

# Correlation between Agrochemicals, Solar Radiation and Mechanical Properties of Greenhouse Plastic Films

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## Abstract

A research was carried out in order to evaluate how agrochemicals contamination and solar radiation influence the mechanical properties of ethylene-vinyl acetate copolymer (EVA) films. The films, manufactured adding several different combinations of light stabilizers, were subjected to natural and artificial weathering and to three agrochemicals commonly used during the cultivation practices. Two sets of field trials were carried out from 2006 to 2007 at the experimental centre of the University of Bari (Italy). The films, installed on steel arches of low tunnels, were periodically sprayed with the agrochemicals containing iron, chlorine and sulphur. For control the same films, mounted over other low tunnels, were not sprayed. Stress and strain at break of the film samples, taken at fixed time intervals in the field and after exposure in an artificial ageing chamber, were measured. Tests were conducted to evaluate the chemical contaminants absorbed by the films. Solar radiation falling on the films under the test was continuously measured and recorded by means of a pyranometer and a CR10x Campbell data logger. The results of the tests showed that the different light stabilizers influenced the behaviour of the films in presence of the sprayed agrochemicals. The experimental data were investigated evaluating the cumulative solar radiation, the kind of anti-UV additive and the absorbed contaminants. Concerning the agrochemicals which were absorbed by the films, values up to 6800 ppm of sulphur were recorded during the tests. The research allowed the identification of suitable additives in relation with used agrochemicals. The tests showed that an improved resistance to the agrochemicals was recorded for the EVA film stabilized with NOR-HALS plus UV filter.

## INTRODUCTION

Greenhouse plastic film lifetime is reduced due to the degradation of the polymer induced by the prolonged exposure to solar radiation, wind, high air temperature and relative humidity, and to agrochemicals used during cultivation (Desriac, 1991; Lemaire, 1993; Briassoulis, 2005; Vox and Schettini, 2007). The plastic film degradation is characterised by discoloration, cracking of surface, stiffening and a decrease in the mechanical and physical properties. The ageing degradation process is caused mainly by the ultra violet (UV) radiation in the solar spectrum, especially by UV-B and UV-A radiation, that occur in the wavelength range from 280 to 400 nm (Nijskens et al., 1990). In order to extend film lifetime, UV stabilizers, such as UV absorbers, hindered amine light stabilisers (HALS) and nickel quenchers, can be added to mitigate degradation through the prevention of solar radiation absorption as well as minimizing any subsequent radical oxidation reactions (Sanchez-Lopez et al., 1991). UV stabilised films can react with the agrochemicals sprayed during cultivation in different ways in relation with the composition and concentration of the anti-UV stabilizers (Basfar et al., 2003; Espi et al., 2007; Vox et al., 2008).

The aim of the research is to study the effects of agrochemicals containing iron,

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chlorine and sulphur, which can be sprayed during cultivation, on greenhouse plastic films degradation.

## MATERIALS AND METHODS

Two field tests were carried out at the experimental farm of the University of Bari in Valenzano (Bari, Italy), latitude 41°05'N from 2006 to 2007.

During each test polyethylene-co-vinyl acetate (EVA) films, made with a copolymer including 5% vinyl acetate and different anti-UV stabilizing combinations, were used (Table 1). The UV stabilizers were: triazine UV absorbers, methylate HALS and N-alkoxy (NOR) HALS. During the second test (2007) an ethylene-tetrafluoroethylene copolymer (ETFE) film, produced with Dyneon 6235 copolymer and no additive, and a film made of EVA and thermoplastic polyurethane elastomer (TPU) with UV stabilizers were added (Table 1). All the films were manufactured by P.A.T.I. S.p.A. (San Zenone degli Ezzelini, TV, Italy), using the single layer blow-extrusion technology with a nominal thickness of 100  $\mu\text{m}$ , and not coextrusion technologies, in order to simplify the experimental data interpretation. The EVA and ETFE films had different specific weight: 0.93  $\text{g cm}^{-3}$  for the EVA films and 1.75  $\text{g cm}^{-3}$  for the ETFE film. The thickness of 100  $\mu\text{m}$  was chosen to complete the ageing tests of the various EVA films in one year only, knowing already from experience that ETFE films would not show significant changes even at lower thickness.

Each cladding film, exposed to the atmospheric agents, was tested as covering of two low tunnels: one of which 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 first experiment lasted from April 2006 to November 2006 while the second experiment started in April 2007 and ended in October 2007. The agrochemicals were sprayed onto the cladding films by a system consisting of a pump connected with pipes and nozzles located inside the low tunnels. A water solution containing sulphur, iron and chlorine was sprayed weekly for 6 months; the solution was prepared adding typical commercially-available agrochemicals: a foliar fertilizer containing iron, trade name Sequestrene<sup>®</sup> Life (Syngenta Crop Protection S.p.A., Milan, Italy); a fungicide containing sulphur, trade name Tiovit<sup>®</sup> Jet (Syngenta Crop Protection); a fungicide containing chlorine, trade name Topas<sup>®</sup> (Syngenta Crop Protection). The quantity of active ingredients sprayed weekly over 1  $\text{m}^2$  of film was: for iron 0.26  $\text{g m}^{-2}$  in the 2006 test and 0.16  $\text{g m}^{-2}$  in the 2007 test, for sulphur 3.33  $\text{g m}^{-2}$  in 2006 and 2.00  $\text{g m}^{-2}$  in 2007 and for chlorine 0.21  $\text{g m}^{-2}$  in 2006 and 0.13  $\text{g m}^{-2}$  in 2007.

During the field tests solar radiation falling on the films was measured by a pyranometer (model 8-48, Eppley Laboratory, Newport, RI, USA) in the wavelength range 0.3-3  $\mu\text{m}$ ; 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 periods was calculated.

During each set of field test, 2  $\text{m}^2$  of each film were taken periodically; five samples from each piece were tested in the laboratory in order to assess the variation of their mechanical properties in consequence of the ageing process due to the prolonged exposure to the climatic agents and to the agrochemicals. After their field exposure the samples of the sprayed films were subjected to additional artificial ageing by a SAIREM SEPAP 12/24 chamber (SAIREM s.a.r.l., France) at the P.A.T.I. S.p.A. laboratory. The SAIREM SEPAP unit was characterised by: 4 mercury vapour arc lamps, 400 W each, as radiation sources; useful radiation range from 290 to 450 nm (the part below 290 nm wavelength was filtered); temperature set equal to 55°C. The tests were carried out in a dry environment, with constant temperature and emission; 24 samples were kept in slight tension on a rotary assembly, without backing plates, in order to ensure uniform exposure. One hour of artificial ageing inside the SAIREM SEPAP 12/24 chamber has an average effect on tensile properties equivalent to about 30  $\text{MJ m}^{-2}$  of solar radiation.

Tests on the mechanical properties of the samples were conducted at the

laboratory of P.A.T.I. S.p.A. The tensile stress and the strain at break were measured as indicative of the degradation of the mechanical properties. The tensile tests were performed by a dynamometer (DY 22, Adam-Lhomargy, France), equipped with a 50 daN load cell, according to the ISO 527-3 (1995) standard.

The absorption of selected contaminants, i.e., chlorine, iron and sulphur, was estimated at the Venezia Tecnologie laboratories (Venice, Italy), using fluorescence X-ray elementary semi-quantitative analysis.

## RESULTS AND DISCUSSION

Figures 1-4 show the variation of the longitudinal stress and strain at break, as a function of the cumulative solar radiation, of the film samples subjected to the natural weathering and taken during the field tests. For both experimental tests the highest decreases of the stress and strain at break were recorded for the 0-C film (Figs. 1-4). As a consequence of the decay of its mechanical properties the 0-C film showed several breakings in the field both in the 2006 test and in the 2007 test, after an exposure to a cumulative solar radiation of about 2000 MJ m<sup>-2</sup>.

Among the covering films that were sprayed with the agrochemicals, the 0-S and 1-S films showed the worst behaviour while the 3-S films showed the best performance as the stress and strain at break indicate in both tests.

In the 2006 test, after an exposure to a cumulative solar radiation of 3360 MJ m<sup>-2</sup>, the value of the stress at break decreased from 32 to 20 MPa for the 0-S film and from 29 to 19 MPa for the 1-S film (Fig. 1) while in the 2007 test, after an exposure of 3614 MJ m<sup>-2</sup>, the stress at break decreased from 28 to 16 MPa for both of the films (Fig. 3). The value of the stress at break of the 3-S film decreased to 27 MPa at the end of both field tests starting from the initial value of 31 MPa in the 2006 test and of 28 MPa in the 2007 test (Figs. 1 and 3).

In both tests the 1-C film increased its strain at break, at the end of the field test, to 770% from the initial value of 745% in the 2006 test (Fig. 2) and to 799 from 750% in the 2007 test (Fig. 4).

Among the stabilized films the 1-S film evidenced the highest decrease of the strain at break at the end of the field exposure in both tests: the value of the strain at break reduced to 649% from the initial value of 745% during the 2006 test (Fig. 2) and to 485% from the initial value of 750% during the 2007 test (Fig. 4).

At the end of the 2006 field test, after an exposure to a cumulative solar radiation of 3360 MJ m<sup>-2</sup>, the sprayed film samples were introduced in the SEPAP unit to induce an additional accelerated weathering. For the 2007 test the samples were introduced in the SEPAP after a field exposure to a cumulative solar radiation equal to 1992 MJ m<sup>-2</sup>, when the first differences were evidenced for the mechanical properties of the films. In both tests, after 50 hours of artificial weathering the 2-S and 3-S films recorded a sharp decrease of the stress at break; the value decreased from 26 MPa (value recorded at the end of the natural weathering) to 18 MPa for the 2-S film and from 27 to 20 MPa for the 3-S film in the 2006 test; the value decreased from 27 to 19 MPa for the 2-S film and from 30 to 20 MPa for the 3-S film in the 2007 test (Table 2). After 100 hours of artificial weathering the values of the stress at break of the tested films reached values lower than 14 MPa (Table 2). According to the EN 13206 (EN 13206, 2001), thermic clear covering films must have a tensile stress at break higher than 19 MPa.

The application of the artificial weathering by means of the SEPAP chamber induced differences concerning the strain at break of the different films, as shown in Table 3. After 50 hours of artificial weathering the value of the strain dropped from 604% (value recorded at the end of the natural weathering) to 361% for the 0-S film for the 2006 test and from 643 to 292% for the 0-S film and from 692 to 360% for the 1-S film for the 2007 test, while the values of the other films were higher. The 3-S film showed the best performance after 100 hours of artificial weathering, recording a value of 315% in the 2006 test and of 469% for the 2007 test. According to the EN 13206 (EN 13206, 2001), thermic clear covering films must have a tensile strain at break higher than 400%

The ETFE film, which was tested during the 2007 test, showed no significant variation of its mechanical properties after the field exposure. The tensile stress at break varied from 51 to 52 MPa for the sprayed ETFE and to 49 MPa for the control after an exposure to solar radiation of 3614 MJ m<sup>-2</sup>. Strain of the ETFE film varied from 352 to 377% for the sprayed film and to 333% for the control film.

The H-LUX film that was not sprayed, showed a slight decrease of the mechanical properties during the natural weathering; higher variations were pointed for the sprayed film and after 100 hours of artificial weathering for the sprayed and the un-sprayed film.

Table 4 shows the chemical contamination of the sprayed films. The limited chemical contamination of the ETFE film in comparison with the other films sprayed in the same way and at the same time intervals was noticeable.

Based on the mechanical degradation of the films (Figs. 1-4) and on the chemical contamination of the sprayed films (Table 4), threshold values for planning of additional tests can be assumed: 3000 ppm for sulphur, 300 ppm for chlorine and 200 ppm for iron.

Among the stabilized films, the decay of the mechanical properties of the sprayed films was higher in comparison with the control films; this result was consistent with the results obtained by Desriac (1991) and Rooze (1992).

## CONCLUSIONS

The two tests showed similar results concerning the correlation between solar radiation, the agrochemicals and the additives. The variation of the mechanical properties of the stabilised films subjected to natural weathering showed that the sprayed films degraded faster than the un-sprayed films. Among the sprayed films the EVA film additived with methylate HALS, NOR HALS and UV absorber triazine recorded the best performance.

## ACKNOWLEDGEMENTS

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## **Tables**

Table 1. Formulation of the films used during the 2006 test (I) and 2007 test (II).

Film code	Polymeric base	Ultra violet stabilizers	Test
0	EVA	---	I and II
1	EVA	methylate HALS and NOR HALS	I and II
2	EVA	methylate HALS and UV absorber triazine	I and II
3	EVA	methylate HALS, NOR HALS and UV absorber triazine	I and II
H-LUX	EVA and TPU	methylate HALS and NOR HALS	II
ETFE	ETFE	no stabilizer	II

Table 2. Tensile stress at break in the longitudinal direction of the sprayed film samples after accelerated ageing in the SEPAP unit; the samples of the 2006 test, taken at the end of the field exposure (A), were aged for 300 hours; the samples of the 2007 test, taken after 91 days of field exposure (B), were aged for 150 hours; S: sprayed film.

Hours	2006 test				Hours	2007 test				
	0-S	1-S	2-S	3-S		0-S	1-S	2-S	3-S	HLUX-S
	(MPa)					(MPa)				
A	20	19	26	27	B	24	24	27	30	22
50	19	16	18	20	50	17	14	19	20	18
100	14	12	12	12	100	13	12	11	14	9
300	15	14	13	12	150	--	--	12	11	9

Table 3. Tensile strain at break in the longitudinal direction of the sprayed film samples after accelerate ageing in the SEPAP unit; the samples of the 2006 test, taken at the end of the field exposure (A), were aged for 300 hours; the samples of the 2007 test, taken after 91 days of field exposure (B), were aged for 150 hours; S: sprayed film.

Hours	2006 test				Hours	2007 test				
	0-S	1-S	2-S	3-S		0-S	1-S	2-S	3-S	HLUX-S
	(%)					(%)				
A	604	649	721	748	B	643	692	744	775	682
50	361	517	545	618	50	292	360	572	608	584
100	73	51	64	315	100	58	91	86	469	71
300	21	22	22	34	150	--	--	40	143	43

Table 4. Chemical contamination of the sprayed films after an exposure in the experimental field of 193 days for the 2006 test and of 91 days for the 2007 test; S: sprayed film.

	2006 test				2007 test					
	0-S	1-S	2-S	3-S	0-S	1-S	2-S	3-S	HLUX-S	ETFE-S
S (ppm)	6600	6800	5400	4800	5200	4000	3300	3000	3000	60
Cl (ppm)	260	470	600	650	440	290	330	400	230	330
Fe (ppm)	30	70	50	40	20	190	200	205	210	40

## Figures

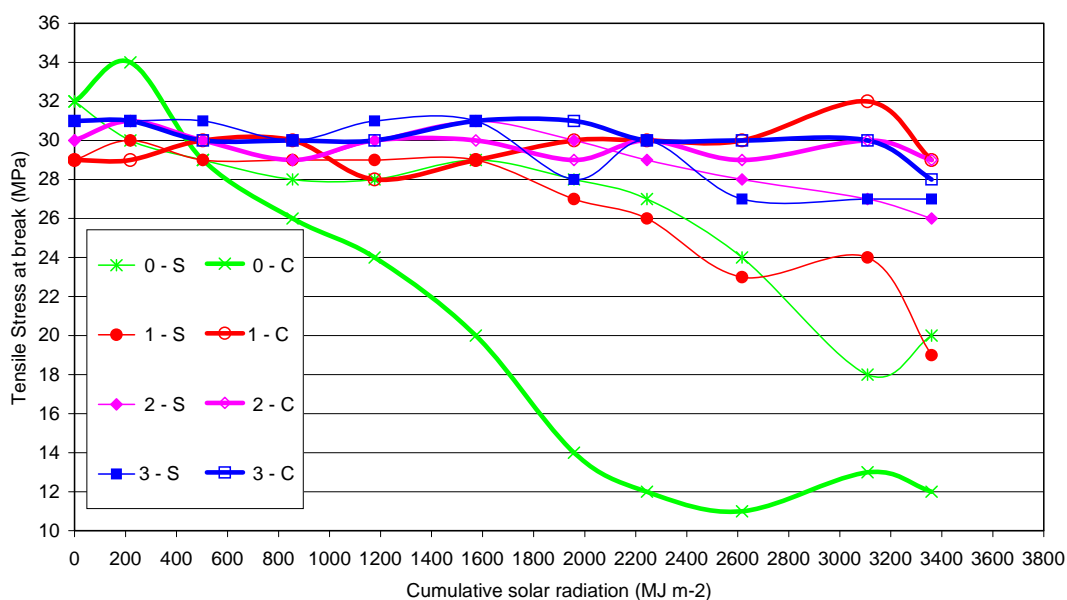


Fig. 1. Tensile stress at break in the longitudinal direction of the film samples taken during the 2006 experimental field test as a function of the cumulative solar radiation; C: control film; S: sprayed film.

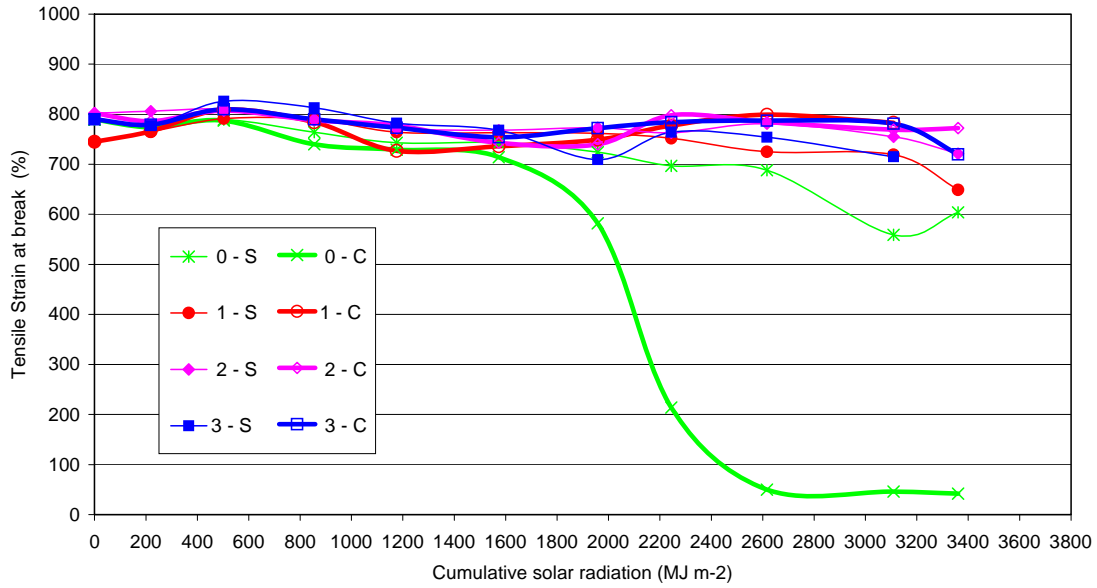


Fig. 2. Tensile strain at break in the longitudinal direction of the film samples taken during the 2006 experimental field test as a function of the cumulative solar radiation; C: control film; S: sprayed film.

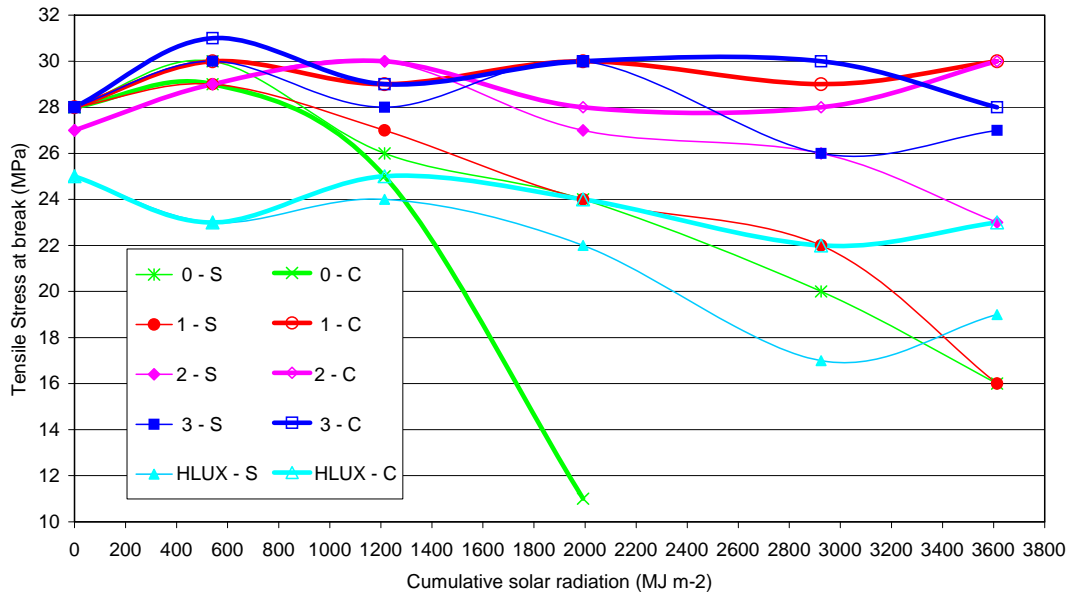


Fig. 3. Tensile stress at break in the longitudinal direction of the film samples taken during the 2007 experimental field test as a function of the cumulative solar radiation; C: control film; S: sprayed film.

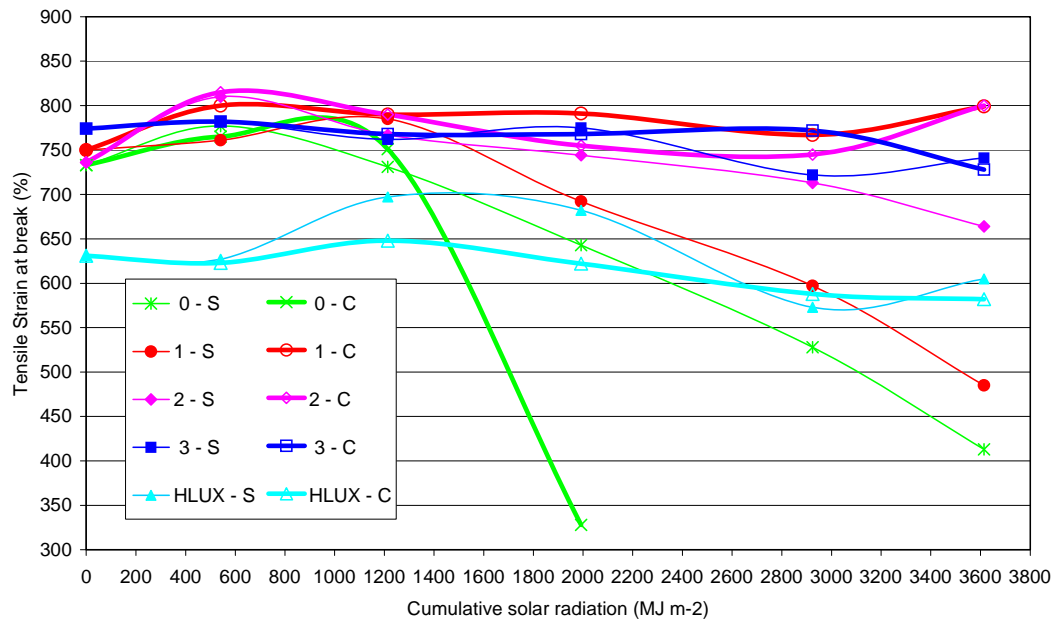


Fig. 4. Tensile strain at break in the longitudinal direction of the film samples taken during the 2007 experimental field test as a function of the cumulative solar radiation; C: control film; S: sprayed film.