

Degradation of Polyethylene Designed for Agricultural Purposes

Pierre Feuilleley,¹ Guy César,² Ludovic Benguigui,³ Yves Grohens,^{4,6} Isabelle Pillin,⁴
Hilaire Bewa,⁵ Sandra Lefaux,³ and Mounia Jamal³

For many years now, scientific articles have been published on the potential biodegradability of polyethylene. Polyethylene (PE) with peroxidant additives, in the form of agricultural films, is sold by various suppliers as biodegradable mulch. Even though, the photo-chemical and thermal degradation of these products under artificial laboratory conditions is highlighted, several extrapolation on the biodegradation and, moreover, on the neutral environmental impact of PE are made. In this study, three different commercial mulch films have been submitted to standardised biodegradation tests and the results are discussed. The first conclusions are that a very low degree of biodegradation of the commercial PE films is achieved from these tests and that crosslinked PE micro-fragments are found in soil after a very long period of time.

KEY WORDS: Biodegradability; polyethylene; fragments; crosslinking.

INTRODUCTION

Biodegradable material is defined as an industrial product which if abandoned, is destroyed by bacteria or other biological agents. Paraphrasing this definition, we can say that a biodegradable material is a material that takes on the task of destroying itself in the environment. However, the above mentioned definition is not complete and other definitions have been described by many authors according to the evaluation experiments and situation in which biodegradation takes place (soil, water, compost and waste). Thus, from the

standards currently in force (ISO, ASTM, DIN, JPBS, CEN), at least five different definitions can be found based on the attack of material by microorganisms and the production of CO₂ and/or CH₄ and water (David, 1994, NF EN 13432). Such a definition has been validated by ISO and the vocabulary has been established (ISO 14851, 14852, 14855, ISO/CD 472). Furthermore, and to be more complete, it is claimed that biodegradation also includes other phenomena such as *bioassimilation*, i.e., the conversion into biomass via biological phenomena under certain conditions and *mineralisation*, i.e., the conversion of compounds into CO₂, H₂O and mineral substances [1].

UV and Thermal Degradation of PE

Many sources clearly indicate that polyethylene (PE) is perfectly stable. Thus, we find that PE is not directly oxidisable [2–5], or that PE is inert [6] and not biodegradable [7]. Two preliminary treatments (heat and ultra violet light) are essential to modify its chemical structure. These are found to oxidise (introduce oxygen in the form of hydroxyls,

¹ CEMAGREF, 361, Rue JF Breton, BP 5095, 34033 Montpellier Cedex 1, France.

² Station Experimentale Horticole de Bretagne Sud, Route du Bono, 56400 Auray, France.

³ Université du Maine, UCO2M – UMR CNRS, 6011Av., Olivier-Messiaen, 72085 Le Mans Cedex 09, France.

⁴ Laboratoire Polymères, Propriétés aux Interfaces et Composites, Université de Bretagne Sud, Rue de St Maudé, 56321 Lorient Cedex, France.

⁵ ADEME, 2 square, La Fayette, BP 406, 49004 Angers Cedex 01.

⁶ To whom all correspondence should be addressed. E-mail: yves.grohens@univ-ubs.fr

carbonyls, peroxides), degrade (reduce the molecular weight or increase it by crosslinking reactions) and destructure (modify the crystalline structure) the PE. The first phase is the exposure of the PE to heat and ultra violet light (UV) [8–10].

The second phase is the analysis of the samples, using classical methods, in order to characterise the physical and chemical degradation induced by these treatments. Steric exclusion chromatography, IR, UV spectrometry, X-ray diffraction, electronic microscopy, thermal analysis are predominantly used [8, 10–12]. A first set of qualitative results can be obtained. Certain chemical groups are detected, such as OH, C=O, COOH [13], double bonds such as —C=C— , $\text{H}_2\text{C=C—}$ [6], ketones, and acids [14]. Physical deterioration of the surface has been observed, including phenomena such as fissures, cracks, erosions, globules and destroyed zones [8, 4] probably due to variations in molecular weight and crystallinity at the surface.

The authors have estimated PE oxidation to be very slow, namely, in the order of 1 μg per 100 mg of the product per week or about 0.001% of the product per week [15]. The molecular weight varies between 200,000 and 600 [8, 12, 13, 15], and apparition of the double bonds has been observed at a rate of 0.0035% [11], that is 1 in 30,000. Other contradictory results show notable increases of molar mass during the oxidation of the PE [16, 17]. It is often reported that, in this polymer, crosslinking competes with the chain scission mechanism depending on the oxygen concentration at the reaction site. An almost insoluble part of the aged PE, known as gel, can be measured by extraction in boiling xylene. In one recent paper [18], PE is shown to be partially crosslinked by peroxidation at 60°C and microbial action does not induce any significant reduction of the molecular weight.

Degradation of PE by Micro-Organisms

The irradiated samples are then exposed to micro-organisms [19, 20], to investigate their effect on biodegradation, as defined above. Several experiments have been performed in compost [10, 12, 13, 21], agar–agar [7, 13], soil [9, 22], or other laboratory experiments [6]. These experiments have concerned bacterial growth and various biodegradations.

On the one hand, several experiments were carried out on PE without additives. From the

classical tests on agar–agar, the results obtained show that the bacterial growth increases with the decrease in molecular weight [13]. Using respirometric tests, the oxidised fragments are broken down to various degrees and in different ways; Weiland *et al.* found that mineralisation varies from 28 to 46% [13] of this fraction. Albertsson *et al.* have shown a maximum of 25% [6]. Other workers cite a rate of 3% per year [11]. The results obtained from the samples buried in soil are similar [9, 22] to those obtained from the treated samples. These phenomena are very slow (300 years to break down a thickness of 60 μm) and affect the outer surface of the material [9], they are limited to a thickness of the order of 1 μm . The UV light accelerates the breaking down [9, 22], as much as doubling the breakdown speed process.

On the other hand, the commercial development of PE with additives containing oxidants and/or starch requires a specific discussion. The purpose of the additives is to favour the creation of double bonds, oxidation and fragmentation [7, 8, 14, 15, 21, 23]. The types of additives are cobalt acetylacetonate, nickel or ferrous dithiocarbamate, magnesium stearate or carboxylate, styrene-butadiene copolymer, starch [7, 8, 14, 15, 21, 23]; where incorporated amount is up to 20%, of which 7% is generally starch, which is often associated with peroxides [7, 8, 14, 15, 21, 23]. The biodegradation rate in soil of PE is independent of the nature of these additives [9], therefore the degradation is often important [24]. The additives accelerate the breakdown and increase the production of oxides derivatives [15]. The result is biodegradation with a higher level of oxides formation [6, 21]. Recent documents [10, 12] reported assimilation, of the order of 60%, of the total carbon after 180 days in an artificial soil maintained at 60°C [10, 12]. After 426 days, 27.8% mineralisation is obtained in compost [10]. Some theory has been established to demonstrate the role of additives in the PE degradation mechanism [6, 14, 23].

The contradictory results described in several publications and the lack of significant experimental details have led us to perform rigorous study with numerous biodegradability experiments such as Sturm, compost, soil and agricultural tests. In this paper, we have compared and discussed on results obtained on three commercial so-called “biodegradable” materials.

MATERIALS AND METHODS

A comparison of the biodegradability of three materials was conducted using 10 standardised measuring methods [24]. These three materials were tested as a part of an international team funded by the European Community and aiming at developing guidelines, testing schemes and predictive models for labelling biodegradability of agro-industrial polymers in relation to their environmental fate in agriculture and waste treatment.

Tested Materials

The material A, Mater-bi (Novamont) film supplied by Deltalène, is a 50 microns thick film made of polycaprolactone/starch blend (60/40 w/w). For the compatibility of that blend, starch was desaturated and complexed with a biodegradable surfactant. Material B, Ecoflex (SASF) is a 60 microns thick film made of an aliphatic/aromatic polyester. Material C (Actimais, SMS Trioplast) is a 36 microns thick film made of PE with pro-oxidant additives. The main characteristics of these polymers are given in Table I. The choice of the three materials tested was based on the commercial products yet proposed to the farmers as mulch films.

Paper (70 g/m²) has been used to compare respirometry tests on natural soil.

Biodegradability Tests

The name of biodegradability tests and standards of the different methods used are listed below:

Stürm	Stürm test (OCDE 301B, ISO 14852) for 180 days
Bodis	Test on the oxygen demand in solid medium (ISO 14851) for 117 days
Compost	Compost test under laboratory conditions (ISO/DIS 20200, EN 261085, ISO 14855) for 50 days
Anaerobic	Anaerobic tests (EN 13432, ASTM D5210) for 58 days
Headsp 25°C	Closed bottle at 25°C (OCDE 301D, ASTM D5988-96 modified) for 48 days
Headsp 50°C	Closed bottle at 50°C (OCDE 301D, ASTM D5988-96 modified) for 48 days
Compost pilot scale	Pilot compost test (EN 14045) for 84 days
Soil test (lab)	Test on reconstructed soil in the laboratory (DIN 53739) for 84 days
Agricultural soil test	Buried sample test in real agricultural soil for 330 days
Enzyme test	Enzyme test

Table I. Principal Characteristics of the Polymers Films

	Thickness (micron)	Tensile strength (Mpa)	Modulus (Mpa)	Glass transition/ melting point (°C)	Permeability
A: Mater-bi	50	30	210	-/122	Very high
B: Ecoflex	60	15	81	-30/110	High
C: Actimais	36	20	150	-100/120	Low

These test have been validated at least by two laboratories and the reproducibility is validated on three replicate samples of each polymer in the different tests.

Observation of Micro-Fragments

After agricultural soil tests for 1 years, the ground was remove in a depth of 20 cm. The stones and other large earth aggregates were removed by sieving the ground at 2 mm. The micro-fragments were separated from the earth using solution of glycerol–water (90–10 by weight) in which the earth is stirred for 2 h. The PE micro-fragments were separated by flotation because its density (0.95–0.97) compared to density of the solvent mixture. The suspension was centrifuged for 1 h at 2000 rpm. The supernatant was withdrawn and placed on a microscope slide until the solvent evaporation. The residual material was observed using optical microscopy on LEICA DMLP apparatus with eyepiece 10*/20M and lens PLAN H40*/0,40M (×400). A camera JVC-TKC1381 was used for photo acquisitions with LIDA software.

The recovered plastic fragments were studied by FT-IR ATR microscopy after deposition of the fragments on a microscope glass slide. The FT-IR absorbance spectra are normalised compared to the pure PE spectra.

Since PE is known to be dissolved in xylene at high temperature (90°C), the same test was performed for the PE fragments recovered from soil.

RESULTS AND DISCUSSION

All the experiments on PE film have been performed without UV or heat pre-treatment. The main pragmatic reason for that experimental choice is that non-negligible part (30–50%) of the agriculture film is buried in soil during film casting and will, therefore, not be exposed to UV light and to strong temperature variations.

Respirometric tests on natural soil show that the PE film does not degrade by much more than 10–15% after 1 year of incubation at 28°C as shown in Fig. 1. The plateau in the percentage of CO₂ produced for PE is achieved after 200 days and the biodegradation observed is no more than 15% of CO₂. Moreover, it is not possible to clearly state if this is the biodegradation of the additives by themselves, or the PE by itself, or both together. For the paper, 91% of CO₂ is obtained after 365 days, which represents the CO₂ which was theoretically expected.

Similar biodegradation tests were performed on three films. Whatever the methods used, material A is the most biodegradable polymer, then comes the material B and finally the material C. The higher biodegradation of polymer A compared to B can be explained by the presence of starch (40 by weight) that is very fast degraded and which rapidly increases the surface area of the remaining polymer attacked by micro-organisms. Whatever the aerobic test used (Sturm, Bodis, composting, headsp, soil

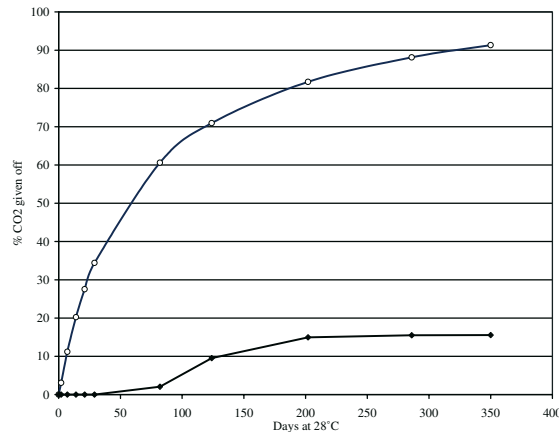


Fig. 1. Respirometric test on real soil (ASTM D5988-96 modified). The percentage of CO₂ released as a function of time for the reference paper and PE with additives. °, represents reference paper; and ◆, represents material C (PE with peroxidant).

and enzymatic tests), material A is biodegraded about 75–88% and material B about 5–95%.

The tests performed on polyethylene films provide very different results: breakdown is close to 1.8% after 56 days at 23°C and around 1.1% according to composting tests after 50 days as shown in Fig. 2. The results obtained from the other tests are plotted in Fig. 2 and generally show very low biodegradability of the PE with additives.

The only positive test is the one on agriculture soil for which the visual observation of the remaining plastic leads to the “biodegradation” of 90% of

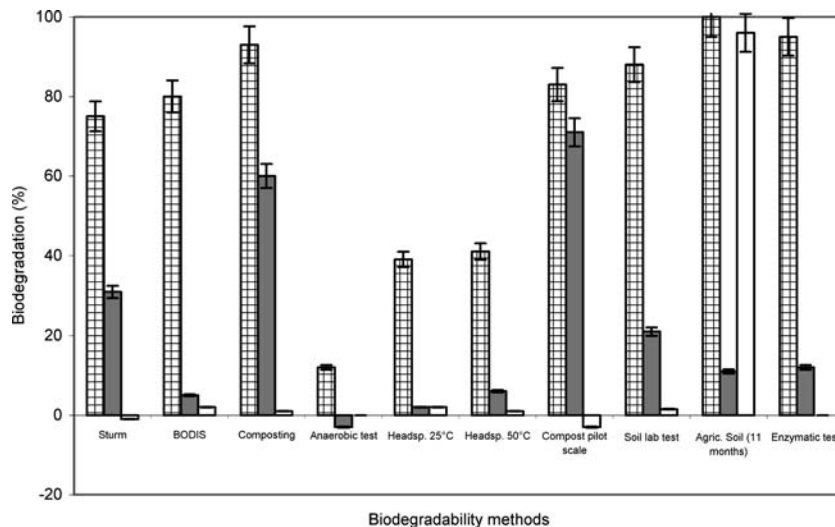


Fig. 2. Comparison of the percentage of biodegradation for material A, B and C according to the nature of the test used. The standards used for each test is described in the Materials and methods part of the paper. ▤, Represents polymer A (starch based); ■, represents polymer B (aliphatic/aromatic polyester) and □, represents polymer C (PE with peroxidant).

the PE film. In fact, an underground test shows total fragmentation at about 11 months [21]. The fragmentation of polyethylene film in soil was analysed by centrifugation of a sample of ground in a blend glycerine/water (90/10) where density is 1.2. This sample of ground was withdrawn from a field which was 100% recovered by PE mulch film 2 years ago and the top soil layer buried at 40 cm after 1 year. The supernatant dispersion was then withdrawn and observed by polarised optical microscopy. Numerous micro-fragments from 5 to 70 μm have been observed as shown in Fig. 3. No quantitative data is available yet on the proportion of fragment remaining in soil according to the initial PE film weight per square metre of soil. However, it can be unambiguously stated that these fragments are made of oxidised PE since the Malte cross-typical of PE spherulitic crystallisation is observed in polarised light as observed in Fig. 3. Micro-ATR infrared spectroscopy also confirms that the fragments are made of oxidised PE as shown in Fig. 4. The peaks at 2919, 2850 and 1471 are assigned to the PE CH_2 and C—C, 719 cm^{-1} could be attributed to CH_2 (rocking) and 3400 cm^{-1} could be linked to absorbed water or COOH groups. Thousand seven hundred and forty per centimetre is assigned to $\nu(\text{C}=\text{O})$ of ester groups. This is the evidence of a strong oxidation of the PE chains due to the UV action.

The solubility test in hot xylene only yields partial swelling of the PE fragments and not to their total dissolution in the solvent. This is a strong evidence of crosslinking between PE chains which is undoubtedly unfavourable for enzymatic attack. Therefore, that large PE fragments in this state cannot be bioassimilated by soil bacteria, neither

further photo-degradation, nor large cumulative effects in soil cannot be, therefore, ruled out.

The results described above shows a fragmentation of polyethylene film but the biodegradation by micro-organisms is still questioning and bioassimilation not achieved. In light of these results, we have to discuss on the validity of methodology and conclusions found in recent publications concerning “biodegradable” PE films. First the so-called “biodegradable” products, which are destined to be broken down in the environment (agricultural, compost), are tested using trials and methods based on physico-chemical treatments (UV, temperature) that are not representative of the environment in which they will be used.

During the pre-treatment for PE films, temperatures about 90–100°C [3, 9, 18] are applied over a period of a few weeks. These temperature ranges do not exist under normal agricultural conditions, not even in the warmest of climates. For example, the maximum temperature, 10 cm below the ground, on the site in south of France, in July 2001, was 1.1°C higher than the air temperature. At 50 cm it was 5.2°C below the air temperature meaning 35°C for the warmest 2 h of the day. Only 55°C at the highest would simulate the correct conditions in compost. The same observation is true for the exposure to UV light: especially for agricultural film, they are exposed to UV for a short amount of time as the vegetation rapidly re-covers it and once again provides protection from UV and heat. Moreover, the buried part of the film, which represents 30–50% of the film, is protected and will never be exposed to UV or heat.

In a recent paper [18], PE polymer film with additive was shown to decrease in molecular weight



Fig. 3. PE fragments (material C) recovered from soil after centrifugation in glycerol/water solution. The observation is made by optical polarised microscopy.

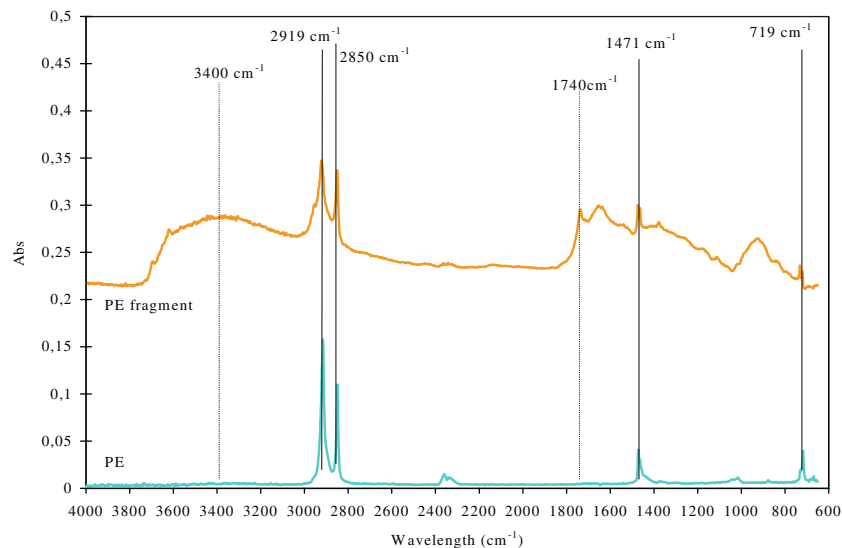


Fig. 4. ATR microscopy FT-IR spectra of PE initial film and of one PE fragment.

when maintained at 20°C but the increase of temperature or a lack of oxygen induces crosslinking. This is in contradiction with previous results for which degradation is induced by heat [3, 9]. Nevertheless, even though rigorous temperature conditions (20, 60 or 80°C) can be achieved in laboratory, in the nature variable uncontrolled temperature cycles are encountered. Extrapolating scientific conclusions achieved in laboratory on the exact nature of the degradation reaction taking place in real soil is rather optimistic. For instance, atmospheric conditions leading to crosslinking reactions and, therefore to non-biodegradable fragments cannot be ruled out. Crosslinking reactions between PE chains leading to an increase of the molecular weight, if sometimes cited, is often underestimated and its consequence on bioassimilation is never discussed.

The environmental impact of the PE micro-fragments that were revealed in the soil by the present study is totally unknown (slow, invisible pollution and the consequences for the mechanical and physical chemistry of the soil). These micro-fragments are electrically charged [25] and their impact, if accumulated, on the argilo humic compound is unknown. Moreover, the micro-fragments of PE, which are not eliminated, are contrary to current legislation on the elimination of waste. As a consequence, no one knows the impact of the micro-fragments present, invisible to the naked eye but evidenced by optical microscopy. Further scientific investigations are required in this field to provide

accurate data to feed software developed to forecast realistic cumulative effects in soil.

CONCLUSIONS

Three “biodegradable” materials were studied using standardised biodegradability experiments. Materials A and B offers a significant percentage of biodegradation after several months. Material C, (polyethylene with additives) does not biodegrade from the standardised biodegradation tests but fragmentation occurs under combination of heat and sun in real soil. It seems clear from our experiments that the biodegradation of PE with peroxidant is very limited and oxidised crosslinked PE fragments are found in soil after 2 years. It is therefore difficult to foresee the accumulative effects of PE fragments and the impact on the environment of the repeated use of these PE films.

REFERENCES

1. M. Vert (2000) Definitions, CEN TC 249 WG 9–21.
2. L. Costa, M. P. Luda, L. Trossarelli, E. M. Brach del Prever, M. Crova, and P. Gallinaro (1998) *Biomaterials* **19**, 1371–1380.
3. M. Zeni, R. Riveros, A. Keller, and A. C. Grisa (1999) *Polym. Deg. Stab.* **66**, 320–327.
4. M. Matsumaga and P. J. Whitney (2000) *Polym. Deg. Stab.* **70**, 325–332.
5. A. Maaroufi (1993) PhD, University Clermont Ferrand 2.
6. A.-C. Albertsson, S. O. Andersson, and S. Karlsson (1987) *Polym. Deg. Stab.* **18**, 73–87.

7. R. Arnaud, P. Dabin, J. Lemaire, S. Al-Malaika, S. Chohan, M. Coker, G. Scott, A. Fauve, and A. Maaroufi (1994) *Polym. Deg. Stab.* **46**, 211–224.
8. A.-C. Albertsson, C. Barenstedt, S. Karlsson, and T. Lindberg (1995) *Polymer* **36**, 3075–3083.
9. Y. Ohtake (1998) *J. Appl. Polym. Sci.* **70**, 1643–1659.
10. E. Chiellini, A. Corti, and G. Swift (2002) 7th World Conference on Biodegradable Polymers & Plastics, Tirrenia (Pisa), Italie, 4–8 juin.
11. E. Brach del Prever, M. Crova, L. Costa, A. Dallera, G. Camino, and P. Gallinaro (1996) *Biomaterials* **17**, 873–880.
12. I. Jakubowicz (1999) 2nd International Conference on Polymer Modification & Stabilisation, Budapest, Hungary, 1–5 August.
13. M. Weiland, A. Daro, and C. David (1995) *Polym. Deg. Stab.* **48**, 275–289.
14. S. Karlsson, M. Hakkarainen, and A. C. Albertsson (1997) *Macromolecules* **30**, 7721–7728.
15. S. Karlsson, and A.-C. Albertsson (1998) *Polym. Eng. Sci.* **38**, 1251–1253.
16. M. Weiland, A. Daro, and C. David (1995) *Polym. Deg. Stab.* **48**, 275–289.
17. R. Broska and J. Rychly (2001) *Polym. Deg. Stab.* **72**, 271–278.
18. S. Bonhomme, A. Cuer, A.-M. Delort, J. Lemaire, M. Sancelme, and G. Scott (2003) *Polym. Deg. Stab.* **81**(3), 441–452.
19. S. Lefaux, L. Benguigui, J. C. Brosse, L. Campistron, A. Laguerre, M. Laulier, V. Leignel, A. Manceau, and G. Tremblin (2002) Journées Scientifiques 2002 – Sections Locales SFC Caen-Le Mans, France, 2 mai.
20. V. Monti, L. Benguigui, and J. C. Brosse (2002) XXIII èmes journées du GFP Ouest. Brest, France, 6 et 7 juin.
21. C. David (1994) *Angew. Makromol. Chem.* **216**, 21–35.
22. Y. Ohtake (1998) *Polym. Deg. Stab.* **60**, 79–84.
23. G. Scott (1999) *J. Polym. Environ.* **8**, 134–152.
24. Labelling biodegradable products (2002) Contract SMT 4 CT97–2167.
25. A. Calmon-Déciaud (1998) PhD, INPT, France.