystallinity upon natural ageing (Sebaa *et al.*, 1993). This

discrepancy can have its origin, either with the instrument used, or more likely with the exact formulation of the films tested and the extent of ageing achieved. However, all agree that the photo-oxidation in the case of LDPE films occurs in the amorphous region of the polymer matrix. Unfortunately, no simple correlation can be found between the carbonyl content and the decrease in mechanical properties, while there seems to be some correlation between the mechanical properties and the results of the thermal analysis by differential scanning calorimetry (DSC) (Liu *et al.*, 1995).

The basic mechanisms which have been put forward in order to explain the production of the degradation species are given below (for more details, see Rabek, 1995). Various mechanisms, such as photolysis of isolated hydroperoxides according to a six-membered transition state, bimolecular reactions of secondary peroxy radicals, free oxidation of secondary hydroxyl groups, reactions of carbonyl groups with hydroperoxide groups and reactions of carbonyl groups with hydroxyl groups, have been proposed for the formation of carbonyl groups.

The production of carboxylic groups can proceed by Norrish Type I reactions followed by secondary reactions, or by reactions of carbonyl groups with hydroperoxy groups, or by peroxy-ketal formation, or finally by decomposition of α -keto-hydroperoxides.

One other group of products, the vinyl group, can be formed by Norrish Type II reactions or intramolecular decomposition of tertiary hydroperoxides. However, the vinyl group is also very reactive and can also disappear during UV irradiation by reaction with singlet oxygen ($^1\text{O}_2$) and reactions with free radicals. Finally, trans-vinylene groups are formed directly by the cleavage of hydroperoxy groups, which also leads to hydroperoxy radicals as byproducts.

The rate of photo-oxidation of polyethylene is temperature dependent and roughly doubles for every 10°C of increase in the temperature (Rabek, 1995). It has also been shown that the rate of oxidation decreases with increasing orientation of the polymer film and this has been attributed to both lower gas solubility as well as lower chain segment mobility (Popov *et al.*, 1983). In any case, the effect of a specific factor on the rate of degradation is also dependent on the time elapsed since the initiation of the particular degradation action.

3.3. Mechanical degradation

Mechanical degradation of materials is a large field comprising fracture phenomena, as well as chemical changes imposed by mechanical stress. The difference between mechanical degradation of polymeric material and

that of low molecular weight organic material is that only in macromolecules are free radicals produced by chemical bond rupture during mechanical treatment. While small molecules are generally free to change positions and accommodate the applied stress, the local high stresses that lead to rupture of chemical bonds are produced in macromolecules which possess lower mobility (Mills, 1993).

Similar to the fracture phenomena, the rupture of bonds due to mechanical loading depends on the amount of elastic energy that a macromolecule is capable of storing and on the time the macromolecule remains under strain. However, studies have shown, that bond scission is still a relatively rare event when compared to other energy dissipation processes. Such non-chemical processes include slippage of the chains, changes in chain conformation and crystallinity.

Those two categories, chemical and non-chemical energy dissipation, compete with each other. In cases where the non-chemical processes are inhibited, such as in stiff polymers, *e.g.* nylon, the bond scission occurs with higher frequency. In contrast, more supple polymers, such as polyethylene, where strong bonding between macromolecules does not exist, slippage of chains occurs more frequently and bond scission less so (Igarashi & De Vries, 1983).

However, LDPE still suffers to some extent of degradation due to mechanical loading. For linear macromolecules, such as PE, it has been shown that the probability of scission is higher in the middle of the chain (Schnabel, 1981). In another work (Popov *et al.*, 1983), increased degradation has been observed for LDPE held under tension (from 0 to 34 kg/mm^2) in an ozone environment, that could not be explained by changes in the degree of crystallinity, orientation or chain mobility. The rate of oxidation decreased with increasing orientation and a linear relationship was observed between the level of stress and the degradation. Finally, increased reactivity of the stretched macromolecules, especially at the parts of the chains which are held in high tension, was put forth as a plausible explanation of the observed behaviour.

3.4. Chemical degradation

3.4.1. Solvents

The effect of a solvent on the structure of the polymer material can be significant at times. Most thermoplastics are soluble in several solvents. Usually, a swelling stage precedes the dissolution. Polymeric materials capable of forming crystallites, such as LDPE, tend to be rather resistant to physical interaction with solvents. Dissolution is impeded by the strong intermolecular interactions

between macromolecules. Only when these interactions are overcome by thermal activation will the polymer swell and eventually dissolve. However, apart from the physical action of dissolution, solvents can also chemically attack such polymers. Immersion tests show that while PE had satisfactory resistance at ambient temperature to methanol and only limited resistance to acetone, it exhibits unsatisfactory resistance to other saturated hydrocarbons, benzene, carbon disulphide and carbon tetrachloride (Schnabel, 1981).

3.4.2. *Environmental pollutants*

Environmental pollution can also be harmful to the structural integrity of the polyethylene due to chemical attack of the polymer bonds. Atmospheric pollutants such as nitrogen oxides, sulphur oxides, hydrocarbons and particulate can enhance the degradation of the polymers (Ranby & Rabek, 1983; Schnabel, 1981; Dilara & Briassoulis, 1998), especially when combined with applied stress (Igarashi & De Vries, 1983) and must also be taken into account. For instance, infrared studies have revealed that polyethylene reacts with NO_2 at elevated temperatures, and that chemical attack is observed even at 25°C , probably due to the presence of impurity olefinic bonds which react readily with NO_2 (Schnabel, 1981). Similarly, SO_2 is rather reactive, especially in the presence of UV irradiation, which it readily absorbs and forms triplet excited sulphur dioxide ($^3\text{SO}_2^*$). This species is capable of abstracting hydrogen from the polymer chains leading to the formation of macroradicals in the polymer structure, which in turn can undergo further depolymerization (Schnabel, 1981).

3.4.3. *Agrochemicals*

Even more severe is the chemical attack brought upon the polymer films by the use of agrochemicals combined with the UV irradiation in greenhouses. The agrochemicals most commonly used are sulphur and halogen containing compounds. Trials have shown that combinations of agrochemicals can severely limit the service life of the LDPE greenhouse coverings (Dilara & Briassoulis, 1998; Henninger, 1992; Desriac, 1991). Sulphur containing pesticides were shown to be particularly harmful and extremely high concentrations of sulphur have been found in LDPE films after pesticide use. In a relevant study (Desriac, 1991), the effect of the daily spray of cyspermethrin on three types of films, long-life PE, filled PE and EVA, was studied in conjunction with accelerated ageing. All films showed increased degradation, compared to the non-sprayed films, starting at 12–16 d of accelerated ageing depending on the film. The problem of rapid degradation due to pesticide use could not be controlled by increased concentration of stabilizers, but increased thickness seemed to improve the situation.

Similar results were reported from studies of natural ageing performed in Spain (Barahona & Gomez-Vasquez, 1985) and Italy (Henninger & Pedrazetti, 1988). In fact, it is clear that the problem depends heavily on the type of pesticide applied, the method and frequency of application, ventilation and the structure of the greenhouse.

4. Mechanisms of stabilization

As was discussed in the previous section, polyethylene deteriorates rapidly on continuous exposure to the various types of degradation. Indeed, degradation can sometimes set in within only a few months, resulting in a marked decrease in strength leading ultimately to disintegration.

Other additions to the formulation of greenhouse films include antioxidants and photostabilizers.

4.1. *Photostabilizers*

In theory, PE should be photo-oxidatively stable, however, the presence of impurities impart photosensitivity on the LDPE films. Special measures are therefore needed in order to protect the polyethylene films against the solar radiation (with wavelengths of 290–1400 nm) and especially its most energetic and therefore harmful portion, the part of UV radiation contained between 290 and 400 nm.

The first class of UV stabilizers are UV absorbers. This class of chemicals act by absorbing the harmful UV radiation above 290 nm and not allowing it to reach the chromophores. The corresponding energy has then to be dissipated without initiating photosensitization. This is achieved by various mechanisms, either by an extremely fast non-radiative decay from the excited state to the ground state, or by formation of internal bonds (Gugumus, 1979). However, this class of stabilizers seems to perform better in more thick sections, (thicker than 100 μm), and further development may lead to increased performance of thin plastic films as well. Alternatively, they may be used in combination with other stabilizers, such as Ni quenchers or hindered amine light stabilizers (HALS), achieving synergetic results.

The second widely used class of chemicals for improving the resistance to the UV radiation of the PE films is Ni quenchers. Chemicals classified as quenchers act by deactivating the excited states of the chromophoric groups responsible for the photoinitiation by energy transfer, instead of relying on direct absorption of the UV radiation. With proper selection of the Ni quencher, the results of the UV stabilization are satisfactory. However,

in order to limit the environmental impact of Ni, such formulations are expected to be limited by law in the near future.

The discovery of the hindered amine light stabilizers (HALS) was the next significant step in the stabilization of polymers. This class of chemicals, being stable free radicals based on piperidine, or piperazine have the capability of trapping radicals produced from photochemical oxidation (Gugumus, 1979; Klemchuk, 1985). These stabilizers are colourless, compared with the greenish/yellow films resulting from the use of Ni quenchers and can result in accelerated growth of the crop. They also pose no environmental problems and can have superior light and heat stability. However, many unexpected problems of premature failure can occur during their use in greenhouses due to their interaction with the pesticides used. Both sulphur and chlorine containing agrochemicals inhibit the functioning of the HALS and can have a very detrimental effect on the life of the greenhouse film (Henninger, 1992). However, HALS stabilized greenhouse films were shown to last 33% longer than Ni stabilized films in testing under real conditions and being sprayed with a variety of agrochemicals. It should also be noted that HALS additives act also as heat stabilizers and minimize the effect of high temperatures.

5. Degradation of low-density polyethylene used as greenhouse covering material

The performance of the plastic film used as covering material in protected cultivation, as well as its service life depend strongly on (a) the original properties of the materials and (b) how these material properties are altered by the various factors which can induce ageing of the plastic film (Briassoulis *et al.*, 1997b; Dilara & Briassoulis, 1998). Various factors, some of which are particular to the greenhouses, affect the ageing of the material. Such factors include the structure and the micro-climate of the greenhouse, the climatic conditions of the area where the structure is installed, the use of agrochemicals and others (Khan & Hamid, 1995). The methods by which the degradation may be detected and measured are described elsewhere (Dilara & Briassoulis, 1998).

5.1. Degradation parameters

The environmental parameters that affect the degradation of greenhouse cladding films in general can be divided in the following three categories:

(a) *the climate*, such as the solar radiation, temperature, wind, rain, hail and snow;

(b) *the greenhouse* itself, such as the structure and geometry, the adequate fixing of the film, the protection of the film at the point of contact with the greenhouse structure and the microclimate inside the greenhouse; and

(c) *the cultivation practices*, such as type of crop, use and type of pesticides and active ingredient.

5.1.1. Climate

5.1.1.1. Solar irradiation

Stabilization of various grades of commercial greenhouse films of LDPE with a mixture of UV absorber, Ni quencher and antioxidant results in life expectation, measured under artificial ageing, to the equivalence of 18–24 months (Ram *et al.*, 1980). In the same study, degradation, as shown by the increase in carbonyl content, started only after 1000 h of artificial ageing (the equivalent of 9–12 months of natural weathering), while studies of natural ageing (Amin *et al.*, 1995) showed an increase in carbonyl content from the start of the exposure. Significant degradation, exhibited by 22% drop in stress at break, was observed after 36 months of exposure of similar films on aluminium racks in a harsh environment, with high heat, solar irradiation, humidity, salt content in the air and low rainfall (Amin *et al.*, 1995). It should be noted that unprotected LDPE films were shown to fail to function (50% retained elongation) in the equivalent of less than two months of exposure (Ram *et al.*, 1980), while linear low-density PE (LLDPE) films showed a 50% drop of tensile strength at break after only three months of natural exposure in a hot country (Qureshi *et al.*, 1990). It is apparent that the rate of degradation is significantly affected by the time elapsed since the initiation of the process. This effect, being a function of time, varies in a rather complicated way depending on several interacting factors and it is not yet fully understood.

In the same studies (Amin *et al.*, 1995; Qureshi *et al.*, 1990), the predominant reaction mechanism was believed to be chain scission due to a drop in molecular weight. Further studies (Khan & Hamid, 1995) have revealed that exposure of HALS stabilized PE films on a scale model greenhouse leads to increased degradation, as seen by higher carbonyl content and worse mechanical properties, when compared to exposure on aluminium racks, due to the special micro-environment created in the greenhouse and the pesticides used. However, LDPE agricultural films, due to their method of production (blow-extrusion) which imparts orientation in the films, are approximately twice as stable as isotropic specimens of the same material (Komitov, 1989).

Photo-degradation is further complicated by various interacting factors. In cases where the effect of UV radiation is combined with varying temperature conditions, water absorption, critical mechanical loads, friction,

abrasion and exposure to agrochemicals, ageing can be accelerated at various rates. For instance, high abrasion of the film by sand or soil particles carried by the wind in Crete, Greece, and other Mediterranean countries leads to the creation of high concentrations of active centres which induce increased photo-degradation (Dilara & Briassoulis, 1998).

5.1.1.2. *Temperature*

Cyclic temperature changes, with high temperatures, such as those developed at the metal parts of the greenhouse construction during a hot and sunny day, combined with low temperatures during the night can also lead to increased degradation. Simulated weathering experiments showed a fourfold increase in the oxidation rates of polyethylene exposed to 300 nm radiation between 10 and 50°C (Winslow, 1972).

5.1.1.3. *Humidity and rainfall*

Increased humidity, as well as rainfall, can lead to the gradual removal of any water-soluble performance enhancing additives, and thus to lower resistance to oxidation and speedy degradation. In fact, it has been shown that thicker films perform better because there exists a reservoir of stabilizers in the centre of the film (Ram *et al.*, 1980). Another way in which the humidity can affect the degradation of the plastic film is photochemical, by the generation of hydroxyl radicals or other reactive species which can promote various free-radical reactions (Hamid *et al.*, 1992). However, in a study in which a lightly stabilized LDPE film underwent artificial ageing under UV and UV combined with rain cycles, it was shown that the water spray acted as inhibitor of the ageing process (Nijskens *et al.*, 1990).

5.1.1.4. *Snow*

Accumulation of snow on the roof of greenhouse structures, especially for prolonged periods of time, can lead to problems of creep, due to constant loading. Also, the low temperatures and humidity occurring due to the snow may impose additional strain to the polymer network. Furthermore, if the film is stressed tightly over the greenhouse structure the change of dimensions occurring due to the temperature changes might also impose additional stresses on the film. All this leads to high mechanical degradation of the film. In cases of tear initiated by sharp objects or otherwise introduced in the film, tear propagation under critical snow loading may become an important factor of mechanical degradation and eventually failure.

5.1.1.5. *Hail*

Hail can and regularly does lead to failure due to puncturing or localized material yielding of the films. However, this is catastrophic failure and cannot be considered as degradation of the polymer.

5.1.1.6. *Wind*

Wind loads can impose increased tensile and shear stress on the plastic film leading to premature failure of the film (yielding, rupture or tearing), or in certain cases even to destruction of the greenhouse structure. Furthermore, a study suggests that tearing due to high wind can be a major problem in greenhouses (Tsirogiannis, 1996). Another problem connected with windy areas is the abrasion caused by soil or sand and other particles which are carried by the wind and impinge the surface of the greenhouse film. Finally, dynamic loading due to wind may lead to fluttering of the film against wires supporting the film with local oxidation of the film and adverse consequences for its resistance. Wind loading may also affect the load transfer and load distribution mechanisms developed by the cover-greenhouse frame system (Briassoulis *et al.*, 1997a). Such an effect may result in over-stressing of the covering material.

5.1.2. *Greenhouse construction*

All of the following parameters can affect the degradation of the greenhouse covering film, by various combined mechanisms. The structure, geometry and the adequate fixing of the film can lead to mechanical degradation. By imposing unnecessarily large design loads on the film itself, the mechanisms for mechanical degradation occur, leading to bond scission.

The protection of the film at the point of contact with the greenhouse structure is also of great importance, because its absence can lead to chemical degradation. Indeed, a lot of damage is usually observed in the places where the plastic film comes in contact with the metallic greenhouse structural elements (Khan & Hamid, 1995), especially if proper care to minimize overheating of the metal parts with painting is not taken (temperatures at those contact points may reach up to 70°C (von Elsner, 1997)). Note that painting of the metal parts of the greenhouse construction that come into direct contact with the plastic films is also recommended for another reason. Metal particles may catalyse the reactions of photo-oxidation, leading to unnecessarily high rates of degradation (Khan & Hamid, 1995).

The microclimate inside the greenhouse with increased humidity can lead to premature removal of any film additives. The problem can occur especially in the new generation of anti-fogging films. These films, in order to avoid droplet formation, create a water film on the internal surface of the polyethylene film. As explained in the section on humidity above, this may lead to increased removal of all water-soluble film additives and therefore to a worse overall performance of the covering material.

Another important factor of the microclimate is the internal temperature of the greenhouse. As studies have shown (Papadakis *et al.*, 1989), temperature differences of

+17°C from the outside temperatures can develop inside a greenhouse, due to poor construction, poor management of the equipment (*e.g.* shading) or poor ventilation. This puts an additional strain on the plastic film and in extreme cases it can lead to a rapid deterioration of the film's structure. Thus, for example, it has been observed in cases of using internal curtains for shading during summertime in Crete, Greece, that the hot air trapped between the covering and the curtain may result in severe degradation of the film (*e.g.* reduction of the useful life of the plastic film by one year).

5.1.3. Cultivation practices

The type of crop in cultivation, although it may have no direct influence on the degradation mechanisms for the greenhouse covering films, dictates the type of agrochemicals to be used, basically the active ingredient, the frequency and method of application. Also, the micro-climate control is directly related to the cultivation needs and may affect several critical factors (such as temperature, humidity, ventilation and ventilation openings, wind pressure). For instance, high temperatures lead to an increase in the rate of reaction for both photo-oxidation and chemical oxidation by the agrochemicals and thus to higher degradation rates.

5.2. Film formulation

Photostabilizers are a necessary addition to the PE films, because LDPE films are easily influenced by solar radiation, heat and oxygen and degrade in only a few months by the combined action of all three elements.

Most LDPE greenhouse films in the market today comprise of co-extruded multi-layered films with 4–10% EVA. Other additions to the formulation include photostabilizers (HALS, Ni quenchers) and special anti-fog materials. Three-layered structures are the norm, and five- to seven-layered films are produced for specific applications.

Such advanced layered films possess several advantages over a single film. The individual layers can be provided with specific compositions according to need. For instance, the concentration of the special anti-fog additive is usually significantly higher in the innermost layer. This provides a deposit of this performance enhancing component in the layer which is the least affected by weathering. Indeed, as the anti-fog additive is depleted from the film surface, its diffusion from the innermost to the surface layer is caused by a gradient in its concentration (Ram *et al.*, 1980). Another example is the use of EVA additive in the middle layer. This additive is used in order to improve the properties of the PE films, as was explained earlier. However, along with the useful

properties, EVA-doped films have some disadvantages. They are elastic, with higher creep rate, sticky and tend to attract dust and therefore lose their transparency in short time. These problems can be overcome if the high EVA-doped film is introduced in the middle of two PE films. Such clever engineering of the LDPE films has proven to prolong both their performance and service lifetime. In other attempts at improving the service life of the films (Sanchez Lopez *et al.*, 1994), use was made of blends of LDPE with linear low-density PE (LLDPE) which possess superior mechanical properties. These blends, appropriately stabilized, were shown to have satisfactory resistance.

6. Conclusions

A very large quantity of plastics is used world-wide, on a yearly basis, for the purpose of protecting cultivation. A significant portion of this amount is made of low-density polyethylene (LDPE) films, whose use is widely spread in the countries of the Mediterranean region. Thin LDPE films are used due to their relatively good mechanical and optical properties, combined with a competitive market price. However, contrary to other agricultural applications, LDPE films for protected cultivation are easily affected by the harsh environmental conditions met during their use. A combination of harmful factors, such as solar radiation, temperature, agrochemical use, humidity and others can eventually alter the chemical structure of the polymer and compromise both its mechanical as well as its optical properties. Among others, a significant reason for this rapid degradation is the reduced thickness of these plastic films when compared to other agricultural applications. Consequently, the life of plastic films used for protected cultivation varies from a minimum of one cultivating season to a maximum of two to three years, and, at the end of its useful life all this plastic is classified as waste.

It was shown that the degradation of LDPE films used as greenhouse covering materials, involves complex and to some extent interacting processes, such as photo-degradation through reactions catalysed by the presence of UV-irradiation, chemical degradation through reactions with air pollutants and agrochemicals and finally mechanical degradation by bond rupture under the influence of mechanical stress. However, clever engineering of the films, based on a better knowledge of the degradation mechanisms, may lead to improved performance and extended service life.

While research in the degradation of LDPE films in general, is rather extensive, a knowledge gap has been identified in this paper concerning the degradation mechanisms and processes of LDPE greenhouse covering

films. In the future, scientific research in the area should focus into elucidating the influence on the degradation characteristics of the parameters connected with the use of various qualities of LDPE films in greenhouses. Further research is also needed in specialized protection measures and stabilization processes for such films. In particular, emphasis has to be placed on improving the performance of the stabilizers with respect to their functioning under the combined effect of the various interacting factors involved in the complicated degradation process.

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