Effects of agrochemicals, ultra violet stabilisers and solar radiation on the radiometric properties of greenhouse films

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Abstract

Agrochemicals, based on iron, sulphur and chlorine, generate by products that lead to a degradation of greenhouse films together with a decrease in their mechanical and physical properties. The degradation due to agrochemicals depends on their active principles, method and frequency of application, and greenhouse ventilation. The aim of the research was to evaluate how agrochemical contamination and solar radiation influence the radiometric properties of ethylene-vinyl acetate copolymer greenhouse films by means of laboratory and field tests. The films, manufactured on purpose with the addition of different light stabiliser systems, were exposed to natural outdoor weathering at the experimental farm of the University of Bari (Italy; 41° 05' N) in the period from 2006 to 2008. Each film was tested for two low tunnels: one low tunnel was sprayed from inside with the agrochemicals containing iron, chlorine and sulphur while the other one was not sprayed and served as control. Radiometric laboratory tests were carried out on the new films and on samples taken at the end of the trials. The experimental tests showed that both the natural weathering together with the agrochemicals did not modify significantly the radiometric properties of the films in the solar and in the photosynthetically active radiation wavelength range. Within six months of experimental field tests the variations in these radiometric characteristics were at most 10%. Significant variations, up to 70% of the initial value, were recorded for the stabilised films in the long-wave infrared radiation wavelength range.

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Introduction

The radiometric properties of covering greenhouse films influence both the energy balance of the greenhouse and the crop behaviour (Kittas and Baille, 1998; Papadakis *et al.,* 2000; Vox *et al.,* 2010). The microclimate of the protected volume modifies the growing conditions of the crop in comparison with the external climatic conditions according to the quantity and quality of the solar radiation passing through the covering. The stability over time of the radiometric properties of the film during the crop cultivation cycle is an important goal for growers.

Physical and mechanical properties decrease when the plastic film covering degrades in the field by discolouration, cracking of the surface, and stiffening. The average service life of plastic greenhouse films depends on parameters related both to the film itself and to the environment in which the film is used (Briassoulis, 2005; Briassoulis and Schettini, 2003; Desriac, 1991; Dilara and Briassoulis, 1998, 2000; Khan and Hamid, 1995; Martin-Closas *et al.,* 2008; Ruiz *et al.,* 2006), varying from 3-6 months, for one cultivation season, to a maximum of 3-4 years in the Mediterranean area. The ultra violet (UV) radiation in the solar spectrum absorbed by the plastic films is one of the factors that have the biggest influence on the ageing and degradation process (Nijskens *et al.,* 1990; Dilara and Briassoulis, 1998). The UV radiation, especially the UV-B and UV-A radiation that occurs in the wavelength range 280-400 nm, causes photo-degradation by leading to bond cleavage and depolymerisation. Film lifespan in greenhouse applications can be extended by adding UV-stabilisers to mitigate degradation through the prevention of solar radiation absorption, as well as by minimising any subsequent radical oxidation reactions (Sanchez-Lopez *et al.,* 1991). UV absorbers, hindered amine light stabilisers (HALS) and nickel quenchers are UV stabilisers. UV stabilisers absorb UV radiation and dissipate it into heat; HALS additives decompose radicals while nickel quenchers deactivate radicals, hampering the degradation process (Sanchez-Lopez *et al.,* 1991).

Film lifespan is also affected by agrochemicals commonly sprayed by the growers due to a generation of by products that lead to a deterioration of the covering materials together with a variation in their mechanical and physical properties (Khan and Hamid, 1995; Espí *et al;* 2007; Rull and Marin, 2006). The degradation due to agrochemicals depends on their active principles, application method and frequency, ventilation and greenhouse structure (Dilara and Briassoulis, 2000).

The aim of the research is to study the effects of agrochemicals containing iron, chlorine and sulphur combined with solar radiation on the radiometric properties of ethylene-vinyl acetate copolymer (EVA) films used in greenhouse cultivation. The films were manufactured with the addition of different light stabiliser systems and were subjected to natural outdoor weathering in the experimental field. Radiometric tests were carried out in the laboratory on the new films and on samples taken at the end of the trials.

Materials and methods

The films, manufactured for the purpose by the P.A.T.I. S.p.A. company (San Zenone degli Ezzelini, Treviso, Italy), were tested during three different campaigns of trials in the period 2006-2008. All the films were 100 μm thick and were made using the single layer blow-extrusion technology. Each film was identified by a code (Table 1): the letter (from *A* to *E*) indicates the type of stabilisers used; the number (from *1* to *3*), the year of the field trial. The percentages of the basic polymers and additives represent proprietary information and as such were not disclosed. UV stabilisers, *i.e.* triazine UV absorbers (Cytec Cyasorb® 1164), photoluminescent UV absorbers (VIBA UV Master 03081), methylated HALS (Cytec Cyasorb® UV-3529), and aminoether type hindered amine light stabiliser (NOR-HALS) (Ciba, now BASF, Tinuvin® NOR371), were added, alone or in combinations, to the basic polymers. EVA films, made with a copolymer including 5% vinyl acetate, were tested during 2006, 2007 and 2008. The E films were made of EVA and thermoplastic polyurethane for the 2007 and 2008 tests. In addition, each year an EVA film without stabilisers was also tested.

The greenhouse covering films were tested at the experimental farm of the University of Bari (Valenzano, Bari, Italy; 41° 05' N) (Figure 1). Each film was exposed to natural outdoor weathering and was used to cover two low tunnels without vegetation: one of the two tunnels was sprayed from inside with the agrochemicals (coded S) while the other one was not sprayed and used as control (coded C). Each low tunnel was 20.0 m long, 1.0 m wide and 0.8 m high, with a North-South orientation. Each year the natural outdoor weathering started in spring and ended in autumn allowing the highest solar irradiation of the films during the warmest period of the year. The first test started on 20/04/2006 and ended on 30/10/2006 after 193 days, the second test started on

Table 1. Stabiliser systems used in the manufacturing of the greenhouse films tested at the University of Bari, Italy.

Film code	Stabilisers				
	No stabilisers	Polymeric HALS	NOR-HALS	Triazine UV filter	Photoluminescent UV filter
A1	X				
B1		X			
C1			X		
D1			X	X	
A2	X				
B2		X			
C2			X		
D2			X	X	
E2					X
A3	X				
B3		X		X	
D3			X	X	
E3			X		

HALS, hindered amine light stabilisers; NOR-HALS, aminoether type hindered amine light stabilisers; UV, ultra violet. Letter in the film code indicates the stabiliser system. Number indicates the trial year: 1, 2006; 2, 2007; 3, 2008.

Table 2. Radiometric coefficients of the films tested during the 2006 trial.

Film	Exposure time, days	Cumulative solar radiation, MJ/m^2	Solar trans, %	PAR trans, %	UVA trans, %	LWIR trans, %
A1_0	0	0	89.5	89.1	80.8	62.3
A1_C	193	3360	88.6	87.3	73.9	47.5
A1_S	193	3360	86.0	84.2	62.6	34.7
B1_0	0	0	88.1	88.3	45.7	59.3
B1_C	193	3360	87.6	87.1	48.8	58.1
B1_S	193	3360	88.7	87.8	45.0	49.6
C1_0	0	0	90.2	90.1	78.6	57.3
C1_C	193	3360	88.4	87.5	77.3	56.6
C1_S	193	3360	89.9	88.8	71.5	40.9
D1_0	0	0	90.2	91.0	37.2	57.9
D1_C	193	3360	89.2	89.2	34.5	55.6
D1_S	193	3360	88.7	88.5	35.4	50.0

PAR, photosynthetically active radiation; UVA, ultraviolet radiation; LWIR, long wave infrared radiation; 0, new film; C, control film; S, sprayed film; trans, transmissivity. Solar wavelength range, 300-2500 nm; PAR wavelength range, 400-700 nm; UVA wavelength range, 320-380 nm; LWIR wavelength range, 7500-12,500 nm.

20/04/2007 and ended on 19/10/2007 after 182 days, and the third test started on 29/04/2008 and ended on 4/11/2008 after 189 days.

The greenhouse films were sprayed with a water solution containing agrochemicals based on sulphur, iron and chlorine weekly for six months in each year-test by a system consisting of a pump connected with pipes and nozzles located inside the low tunnels. The choice of iron, chlorine and sulphur was based on a private communication by P.A.T.I. S.p.A. (2006) that made available the results of a survey into the causes of early film failures, including detected contamination as chemical elements and their concentration in the film. The commercially available agrochemicals applied were: i) a foliar fertiliser containing iron with the trade name Sequestrene® Life (Syngenta Crop Protection S.p.A., Milan, Italy); ii) a fungicide containing sulphur with the trade name Tiovit® Jet (Syngenta Crop Protection); iii) a fungicide containing chlorine with the trade name Topas® (Syngenta Crop Protection). The doses of the active principles of the agrochemicals sprayed weekly per square meter of film surface area during the tests were: 3.35 g/m^2 for sulphur; 0.21 g/m^2 for chlorine; 0.26 g/m^2 for iron during 2006; 2.00 g/m^2 for sulphur; 0.13 g/m^2 for chlorine; 0.15 g/m^2 for iron during 2007; and 0.500 g/m^2 for sulphur; 0.03 g/m^2 for chlorine; 0.03 g/m^2 for iron during 2008. The doses of the active principles of the sprayed agrochemicals were modified every year in order to tentatively approach the concentrations of contaminants corresponding to the limits of contamination suggested by CEPLA (2012) and according to the confidential releases by the P.A.T.I. (2006).

Solar radiation hitting the films was measured by a pyranometer (model 8-48, Eppley Laboratory, Newport, RI, USA) in the wavelength range 0.3-3 μm. Air temperature inside and outside the tunnels was measured by means of thermistors. Data were recorded every 60 s by two data loggers (CR 1000 and CR 10X, Campbell, Logan, USA) and stored as 15 min average values.

Radiometric tests were carried out at the University of Bari by means of two spectrophotometers in order to evaluate the spectral transmissivity of film samples at the beginning and at the end of the trial. Spectral transmissivity $\tau(\lambda)$ of a greenhouse film is the fraction of the incident energy radiant flux that is transmitted at a specific wavelength λ. Radiometric properties of the covering materials were defined by means of the transmissivity coefficients calculated as average values of the spectral transmissivity over different wavelength bands: the solar wavelength range (300-2500 nm), the photosynthetically active radiation (PAR) range (400-700 nm) and the long wave infrared radiation (LWIR) range (7500-12,500 nm).

Spectral direct transmissivity was measured in the solar range, from 200 to 2500 nm, by a double beam UV-VIS-NIR spectrophotometer (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, with a double beam comparative method (Wendlandt and Hecht, 1966). Spectral diffuse transmissivity was calculated by subtracting the direct transmissivity from the total transmissivity. The transmissivity coefficient in the solar range was calculated as the weighted average value of the spectral transmissivity using the spectral distribution of the solar radiation at the ground level as weighting function (Duffie and Beckman, 1991; Papadakis *et al.,* 2000; Vox *et al*., 2005; Vox and Schettini, 2007; Sica and Picuno, 2008; De Salvador *et al.,* 2008).

Spectral transmissivity in the LWIR range, between 2500 and 25,000 nm, was measured by an FT-IR spectrophotometer (1760 X, Perkin-Elmer Instruments, Norwalk, CT, USA) in steps of 4 cm^{-1} using radiation with a direct perpendicular incidence. The transmissivity coefficients in the LWIR range were calculated as average values of the spectral transmissivity in the wavelength range from 7500 to 12,500 nm (Papadakis *et al.,* 2000; Vox and Schettini, 2007).

Results and discussion

The radiometric parameters of the films tested, *i.e.* the total transmissivity coefficients calculated in the solar, in the PAR, in the UVA and in the LWIR wavelength ranges, are shown in Tables 2-4. The radiometric tests were carried out on samples taken 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 2008 trial, the average values of the maximum, minimum and mean daily air temper-

Table 3. Radiometric coefficients of the films tested during the 2007 trial.

Film	Exposure time, days	Cumulative solar radiation, MJ/m^2	Solar trans, %	PAR trans, %	UVA trans, %	LWIR trans, %
A2_0	0	0	94.3	94.3	91.8	62.1
A2_C	182	3614	87.0	85.8	73.7	51.7
A2_S	182	3614	86.0	83.8	55.6	18.6
B2_0	0	0	91.6	92.0	56.6	58.9
B2_C	182	3614	86.8	86.0	53.3	56.5
B2_S	182	3614	86.3	84.3	56.9	26.2
C2_0	0	0	94.0	94.3	81.9	57.8
C2_C	182	3614	88.1	87.3	76.4	56.4
C2_S	182	3614	88.6	86.4	58.3	18.4
D2_0	0	0	93.3	94.6	37.4	56.8
D2_C	182	3614	86.7	86.4	40.6	57.3
D2_S	182	3614	90.8	90.5	41.4	42.7
E2_0	0	0	91.8	92.1	63.7	30.5
E2_C	182	3614	87.3	86.4	65.4	29.9
E2_S	182	3614	86.8	84.9	49.9	18.5

PAR, photosynthetically active radiation; UVA, ultraviolet radiation; LWIR, long wave infrared radiation; 0, new film; C, control film; S, sprayed film; trans, transmissivity. Solar wavelength range, 300-2500 nm; PAR wavelength range, 400-700 nm; UVA wavelength range, 320-380 nm; LWIR wavelength range, 7500-12,500 nm.

Table 4. Radiometric coefficients of the films tested during the 2008 trial.

Film	Exposure time, days	Cumulative solar radiation, MJ/m^2	Solar trans, %	PAR trans, %	UVA trans, %	LWIR trans, %
A3_0	0	0	90.1	89.5	78.5	57.1
A3_C	189	3529	89.8	88.4	68.5	41.4
A3_S	189	3529	85.7	84.0	63.6	32.0
B3_0	0	0	86.4	86.4	36.5	39.8
B3_C	189	3529	90.4	89.9	50.9	51.8
B3_S	189	3529	92.1	92.1	49.8	45.4
D3_0	0	0	82.7	81.6	16.1	34.2
D3_C	189	3529	89.2	89.1	30.6	49.0
D3_S	189	3529	91.2	90.7	40.9	46.3
E3_0	0	0	92.2	92.7	62.5	30.3
E3_C	189	3529	92.7	93.0	80.1	29.6
E3_S	189	3529	94.1	94.1	77.3	26.7

PAR, photosynthetically active radiation; UVA, ultraviolet radiation; LWIR, long wave infrared radiation; 0, new film; C, control film; S, sprayed film; trans, transmissivity. Solar wavelength range, 300-2500 nm; PAR wavelength range, 400-700 nm; UVA wavelength range, 320-380 nm; LWIR wavelength range, 7500-12,500 nm.

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

ature were calculated from 30/4 to 30/9. Maximum temperatures were 56.2°C for the tunnel covered with B3 film, 55.9°C in the tunnel covered with B3_S film, 54.5°C in the tunnel covered with A3 film; maximum external air temperature was 32.0°C. Minimum temperatures were 14.4°C for the tunnel covered with B3 film, 15.5°C in the tunnel covered with B3_S film, 14.7°C in the tunnel covered with A3 film; minimum external air temperature was 16.4°C. The mean temperature was 32.7°C for the tunnel covered with B3 film, 32.3°C in the tunnel covered with B3_S film, 31.8°C in the tunnel covered with A3 film; mean external air temperature was 23.6°C.

Greenhouse covering films must satisfy the UNI EN 13206:2002 standard (UNI, 2002). This establishes that films with a thickness of 100 μm must have a PAR total transmissivity coefficient higher than 85%. The PAR total transmissivity coefficient of the stabilised films ranged from 84.3% (B2_S) to 94.6% (D2_0) (Tables 2-4).

In the solar and in the PAR wavelength range, the radiometric properties of all the films varied at most by 10%, while some of the stabilised films showed in the LWIR range higher variations between the values measured at the beginning of the trial and at the end of the trial. The variation in the transmissivity in the LWIR range suggests changes in the chemical structure of the films with a reduction in their mechanical characteristics (Stefani *et al.,* 2008; Vox *et al.,* 2008; Stefani *et al.,* 2011, Schettini and Vox, 2012). The parallel evaluation of the radiometric characteristics and the mechanical properties of the stabilised films showed a relationship between the variation of the radiometric properties in the LWIR range and the changes of the mechanical properties (Stefani *et al.,* 2011).

The radiometric properties of the A films, made with the basic polymers without UV stabilisers recorded a decrease in the transmissivity coefficients after the exposure in the field (Tables 2-4).

Among all the stabilised films tested, as far as LWIR transmissivity coefficient is concerned, the C2_S film showed the highest decrease from the value measured at the beginning of the test (almost 70%) (Tables 3). A decrease in the LWIR transmissivity reduces LWIR thermal energy losses.

There was no regular variation in the radiometric coefficients of the B, D and E films in the three trials; the values recorded for the control films were often higher than the values measured for the sprayed films (Tables 2-4). In 2008, the solar total transmissivity coefficient and the PAR transmissivity coefficient of the stabilised film aged in the field were higher than the corresponding values measured at the beginning of the test (Table 4). It seems that a considerable reduction in the agrochemicals has improved the solar transmissivity of the films.

Conclusions

It is well known that greenhouse plastic films exposed to natural weathering and to agrochemicals are subjected to the degradation of their mechanical properties. The research showed that there was no significant change in the radiometric properties of the films in the solar and in the PAR wavelength range during their exposure to climatic agents and to the agrochemicals. The variation in the transmissivity coefficients was at most 10% within six months of experimental field test. Higher variations between the values measured at the beginning and at the end of the test (up to 70% of the initial value) were recorded for the radiometric coefficients of the stabilised films in the LWIR wavelength range.

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