

## Degradation in soil behavior of artificially aged polyethylene films with pro-oxidants

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**ABSTRACT:** Bio-based, biodegradable in soil, as well as degradable polyethylene mulching films with pro-oxidants, have been introduced in the market in an effort to deal with the serious problem of managing plastic waste streams generated from conventional mulching films. In a previous experimental investigation, a series of naturally degraded under water melon cultivation conditions linear low density polyethylene (LLDPE) mulching films with pro-oxidants, buried in the field for 8.5 years, were recovered intact even though undergoing a continuous slow abiotic degradation in soil. The aim of the present article was to simulate the behavior of the LLDPE mulching films with pro-oxidants under a much longer time-scale (e.g. some decades). Toward this purpose, samples of LLDPE with pro-oxidants film were artificially degraded to simulate severe degradation/fragmentation of these films while been buried in the soil for many years, following the end of the cultivation season. Further degradation of these severely degraded samples was investigated by burying them in the soil over a period of seven years. During this burial period, all degradation parameters and their evolution with time were measured. The artificially degraded LLDPE film samples with pro-oxidants, in contrast to the naturally degraded film that remained intact for 8.5 years, were gradually transformed into tiny micro-fragments in the soil. These fragments, through a continuing abiotic degradation process under natural soil conditions are eventually transformed into invisible micro-fragments. The fate of these micro-fragments and their long-term impact to the environment and human health is unpredictable. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42289.

**KEYWORDS:** ageing; biodegradable; degradation; films; mechanical properties

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### INTRODUCTION

Polymers are increasingly used in agriculture and horticulture during the last 50 years. This enabled farmers to protect and increase their crop production, enhance the produce quality, reduce the use of herbicides and pesticides and conserve water. Mulching films are used extensively to create a favorable micro climate at the zone of rapid growth of plant roots by modifying the soil temperature, limit weed growth (reducing the use of herbicides), reduce moisture losses (conserving water) and improve crop yields and precociousness. The mulching films consumed exceed the quantities of 130,000 t/year in Europe and 2,600,000 t/year worldwide (2003–2005 data).<sup>1</sup>

The growing use of plastic films in agriculture requires the disposal of thousands of tons of agricultural plastic wastes produced each year. The cost of collection, sorting, and consolidation of these plastic waste streams and the difficulties

of recycling due to their contamination with soil and their serious degradation results in their mismanagement: a large portion of these waste are left in the field, buried or burned uncontrollably by the farmers releasing harmful or toxic substances.<sup>2</sup>

In order to overcome this serious environmental problem, innovative, mostly bio-based, biodegradable in the soil materials have been developed during the last years.<sup>3–5</sup> Materials biodegrading within a limited defined period of time under natural field conditions with no negative environmental impact, are defined as “biodegradable in soil” according to the international standards.<sup>3</sup> However, biodegradable in soil mulching films, although commercially available, are still expensive, and as long as the current illegal (cost free) disposal practices for conventional films are allowed, they cannot be competitive.

A second alternative to overcome the environmental problems associated with the use of conventional mulching films, has

been based on the use of the conventional PE material, additivated with pro-oxidant components to control the PE UV-induced and/or thermal degradation. The use of specialized pro-oxidants as additives in polyethylene films, results in acceleration of the breakdown of polyethylene exposed to UV and/or heat, to very small fragments (these materials are known as fragmentable). These relatively low cost oxo-degradable (or fragmentable, or degradable) mulching films have already been introduced in the market and they are used in agricultural applications.<sup>6,7</sup>

Pro-oxidant additives, usually transition metals, present in the polyolefin backbone catalyze chain scission producing free radicals. These free radicals can attack the polymeric chain producing hydrophilic oxidation products of low molecular mass (e.g.  $-\text{COOH}$ ,  $-\text{OH}$  and  $>\text{C}=\text{O}$  groups). Several published research results suggest that the oxidation products of oxo-degradable polyolefins may be biodegradable under certain conditions.<sup>8–10</sup>

Unfortunately, as described by Narayan,<sup>11</sup> the introduction of some of the oxo-degradable materials in the market is also associated with “a growing number of misleading, deceptive and scientifically unsubstantiated biodegradability claims proliferating in the marketplace”. Several publications,<sup>3,11–16</sup> question the biodegradability of the oxo-degradable film fragments. There is no adequate evidence to support the complete consumption of these fragments by the microorganisms that inhabit natural environments within a reasonable time frame.<sup>11</sup>

According to the results of a study conducted by the European Bioplastics association<sup>17</sup> fragmentation of oxo-fragmentable plastics is the result of a chemical reaction (abiotic degradation) rather than the result of a biodegradation process. According to this study: “The resulting fragments will remain in the environment.”<sup>18</sup>

The so called “oxo-biodegradable” plastic bags have been introduced in the market during the last decades. Independent biodegradation testing of several of these bags using standard respirometric test methods, such as ASTM D5338<sup>19</sup> and ISO 14855,<sup>20,21</sup> have not shown biodegradation. Moreover, these materials fail the biodegradability norms and standards specifications of ASTM 6400<sup>22</sup> and ISO 17088.<sup>23–25</sup> This is confirmed also by a study commissioned by the State of California's Waste Management Board to a California public University<sup>26</sup> that led to laws restricting such unverified claims in the State of California.

The present work is part of an experimental study aimed at investigating the long-term degradation behavior of the remains and fragments of mulching films made out of LLDPE with pro-oxidants (oxo-degradable or photodegradable or fragmentable films), under real soil burial conditions. To this end, a first series of LLDPE mulching films with pro-oxidants were used in full-scale water melon cultivation in the experimental field of the Agricultural University of Athens (AUA). Their degradation behavior during the cultivation season is described in Ref. 27. Following the harvesting of the produce, the remains of the films were collected and incorporated into the soil, along with the plants remains in the same field, for a total period of 8.5

years. The remains of these naturally aged materials remained intact after 8.5 years in the soil, even though they were further degraded.<sup>28</sup>

The aim of the present work was to simulate the behavior of LLDPE mulching films with pro-oxidants (same films were used as in Ref. 28 for comparison purposes) under a much longer time-scale (e.g. some decades). Toward this purpose, samples of the LLDPE with pro-oxidants film were artificially degraded to simulate the degradation/fragmentation of these films as if they had been buried in the soil for many years, following the end of the cultivation season. Further degradation of the already severely degraded samples was investigated by burying them in the soil over a period of seven years during which all degradation parameters and their evolution with time were measured.

## EXPERIMENTAL

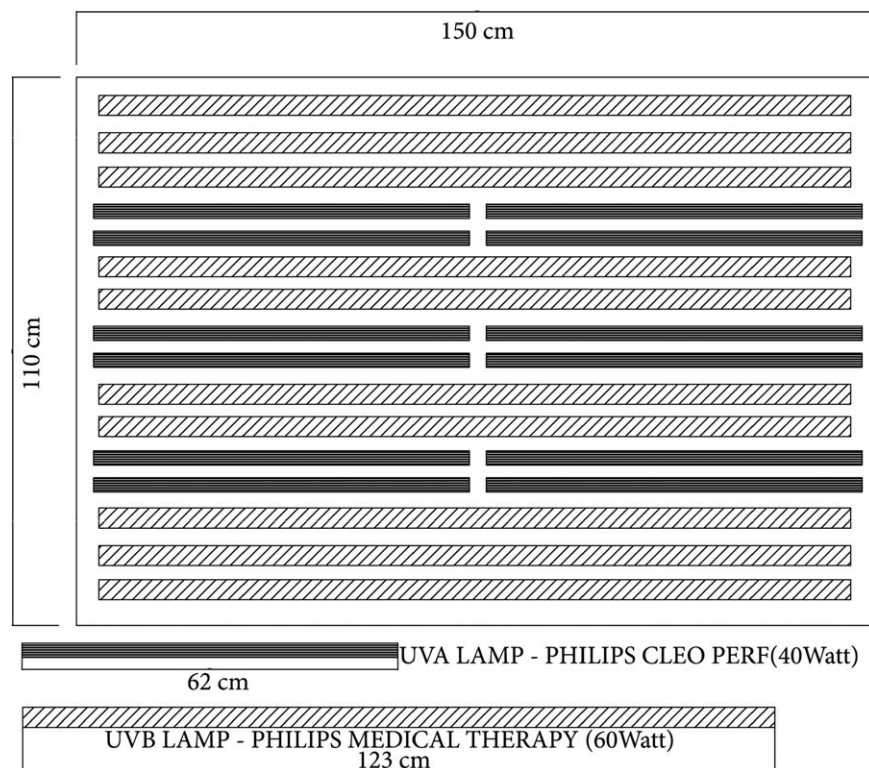
### Materials

The experiments were performed with a 20  $\mu\text{m}$  thick LLDPE experimental mulching film labelled LLDPE-P1, containing as additives: carbon black 350 at 16.0%, a commercial pro-oxidant at 2.5% (Ciba® Envirocare® AG1000) and 3000 ppm of Tinuvin 783 (with components Chimassorb 944 and Tinuvin 622;<sup>29</sup> made by Ciba SC). The LLDPE-P1 mulching film was used in the full-scale water melon experiments of Refs. 27 and 28. In the present study, the same film was used to investigate the long-term degradation behavior of the material under natural soil burial conditions following its accelerated artificial degradation under controlled laboratory conditions.

### Pretreatments

The original LLDPE-P1 mulching film used with the full-scale experiments described in Ref. 27, was artificially aged in the laboratory to investigate the accelerated degradation effect (high UV radiation and/or heat) and compare it to the film degraded naturally under field cultivation conditions.

A set of LLDPE-P1 samples was exposed in a high intensity UV accelerated ageing system designed and constructed in the AUA lab. The system consists of 10 UVB Philips TL 40W/12RS Medical lamps (broadband UV 10 lamps emitting in the range UVB 280–315 nm with peak at 310 nm)<sup>30</sup> and 12 UVA Philips Cleo Performance 40W broadband lamps (emitting relatively moderate energy in the range of 310 to 400 nm with peak at 350 nm).<sup>31</sup> The lamps were arranged in a staggered pattern over an area of 1  $\text{m}^2$  (Figure 1). The resulting total irradiance in the UV region is 35–45  $\text{W}/\text{m}^2$  with peaks at 350 nm and 310 nm wavelengths where polyethylene is sensitive. This accelerated ageing system provides higher UV radiation than the sun radiation during a sunny day, and is more detrimental to polyethylene than the standard artificial weathering equipment (since it emits also UVB radiation). As a result a faster and more severe degradation of polyethylene is achieved as compared to the artificial ageing induced by means of the equipment described in the standard ISO 4892-2.<sup>32</sup> The radiation intensity emitted by the system above 360 nm does not follow the sunlight radiation curve but falls abruptly to very low levels in the visible range and becomes zero in the infrared wavelength range.<sup>33</sup> The LLDPE-P1 samples were placed at a distance of about 25 cm



**Figure 1.** Pattern of UVA and UVB lamps arrangement in the accelerated ageing system.

below the lamps, under conditions of constant temperature, at 50°C and without humidity for a period of 800 h. The so artificially degraded samples are labelled: “exposure in the lab to UV”.

Another set of LLDPE-P1 samples was exposed in the oven to artificial thermal ageing at 50°C for 800 h. These samples are labelled: “exposure in the lab to heat”.

Samples (of A4 paper size) were collected weekly during the accelerated ageing (UV and heat) to analyze the evolution of their mechanical and chemical properties.<sup>27</sup>

### Soil Burial Experimental Set-Up

To follow the evolution of the degradation of the three groups of film samples (“LLDPE-P1 untreated”, “LLDPE-P1 oven-treated” and “LLDPE-P1 UV-treated”) during their burial exposure in the field, it was decided to conduct four recalls for each group. Consequently 12 pouches were prepared as follows (Figure 2): A 3 kg mass of soil containing a 2 g mulching film sample was placed in each pouch made of a PP net (dimensions of the net: 0.35 mm×1 mm). The soil was collected from the experimental field and sieved (2 mm). The pouches with the samples were buried in October 2005 in the field in the configuration shown in Figure 3. The first recall was planned to take place after one year (October 2006) but since the field was flooded at that time, the recall was postponed for April 2007 (total burial time: 19 months). The second set was recovered one year after the first recall, in April 2008 (total burial time: 31 months). The third set of samples was recovered in June

2011 (total burial time: 69 months). The fourth set of samples was removed from the soil in July 2012 (total burial time: 82 months; almost 7 years).

### METHODS OF ANALYSIS AND TESTING

#### Recovery and Weighing of Samples After Their Soil Burial Exposure

**First recall (19 months burial exposure in the field).** The mulching film samples “LLDPE-P1 oven treated” and “LLDPE-P1 untreated” during the first recall were found intact inside their pouches. The soil was easily separated from both samples.

The “LLDPE-P1 UV treated film” (Figure 4) was found fragmented into small pieces. In this case, a special separation procedure was introduced to recover the small plastic fragments from the soil as follows:

The visible fragments were first manually removed from the soil. In order to separate the remaining plastic micro-fragments from the soil, a solution of glycerol-water (9 : 1 by weight) was added to the soil containing the plastic fragments. The mixture was stirred for about 5 min. The visible floating fragments were collected first. Then, the mixture was filtered through a “gooch” crucible (porosity 2). The visible plastic remains were collected from the walls of the filter and placed on a Petri-dish. This procedure (Figure 5) was repeated until no visible fragments were left for collection. The larger fragments were washed with diluted water to remove the soil adhered on them and they were dried in the oven at 104°C





**Figure 2.** Typical PP net-pouch with 3 kg soil from the experimental field containing an LLDPE-P1 film sample. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

for 2 h. After cooling at ambient temperature, they were weighed in an electronic OHAUS Explorer analytical balance, along with all other collected fragments, to calculate the percentage of weight loss.

**Second recall (31 months burial period in the field).** The second recall took place in April 2008. The “LLDPE-P1 oven treated” sample was composed of a portion (half of it) fragmented into small pieces while the rest of the sample was still intact. The part of the sample that was found intact was directly separated from the soil. This part is shown in Figure 6(a) as it was extracted from the pouch. The fragmented part of the sample was recovered using the procedure described above. A change in the concentration of the glucose solution was made in this procedure by using 16 g glucose in 500 g water (16/500).

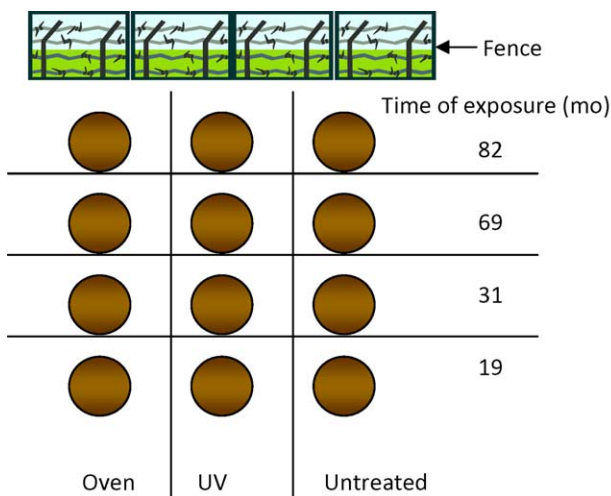
The “LLDPE-P1 UV treated film” was found fragmented into small pieces like the sample of the first recall described in the previous paragraph. The separation of the small pieces of the film was more difficult this time since they were broken into



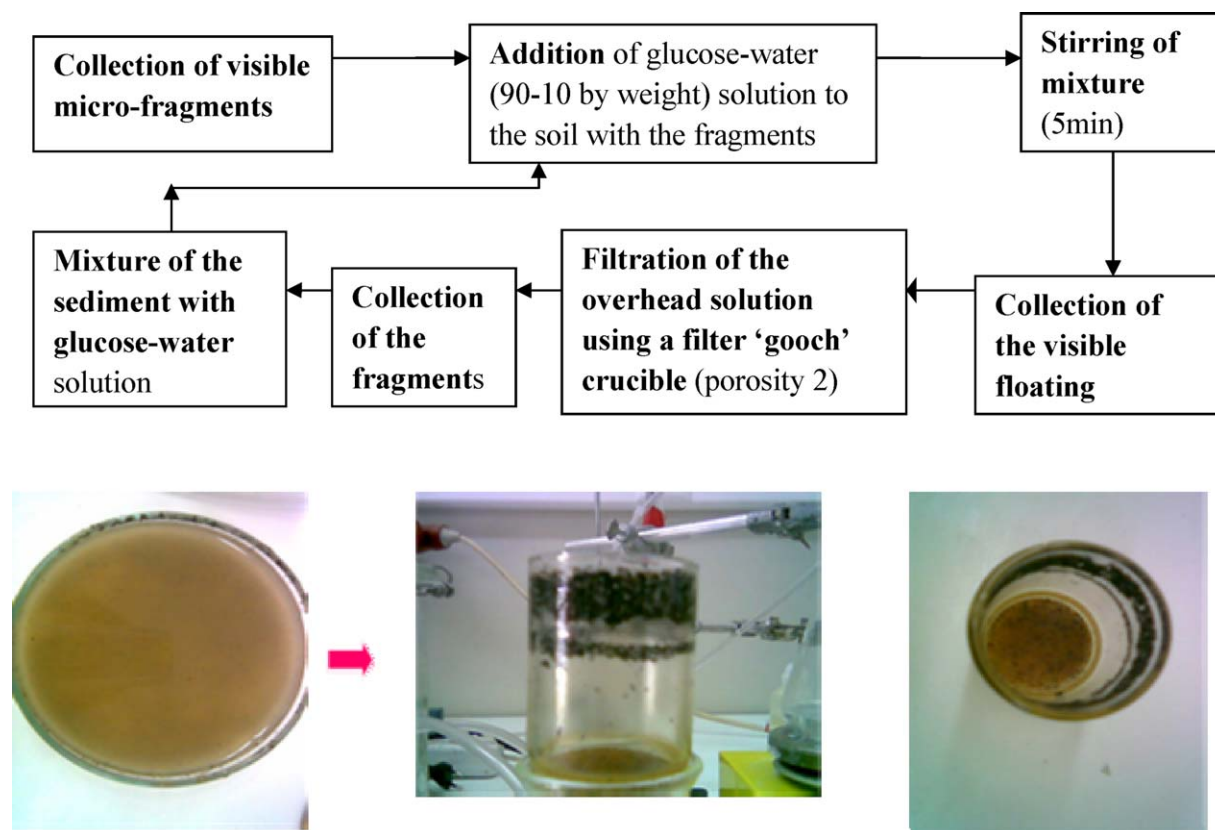
**Figure 4.** Pouch with soil and micro-fragments from UV pre-treated sample after 19 months soil burial. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

even smaller fragments. This suggests a progressive embrittlement that leads to “pulverization” of the material under pure mechanical stress (e.g. in the field such stress could be induced by water movement, roots, earthworms, temperature changes, etc.). Despite the difficulties, some of the bigger-size pieces were collected carefully and placed on a Petri-dish using pincers [Figure 6(b)].

Another difficulty encountered in the effort to recover the plastic fragments from the soil, was that many very small-size fragments of the film could not be distinguished from the soil aggregates [Figure 6(c)]. To deal with this, de-ionized water was added to disperse the soil aggregates. The water solution with the soil aggregates and sample fragments was stirred carefully with pincers in order to dissolve the soil and keep the film fragments intact. Then, the visible floating fragments were collected manually and placed in a Petri-dish. For the separation of the remaining visible micro-fragments from the soil, the same separation procedure was followed as the one described in the first recall. In the case of the second recall, 10 filters were used instead of one in order to accelerate the procedure due to the increased number of the micro-fragments to be collected. It



**Figure 3.** Experimental set-up for soil burial of samples degraded under laboratory conditions. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 5.** Separation of micro-fragments using a filter 'gooch' crucible with porosity 2. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

should be noticed that very small, almost invisible fragments could not be collected with this procedure. The percentage of the almost invisible and unrecoverable fragments is expected to increase with the time of soil burial exposure due to the ongoing degradation process. The same weighing procedure described in the first recall was followed to calculate the percent of LLDPE-P1 micro-fragments recovered.

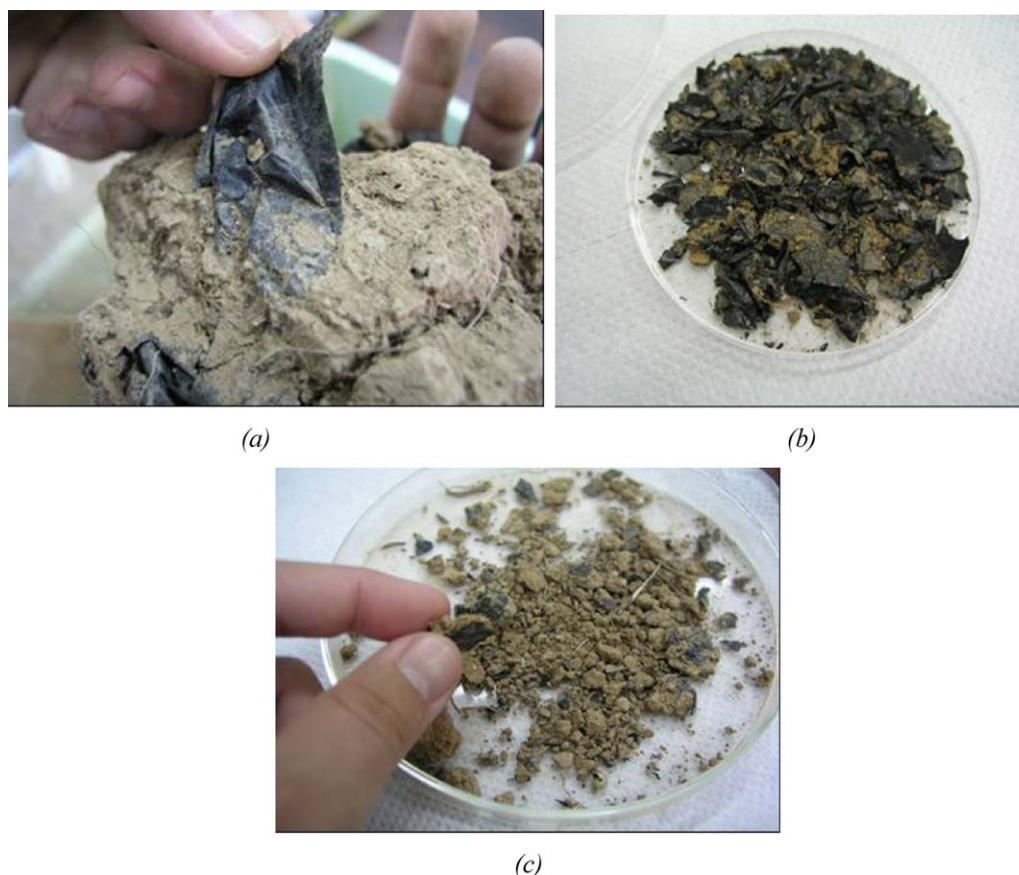
**Third recall (5 years and 9 months in the field).** The third recall took place in June 2011, 3 years and 2 months from the second recall (total burial exposure of 69 months). The "LLDPE-P1 oven-treated" sample was easily extracted from the pouch in the form of five large pieces. The "LLDPE-P1 untreated" sample separated from the soil had the form of the initial film sample, with a number of very small holes visible on its surface [see Figure 7(a,b)]. The "LLDPE-P1 UV treated film" sample was found totally fragmented into many very small fragments adhered to the soil. These fragments were, in their majority, indistinguishable from the soil aggregates as in the case of the corresponding sample of the second recall [see Figure 7(c)].

The procedure followed to separate the adhered small fragments from the soil in the case of the UV-treated sample is described in Figure 8. The micro-fragments recovered following this method were put in a glass beaker. To ensure the purity of these parts and in order to further separate them from the organic phyto-genic impurities usually found in the soil, butyl alcohol was added in the glass and the solution was stirred for 5 min. The

differences in the specific gravity of the organic phyto-genic residues (e.g. wheat straw:<sup>34</sup> 24–323, hay: 40–350, pine wood: 370–660 kg/m<sup>3</sup> etc.) compared to the polyethylene (specific gravity of 910 kg/m<sup>3</sup>) in butyl alcohol (specific gravity: 809.7 kg/m<sup>3</sup> (20°C)), causes the phyto-genic residue to float and the PE to sink. After the removal of the organic residues, the solution with the PE micro-fragments was filtered through a pre-weighed paper filter. The filter containing the PE micro-fragments was dried in an oven with circulating air for 24 h at 50°C and then weighed in order to calculate the weight of the recovered micro-fragments. The same weighing procedure as before was followed to calculate the weight of collected LLDPE-P1 micro-fragments.

**Fourth recall (6 years and 10 months in the field).** The LLDPE-P1 samples of the fourth recall were unburied in July 2012, 1 year and 1 month from the third recall (total burial exposure of 82 mo). The "LLDPE-P1 untreated" sample was separated from the soil in the form of one large plastic piece with small holes visible on its surface, one plastic piece of smaller size and several other even smaller plastic pieces Figure 9(a). All of them were removed using pincers. One portion of the "LLDPE-P1 oven-treated" sample was separated from the soil using pincers (in the form of two large pieces and one smaller) while the rest of the plastic sample was shattered into very small fragments adhering to the soil. The same procedure described in the previous section for the UV-treated plastic material was followed to recover the small plastic fragments. A photo of the small pieces recovered is shown in Figure 9(b).

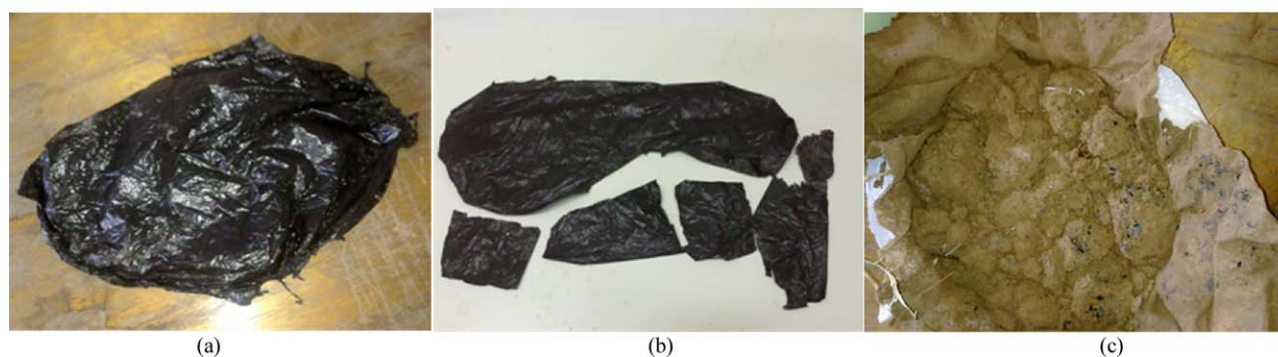




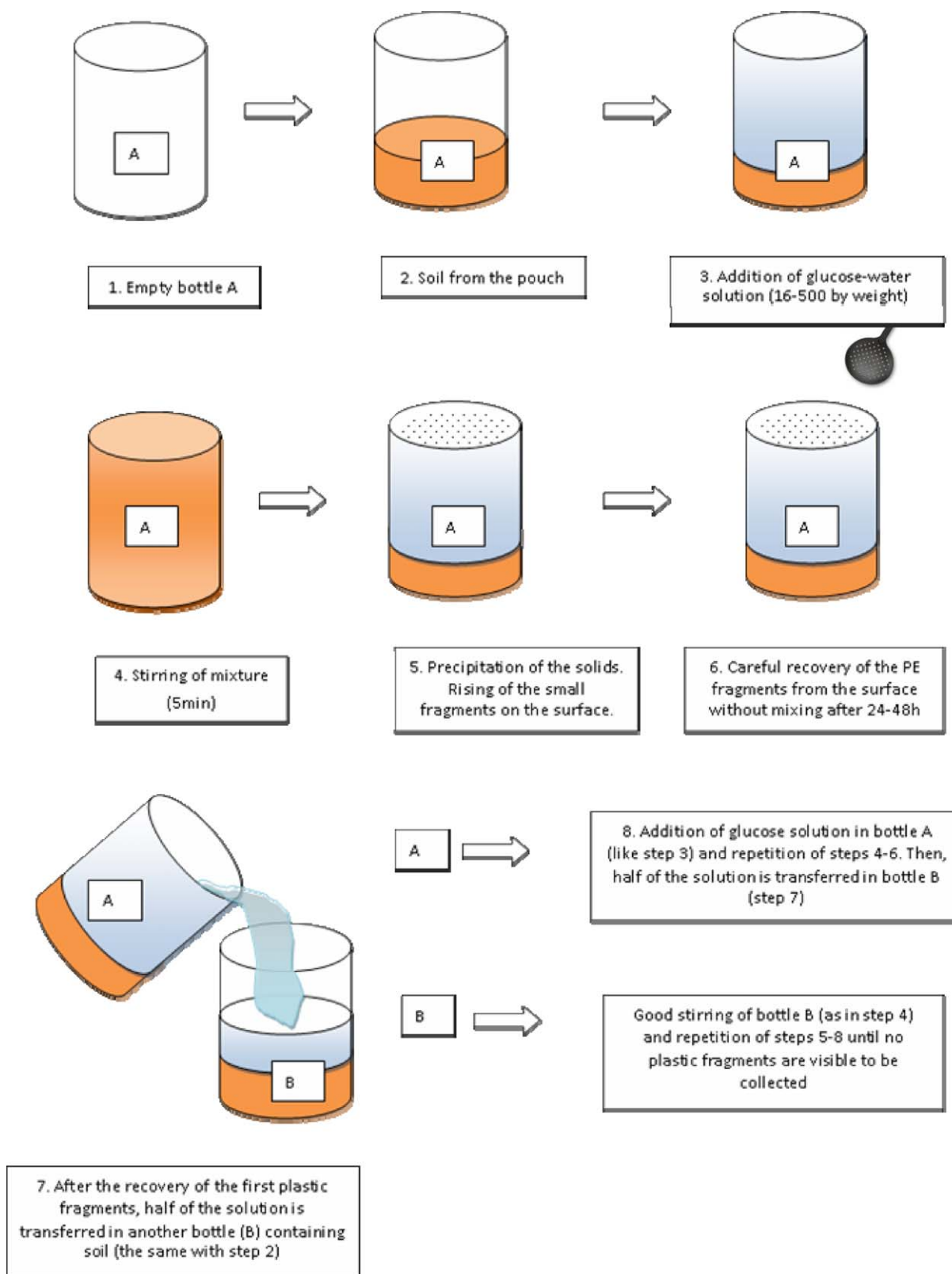
**Figure 6.** (a) Extracting the intact part of the “LLDPE-P1 oven treated” sample after 31 months soil burial; (b) LLDPE-P1 UV treated film pieces collected in a petri dish (31 months); and (c) solid aggregates of fragments and soil (31 months). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

In the case of the “LLDPE-P1 UV-treated” sample removed from the soil after 82 months of soil burial exposure, it was impossible to distinguish visually the plastic material from the soil. The procedure used in the previous recalls to remove the plastic from the soil aggregates did not succeed. Another approach for the collection of even smaller micro-fragments that remained attached to the soil aggregates was tested by means of metallic pincers electrically charged. The negatively

charged pincers were held near the black spots that could be distinguished in the soil- of dimensions less than 1 mm and bearing a resemblance to the black plastic film pieces. Since plastics are insulators, the electrons in their atoms and molecules are able to move slightly to one side, away from the pincers, leaving more positive charges closer to the negatively charged pincers and causing the attraction of the black plastic fragments onto the pincers.<sup>35</sup> The collected micro-fragments



**Figure 7.** (a) LLDPE-P1 untreated sample inside the pouch and after washing and drying in room temperature, (b) LLDPE-P1 oven-treated sample, and (c) LLDPE-P1 UV treated sample, all after 69 months in soil burial conditions. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



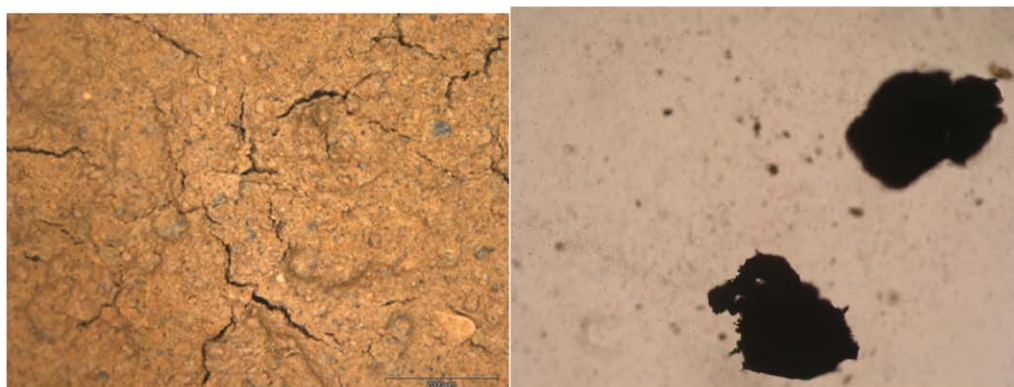
**Figure 8.** Separation of micro-fragments using a system of bottles. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



(a)



(b)



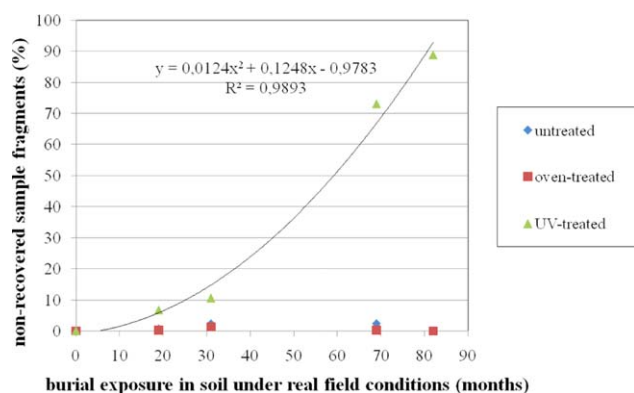
(c)

**Figure 9.** (a) LLDPE-P1 untreated sample inside the pouch and after washing and drying in room temperature (digital photo), (b) LLDPE-P1 oven-treated sample (digital photo), and (c) LLDPE-P1 UV treated sample (digital microscopy photos with magnifications at the scale of 2000  $\mu\text{m}$ , 500  $\mu\text{m}$ ;  $\times 10$ ,  $\times 40$ ), all after 82 months in soil burial conditions. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

were optically observed through digital microscopy in order to confirm that they are indeed plastics. As shown in Figure 9(c), such small pieces were found in dimensions of less than 500  $\mu\text{m}$ . Consequently, it was proved that after 82 months in soil burial conditions, the “UV-treated LLDPE” sample was frag-

mented into very small pieces of dimensions less than 1mm, very difficult to be traced, if visible to naked-eye, and therefore difficult to be collected. The percentage of non-visible micro-fragments should be expected to be higher with longer burial periods.





**Figure 10.** Graph depicting the evolution of non-recovered LLDPE-P1 sample micro-fragments (%) after their exposure under soil burial conditions over a period of 7 years. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Tensile Properties – Measurement of Mechanical Degradation

The mechanical properties (tensile strength (MPa), elongation at break (%) and stress at yield) of the recovered intact samples were measured according to the provisions of the standard EN ISO 527-3<sup>36</sup> (or ASTM D882<sup>37</sup>) by using an INSTRON Model 4204. The results obtained were compared to the evolution of the corresponding mechanical properties measured during the exposure of the same samples to artificial ageing in the lab, before their burial in the field (as reported in Ref. 27).

### DSC – Analysis of Thermal Properties

Heat effects that are associated with phase (thermal) transitions and chemical reactions of the polymer are monitored

as a function of temperature by Differential Scanning Calorimetry (DSC). The thermal properties of the recovered samples were analyzed in a Perkin Elmer Pyris 6 Differential Scanning Calorimeter, calibrated with Indium. The thermograms of small  $15 \pm 5$  mg plastic samples were recorded at a constant rate of  $10^\circ\text{C}/\text{min}$  in two cycles: (a) heating from  $-5$  to  $200^\circ\text{C}$ , followed by (b) cooling from  $200$  to  $-5^\circ\text{C}$ . The cycle was repeated three times in total to eliminate any thermal history effects and to assure thermal stability of the sample under the chosen conditions. The measurements were performed under nitrogen atmosphere, to avoid thermal degradation.

### FTIR Spectroscopy – Identification of Chemical Composition

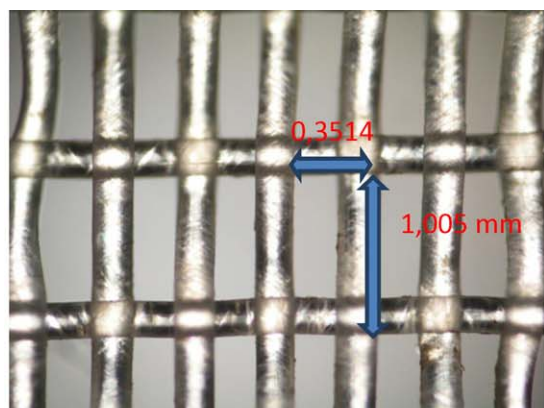
Mid infrared spectra of the recovered samples were obtained through Fourier transform infrared spectroscopy (FTIR) measurements conducted on a Tensor 27 by Bruker Optics FTIR spectrometer (Standard system with OPUS software). Attenuated total reflection (ATR) FTIR spectroscopy was employed in these measurements using a single reflection diamond accessory (Dura-samplIR2, by SENSIR). More details about the technical parameters of these measurements are given in Ref. 27. The presence of carbon black in the samples led to the selection of the FTIR ATR spectroscopy over the FTIR transmission spectroscopy. In the presence of carbon black in the samples, transmission specs suffer higher signal loss than ATR specs, as carbon strongly absorbs infrared radiation over a broad range of frequencies. Furthermore, during aging, the deterioration of the mechanical properties of the film renders the samples too fragile to be handled properly and obtain reliable transmission spectra.

**Table I.** Evolution of the Weight of the LLDPE-P1 Samples Recovered Following Their Exposure in the Soil Under Real Field Conditions (Four Recalls)

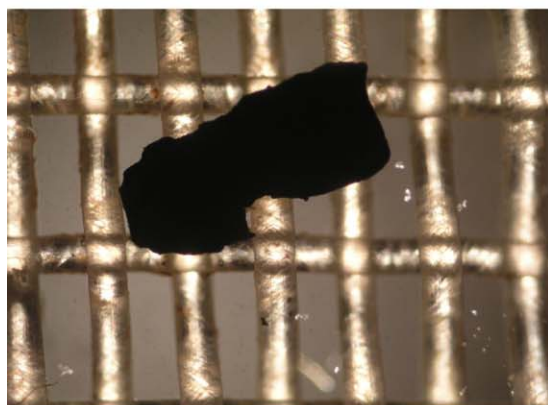
Sample	Initial sample weight (g)	Weight of the collected fragments of sample (g)	Non-recovered sample fragments (%)
Recovered samples after 19 months soil burial (first recall) <sup>a</sup>			
LLDPE-P1 untreated	2.0185	2.0047	0.7
LLDPE-P1 oven-treated	2.0086	2.0031	0.3
LLDPE-P1 UV-treated	2.0283	1.9005	6.7
Recovered samples after 31 months soil burial (second recall)			
LLDPE-P1 untreated	2.0327	1.9856	2.3
LLDPE-P1 oven-treated	2.1452	2.1165	1.3
LLDPE-P1 UV-treated	2.0856	1.8640	10.6
Recovered samples after 69 months soil burial (third recall)			
LLDPE-P1 untreated	2.0125	1.9637	2.4
LLDPE-P1 oven-treated	2.0356	2.0300	0.3
LLDPE-P1 UV-treated	2.1452	0.8301 <sup>b</sup>	61.3 <sup>b</sup>
Recovered samples after 82 months soil burial (fourth recall)			
LLDPE-P1 untreated	2.0477	2.0808	-
LLDPE-P1 oven-treated	2.0288	2.2900	-
LLDPE-P1 UV-treated	2.0086	0.2131 <sup>b</sup>	89.0 <sup>b</sup>

<sup>a</sup>Based on the weight of the sample fragments separated from the soil aggregates.

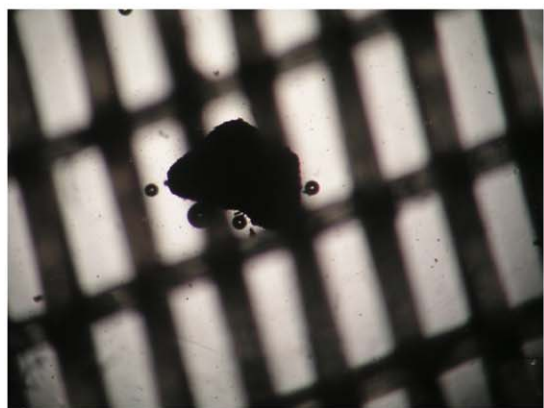
<sup>b</sup>Very small fragments not possible to recover.



(a)



(b)



(c)

**Figure 11.** (a) Digital photo of the pouch net showing the dimensions of the net openings, (b) digital photo of a micro-fragment found attached on the pouch net, and (c) magnification  $\times 40$  of micro-fragments against the pouch net. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

#### Optical Microscopy – Identification of Micro-Fragments Size

The degree of fragmentation of the samples exposed to soil burial degradation was evaluated through digital microscopy by using an OLYMPUS microscope, model B $\times 51$ TRF and a digital camera (OLYMPUS model C-5050ZOOM).

#### Scanning Electron Microscopy (SEM) – Identification of Morphological Degradation of the Films

SEM is a significant and reliable tool to measure the morphological and topographical changes of a degraded polymer. The scanning electron photomicrographs of the three series of LLDPE samples before and after soil burial studies have been taken using an SEM Jeol company model 6360 (2004) after sputter coating their surface with gold. A Denton Vacuum DV 502 sublimator was used equipped with specific components for the sublimation of metals and voltaic arc for covering the samples with carbon and gold using glow evacuation in argon atmosphere.

#### RESULTS AND DISCUSSION

##### Evolution of the Disintegration of the LLDPE-P1 Films in Soil Over a Period of Seven Years

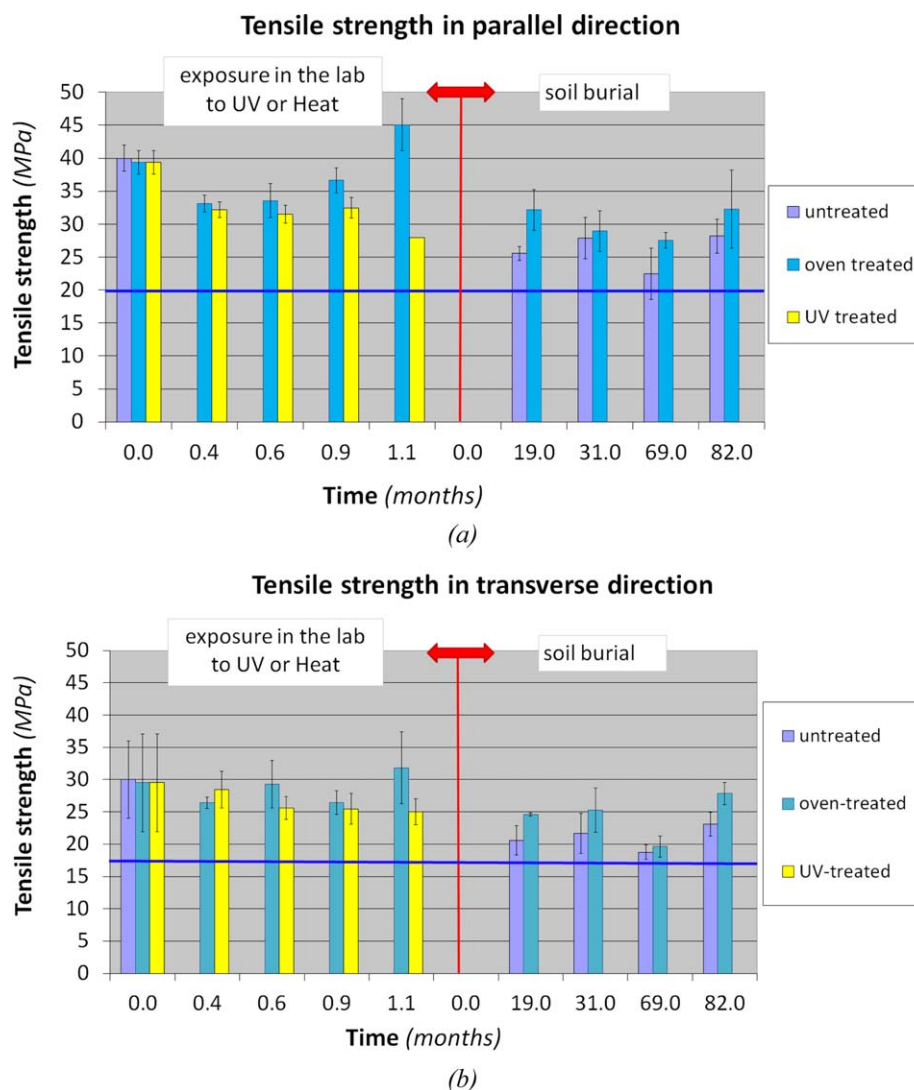
The changes in the weights of the recovered samples during their burial (four recalls) are recorded in Table I and graphically depicted in Figure 10. As it can be inferred from the table, no significant changes were found in the weight of the recovered samples after their burial for 19 months in the field (first recall), taking also into account that the separation method applied offers only a lower bound recovery rate and depends strongly on the degree of fragmentation of the sample.

The samples of the second recall (31 months soil burial in the field) show higher percentages of non-recovered fragments. Specifically, for the UV-treated samples, the sample fragments that were not recovered increased by 4% during the time period from 19 to 31 months. This can be justified by the intensive micro-fragmentation of the UV-treated samples during this period that rendered the recovery of the very small micro-fragments impossible.

The weights of the recovered sample fragments of the third recall (69 months in the field) indicate a significant increase of the non-recovered micro-fragments in the case of the UV treated sample: a high percentage of 61% of the initial weight was not recovered after 69 months vs. the 11% not recovered after 31 months of burial in the soil. No significant changes were recorded for the percentages of the non-recovered fragments of the other two series of samples.

Referring to the fourth recall, the weight of the initial sample not recovered after 82 months in the case of the UV-treated sample, reached a very high percentage of 89%. No changes were observed regarding the other two series of samples.

The large percentage of very small micro-fragments in the case of the intensive UV-treated series, many of which were invisible by naked eye as shown for the sample buried in the soil for 82 months [refer to photographs taken through digital microscopy in Figure 9(c)], introduces a question about the reliability of the method used to recover the micro-fragments. As shown in Figure 11, the size of these invisible fragments was smaller than the size of the net openings (e.g. sample micro-fragment: 500  $\mu\text{m}$ , net dimensions: 0.35–1mm). This suggests the possibility of micro-fragments smaller than the net opening to be transported by the ground water, escaping the pouch. In parallel, the efficiency of the separation method described in Figure 8 is



**Figure 12.** Tensile strength (MPa) of LLDPE-P1 films during the exposure in the lab to UV or heat and during the soil burial exposure (a) in parallel and (b) in transverse direction. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

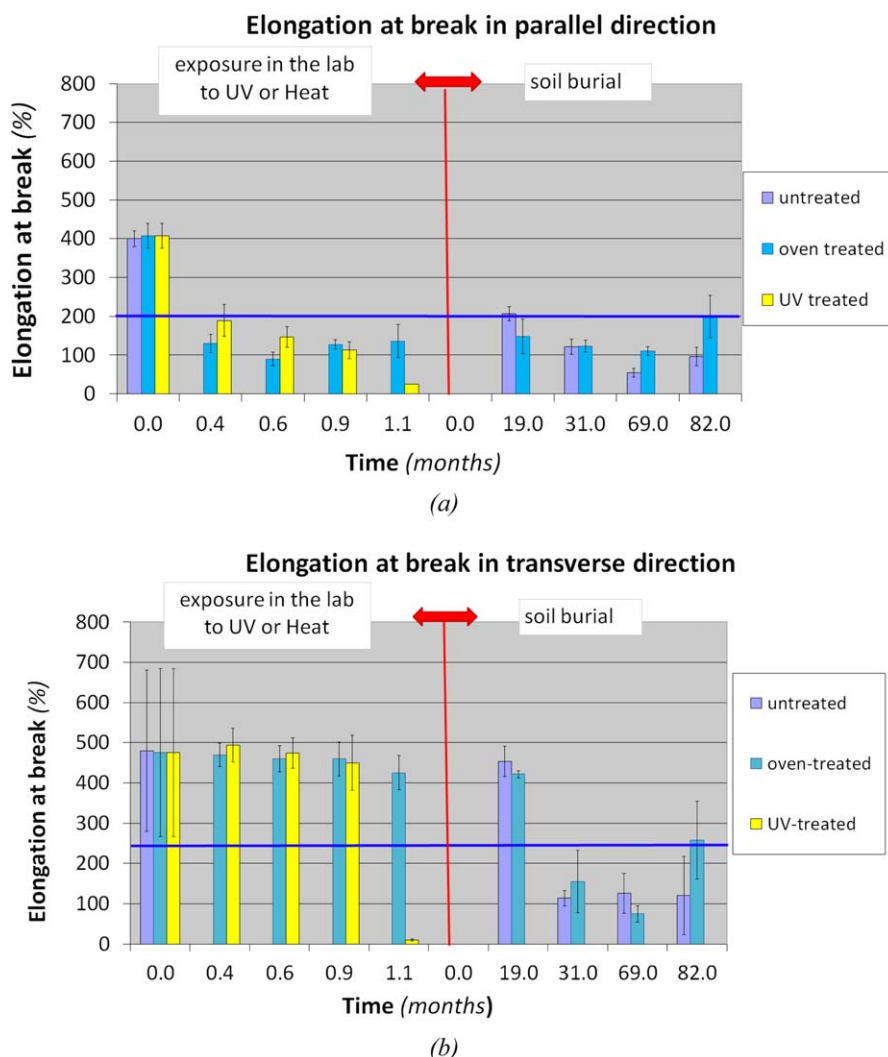
questionable as: (1) it assumes that the micro-fragments are separated from the soil aggregates, which is not possible for all micro-fragments and (2) it is practically impossible to collect quantitatively the invisible or nearly invisible micro-fragments from the water-glucose solution.

Based on the evolution of the percentage of the non-recovered micro-fragments of the LLDPE-P1 samples pre-treated by UV radiation and recovered in four recalls, one may estimate the long term trends of the expected maximum generation of non-recoverable micro-fragments of the UV treated samples under real soil burial conditions. The corresponding behavior of the pre-treated by high temperature samples suggests recovery of most of the initial samples buried during the specific time period while it was possible to recover all the buried non-treated samples.

The naturally degraded mulching films (the same LLDPE-P1 material) used in water melon cultivation) showed no fragmen-

tation during burial for 8.5 years, but only strong embrittlement.<sup>27</sup> This implies that a much longer soil burial period is needed for a possible fragmentation of these remains to the degree of invisible micro-fragments experienced by the samples exposed artificially to intensive UV-A/UV-B radiation. Based on the results of Ref. 27, polyethylene mulching films with pro-oxidants are strongly degraded during their useful life-time under the solar UV radiation and summer temperatures (depending on the composition of the polyethylene mulching films, the type and percentages and the ratio of pro-oxidants to UV-stabilizers). These degraded films, buried in the soil at the end of the cultivation period, are expected to undergo a gradual fragmentation and may be slowly transformed into tiny micro-fragments after a very long period (e.g. after some decades according to the results reported in Ref. 28), polluting the soil and the water. The difference in the long-term degradation behavior of the naturally degraded mulching films in the soil from the samples exposed to high UV radiation is the time





**Figure 13.** Elongation at break (%) of LLDPE-P1 films during exposure in the lab to UV or heat and during the soil burial exposure (a) in parallel and (b) in transverse direction. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

scale. As the practice of burying the used/degraded mulching films after each cultivation period continues for several years, a steady accumulation of remains undergoing gradual fragmentation and the subsequent accumulation of polyethylene micro-fragments should be expected in the soil. The fate of these continuously degrading micro-fragments into invisible micro-fragments and their possible impact for the environment and human health is unpredictable.

#### Evolution of the Critical Mechanical Properties of the Films

Figures 12 and 13 depict the changes of the mechanical properties of the LLDPE-P1 samples during their artificial ageing phase through their exposure to high UV radiation and to thermal degradation<sup>27</sup> and subsequently, during their burial phase in natural soil, along with samples not exposed to artificial aging. No mechanical tests could be performed with the “LLDPE-P1 UV-treated” samples as they were seriously fragmented.

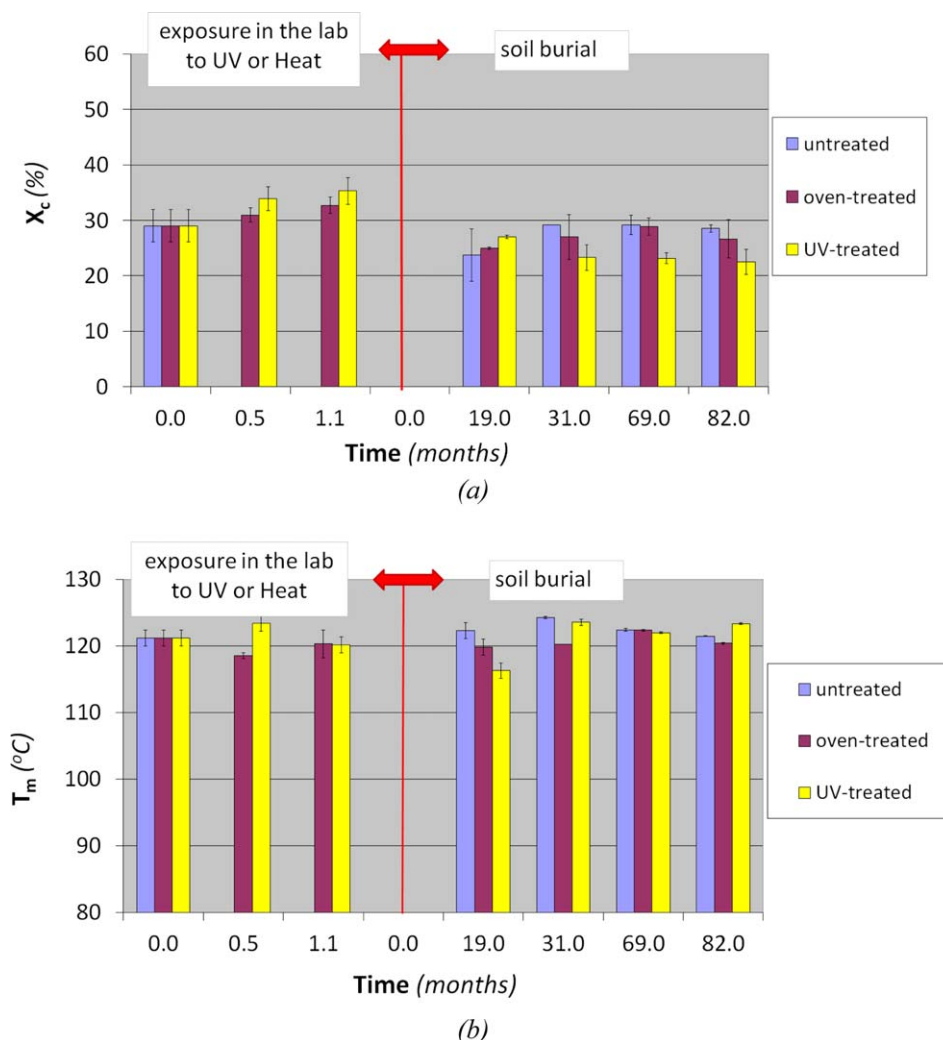
As shown in Figure 12 and Figure 13, during the artificial ageing (UV or heat) the tensile strength of the mulching film sam-

ples in both directions remained almost unchanged. During the soil burial period, the untreated films and the pre-treated in the oven films showed a maximum loss of their tensile strength in the parallel direction up to 43.9% and 40.0% after 69 months and 29.5% and 28.48% after 82 months of exposure, respectively. In both cases the tensile strength never reached the stress at yield value of 20 MPa (degradation criterion<sup>38</sup>).

In the transverse direction, the untreated and oven-treated samples buried for 69 months, lost the 37.5% and the 38.4% of their tensile strength respectively and 23.1 and 12.6% after 82 months of soil burial exposure.

The elongation at break values of the films in the parallel direction, showed a reduction of 93.8%, after 1.1 months of exposure to high UV radiation and 67%, after 1.1 months in the oven. In the transverse direction, the loss was abrupt, at 97.9%, after 1.1 months for the UV-treated materials.

The accelerated UV-A, UV-B induced degradation led to a more drastic embrittlement of the samples as compared to the natural solar UV radiation induced degradation where a maximum



**Figure 14.** (a) Crystallinity values ( $X_c$  %) of the LLDPE-P1 mulching films based on DSC measurements during the artificial ageing procedure and during the soil burial exposure up to 82 months and (b) changes in the melting temperature of the LLDPE-P1 mulching films based on DSC measurements during the artificial ageing procedure and during the soil burial exposure up to 82 months in the field. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

reduction of elongation at break of 73.7% and 47.7% was observed in the parallel and transverse direction.<sup>28</sup> The serious embrittlement explains the high degree of fragmentation experienced during the burial of the UV treated samples compared to the naturally aged ones.

As supported by many authors<sup>39–42</sup> the presence of pro-oxidants in polyethylene increases the rate of oxidation by air oxygen and cleavage of PE chains under the influence of light and/or heat. This leads to polymer fragmentation.

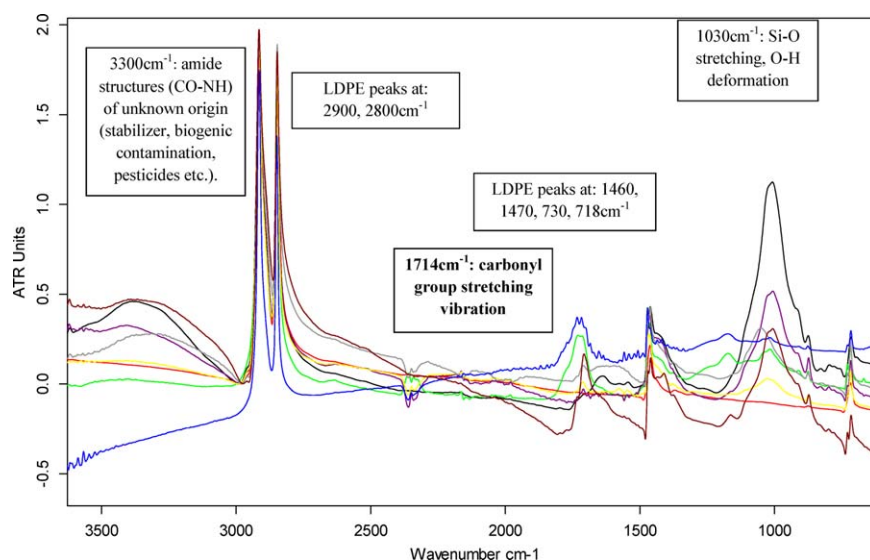
During the soil burial procedure, the elongation at break of the UV pre-treated samples was practically zero (not measurable, as it led to a drastic fragmentation). For the other two samples the maximum losses of the elongation at break in the parallel direction were recorded after 69 months: the untreated films lost 69.7% and 86.4% of their initial elongation at break value after 31 and 69 months of exposure to soil burial conditions, respectively. The oven-pre-treated samples presented a stable trend in the already low values of their elongation at break in parallel

direction during soil burial. The maximum loss of the elongation at break of the oven pre-treated samples in the transverse direction was recorded at 82.5% after 69 months of soil burial. The untreated samples lost 74.9% of their elongation at break after 82 months of soil burial.

The differences observed in the degradation of the mechanical properties of the samples recovered after 69 and 82 months (shown in Figure 12 and Figure 13) may be attributed to differences in the prevailing local soil conditions (i.e. different abiotic degradation conditions like soil characteristics, water content, vegetation etc.).

#### Evolution of Thermal Properties of the Films Through DSC Measurements

Figure 14(a) depicts the evolution of the crystallinity of the LLDPE-P1 samples, based on DSC measurements. The evolution of crystallinity during the artificial ageing period in the lab,<sup>27</sup> and during their exposure for 82 months under soil burial conditions is presented. An increase in crystallinity of the



**Figure 15.** FTIR-ATR spectra of the LLDPE-P1 samples before their exposure (original sample –red), exposed to artificial UV degradation (UV-treated samples) for 0,5 months UV (green), 1,1 months UV (blue), exposed to soil burial conditions for 19 months (brown), 31 months (black), 69 months (grey), 82 months – big plastic fragments (yellow), 82 months – fragments < 1mm (mauve), following the UV-treatment for 1,1 months. Wavenumber range: 3000–600 $\text{cm}^{-1}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

samples exposed to thermal and UV induced degradation for 1.1 months of 12.7% and 21.7%, respectively, was observed. A similar trend to that of the artificially degraded by UV radiation samples [Figure 14(a)] was observed in the crystallinity of the LLDPE-P1 mulching films exposed to real cultivation conditions (natural ageing).<sup>27</sup>

Balasubramanian *et al.*<sup>42</sup> showed that the thermo-oxidation of low density polyethylene (LDPE) films with cobalt stearate as pro-oxidant at 70°C induced chain scission. The chain scission of the LDPE films was found to increase with the thermal-oxidation time, followed by a slight increase in crystallinity and a decrease in the strain at break. Benitez *et al.*<sup>41</sup> confirmed this trend in LLDPE and LDPE with pro-oxidants exposed to environmental or oven induced thermal weathering. The samples showed an increase in crystallinity with the exposure time and higher degradation of samples for all the pro-oxidants used, while those containing a higher pro-oxidant concentration (2%) seemed to be slightly more affected.

The increase in crystallinity of the exposed samples has been associated with a decrease in the average molecular weight of the samples.<sup>39,43,44</sup> Corti *et al.*<sup>40</sup> reported that the DSC of LDPE films with pro-oxidant exposed to the solar UV radiation showed a slight increase in crystallinity as compared to unexposed samples. It was suggested that, the oxidization of the films under sunlight-induced aging produced lower molecular weight products, confined in the amorphous portion of the polymer matrix. The observed crystallinity increase is explained by the fact that the remainder of the polymer mass is more susceptible to molecular reorganization. Little if any change in crystallinity was observed in LLDPE without pro-oxidant additives.<sup>40,45</sup>

The increase in crystallinity has also been related to the mechanical properties degradation, mainly the elongation at

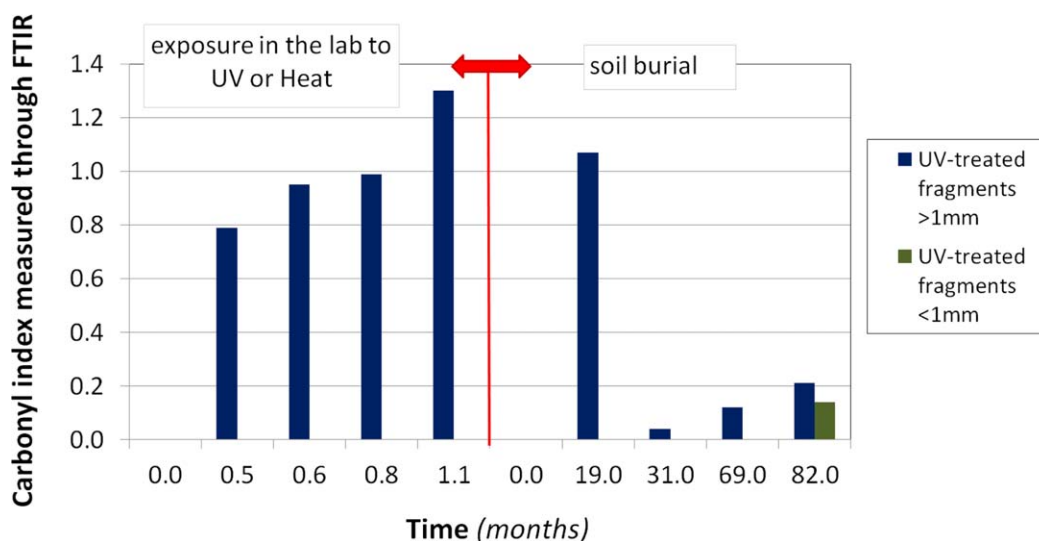
break, of the films exposed to real cultivation conditions.<sup>27</sup> This was confirmed by similar research results in the literature.<sup>39,43,44</sup>

Figure 14(a) shows that the crystallinity of the untreated films remained rather constant during the whole soil burial period, taking into account the standard deviation of the measurements. On the opposite, a reduction of crystallinity is shown for the two artificially aged series of samples during the first period of their soil burial exposure. The values measured are 23.6% below the corresponding increased crystallinity values of the artificially degraded samples in the lab (same decrease value for both the oven and UV-treated materials). Following the initial reduction, the crystallinity values of the thermally degraded samples stay rather constant (from 19 to 82 months of soil burial) taking into account the standard deviation of the measurements. The UV artificially degraded samples show a further decrease of the crystallinity value after 31 months of soil burial that remained constant thereafter. During the 82 months of soil burial, the oven and UV pretreated samples presented a decrease in crystallinity of 17.7% and 36.4%, with respect to the corresponding values of the artificially degraded samples, respectively.

The parallel investigation of Ref. 28 on the long term degradation behavior of the LLDPE with pro-oxidants mulching films after their application in the field under water melon cultivation conditions and their subsequent burial in the soil for 8.5 years, has shown a maximum decrease in crystallinity of 25.8% during burial with respect to the corresponding increased values reached at the end of the cultivation period.

A possible explanation for the decrease of crystallinity during soil burial, given in the work of Ref. 28, considers that the presence of radicals formed during aging can lead to the formation of crosslinks in conditions of oxygen absence (e.g. due to periodically flooded field) during soil burial.



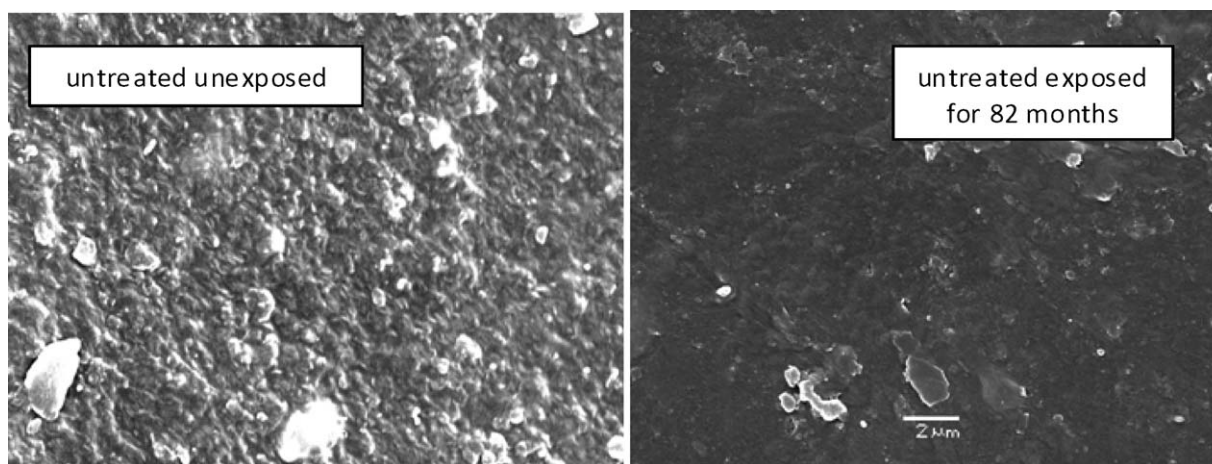


**Figure 16.** Evolution of the carbonyl index (CI) of the LLDPE-P1 mulching film samples during the artificial ageing procedure and during their exposure under soil burial conditions measured through FTIR-ATR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

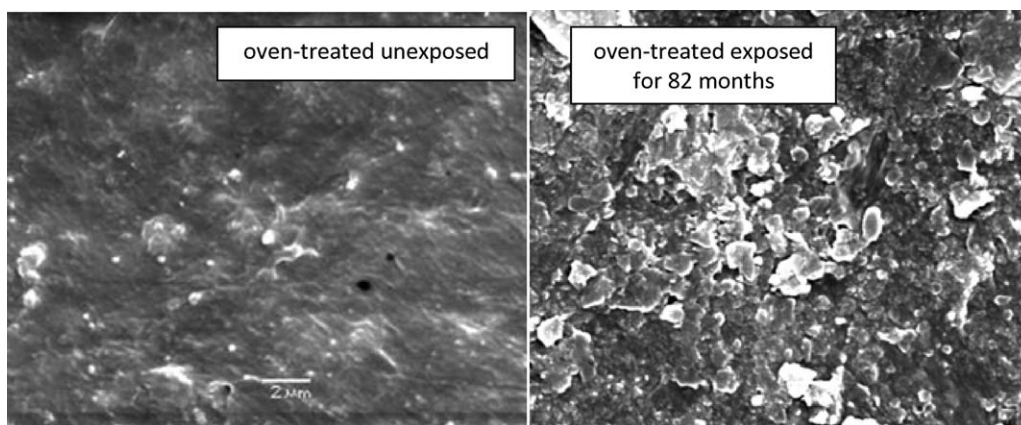
Correspondingly, as mentioned in literature<sup>46,47</sup> for the case of the pre-treatment of film samples through their exposure to heat or/and to light, the pro-oxidants enhance the oxidation of polyethylene, through the generation of free radicals. The free radicals react with molecular oxygen to produce peroxides and hydroperoxides, that, in the presence of heat light and metallic ions, decompose leading to the formation of macroalkoxy radicals. Subsequently, the auto-oxidation of polyethylene proceeds through classical free radical chain reactions<sup>46,47</sup> resulting in chain scission and cross-linking. These reactions are strongly affected by the presence of oxygen. In the presence of oxygen, chain scission and macromolecules oxidation are the predominant reactions.<sup>47</sup> On the opposite, thermal degradation (or photo-degradation) can lead to crosslinking, associated with crystallinity decrease, in conditions of oxygen absence.<sup>28</sup>

In agreement with the above mentioned research works, in the case of the present experiment, the samples that presented a declining trend in their crystallinity values under soil burial conditions were the oven pre-treated and UV irradiated samples. This indicates that the heat and the UV radiation can be important parameters leading to the subsequent deterioration of the thermal and mechanical properties of the degraded films under natural soil conditions, a process that is also affected by the presence of oxygen in the soil and the periods of anoxic conditions.

The histogram of Figure 14(b) gives the changes of the melting temperature of the two series of samples subjected to artificial degradation for 1.1 months as well as of the three series of samples that were subsequently exposed to soil burial conditions for a period of 82 months. As shown in this figure, no significant alterations of the melting point of the film samples were



**Figure 17.** SEM photomicrographs of the untreated series of samples before the soil burial (left photo) and after the soil burial for 82 months (right photo) at magnification 2  $\mu\text{m}$ .



**Figure 18.** SEM photomicrographs of the oven-treated series of samples before the soil burial (left photo) and after the soil burial for 82 months (right photo) at magnification  $2 \mu\text{m}$ .

recorded either due to the artificial aging or due to the soil burial conditions.

Benitez *et al.*<sup>41</sup> showed that crystallinity variations are more sensitive in revealing degradation related structural changes than variations in the melting temperatures during oxo-degradation of LLDPE and LDPE samples containing pro-oxidants.

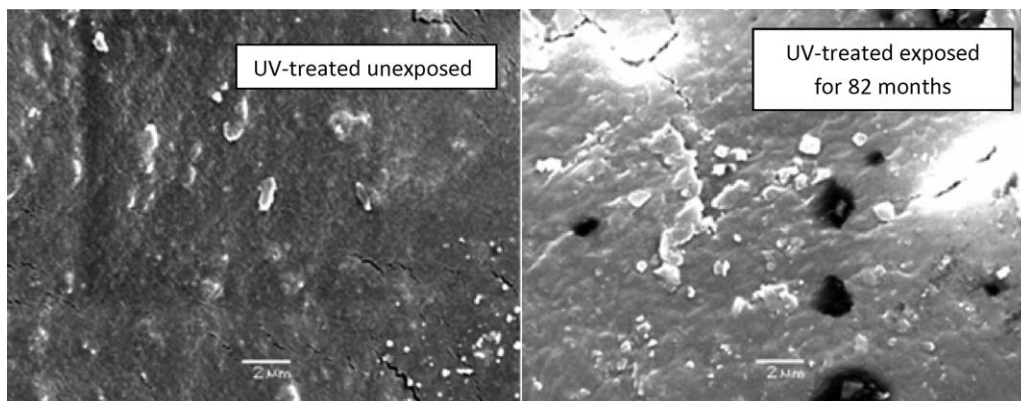
#### Evolution of Chemical Structure by FTIR Analysis

FTIR-ATR spectra run on the untreated and UV-treated series of LLDPE-P1 film samples (no spectroscopic tests had been performed during the thermal ageing of these materials) and on samples of the untreated, oven treated and UV-treated series exposed to soil burial conditions for 19, 31, 69, and 82 months presented strong features at:  $2900, 2800 \text{ cm}^{-1}$  (C–H stretching vibrations),  $1470, 1460, 1370 \text{ cm}^{-1}$  (methylene group scissoring and bending vibrations  $-\text{CH}_2$ ), and  $730$  and  $718\text{--}720 \text{ cm}^{-1}$  ( $\text{CH}_2$  rocking modes), all characteristic peaks of LDPE.<sup>48–51</sup> Additional absorption peaks were observed at the wave number ranges of  $1650\text{--}1580 \text{ cm}^{-1}$  and  $3500\text{--}3180 \text{ cm}^{-1}$  that are usually attributed to N–H bend vibrations found in the structure of primary amines.<sup>51</sup> These amines may originate from biogenic contamination of the films, pesticide residues or the presence of stabilizers. Also, additional bands noted at ca.  $1030\text{--}1040$  and  $910 \text{ cm}^{-1}$  indicated the presence of kaolinitic clay (soil).<sup>49</sup> No

trace of carbonyl band was found in the case of the untreated series of film samples before their soil burial. Figure 15 depicts the FTIR-ATR spectra of the LLDPE-P1 films exposed to UV radiation for 0.5 months and 1.1 months as well as those that were subsequently exposed to soil burial conditions for 19, 31, 69, and 82 months. As shown in these figures, a carbonyl band ( $1715 \text{ cm}^{-1}$ ) is identified after 15 days exposure of the samples to UV radiation.

It is generally known<sup>52</sup> that carbonyl peak ( $1712\text{--}1716 \text{ cm}^{-1}$ , carboxylic acid group absorbance region) increases as a consequence of photo oxo-degradation and thermo oxo-degradation of the oxo-degradable polyolefins.<sup>53</sup>

The carbonyl index (CI) of the spectra was used to express the concentration levels of carbonyl compounds measured by FTIR-ATR. The CI is defined as the carbonyl to methylene absorbances ratio (i.e. the ratio of the optical density of the carbonyl absorption band at  $1714 \text{ cm}^{-1}$  over the optical density of the methylene absorption band at  $1462 \text{ cm}^{-1}$ –  $\text{CH}_2$  scissoring peak<sup>52,54–56</sup>). The results shown in Figure 16 indicate an increasing trend for the carbonyls developed as oxidation products due to the UV radiation exposure. On the opposite, during soil burial, the quantity of accumulated carbonyl compounds appears to be decreasing to very low values. Already during the



**Figure 19.** SEM photomicrographs of the UV-treated series of samples before the soil burial (left photo) and after the soil burial for 82 months (right photo) at magnification  $2 \mu\text{m}$ .

first 19 months of soil burial exposure a 17.7% CI loss is observed as compared to the CI reached during artificial ageing. This loss is shown to be accentuated with longer burial times. This behavior is in agreement with similar observations reported in Refs. 46 and 57 where the carbonyl groups developed during a thermal pre-treatment stage disappeared during the soil burial period.

In the work of Ref. 28, a depletion of the carbonyl groups during the soil burial phase was detected for the same mulching films degraded however under cultivation conditions and experiencing an increase of the CI. The decrease of the CI under soil burial conditions was attributed to the presence of pro-oxidants leading to hydrophilic groups formation in the polymer surface that stimulates a rapid migration/diffusion of the low molecular weight carboxylic acids in the humid soil environment (water in soil).<sup>39</sup> This behavior was confirmed with laboratory experiments.<sup>28</sup>

### Morphological Characterization Through SEM

The SEM images of the untreated, oven-treated and UV-treated samples before and after their soil burial exposure for 82 months (fourth recall) are shown in Figures 17–19.

As seen in Figure 17, the two-phase morphology (LLDPE containing carbon black) of the untreated – unexposed plastic is revealed and is apparent that the film showed no surface damage after 82 months of exposure to soil burial conditions.

The oven treated samples (Figure 18), exposed to soil burial conditions for 82 months show soil particle aggregates on their surface (distinguished from the carbon-black by their size) but no other surface degradation defects.

The UV-treated film samples (Figure 19), after 82 months of soil burial, depict – in addition to the traces of soil – the development of a number of holes of varying sizes (lower than 2  $\mu\text{m}$ ) and micro-cracks. This is an indication of the gradual fragmentation the UV-treated film samples were undergoing during the long soil burial period, as a continuation of the accelerated UV-induced photo degradation in the lab. The high number of micro-cracks and microscopic voids developed justifies a gradual intense embrittlement of the material. The significant decrease of the elongation at break (practically to zero values after 1.1 months of exposure to high intensity UV radiation) was followed by the progressive abiotic fragmentation of the material into tiny or invisible micro-fragments under soil burial conditions.

### CONCLUSIONS

LLDPE mulching films with pro-oxidants used in water melon cultivation, collected after the end of the cultivation and buried in the field for 8.5 years could be recovered almost intact<sup>28</sup> despite the fact that the very low elongation at break values measured and other degradation parameters suggested that the films were at the onset of fragmentation.

In the present work, the behavior of LLDPE mulching films with pro-oxidants under a much longer time-scale (e.g. some decades) was simulated. Toward this purpose, samples of LLDPE mulching films with pro-oxidants were exposed to accel-

erated ageing in the lab through their exposure to a combination of high intensity UV-A and UV-B radiation and to thermal degradation in the oven to simulate the severe degradation/fragmentation of these films while been buried in the soil for many years, following the end of the cultivation season. Further degradation of the already highly degraded samples was investigated by burying them in the soil over a period of seven years during which degradation parameters and their evolution with time were measured.

Samples of the present work exposed to thermal degradation in an oven did not exhibit a significant fragmentation during the 7-years soil burial period, but mainly mechanical degradation. A gradual fragmentation of the UV treated samples was observed under soil burial conditions, leading to tiny and eventually invisible micro-fragments. The very small micro-fragments with diameter smaller than 1 mm could not be recovered quantitatively. The analysis of the recovered micro-fragments indicated that they had not undergone radical chemical or thermal modifications after seven years in the soil under natural field conditions. SEM analysis confirmed abiotic degradation characteristics.

The gradual fragmentation of the UV treated samples into invisible micro-fragments could represent a serious long-term risk of accumulation of micro-fragmented PE in the soil. If this type of mulching film, made out of polyethylene with pro-oxidants, is used in the field for consecutive years during the cultivation seasons and then at the end of each cultivation period it is incorporated into the soil with the plant remains, it will follow the behavior of the UV treated samples (but at considerably lower rate) as shown in the work with the same materials buried in the field after their use with water melon cultivation. In general, PE mulching films with pro-oxidants that are strongly degraded during their useful life-time (depending on the aging conditions and the type and ratio of pro-oxidants to UV stabilizers), and buried in the field at the end of the cultivation season, will be gradually transformed, at relatively low rates (e.g. in decades), into tiny micro-fragments, finally into invisible PE micro-fragments. Such micro-fragments eventually will end up to groundwater, freshwater, and seawater, and, possibly, to the air and the plants. They may enter the respiratory systems of animals and humans, and of course, the food chain. The fate of the continuously degrading micro-fragments into invisible PE micro-fragments and their possible long term impact to the environment, food safety and human health remains unpredictable. It is beyond the scope of this work to investigate such effects.

On the other hand, if the PE mulching film with pro-oxidants is not severely degraded under natural conditions (under solar UV radiation), it is highly probable that the remains of the so degraded LLDPE mulching films with pro-oxidants will not suffer serious fragmentation in the soil within a short period of a few years but will remain and accumulate in the form of large pieces and smaller fragments affecting the physical properties of the soil (e.g. hydraulic properties) and may compromise the agricultural production. As these fragments however, undergo a continuing slow abiotic degradation process under natural soil



conditions, it should be expected that after a long time they will eventually be transformed also into invisible micro-fragments.

## ACKNOWLEDGMENTS

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