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RESEARCH ARTICLE

Behavior of Polyethylene Films in Soil

Viktória Vargha[1*], Gabriella Réthási[2], Tamás Heffner[1],
Krisztina Pogácsás[2], László Korecz[3], Zsolt László[4], Imre Czinkota[2],
László Tolner[2], Ottó Kelemen[5]

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Abstract

A true-to life experiment on the behaviour of polyethylene films in soil was carried out. Commercial middle density polyethylene (MDPE) film, MDPE films containing pro-oxidative additives and thermoplastic starch and a commercially available biodegradable film (Ecovio, BASF) have been buried in soil and monitored monthly for one year. Bags made out of the films were filled with and surrounded with brown forest soil and electrodes were put into the soil inside the bag and into the soil surrounding the bag. The soil served as capacitor. Degradation could be monitored weekly by measuring the capacity and conductivity of the soil without removing the bags from it. Visual, mechanical (Instron), structural (FTIR, ESR) and morphological (POM, SEM) changes in the films and the change in molecular mass were tested monthly. The polyethylene films suffered only some physical degradation and not biodegradation. Our life-like experiments suggest that biopacking will be the future of plastics waste disposal.

Keywords

polyethylene film, degradation in soil, material testing

[1] Department of Physical Chemistry and Materials Science, Faculty of Chemical Technology and Biotechnology,
Budapest University of Technology and Economics,
H-1521 Budapest, P.O.B. 91, Hungary

[2] Department of Water and Waste Management, Institute of Environmental Sciences, Szent István University Department of Control,
H-2103 Gödöllő, Páter K. str. 1. Hungary

[3] Institute of Materials and Environmental Chemistry, Research Center of Natural Sciences, Hungarian Academy of Sciences
H-1117 Budapest, Magyar tudósok körútja 2.

[4] TVK Development, Product- and Application Development,
TVK, Member of the MOL group
H-3581 Tiszaújváros Pf. 20. Hungary

[5] Qualchem Zrt., H-2072 Zsámbék Új Gyártelep Hungary

[*] Corresponding author, e-mail: vvargha@mail.bme.hu

1 Introduction

In the 21st century, plastics became one of the most universally-used, multipurpose materials in the global economy. Plastics production in the world shows a continuous growth for more than 50 years (Fig. 1) [1]. Global production in 2012 rose to 288 million tonnes – a 2.8% increase compared to 2011.

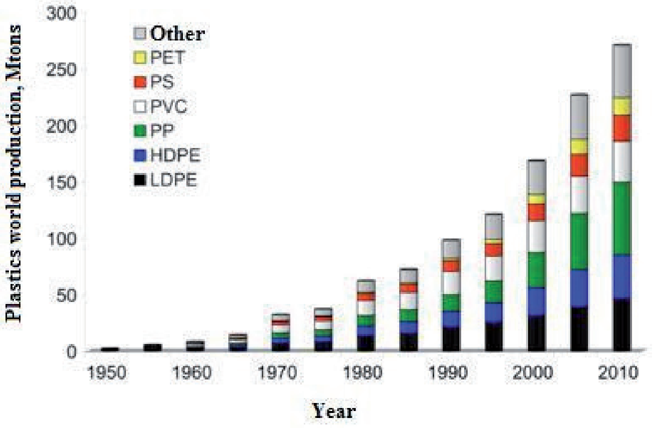

Fig. 1 World plastics production from 1950 to 2010 [1]

Polyolefins (PE, PP) comprise about 48 % of plastics production, and about 40 % of the produced plastics is used for packaging. This is a serious environmental burden. In Europe the tendency is to reduce landfill disposal of plastics waste possibly to zero favouring plastics recycling and energy recovery. Although some countries have almost accomplished this. the majority of plastics waste is still disposed to landfill. Throughout Europe in 2012 26.3 % of post-consumer plastics waste was recycled, 35.6 % was used for energy recovery, and 38.1 % went to landfill disposal [2]. The decreasing oil prices further encourage polyolefin manufacturers to increase their production. Therefore it remains still an essential problem, what happens with polyolefin waste after disposal. A great number of references deal with polyethylene and polypropylene degradation. A systematic study of polyethylene degradation mechanism was carried out by Albertsson et al. [3-9]. Koutny et al. summarize the findings on mechanism and degradation of polyethylene giving an extensive literature survey [10].

A comprehensive review is given on the biological degradation of plastics generally by Shah et al. [11]. Lucas et al. review the mechanisms and estimation techniques of polymer biodegradation [12]. Eubeler and co-workers summarize the test methodologies and procedures of environmental biodegradation of synthetic polymers [13]. He also reports on the environmental biodegradation of synthetic polymers and on the biodegradation of different polymer groups [14]. A comprehensive survey on the biodegradation of polyethylene and polypropylene is given by Arutchelvi and co-authors [15]. Tharanathan summarize the past, present and future of biodegradable films and composite coatings [16]. The use of polyethylene film is especially widespread in agriculture. According to Kyrikou and Briassoulis many polymers that are claimed to be 'biodegradable' are in fact 'bioerodable', 'hydrobiodegradable', 'photodegradable', controlled degradable or just partially biodegradable. Emphasis is placed on the controversial issues regarding biodegradability of some of these polymers [17]. Feuilloley et al. studied the biodegradation of three different commercial PE mulch films [18]. They found a very low degree of biodegradation. Wang et al. monitored the degradation of PE mulching films in soil by visual observation, and loss of weight [19]. Fontanella and co-authors studied the biodegradability of different polyethylene films (HDPE, LDPE and LLDPE) with a balanced content of antioxidants and pro-oxidants [20]. They concluded that the nature of PE matrix is important but the most important parameter is the nature, the composition and the concentration of the metals present in the complexes used as pro-oxidant. Synergistic effects of sunlight exposure, thermal aging and fungal biodegradation on the oxidation and biodegradation of LLDPE films containing pro-oxidant additives were examined by Corti et al. [21]. It was concluded that the degradation of oxo-biodegradable LLDPE is enhanced by the synergistic action of both abiotic and biological factors after its initial oxidation by exposure to direct sunlight. Soni and co-workers developed a bacterial consortium for the biodegradation of porous and nonporous LDPE [22]. The consortium was capable of degrading the poronized form of LDPE much easiler. Muthukumar et al. [23] studied the rate of degradation of commercial pro-oxidant blended and starch blended HDPE, LDPE, and PP under direct sunlight, buried in soil and immersed in marine waters for a period of 150 days. Exposure to sunlight showed highest weight loss (>10%) and samples buried in soil showed the lowest (1%). Therefore it is not suggested burying plastics in soil and no common disposal strategy can be adopted for the different polyolefins [23]. The biodegradability of PE/starch blends was investigated by a great number of authors [23-33]. Ojeda and co-workers [34] believe in an increase in the biodegradation rate of polyethylenes containing pro-oxidant and having preliminary weathering. Although conventional PE films exposed to natural weathering showed small biodegradation. Chiellini and co-workers investigated the biodegradation of LDPE containing pro-oxidant additives in soil and in mature compost [35]. Control of rate and completeness of biodegradation, and cumulative time for oxidation and biodegradation under different environmental conditions remain still to be solved. Matsunaga and Whitney studied the effect of surface treatment of LDPE by corona discharge and UV irradiation on the initial colonisation and possible subsequent biodegradation period [36]. It seemed that the corona discharge treatment was markedly more effective and more practical than UV exposure. Kaur, Gupta and Kumari modified the surface of polyethylene with irradiation grafting with hydrophilic monomers; methacrylic acid and acrylamide [37]. Grafting improved the thermal and swelling behaviors of PE for utilization as a membrane in ion separation, and enhanced biodegradation. Bonhomme et al. report promising results on polyethylene biodegradation, if degradation is carried out in two stages, namely first an abiotic oxo-degradation and second a biotic degradation in compost [38]. Husarova and co-workers partly biodegraded low density polyethylene films in soil and compost after controlled preoxydation [39]. Gilan et al. developed a strain of Rhodococcus ruber for colonization, biofilm formation and biodegradation of polyethylene [40]. Mumtaz et al. report that after 7–9 months of soil exposure, microbial colonization was evident on LDPE film surface. They conclude that biodegradation is seldom due to a single cause, but a combined effect of heat, UV light, microorganisms, stress and water [41].

From a comprehensive literature study on the degradation of polyolefins there are many contradictory results especially concerning their biodegradation. Biodegradation is the chemical dissolution of materials by bacteria, fungi, or other biological means. Biodegradable matter is generally organic material that serves as a nutrient for microorganisms.

After an extensive literature research we have concluded that polyethylene poorly degrades in the environment and does not biodegrade unless it is preliminary fragmented through oxidation. Only specific microorganisms can attack fragmented polyethylene, and the degree of mineralization is variing. It is not known how these specific microorganisms and non-degraded polyethylene fragments effect the soil and the environment in general.

This degradation of polyethylene is not life-like, since packaging materials in municipal waste can neither be selected, nor pre-treated, it goes directly to landfill and buried in soil. This is the practice. We would like to form an ultimate opinion on the suitability of polyethylene for throwaway packaging material in respect to its environmental impact.

Therefore we planned a life-like test on polyethylene revealing its behavior in soil. Our aim was to study the change of a commercial middle density polyethylene film in soil as well as the effect of pro-oxidants and thermoplastic starch on the degradation of MDPE film in soil.

2 Experimental

2.1 Materials and preparation of the samples

Bags out of the plastic films (6 x 10 cm) were made and the experiment was set with 12 repetitions for monthly sampling. The plastic bags were filled with soil and placed in a beaker containing soil, thus the plastic bags were surrounded by soil. Measuring electrodes were put into the soil that was in the plastic bag, and into the soil that surrounded the plastic bag. The soil served as a condenser. The beakers were placed in plastic boxes with previously set moisture content, and aerated on a regular basis. The experimental setup is demonstrated by Fig. 2. Commercial middle density polyethylene (Phillips type MDPE) film, MDPE films containing only pro-oxidant and pro-oxidant plus thermoplastic starch and a commercially available biodegradable film (Ecovio, BASF) as reference were monitored in soil monthly for one year (Table 1). For thermoplastic starch wheat starch (Agrana Staerke GmbH, Austria) was used. Granular native wheat starch with 30 mass% glycerol and 10 mass% water was extruded in a single-screw extruder. The temperature regime was 120°C, 140°C, 120°C, and 90°C (nozzle). From pro-oxidative additives master-batch was made. TPS and master batch have been compounded with MDPE in a single-screw extruder. Films have been blown at Hembach Kft. Polgárdi, Hungary. Temperature of blowing was max. 180°C.

The soil was an acidic brown forest soil originating from Gödöllő Szárítópuszta. It served as a capacitor and its conductivity and capacity were monitored weekly without removing the bags from the soil. During degradation the film becomes thinner, then holes and permeates moisture resulting in the change of electrical properties of the soil as a capacitor. The thinner the film, the higher the capacity. When holes formed, the conductivity of the soil dramatically increased. This type of monitoring degradation was done first time by us. These results are reported in a previous publication [42]. Temperature of the soil was 20±2°C. The main characteristics of the soil are summarized in Table 2. Visual changes, thickness of the films, mechanical, structural and morphological changes in the films and molecular mass were tested monthly.

Fig. 2 Experimental setup

Table 1 Films tested in the soil

Tested PE samples	Composition
PE 340	Commercial Phillips type MDPE (TVK)
PE 238	PE 340 + pro-oxidant (Fe 0.072 %, Co 0.015 %, Zr 0.031 %, Mn 0.006 %, total metal content 0.124 %) (BME-Qualchem Zrt)
PE 242	PE 340 + pro-oxidant (Fe 0.051 %, Co 0.025 %, Zr 0.024 %, Mn 0.044 % - total metal content 0.144 %) (BME-Qualchem Zrt)
PE 297	PE 340 + 8.75% thermoplastic starch + pro-oxidant (Mn 0.0103%, Co 0.0094 %, total metal content 0.0197 %) (BME-Qualchem Zrt)
BASF	polyester + polylactic acid blend (Ecovio - BASF)

Table 2 Parameters of the examined brown forest soil

K_A	25
pH_{KCl}	4.9
pH_{H2O}	5.7
Total C (%)	0.58
Total N (%)	0.08
NO_3^--N + NH_4^+-N (mg/kg)	5.5
AL-P_2O_5 (mg/kg)	33
AL-K_2O (mg/kg)	135

The nutrient and moisture content of the soil was adjusted in order to prepare convenient circumstances for the degradation by the soil microorganisms. Thus, the carbon to nitrogen ratio was adjusted by NH_4NO_3 addition, and the proper moisture content was set by distilled water (60% of outdoor field capacity).

2.2 Testing methods

Samples were taken out of soil monthly, and film thickness was measured by a micrometer, ten parallel measurements were averaged. For mechanical testing an Instron5566 was used. Tensile strength and elongation at break were determined and averaged from five parallel measurements. Structural changes in the films were followed by FTIR spectroscopy using a Bruker Tensor 27 instrument. The wave number range was between 4000–400 cm^{-1}, the resolution 2 cm^{-1}, the number of scans was 16. The radical formation after exposure in soil was checked by ESR spectroscopy using a Bruker Elexsys 500 spectrometer in the X^1 frequency range (~9-10 GHz). For morphological testing polarized optical microscopy (POM) and scanning electron microscopy (SEM) were used. For POM served a Zeiss Axioscop equipped with a Leica DMC 320 digital camera. The micrographs were recorded with Leica IM50 software. For SEM investigations a Jeol JSM 6380LA electronmicroscop was used. Before testing the surface of the samples was covered with Pd-Ag alloy. Images of 250x, 500x, 1000x, 2500x and 5000x magnification were made. Number- and weight average molecular mass of the polyethylene films were determined in 1,2,4-trichlorobenzene solution at TVK, Product- and Application Development, Tiszaújváros Hungary. The equipment was Malvern Viscotek 350 HT-GPC with 2 Phenogel 10u Linear(2) coloumn at 160°C. All samples were monitored monthly. Microbiologists suggested to cut a piece of the films after 7 months in soil to check colonization of microorganisms on their surface. Therefore these film pieces were shaken in mineral salt solution in order to insure their survival. If cells were able to remain metabolically active, it would suggest that they gain energy from the material, hence promoting biodegradation. These shaken samples were also tested for thickness, for morphology by SEM and for molecular mass. The mineral salt solution consisted of 5 g $(NH_4)_2SO_4$, 0.5 g KH_2PO_4, 1 g K_2HPO_4, 0.5 g $MgSO_4 \times 7\ H_2O$, 0.2 g $CaCl_2 \times 6\ H_2O$, 0.01 g $FeSO_4 \times 7\ H_2O$, 0.5 g peptone, 0.5 g yiest extract, 1000 cm^3 distilled water and was sterilized for 15 minutes at 121°C, 1 att superpressure. Incubation took place in a universal benchtop shaker CERTOMAT S II for 3 month. The aim of incubation was the investigation of survival and further activity of microorganisms remained on the film surfaces after exposure in soil.

K_A : Soil water capacity , Arany-type plasticity index : 100 g air-dried soil was mixed with deionised water until a homogeneous paste was formed. The upper limit of plasticity was realized by the so-called thread proof (MSZ-08 0205:1978).

pH were determined in water and in 1 n KCl solution by the potentiometric method (glass electrode). The soil : solution ratio was 1 : 2.5.

Total C % was determined by Walkley-Black methods [42]

Total nitrogen % was measured by using micro-Kjehldal analysis

NO_3-N+NH_4-N: Mineral form of Nitrogen in soil. Determined by Parnas-Wagner distillation from soil extraction (1% KCl solution).

AL-P_2O_5 and AL-K_2O: Easy available phosporus and potassium form of soil. [43]

3 Results

Based on capacity and conductivity measurements among the MDPE films the thermoplastic starch containing film degraded the most. The smallest change showed the commercial polyethylene film. Compared to the polyethylene films the BASF film degraded the most in the soil. Results of conductivity and capacity measurenents are reported in [42].

While little changes could be visually detected on the polyethylene films, the BASF film became more brittle after 11 month exposure in soil.

For biodegradable materials an increase in film thickness may be expected due to biofilm formation. A biofilm is any group of microorganisms in which cells stick to each other on a surface. These adherent cells are frequently embedded within a self-produced matrix of extracellular polymeric substance (EPS). Biofilm extracellular polymeric substance, which is also referred to as slime (although not everything described as slime is a biofilm), is a polymeric conglomeration generally composed of extracellular DNA, proteins, and polysaccharides [45]. As Figure 3 shows non of the polyethylene films changed significantly in thickness in soil. Even after 3 month incubation the film thickness decreased. This means that no microbial growth was on the surface of polyethylene films. However there is a monotonous increase in film thickness of the BASF film with time in soil, although scattering of thickness data is high. The incubated BASF film has somewhat higher thickness, than the non-incubated one. Biofilm formation on the surface of the BASF film has been confirmed by SEM.

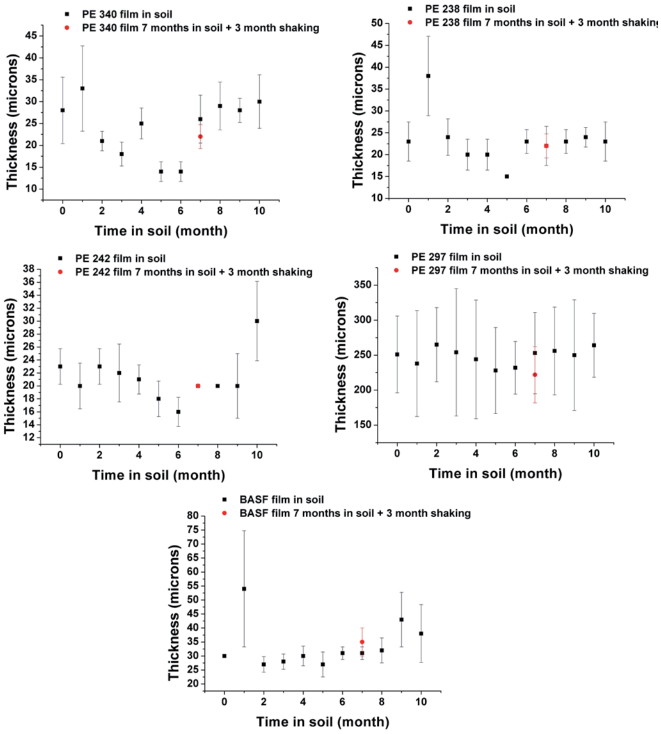

Fig. 3 Change in film thickness of the samples buried in soil with time

Figure 4 represents the change in tensile strength and elongation at break of the films during the 11 month soil test. Tensile strength of commercial MDPE film (PE340) shows a monotonous increase up to six month of exposure in soil, which might be due to initial cross-linking. After 6 month however the tensile strength further decreased and approached the initial value. Elongation at break of commercial MDPE scatters and by the end of the exposure in soil decreased from 400 to 200 %. Similarly behave the polyethylene films (PE 238 and PE 242) containing pro-oxidant, as well as PE 297, which contains pro-oxidant and thermoplastic starch. This film has lower tensile strength and elongation at break then the other MDPE films due to the presence of thermoplastic starch. All MDPE films suffered some physical degradation in soil. The BASF film significantly differs from the polyethylene samples. Its tensile strength changes with time in soil similarly to the polyethylene films, but its elongation at break drastically decreases by the end of the 11 months in soil. The initial increase in tensile strength is in accordance with the results of Feuilloley et al. [18]. They studied three different commercial mulch films submitted to standardised biodegradation tests and concluded that a very low degree of biodegradation of the commercial PE films was achieved. They also found that crosslinked PE micro-fragments could be detected in soil after a very long period of time.

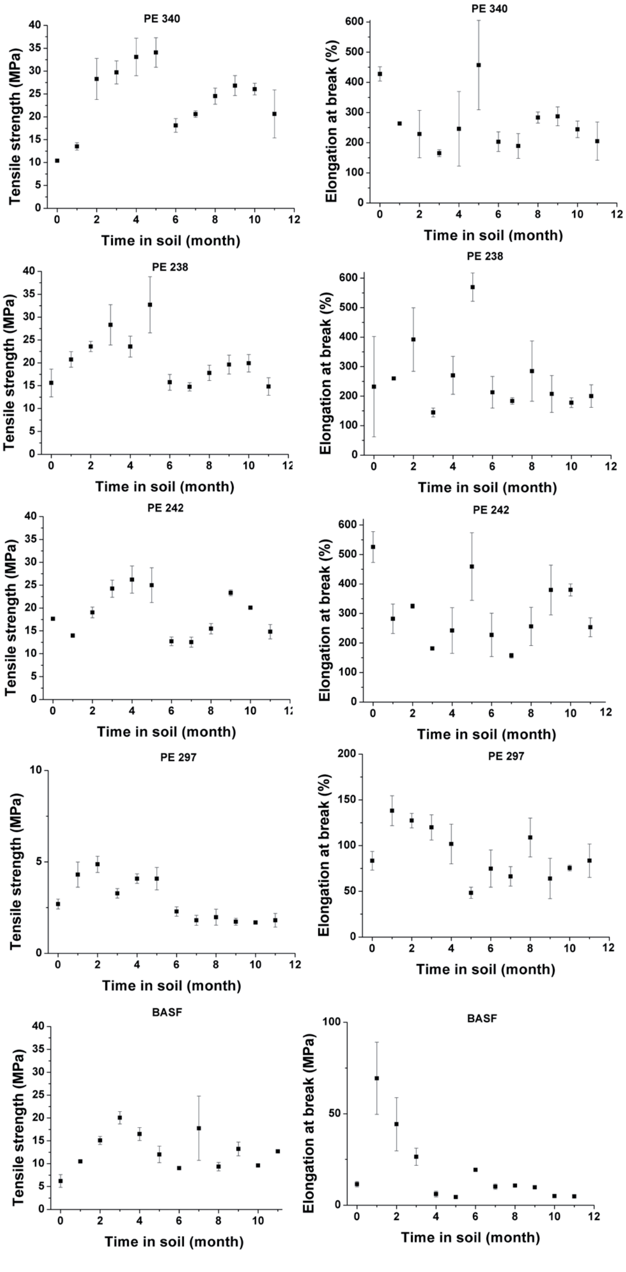

Fig. 4 Change in tensile strength and elongation at break of the tested films with time in soil

There was no perceptible change in the structure of the polyethylene films by FTIR-spectroscopy. Carbonyl index and vinyl index were calculated for polyethylene samples after each month in soil. None of them changed. This means that no oxidation occurred in soil. The BASF film suffered significant degradation in soil based on capacity and conductivity measurements, visual and mechanical testing, although no significant changes in its structure could be detected by FTIR-spectroscopy.

ESR-spectroscopy was used to detect the formation of radicals during soil exposure (Fig. 5). Physical degradation involves radical formation. It can be seen on Fig. 5 that there is a significant intensity of radical concentration especially in the beginning of soil exposure. Unfortunately the ESR tests could not always be made directly after taking the samples out of the soil. In spite of this it may be concluded that radical formation accompanies physical degradation.

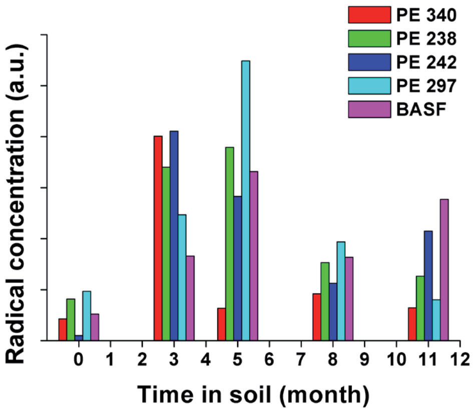

Fig. 5 Detection of radicals during soil test
ESR intensities (a.u.) are given for unit mass

Polar optical images of the films before and 7 months after soil exposure are seen on Fig. 6. These samples were not incubated in mineral salt solution. The polar optical microscopic images of MDPE films reveal smaller or larger changes in each case after storage in soil which may be attributed to some physical aging of MDPE films. Also some decontamination from soil can be seen on their surface. The MDPE film with thermoplastic starch was somewhat heterogenous as it can be seen on the unexposed sample. The BASF film shows remarkable cracking as a result of degradation.

Scanning electron microscopic images were taken before exposure and after seven months in soil following three month shaking in mineral salt solution (Fig. 7). The results are surprising. Very few microorganisms could be detected on the surface of all the MDPE films including the commercial PE 340. Commercial MDPE film seems to be as, or even more susceptible to microorganisms than the pro- oxidant-containing films. This suggests as if the additives would repel the microorganisms. Even the presence of thermoplastic starch did not attract more microorganisms, than were found on the surface of commercial MDPE film. The surface of the BASF film was fully covered with microorganisms after soil burial. Since no significant morphological changes could be found on the PE films after soil exposure, it may be concluded, that even if some degradation

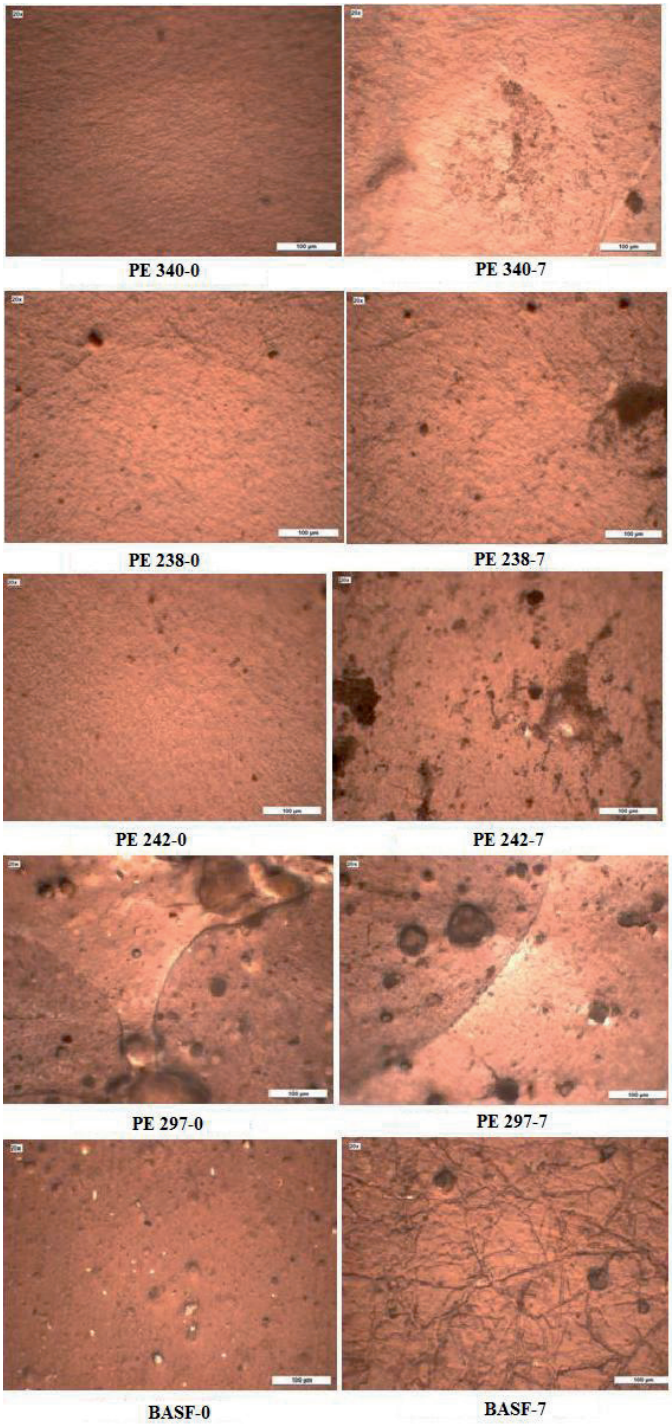

Fig. 6 POM images of the films before (left) and 7 months after exposure (right) in soil (scale bar shows 100μm)

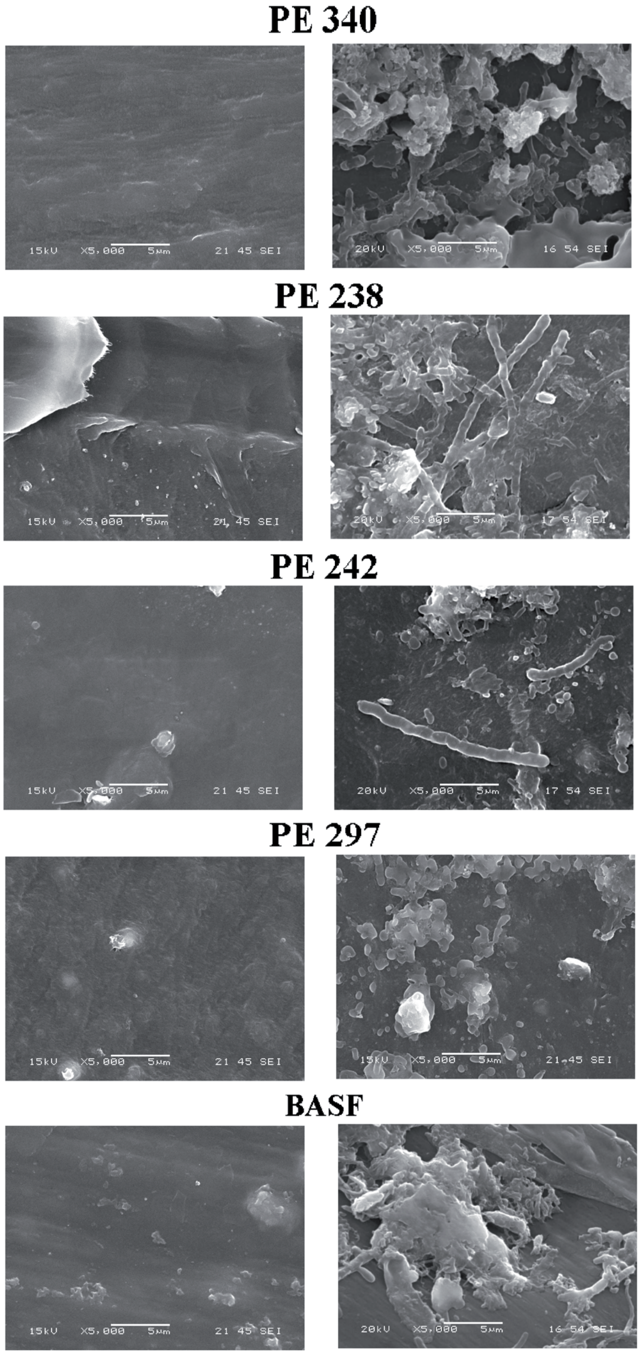

Fig. 7 SEM images of the films before exposure (left) and after 7 months in soil + 3 months shaking in mineral salt solution (right) (magnification 5000x) (scalebar shows 5 μm)

occured, it cannot be declared as biodegradation. This is supported by the results of Feuilloley et al. who submitted three different commercial PE mulch films to standardised biodegradation tests and concluded that a very low degree of biodegradation of the films was achieved [18]. According to Fontanella et al. [20] on the biodegradation of PE the nature of PE matrix is important but the most important parameter is the nature, the composition and the concentration of the metals present in the complexes used as prooxidant additives. Our pro-oxidant additives did not favour biodegradation of MDPE films.

Change in weight-average-, number-average molecular mass and polydispersity of the films after 7 months in soil followed by three-month shaking in mineral salt solution and after 11 monts in soil are summarized in Table 3.

Only the MDPE sample PE 238 which contained pro-oxidative additives showed a significant decrease in molecular mass averages. Since other macroscopic changes did not occur, and only a few microorganisms could be detected on its surface by SEM, this decrease in molecular mass cannot be rendered to biological degradation, better to physical degradation. Cross-linked, non-soluble molecules might also have been filtered out before getting the polymer to the measuring column of GPC resulting in a pseudo-decrease in the average molecular mass.

Table 3 Molecular mass averages and polydispersity of the polyethylene films before soil exposure, after seven month in soil+3 months shaking and after 11 months in soil

Tested film	Mw	Mn	Pd
PE 340-0	120765	13320	9.066
PE 340-7+3	140375	10492	13.379
PE 340-11	128844	15887	8.110
PE 238-0	126108	9831	12.827
PE 238-7+3	89420	10608	8.429
PE 238-11	36420	5925	6.114
PE 242-0	107019	4960	21.572
PE 242-7+3	109004	6995	15.582
PE 242-11	113092	3319	34.072
PE 297-0	128770	10274	12.533
PE 297-7+3	121608	7852	15.486
PE 297-11	117404	6895	17.026

0: before soil exposure

7+3: seven month in soil plus 3 month shaking with microorganisms from soil

11: after 11 month in soil

4 Conclusions

Plastics such as polyethylene are widely used in packaging and other agricultural applications. They accumulate in the environment at a rate of 25 million tons per year. [32]. Biodegradability of plastics needs to be determined in environmentally realistic conditions.

Commercial middle density polyethylene film (PE 340), MDPE films containing pro-oxidant (PE 238 and PE 242) and MDPE film containing pro-oxidant plus thermoplastic starch (PE 297) were tested in soil together with a commercially available biodegradable film (Ecovio, BASF). The bags made from the films were buried in soil and monitored monthly for one year. The soil served as a condenser, and capacity and conductivity of the soil were tested weekly and proved to be adequate tools for monitoring degradability [42]. Macroscopic changes of the films were tested monthly, namely visual appearance, mechanical, structural, morphological changes and the molecular mass. Film thickness of polyethylene samples did not significantly changed. There were great deviations. The biodegradable BASF film showed a monotonous increase in film thickness, which may be attributed to biofilm formation. Mechanical properties i.e. tensile strength and elongation at break of the MDPE-based films did not vary much. There was an initial increase in tensile strength up to 6 month exposure in soil due to cross-linking, which is a sign of physical degradation. Similarly behaves the degradable BASF film. While elongation at break of MDPE films hardly changed in soil, the BASF sample suffered a drastic decrease in elongation at break. Structure of MDPE films did not change during 11 month exposure in soil, even oxydation could not be detected as revealed by FTIR-spectroscopy. In spite of this, presence of radicals could be detected by ESR spectroscopy during soil exposure due to physical degradation. POM revealed some morphological change on MDPE films after buriel in soil, the degradable BASF film however was full of cracks. SEM revealed presence of some microorganisms remained on the surface of both commercial and pro-oxidant containing MDPE films after seven months in soil, although commercial MDPE seems to be more susceptible on the microorganisms than the additive-containing films. This suggests as if the pro-oxydant additives would repel the microorganisms. Even the presence of thermoplastic starch did not attract more microorganisms, than were found on the surface of commercial MDPE film. Molecular mass of MDPE films did not change significantly after buriel in soil.

It can be concluded that the polyethylene films suffered some physical degradation in soil, and it cannot be declared as biodegradation. Our results are in accordance with the findings of Feuilloley et al. [18] that very small degree of degradation occured on PE films in soil. Muthukumar et al. [23] also do not suggest buriing plastics in soil, since they found no degradation.

Our life-like experiments suggest that biopacking will be the future of plastics waste disposal.

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