AGROCHEMICALS CONTAMINATION AND AGEING EFFECTS ON GREENHOUSE PLASTIC FILM FOR RECYCLING

PICUNO P. [1], GODOSI Z. [2], PICUNO C. [3]* AND KUCHTA K. [3]

1 *University of Basilicata – SAFE School, via dell'Ateneo Lucano, n.10, 85100 Potenza (PZ), Italy*

2 *Civil Engineer, Freelance Consultant, via Nicolò Giudice, n.1, 70010 Cellamare (BA), Italy*

3 *Hamburg University of Technology Sustainable Resource and Waste Management, Blohmstraße 15, D-21079 Hamburg, Germany*

* *Corresponding Author: caterina.picuno@tuhh.de*

The contribution to programming and executing this research should be equally shared among the Authors

SUMMARY:

Polymers are employed in agriculture in several applications, the most efficient and fruitful of which is the protection of cultivations through the use of cover placed over plants while they are growing, providing protection from climatic factors, while at the same time increasing yield and/or extending the cropping season. Plastic films used for covering greenhouses, low and medium tunnel and for soil mulching have reached very notable consumptions all over Europe as well as the rest of the World, posing an important environmental problem connected with the impact that plastic material has on the sustainability of the agricultural production, whose environmental footprint may be deteriorated. Recycling agricultural plastics is a common technique, but it has not yet solved the problem of their re-use in the framework of a circular economy, since many factors are still anyway limiting the mechanical recycling of agricultural plastic materials. Among these limiting factors, the loss of mechanical properties of plastic film, due to its ageing after being exposed to direct solar radiation plays a crucial role, mostly if aggravated by the contamination with agrochemicals ordinarily used for crop health and pest management. In the present paper, the results of some laboratory tests on agricultural plastic film artificially aged for different periods contaminated with two different agrochemicals, are reported. These results have showed that the impact of agrochemicals on the plastic film is considerable already in the use-phase, so when entering the recycling stage, the material carries a low potential for being transformed into a closed-loop recycled material. The results in terms of Carbonyl Index (CI) have confirmed the tendency of the material to degrade rapidly when in contact with anti-aphid or fungicide contaminants. The samples sprayed with agrochemicals

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experience a considerable increase in CI values after 4 weeks of ageing, which makes impossible the mechanical recycling of this material.

1. INTRODUCTION

Agriculture is the most important sector for the application of plastic material as a primary building component. Within civil and industrial constructions, the use of this material is limited to complementary applications, as window or door frames, flooring, insulating or facing covers, *etc*. In agriculture, when employed as a covering material for protecting cultivation, plastic plays a central role, by performing a passive effect – protecting crops from negative weather conditions – and, at the same time, an active effect, realizing a more favourable microclimate for the crops, while contributing to the valorisation of the solar radiation (Picuno C. et al., 2019). The total agricultural plastic films market consists mainly of greenhouse and mulching films. According with the most updated estimations, the total plastic film used for greenhouse production in the European countries is almost 300,000 tons/year (Briassoulis et al., 2013), with an estimated total area of around 120 x 10^3 hectares. On the other hand, in 2016, China alone had the largest area under protected cultivation, mainly under plastic greenhouse, estimated to be of 2.76 x 10^6 hectares. Together with Korea and Japan, they account for 80% of the total area covered with greenhouses (Jansen et al, 2017).

The increasing use of plastic films in protected cultivation calls for further research on their durability and suitability to the Circular Economy concept, to contribute to reducing the plastic footprint in agriculture (Cruz-Sanchez et al., 2020; Pazienza & De Lucia, 2020; Beriot et al., 2021). The use of plastics in agriculture generates, in fact, serious environmental problems, as those connected with the management of large amounts of post-consume material. In order to explore new possibilities in the use of plastic material in the agricultural sector, characterized by a lower environmental impact, a better understanding of the factors hindering its mechanical recycling is needed. In this sense, the conditions in which plastic materials conclude their useful life after application in agriculture play a decisive role.

The study of the ageing of polyethylene through weathering is of great importance for the development of more resistant materials, together with the formulation of additives able to extend the durability of such polymers (Guadagno et al., 2011). The main factor playing a role in the ageing of a plastic material used for application in protected cultivation is solar radiation, mainly in its Ultra-Violet (UV) component (Abdel-Bary et al., 1998; Gulmine et al., 2003). Based on this assumption, the global energy arriving in an area by the sun is usually accepted within the international technical and scientific literature as a general parameter expressing the global conditions of the area where the plastic material will be installed. This global energy amount, calculated as the integral of the solar power coming from the sun, is expressed in Langleys (Ly), the unit of energy distribution over an area (1Ly = 1 cal/ cm^2 = 41840 Joule/m^2).

Briassoulis et al. (2004) analysed the quantitative criteria which may be combined to base the characterisation of degradation of low-density polyethylene (PE-LD) films, which are currently the most widespread greenhouse covering material in the Mediterranean countries. They argued that, even if the final characterisation of degradation of a greenhouse plastic film is at present mainly based on the changes in percentage elongation at break, the exposure of PE-LD film to weathering conditions - especially to solar irradiation in the range of 290–400 nm - affects its chemical structure and consequently its mechanical and physical properties. A more suitable and realistic combination of criteria, may represent critical properties, which should be measured in a very specific and well-harmonised way under pre-defined conditions.

The scientific investigations so far performed have examined the combined effect of ageing and contact with agrochemicals on the greenhouse plastic film, mostly focusing on the technical properties of this material. By means of laboratory and field tests, these studies have investigated, the effects of ageing on the main technical characteristics of plastic films for their working life when installed to cover the greenhouse, so as to protect the crops cultivated inside, *i.e.*: radiometric properties, mechanical strength, etc. Briassoulis (2005) analysed the effect of tensile stress and of a drastic agrochemical (Vapam) on the ageing of PE-LD greenhouse films. The synergistic effect of these two critical ageing factors with UV radiation and temperature on the ageing of selected PE-LD films was investigated under artificial ageing conditions. The PE-LD was non-stabilised, in order to investigate the basic characteristics of ageing in a very short period. The ageing was monitored through the changes of selected mechanical properties of the polyethylene film before and after ageing. A modified artificial ageing procedure has been finally proposed, considered to simulate in a more realistic way the weathering of PE-LD greenhouse films. More experimental investigations were carried out by Schettini & Vox (2013), to evaluate how agrochemicals contamination and solar radiation influence the physical properties of PE-LD films. 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. The same Authors (Vox & Schettini, 2013), have evaluated how agrochemical contamination and solar radiation influences the radiometric properties of ethylene-vinyl acetate copolymer (EVAC) greenhouse films by means of laboratory and field tests. 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 in the photosynthetically active radiation wavelength range.

So far, no research has been conducted with the aim to assess the influence of a non-natural ageing factor – as the contact of the plastic film with agrochemicals (Picuno P. et. al., 2018; Picuno C. et al., 2020) – on the alteration of these materials in view of their mechanical recycling. The present paper contributes to covering this gap, discussing the results of laboratory tests on agricultural plastic film artificially aged for different periods contaminated with two different agrochemicals.

2. MATERIALS AND METHODS

Plastic film samples obtained from a PE-LD film commonly available in the market were alternatively contaminated with two agrochemicals. The first one was the anti-aphid insecticide EPIK SL VITHAL (active ingredient: *Acetamiprid 50 g/l*, producer: Ital-agro srl.), classified as hazardous for the environment - *GHS09, H410, "very toxic to aquatic life with long-lasting effects"* (United Nations, 2019) - (Ital-Agro srl, 2021). The second agrochemical used was the fungicide CUMETA FLOW (active ingredients: *Metalaxil-m 1,85%, copper hydroxide sulfate 15,40%*, producer: Diachem S.p.A.), classified as irritant - *GHS07, H317 "May cause an allergic skin reaction + H319 Causes serious eye irritation"* - and hazardous for the environment - *GHS09, H410, "very toxic to aquatic life with long-lasting effects"* (United Nations, 2019) – (Chimiberg, 2021). These were sprayed on one side of the plastic film, that were then aged for 2 and for 4 weeks in an ageing chamber (Fig.1). The PE-LD plastic film was also analysed without any contamination, so as to have a reference sample. The tested materials are reported in Table 1.

Table 1: Nomenclature of the tested PE-LD films

LD-PE film typologies	
Contamination (1st Letter)	Number of weeks in the ageing chamber
N = **N**ot contaminated	**0** = no ageing
A = contaminated with anti-**A**phid	**2** = **2** weeks ageing in the ageing chamber
F = contaminated with **F**ungicide	**4** = **4** weeks ageing in the ageing chamber
Example: N2 = LD-PE film **N**ot-contaminated, aged **2** weeks in the ageing chamber	

The material was aged keeping a constant temperature of 20°C in the ageing chamber. The ageing period was selected so as to simulate a corresponding ageing in open field in southern Italy - Municipality of Cellamare. There, a yearly global energy arriving from the sun of 5554 MJ/m^2 = 132.74 kLy was detected in 2018. Since the energy released by the lamp of the ageing chamber has a power of 1000 W/m^2, this value approximately corresponds to 8 weeks of artificial ageing. Therefore, the tested periods of 2 and 4 weeks respectively corresponds to three and six months in real conditions.

After the ageing process, each plastic film was tested through tensile tests and radiometric properties. The mechanical properties were determined by tensile tests (fig. 1) on 10 specimens for each LD-PE film typology. Results were expressed in terms of maximum strength and percentage elongation at break.

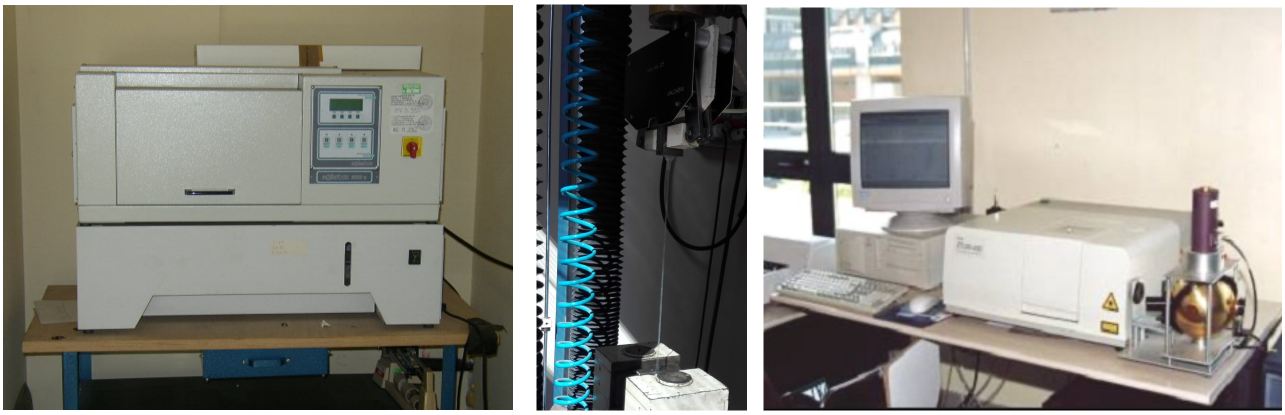

Figure 1: Ageing chamber (*left*), tensile test (*center*) and radiometrical test (*right*) on greenhouse plastic films

Additionally, the optical characteristics were analysed by determining in a Iasco FT-IR spectro-radiometer the absorbance in the wavenumbers' range of 1650 - 1860 cm^{-1}. This allowed to assess the change in the Carbonyl Index (CI) of the material during the ageing period, of which evolution on time was calculated with the following equation (Picuno P., 2014):

$$C_I = \varepsilon \frac{A^t - A^0}{S}$$

where:

CI = Carbonyl Index, [%];

At = absorbance in the range [1650 – 1860] cm^{-1} at time t (respectively 0,2 and 4 weeks), [%];

A0 = absorbance in the range [1650 – 1860] cm^{-1} at time 0, [%];

ε = Molar absorbance coefficient, m;

S = film thickness, m.

3. RESULTS AND DISCUSSION

The results of the mechanical tests are reported in Table 2.

Table 2. Results of the mechanical tests

LD-PE film	Maximum strength [N/mm^2]	Percentage elongation at break [%]
N0	26,00	716,06
N2	24,63	687,44
A2	20,75	601,16
F2	16,30	402,33
N4	20,18	580,87
A4	13,80	402,33
F4	10,01	51,06

In Figure 2 the results of the mechanical tests are reported in terms of percentage variation over time compared to the material as new (*i.e.*, initial value = 100%). Specifically, Figure 2a and 2b picture the variations of, respectively, maximum strength and elongation at break due to ageing in contact with the respective contaminants. From these results it is evident that the ageing of LD-PE plastic films in contact with agrochemicals greatly reduces their mechanical characteristics. After 4 weeks of artificial ageing – *i.e.*, around six months in real conditions of ageing in Southern Italy – the material in contact with a pesticide/fungicide has reduced its elongation at break below 50% of the value as new, so it has to be removed. Indeed, this is the current criterion basing on which the material should be replaced - because it is considered having concluded its working life.

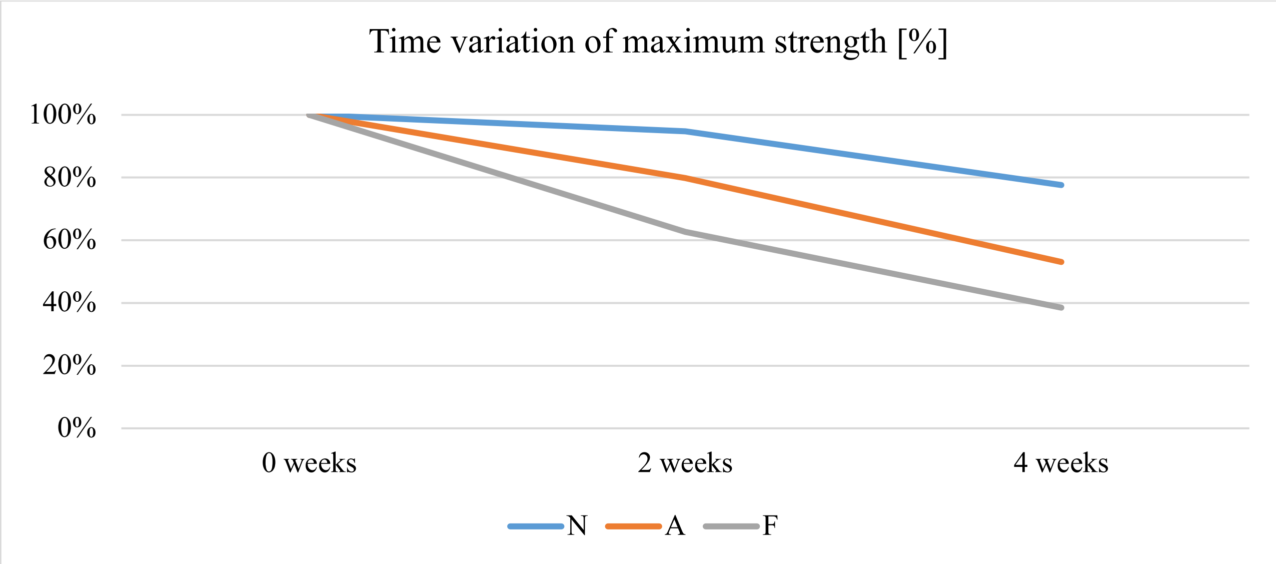

Figure 2a: Maximum strength variation on aged LD-PE plastic film with no contamination (N), one spraying with anti-aphid insecticide (A) and one spraying with fungicide (F).

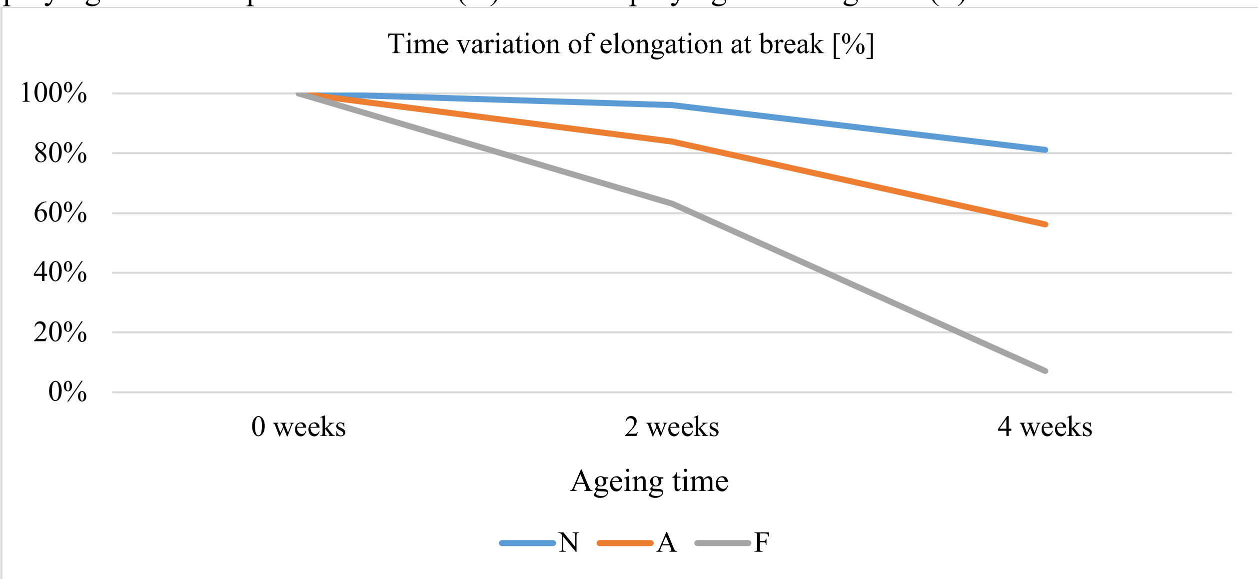

Figure 2: Elongation at break variation on aged LD-PE plastic film with no contamination (N), one spraying with anti-aphid insecticide (A) and one spraying with fungicide (F).

Hence, the impact of agrochemicals on the plastic film is considerable already in the use-phase. This entails that when entering the recycling stage, the material carries a low potential for being transformed into a closed-loop recycled material. This phenomenon is particularly clear in the case of LD-PE plastic film having been in contact with the fungicide, that has almost lost every mechanical property after 4 weeks of artificial ageing. In this case, its mechanical recycling would deliver a recycled material with no potential applications as a film. This is particularly true when considering the degradation occurring in polymers consequent to mechanical recycling, due to thermo-mechanical processes (Saikrishnan, S. et al., 2020; Jin, H. et al., 2012).

The results in terms of Carbonyl Index (CI) confirm the tendency of the material to degrade rapidly when in contact with anti-aphid and fungicide contaminants. More specifically, as reported in Table 3, the CI of the uncontaminated sample decreases, clearly suggesting degradation effects taking place (mostly chain scissioning). On the other hand, the samples sprayed with agrochemicals experience a remarkable increase in CI values after 4 weeks of ageing. These samples are most likely undergoing degradation of the polymeric chains, whereby new carbonyl groups are being created, justifying an increase in the value (Beltrán-Sanahuja, A. et al, 2019). As in the case of mechanical performances, the sample contaminated with fungicide is subject to the most extensive degree of degradation through carbonyl bonds formation.

Table 3. Variations of the Carbonyl Index during the ageing period

LD-PE film	0 – 2 weeks	0 – 4 weeks
N	31,3	28,5
A	16,1	26,0
F	21,4	42,4

5. CONCLUSIONS

The final results enabled to evaluate how agrochemical contamination and solar radiation influence the technical properties of a PE-LD greenhouse film, as well as its feasibility to be recycled into a new secondary product. It was shown that the contact with agrochemicals plays a decisive role in the degradation process of the plastic film, confirming that agrochemicals generate by-products leading to degradation of greenhouse films together with a decrease in their mechanical and physical properties. The degradation due to agrochemicals was found to be dependent on their active principles, as well as on method and frequency of application. In general, the effect of the UV radiation on the PE-LD film revealed to be dominant, as expected, while the synergistic effects and the relative importance of exposure to the two different agrochemicals in the degradation of the films were significant as well. Hence, the effect of its exposure may result in dramatic deterioration of the film when applied alone, since it may accelerate ageing, with highly probable unfavourable repercussions on the feasibility of this material to undergo mechanical recycling processes. In this sense, future research should investigate the possible changes in the polymeric chain occurring after ageing in contact with the anti-aphid and the fungicide (e.g. through FTNIR). Additionally, variations in the processability should be assessed, comparing the values of the Melt Flow Index and the density of the different tested samples.

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