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Variation of physical properties of LDPE greenhouse films due to agrochemicals used during cultivation

Evelia Schettini*, Giuliano Vox

Department of Agricultural and Environmental Science, University of Bari, Italy

Abstract

During protected cultivation, the use of agrochemicals influence the degradation of the greenhouse plastic films. A research was carried out to evaluate how agrochemicals contamination and solar radiation influence the physical properties of low density polyethylene (LDPE) films. The LDPE films were manufactured on purpose adding different anti-UV stabilizer systems and were exposed to natural outdoor weathering at the experimental farm of the University of Bari (Italy; 41° 05' N). Each film was tested as covering of two low tunnels: one was sprayed from inside with commercial agrochemicals containing iron, chlorine and sulphur while the other one was not sprayed and used as control. Radiometric tests were carried out on the new films and on film samples taken at the end of the trial. Analyses on absorption of the selected contaminants were carried out in laboratory on the samples taken at the end of the exposure in the field in order to compare the relative effectiveness of the stabilizing systems under evaluation. The experimental tests showed that the natural weathering together with the agrochemicals did not modify significantly the radiometric properties of the films in the solar and PAR wavelength range. Significant variations were recorded for the stabilised films in the LWIR wavelength range.

Correspondence: Evelia Schettini, Department of Agricultural and Environmental Science, University of Bari, via Amendola 165/A – 70126 Bari, Italy.
Tel. +39 080 5443060- Fax+39 080 5442977.
E-mail: evelia.schettini@uniba.it

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Introduction

The radiometric properties of films used for crop protection influence the microclimate of the protected volume, i.e. the air temperature and relative humidity, the soil temperature, the quantity and quality of the solar radiation, modifying the growing condition of the crop in comparison with the external climatic conditions. The time stability of the radiometric properties of the film during the crop cycle cultivation is important when assessing the potential benefits of different materials on microclimate and on crop growth. The average service life for plastic films used to cover greenhouses ranges from some months up to three or four years in the Mediterranean region. Film lifetime is influenced by parameters related both to the film itself and to the environment in which the film is used (Desriac, 1991; Dilara and Briassoulis, 2000; Briassoulis, 2005; Ruiz *et al*., 2006; Stefani *et al*., 2008).

The ultra violet (UV) radiation in the solar spectrum, especially the UV-B and UV-A radiation that occur in the wavelength range from 280 nm to 400 nm, is one of the factors that mainly influences the ageing degradation process by leading to bond cleavage and depolymerisation (Nijskens *et al*., 1990; Dilara and Briassoulis, 1998). The use of UV-stabilizers, such as UV absorbers, hindered amine light stabilizers (HALS) and nickel quenchers, mitigates the degradation through the prevention of solar radiation absorption as well as minimizing any subsequent radical oxidation reactions. UV stabilisers absorb UV radiation and dissipate it into heat; HALS additives decompose radicals while nickel quencher deactivate radicals, hampering the degradation process (Sanchez-Lopez *et al*., 1991).

Agrochemical substances influence greenhouse film degradation due to their active principles, method of application and frequency, greenhouse ventilation and structure (Dilara and Briassoulis, 2000). Agrochemicals based on sulphur and chlorine generate sub-products of the used pesticides that lead to a deterioration of the covering films together with a reducing of their mechanical and physical properties (Kham and Halim, 1995; Rull and Marin, 2006; Espi *et al*, 2007; Vox *et al*., 2008; Stefani *et al*., 2011; Schettini and Vox; 2012).

Aim of the research is to study the effects of agrochemicals containing iron, chlorine and sulphur, which are sprayed during cultivation, on greenhouse plastic films degradation. Three low density polyethylene (LDPE) greenhouse films were tested changing the UV-stabilizers added to the base polymer. Natural outdoor weathering, radiometric tests, and analyses on the absorption of selected contaminants were carried out to evaluate the detrimental effect of ageing and of agrochemical application on different covering films actually used in the Mediterranean region.

Materials and methods

Low density polyethylene (LDPE) films were manufactured on purpose by P.A.T.I. S.p.A. company (San Zenone degli Ezzelini, TV, Italy) with a nominal thickness of 100 μm, using the single layer blow-extrusion technology. The UV stabilizers, such as triazine UV absorbers, benzophenone UV absorbers, polymeric HALS, and N-alkoxy (NOR) HALS, were added to the basic polymers with a percentage not revealed, since these formulations are proprietary. Each film was identified by a code as shown in Table 1.

The films were exposed to natural outdoor weathering at the experimental farm of the University of Bari (Valenzano, Bari, Italy; 41° 05' N, 16° 53' E, 85 m asl). The test started in Spring 2009, allowing the highest solar irradiation of the films during the warmest period of the year, and ended when the first film was broken. Each film was used to cover two low tunnels (Figure 1): one of the tunnels was sprayed (code S) with the agrochemicals while the other one was not sprayed and used as control (code C). Each low tunnel had a length of 20.0 m, a width of 1.0 m and a height of 0.8 m, with N-S orientation.

The agrochemicals were sprayed onto the films by a system consisting of a pump connected with pipes and nozzles located inside the low tunnels. A water solution with a foliar fertilizer containing iron (Sequestrene® Life, Syngenta Crop Protection S.p.A., Milan, Italy), a fungicide containing sulphur (Tiovit® Jet, Syngenta Crop Protection) and a fungicide containing chlorine (Topas®, Syngenta Crop Protection) was sprayed weekly during the period test. The doses of the active principles of the agrochemicals were: 0.500 g/m^2 for sulphur; 0.028 g/m^2 for chlorine; 0.034 g/m^2 for iron.

Table 1. LDPE greenhouse covering films.

Film code	Stabilizers
A4	No stabilizers
D4	NOR-HALS + triazine UV filter
H4	HALS + benzophenone UV filter

Figure 1. The experimental field at the University of Bari (Italy).

Solar radiation was measured by a pyranometer (model 8-48, Eppley Laboratory, Newport, RI, USA) in the wavelength range 0.3-3 mm; data were recorded by a data logger (CR10X, Campbell, Logan, USA) every 60 s and stored as 15 min average values. The cumulative solar radiation for the exposure period was calculated.

Radiometric tests on the new films and on samples taken at the end of the trial were carried out at the University of Bari. Spectral transmissivity $\tau(\lambda)$ of a material is the fraction of the incident energy radiant flux that is transmitted at a specific wavelength λ. Spectral direct transmissivity in the wavelength range between 300 and 2500 nm were measured by means of a spectrophotometer (UV-VIS-NIR Lambda 950, Perkin-Elmer Instruments, Norwalk, CT, USA) in steps of 10 nm using radiation with a direct perpendicular incidence. Spectral total transmissivity was measured by means of an integrating sphere (diameter 60 mm) used as receiver of the Lambda 950 spectrophotometer. Spectral diffuse transmissivity was calculated by subtracting the direct transmissivity from the total transmissivity. The transmissivity coefficients were calculated as weighted average values of the transmissivity over the wavelength interval between 300 and 2500 nm for the solar range, and between 400 and 700 nm for the photosynthetically active radiation (PAR) range using the spectral distribution of the terrestrial solar radiation as weighting function (Vox and Schettini, 2007). The transmissivity in the long wave infra-red radiation (LWIR) range between 2500 and 25000 nm was measured by a spectrophotometer (FT-IR 1760X, Perkin-Elmer Instruments, Norwalk, CT, USA) in steps of 4 cm^{-1}. Spectral transmissivity was measured using radiation with a direct perpendicular incidence. The transmissivity coefficient in the LWIR range was calculated as average value of the spectral transmissivity in the wavelength range from 7500 to 12500 nm, where the bodies at ambient temperature have the maximum energy emission as expressed by Planck's spectral distribution of emissive power (Vox and Schettini, 2007).

The absorption of chlorine, iron and sulphur was estimated at the Venezia Tecnologie laboratories (Venice, Italy), using fluorescence X-ray elementary semiquantitative analysis.

Results and discussion

Table 2 show the radiometric parameters of the films tested, i.e. the total transmissivity coefficients calculated in the solar (300-2500 nm),

Table 2. Radiometric coefficients of the LDPE films; 0: new film; C: control film; S: sprayed film; trans.: transmissivity.

Film	Exposure time, days	Cumulative solar radiation, MJ/m^2	Total solar trans., %	Total PAR trans., %	Total UVA trans., %	LWIR trans., %
A4_0	0	0	89.2	88.6	80.5	78.8
A4_C	108	2428	90.7	90.9	79.6	67.9
A4_S	108	2428	89.8	89.0	72.4	55.5
D4_0	0	0	89.4	90.2	49.3	74.2
D4_C	108	2428	90.0	90.3	50.5	71.9
D4_S	108	2428	89.2	88.6	55.3	60.8
H4_0	0	0	88.1	88.4	30.2	72.1
H4_C	108	2428	88.2	87.3	28.1	70.4
H4_S	108	2428	87.7	86.6	31.6	60.4

in the PAR (400-700 nm), in the UVA (320-380 nm) and in the LWIR (7500-12500 nm) wavelength range. These coefficients were evaluated at the beginning of each trial for the new films (coded 0) and at the end of the trials both for the control films (coded C), subjected only to the natural weathering, and for the sprayed films (coded S), subjected to the natural weathering and to the spray of the agrochemicals. The cumulative solar radiation was calculated from the day of the film installation. In the solar and in the PAR wavelength range the radiometric properties of all the films varied less than 5% between the values measured at the beginning of the trial and the end of the trial.

In the LWIR range the stabilised films showed variations less than 20% between the values measured at the beginning of the trial and the end of the trial; the A4 film, a not stabilised film, showed a higher decrease (about 30% from its initial value). Figures 2 shows the spectral transmissivity of the H4 films in the LWIR wavelength range, between 2500 and 25000 nm; the curves concern the new film (H4_0), the control film (H4_C) and the sprayed film (H4_S) after the exposure in the field. The H4 film showed changes of its radiometric properties at the end of the exposure in the field. The variation of the transmissivity in the LWIR range suggests changes in the chemical structure of the films. Greenhouse covering films must satisfy the EN 13206 (2001) standard; it establishes that the films, with a thickness of 100 m, must have a PAR total transmissivity coefficient higher than 85%. The films were always characterised by higher values for the PAR total transmissivity coefficient, ranging from 86.6% (H4_S) to 90.9 % (A4_C).

Table 3 shows the absorption of the chemical contaminants, such as chlorine, iron, and sulphur, of the films tested at the end of their exposure in the field. The H film was characterised by the highest sulphur and chlorine absorption in comparison with the other films sprayed in the same way and at the same time intervals.

Table 3. Contaminants in the LDPE films at the end of film exposure in the field.

Film	S (ppm)	Cl (ppm)	Fe (ppm)
A4_S	1600	250	150
D4_S	2100	170	150
H4_S	3600	300	150

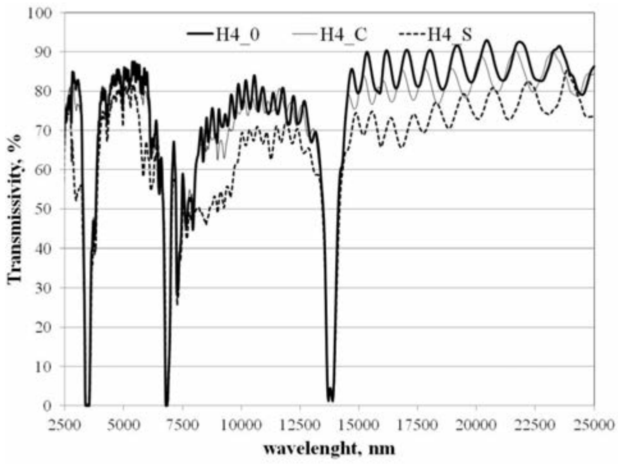

Figure 2. Long wave infrared (LWIR) spectral transmissivity of the H4 film in the wavelength range 2500-25000 nm; H4_0, new film; H4_C: control film exposed only to natural weathering; H4_S: film exposed to natural weathering and to agrochemicals.

Conclusion

The research showed that the radiometric properties of the films in the solar and in the PAR wavelength range were not significantly modified during their exposure to climatic agents and to the agrochemicals; the variation of the transmissivity coefficients was less than 5%. Variations less of 20% of the initial value were recorded between the values measured at the beginning and the end of the test for the radiometric coefficients of the stabilised films in the LWIR wavelength range.

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