This article was downloaded by:
On: *24 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Can Polyethylene be a Photo(bio)Degradable Synthetic Polymer?

Jacques Lemaire[a]; René Arnaud[a]; Philippe Dabin[a]; Gerald Scott[b]; Sahar Al-Malaika[b]; Sukhinder Chohan[b]; Annie Fauve[c]; Abderrazek Maaroufi[c]
[a] Laboratoire de Photochimie Moléculaire et Macromoléculaire, URA CNRS 433 Ensemble Universitaire, Aubiere, Cedex, France [b] Department of Chemical Engineering and Applied Chemistry, Aston University, Birmingham, UK [c] Laboratoire de Chimie Organique et Biologique, URA CNRS 485, Ensemble Universitaire des Cézeaux, Aubiere, Cedex, France

To cite this Article Lemaire, Jacques , Arnaud, René , Dabin, Philippe , Scott, Gerald , Al-Malaika, Sahar , Chohan, Sukhinder , Fauve, Annie and Maaroufi, Abderrazek(1995) 'Can Polyethylene be a Photo(bio)Degradable Synthetic Polymer?', Journal of Macromolecular Science, Part A, 32: 4, 731 — 741
To link to this Article: DOI: 10.1080/10601329508010284
URL: http://dx.doi.org/10.1080/10601329508010284

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J.M.S.—PURE APPL. CHEM., A32(4), pp. 731–741 (1995)

CAN POLYETHYLENE BE A PHOTO(BIO)DEGRADABLE SYNTHETIC POLYMER?

JACQUES LEMAIRE,* RENÉ ARNAUD, and PHILIPPE DABIN

Laboratoire de Photochimie Moléculaire et Macromoléculaire
URA CNRS 433
Ensemble Universitaire des Cézeaux
F-63177 Aubiere Cedex, France

GERALD SCOTT, SAHAR AL-MALAIKA, and SUKHINDER CHOHAN

Department of Chemical Engineering and Applied Chemistry
Aston University
Birmingham, UK

ANNIE FAUVE and ABDERRAZEK MAAROUFI

Laboratoire de Chimie Organique et Biologique
URA CNRS 485
Ensemble Universitaire des Cézeaux
F-63177 Aubiere Cedex, France

Downloaded At: 15:38 24 January 2011

ABSTRACT

A polymeric system based on LDPE would be qualified as a "photo(bio)degradable synthetic polymer" for use as films or thin systems in plasticulture and later in packaging where severe specific criteria should be respected. The evolution of such a system in environmental conditions should present three phases. In Phase I, corresponding to storage and use, in the presence of physicochemical and biological aggression, chemical evolution should be very limited and resistance to any microorganism should be observed. In Phase II a rapid abiotic degradation should occur until the complete destruction of physical (mechanical) properties and spontaneous fragmentation of the thin systems into more and more di-

Copyright © 1995 by Marcel Dekker, Inc.

vided parts. Phase III corresponds to bioassimilation of heavily transformed (oxidized) solid particles. Phase I should be predicted and controlled on the basis of artificial photoaging or thermoaging experiments. Depending on the desired lifetime of the system, nonaccelerated, accelerated, or ultra-accelerated photoaging techniques could be used. The earliest fragmentation, which should be observed in Phase II, should be predicted within the same experiment. The prediction of the long-term fate of the polymeric materials should be based not only on the variations of physical properties but on a full analysis of the chemical evolution, i.e., determination of the major final transformed groups of the macromolecular chains (and especially the acidic end groups) and the molar mass distribution. In a recent BRITE-EURAM European contract, we developed an experimental protocol for the control of Phase III based on the use of pure cultures of strains from collections or selected adapted wild strains (from industrial polyethylene site dumpings) which had been examined. Abiotically oxidized LDPE was the only carbon source in a starving mineral medium. Bioerodibility caused by the carboxylic acid formed throughout abiotic degradation has been observed.

Downloaded At: 15:38 24 January 2011

INTRODUCTION

In response to public concern about the effects of plastics in the environment, and in particular the damaging effects of sea litter on animals and birds, legislation is being enacted or is pending in many countries to ban nondegradable packaging, fishing nets, etc. In response to these concerns a variety of new polyolefin-based packaging materials have recently appeared on the market which claim to be photodegradable, biodegradable, or both. A problem for the manufacturers and users of plastics products, and ultimately for legislators, is the absence of objective criteria to distinguish between the performance of competing products and processes.

In a recent European research contract (BRITE EURAM BREU 170) entitled "An Investigation of the Parameters Involved in the Environmental Ultimate Degradation of Plastics," Université Blaise Pascal and Aston University collaborated on a program whose main objectives were to provide:

1. Guidance for the manufacturers and users of degradable plastics which will allow them to distinguish between the claims of different producers
2. The basic principles underlying the developments of industrial standards for quality and assurance and for quality control

The research was carried out on most types of "photodegradable" polyethylene systems commercially available and on fully controlled on-purpose-made films. As later reported, the experimental results collected in the 3-year cooperation appear as a first approach to answer the general question: "Can polyethylene be a photo(bio)-degradable synthetic polymer?"

DEFINITION OF A PHOTO(BIO)DEGRADABLE SYNTHETIC POLYMER

A polymeric system based, for example, on LDPE or LLDPE would be qualified as a photo(bio)degradable synthetic polymer for use as films or thin systems in

plasticulture or in the packaging industry when the following severe specific criteria are respected. The evolution of such a system should present three phases.

Phase I corresponds to storage in usual conditions where the physicochemical strains could be limited to O_2, heat corresponding to room temperature, humidity, and microorganisms. Such storage conditions are usual in the plasticulture industry. However, if extension to the packaging industry is considered, the environmental strains during Phase I should include daylight (more or less filtered according to external or internal use). Any packaging systems should maintain their initial physical properties (including permeability) during use, even in the presence of daylight. Chemical evolution in Phase I, should be very limited as should variations in macroscopic physical properties and resistance to any microorganisms. Phase I should extend for several months in plasticulture and from several months to more than 1 year in packaging.

In *Phase II* a rapid abiotic degradation should proceed until the complete destruction of mechanical properties is attained, and there should be spontaneous fragmentation of thin systems into more and more divided parts. Such an abiotic degradation results from the concerted action of daylight, heat, and O_2. Water as humidity does not affect LDPE and LLDPE photothermal oxidation, and biodegradation is not required at this level.

Phase III corresponds to the bioassimilation of heavily transformed (oxidized) solid particles.

Phase I should be predicted and controlled on the basis of artificial photoaging or thermoaging experiments. Depending on the desired lifetime of the system, nonaccelerated, accelerated, or ultra-accelerated photoaging techniques could be used. The earliest fragmentation, which should be observed in Phase II, should be predicted within the same experiment. The prediction of the long-term fate of the polymeric materials should be based not only on the variations of physical properties but on a full analysis of the chemical evolution, i.e., the determination of the major final transformed groups of the macromolecular chains (and especially the acidic end groups) and the molar mass distribution.

The control of Phase III, i.e., evaluation of the biodegradability of heavily oxidized LDPE fragments, requires definition of an uncontroversial protocol, which is far beyond the present status of the art. An experimental protocol based on the use of pure cultures of strains from collections or selected adapted wild strains (from industrial polyethylene site dumpings) will be presented in the next sections. Abiotically oxidized LDPE was the only carbon source in a starving mineral medium.

CONTROLLED ABIOTIC DEGRADATION OF LDPE SYSTEMS

It has been recognized during the past 20 years that for some applications, particularly in packaging and in some agricultural applications such as mulching films and binder twines, the polyolefins as normally formulated are too stable for their intended purposes. This has led to the development of commercial products with enhanced degradability. The following classes of "degradable polyolefins" (i.e., abiotically fragmentable) have been identified.

Downloaded At: 15:38 24 January 2011

Photolytic polymers (type A) contain a carbonyl group which is either built into the polymer chain (e.g., ethylene-carbon monoxide polymers) or they contain a copolymerized vinyl ketone in the side chain (the Guillet process) [1]. Both modifications undergo photolysis by the Norrish II (and to a lesser extent the Norrish I) process with chain scission.

Polymers with enhanced photooxidability (type B). There are two subdivisions of this class. 1) Polymers which contain an organo-soluble metal ion (generally in the form of a carboxylate), which acts as a thermal- and photoprooxidant for the polymer. 2) Polymers which contain a sulfur complexed metal ion [e.g., Fe(III) dithiocarbamate] which is photolyzed during outdoor exposure, liberating the free metal ion which then assumes its normal prooxidant function (Scott-Gilead process) [2].

Starch-filled polyethylene (type C). Again, there are two modifications of this system (the Griffin process) [3]. 1) This polymer contains only starch, normally at a 6–8% concentration. 2) This polymer contains, in addition to starch, an iron carboxylate (generally stearate), which, as in B(1), catalyzes the photooxidation of the polymer, thus releasing the starch filler.

Downloaded At: 15:38 24 January 2011

CONTROL OF PHASE I IN STORAGE CONDITIONS

In the absence of light, LDPE and LLDPE are only involved in room temperature thermooxidation. As reported later, among the 70 strains examined in the bioassimilate experiments, not one was able to grow on unoxidized LDPE. Considering the thermal stability of the main intermediate and first oxidation products (associated ROOH, isolated ROOH, ketonic groups, alcoholic groups, acidic groups), the thermooxidation mechanism observed at room temperature should be unchanged up to 90–100°C, and the apparent activation energy should be constant in the 20–100°C range.

Thermooxidability of the various systems was examined in an oven under constant air flow or without constant air flow between 90 and 110°C. With the exception of starch-filled LDPE films, all other samples exhibit an induction period (400–600 hours at 80°C, 200–300 hours at 100°C). From the determined activation energy, it is possible to predict that significant oxidative conversion should not be observed before 100–200 days for the various systems at 20°C.

The limitation of chemical evolution or induction period which should be observed in Phase I when such a system is used in the presence of light is controlled in the same experiment as Phase II.

CONTROL OF PHASE II

Various experimental conditions have been used.

A nonaccelerated photoaging cabinet designed in Aston University, using 7 sunlamps and 21 actinic blue lamps arranged in a symmetrical sequence. The maximum in relative intensity was found to occur within the range 280–370 nm, and the average relative radiation output in the cabinet is estimated to be in the 4.5 $W \cdot h \cdot m^{-2}$ range.

An accelerated photoaging SEPAP 12-24 unit was designed in Laboratoire de Photochimie in Clermont-Ferrand. This device is fitted with four 400-W medium-pressure mercury lamps located at the four corners of a square chamber. The samples were irradiated on a rotating support located at the center of the chamber. The radiations were filtered at $\lambda > 300$ nm, and the temperature of the samples was 60°C.

An ultra-accelerated photoaging SEPAP 50-24 unit was designed in Laboratoire de Photochimie in Clermont-Ferrand. This device is similar to the SEPAP 12-24 unit, but it includes 8 lamps and operates at 70°C.

The "mechanism" of LDPE photooxidation is fairly well established [4, 5]. The photochemical evolution of LDPE can be described through variations in the concentration of acidic end groups, considered as critical photoproducts and determined by FT-IR spectrophotometry as compounds absorbing at 1710–1715 cm^{-1}. The samples were exposed to UV radiation until complete degradation was reached, i.e., the fragmentation under minor strain usually observed when the absorbance at 1715 cm^{-1} is close to 0.3 for 30 μm films.

As an example, the variations of the absorbance at 1715 cm^{-1} for A_2, B_5, and C_2 films exposed in a SEPAP 12-24 unit are presented in Fig. 1 and compared to the corresponding variations of an untreated PE film.

GPC measurements have been carried out with a Waters unit, model 150C ALC/GPC. 1,2,3-Trichlorobenzene containing 250 ppm of Santonox R, a phenolic antioxidant, has been used as the solvent at 135 and 160°C. Prior to any GPC run, the complete dissolution of the unoxidized or photooxidized LDPE samples was obtained when the solvent was heated at 160°C for 4 hours. The solution was thoroughly filtered. The GPC runs were carried out at 135°C, the Waters unit being equipped with four μ-Styragel columns (pore sizes 10^3, 10^4, and 10^5Å ; particle size 10 μm; length 30 cm;

Downloaded At: 15:38 24 January 2011

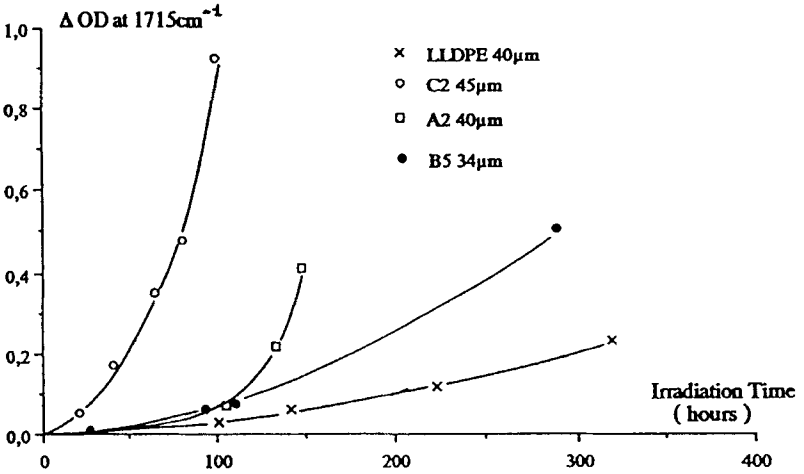

FIG. 1. Variations of absorbance at 1715 cm^{-1} vs exposure time for A_2, B_5, and C_2 films and untreated LDPE film samples (SEPAP 12-24 unit, 60°C).

diameter 7.8 mm). Detection was based on refractometry. For calibration, TSK monodisperse polystyrene standards from Varian were used after dissolution in trichlorobenzene at 145°C in less than 1 hour and requiring no filtering.

A direct comparison of the rates of photooxidation of commercial degradable polyethylenes showed a rapid rate of carbonyl formation and a molar mass reduction for all the polymers which were claimed to be photodegradable. Three different accelerated weathering devices (S/B cabinet, SEPAP 12-24, SEPAP 50-24) were used, and a good correlation was found between them and outdoor exposures.

From the results reported in Table 1, it appears that the changes of the absorbance at 1715 cm^{-1} can be related to the variations of the average molar mass ($\overline{M}_n$, $\overline{M}_w$). An oxygen starvation effect was not observed in thin films (12–45 μm) which behaved like a homogeneous photoreactor, whatever the acceleration conditions were.

It is quite clear that UV exposure under all conditions led to a considerable reduction in the molar mass ($\overline{M}_n$, $\overline{M}_w$). Note the following important points:

Values of $\overline{M}_w$ at embrittlement for the photooxidizing polymers were generally in the 10,000–20,000 region ($\overline{M}_n$ = 5,000–10,000); these samples were subsequently studied in biodegradation.

As shown, for example, on the C_2 films, in ultra-accelerated, medium accelerated, and nonaccelerated conditions, a very similar relationship between the reduction of molar mass and the build up of the acidic groups was observed (see Fig. 2). This means that even in the presence of the highest concentrations of radicals, crosslinking never competes in chain scissions throughout the photooxidation of C_2 films.

Molar mass reduction was particularly rapid during the initial stages of UV exposure in the case of the ethylene-carbon monoxide copolymer (A_2), but the degradation (as measured by this parameter) apparently ceased at a limiting $\overline{M}_w$ of about 50,000, whereas all the transition metal systems continued to much lower values of $\overline{M}_w$. This behavior of the photolytic polymers has been reported previously [6], and it has been suggested that crosslinking through vinyl competes with chain scission at a relatively early stage in photolysis [7].

CONTROL OF PHASE III: BIODEGRADATION STUDIES

Assuming that Phase II abiotic oxidation of polyethylene may favor the biotic attack of the matrix by creating assimilable long-chain carboxylic acids, as already reported by several authors (cf., for example, Refs. 8 and 9), a comparative study of the bioassimilation of nonoxidized and oxidized plastic films was carried out. After selection of the microbial species from collections or from polyethylene-rich areas, various types of commercial photo(bio)degradation polyethylene films were incubated under controlled starving conditions. Besides molecular weight modification analysis by GPC and FT-IR of the matrix, microbial action was especially monitored by scanning electron microscopy analysis of the surface.

Downloaded At: 15:38 24 January 2011

TABLE 1.

Films references	Exposure conditions	e, μm [b]	Exposure time	$\Delta_{absorbance}$ at 1715 cm^{-1}	M_n [a] (±5%)	M_w [a] (±5%)
A_2	SEPAP 12-24 (60°C)	12	–	–	72,500	291,400
			85 hours	≃0	17,300	131,900
			105	0.020	9,600	48,800
			133	0.065	7,400	40,400
			148	0.124	6,800	36,600
B_5	SEPAP 12-24 (60°C)	34	–		33,200	229,500
			26 hours	0.008	37,600	214,500
			93	0.063	17,400	143,700
			110	0.077	13,700	113,000
			289	0.508	5,100	29,300
	S/B Cabinet	35		2.132	1,800	4,500
	Weathering	34	–	–	33,200	229,500
	(45° south)		23 days	0.142	53,200	239,300
			40	0.173	26,800	208,800
			86	0.305	14,300	105,100
			124	0.428	10,700	63,600
C_2	SEPAP 12-24 (60°C)	45	–	–	55,000	271,000
			20 hours	0.05	31,690	116,300
			40	0.17	12,100	78,600
			65	0.35	13,900	52,100
			80	0.48	11,500	43,000
			100	0.924	3,500	13,800
			–	0.959	2,700	11,000
	SEPAP 50-24 (80°C)	45	–	–	55,000	271,000
			11 hours	0.142	16,090	58,100
			33	0.173	13,500	51,500
			–	0.305	7,500	34,200
			41	0.428	6,600	26,300
			–	0.618	4,900	16,700
	S/B Cabinet	45		2.075	2,600	8,500
	Weathering	45	–	–	55,000	271,000
	(45° south)		23 days	0.113	20,000	125,900
			40	0.249	14,000	76,700
			86	0.630	6,400	27,100

[a] Molecular weight in equivalent weight of polystyrene.
[b] e is the film thickness.

Downloaded At: 15:38 24 January 2011

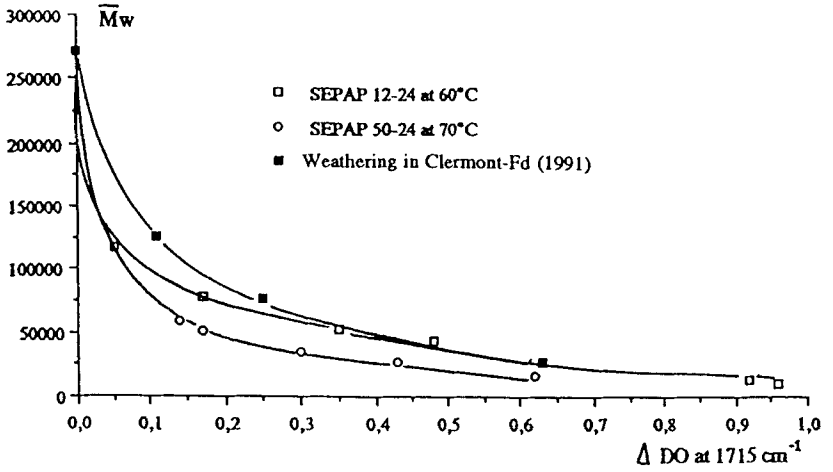

FIG. 2. Variations of M_w vs variations of the absorbance at 1715 cm^{-1} in various photoaging conditions.

Downloaded At: 15:38 24 January 2011

Selection of Strains

Biodegradation of long-chain molecules is well documented, and 32 different species were tested first in the selection procedure. Plastic-degrading strains, rubber-degrading strains, and hydrocarbon-degrading strains used for waste degradation were tested. They were mainly bacteria and fungi with simple nutritional requirements, nonpathogenous, and easily available from collections. Evolution of the microbial population according to chemical modifications is generally observed in the environment. Adapted species may be found in polyethylene-rich areas, and four different locations were investigated. Considering the enormous range of microorganisms in soil, a selective technique, the enrichment culture procedure, was used. In the procedure, oxidized polyethylene films were the growth-limiting and sole carbon source, and only organisms with the necessary polyethylene-degradative ability could grow and outgrow the large number of strains added at the start. Thirty-eight pure cultures were isolated and purified. They were mainly fungi and bacteria, and they were fully characterized after selection.

Pure cultures of microorganisms were incubated in a classical mineral medium in which the only carbon source was the plastic film. Photodegraded copolymer A_2, photosensitive B_5, and iron stearate-starch containing C_2 were used as the carbon sources in a starving medium in which all nutrients were minerals. Samples were sterilized and inoculated with each of the 70 selected strains. After 6 months of incubation in weathering ovens, the microbial growth was observed by visual rating and comparison with various controls (nonoxidized films, abiotic and viability controls). Only strains which displayed a visual growth ranking of at least 2 on a scale of 4 for the three types of films were selected. After analysis of the chemical modifications as described further, the following strains were selected:

Cladosporium cladosporioides (no. 9), a fungus from the American Type Culture Collection (20251)

Norcardia asteroides (no. 13), a bacterium isolated and characterized earlier in our laboratory (911)

Rhodococcus rhodochrous (no. 28), a bacterium from the American Type Culture Collection (29672).

Adapted species (two strains of the same fungus *Aspergillus* isolated at the surface of plastic films and five isolated from a factory dumping site) were also studied. However, their biodegradative abilities will not be fully presented here.

Bioassimilation of Commercial Degradable Films

Comparative bioassimilation studies of nondegraded, photodegraded, and thermodegraded films were carried out. Emphasis was given to the modifications at the surface of the film as shown by scanning electron microscopy observations. Changes in polyethylene chemical structures were monitored through the variations of carbonyl, carboxyl, and ester end-groups detected by FT-IR, through molecular weight distribution analysis by GPC, and through the decrease of thickness, also measured by FT-IR at 1375 cm^{-1}

Downloaded At: 15:38 24 January 2011

Model films in each series were also A_2, B_5, and C_2. Because the inherent heterogeneity of the polymers can lead to false conclusions, we used a procedure in which the blank (zero incubation), control (abiotic incubation), and assay (biotic incubation) test materials were cut from the same sample. Films were photodegraded in an SEPAP unit until the first stage of embrittlement was observed. Thermodegradation was performed at 90°C in an oven without a constant air flow. No embrittlement appeared after weeks of thermal treatment, whereas oxidation had occurred. The solid incubation medium was all-mineral. Assays and controls were incubated 6 months with all selected pure strains and harvested every 2 months. Because the thermal treatment was too long for A_2 and B_5 films, comparison by oxidative treatment for the three diffferent matrixes was made with only one strain, Nocardia; only C_2 was incubated with the three strains after both photo- and thermoxidation. Biodegradation was evaluated in terms of oxidation treatment and polymer content, microbial species, and incubation time.

As-received nondegraded photodegradable LDPE films (M_w = 300,000) were not attacked by the microbial species tested. By looking at SEMs of incubated samples it appeared that abiotic degradation due to the incubation conditions was not significant compared to the modifications due to microbial cells observed at the surface of degraded films. A biotic degradation of the surface of photoxidized and/or thermooxidized samples was evidenced, especially for B_5 and C_2 films (cf. Table 2).

GPC analysis showed a slight decrease of average M_w after biotic incubation, but this reduction was not significant enough to be used as a quantitative predictive technique in biodegradability studies. Data obtained by FT-IR spectra analysis at 1375 cm^{-1} showed a decrease of thickness as determined by a decrease of absorbance, and this was used to quantify the biodegradability of the films.

SEM observations and FT-IR measurements of the surface erosion showed that:

No strain was found to assimilate nonoxidized material.

Only one strain, *Nocardia*, was found to modify copolymer A_2 and then only

TABLE 2. Optical Density and Mass Distribution Values of A_2, B_5, and C_2 Films vs Oxidation Treatment after 6 Months of Incubation with *Nocardia*, Blanks, Abiotic Controls, and Assays

		Blank		Abiotic control		*Nocardia* no. 13	
Film	Abiotic treatment	O.D. 1715 cm^{-1}	M_w ($\times 10^3$)	O.D. 1715 cm^{-1}	M_w ($\times 10^3$)	O.D. 1715 cm^{-1}	M_w ($\times 10^3$)
A_2	Nontreated	0.05	280	0.05	310	0.04	320
	Photodegraded	0.12	17	0.10	16	0.11	12
	Thermodegraded	0.45	21	0.40	19	0.20	17
B_5	Nontreated	0	250	0	250	0	250
	Photodegraded	0.35	40	0.30	32	0.25	19
	Thermodegraded	1.05	16	0.90	16	0.75	15
C_2	Nontreated	0.10	200	0.11	280	0.11	280
	Photodegraded	1.15	16	1.08	15	0.70	12
	Thermodegraded	1.90	ND	1.95	ND	1.55	ND

Downloaded At: 15:38 24 January 2011

after thermal treatment. In general, it was observed with all strains, even the adapted species, that this degraded copolymer A_2 was not a good substrate for biodegradation at the embrittlement stage. This may be because, in this series, photolytic fragmentation according to a Norrish II type reaction did not afford, at this early stage, the long-chain carboxylic acids assumed to favor microbial assimilation.

Strains of particular genera, especially *nocardioforms* and *aspergilli*, from collections or adapted sites, strongly alter B_5 and C_2.

Photosensitive film B_5 was a good substrate for microbial growth after photo- and thermooxidation, depending on the species used. Iron stearate-starch-containing photo(bio)degradable C_2 film was an even better substrate for microbial growth after oxidation. All the strains tested could assimilate starch, thus increasing the rate of growth. However, this biodegradable additive must be released from the polymer matrix by abiotic treatment prior to incubation.

The kinetics of bioassimilation were monitored for each *phototreated* model film with the selected strains. Film samples were analyzed as already reported, and the results varied according to the type of film:

Untreated films showed no modifications within 6 months of incubation.

Phototreated A_2 presented no modifications after 6 months of incubation with all strains. After 4 months, thermotreated A_2 was eroded (-4%).

Bioassimilation of photooxidized B_5 was observed after 4 months of incubation with *Rhodococcus* whereas 6 months were required for the measurement of a decrease of thickness of the film with the other efficient strains (Table 3).

Photooxidized starch-containing film C_2 was rapidly covered with a biomass,

TABLE 3. Bioassimilation of Photooxidized B_5 and C_2 Films vs Time. Decrease of Thickness vs Controls and Blanks

Microorganisms	Films	2 months, %	4 months, %	6 months, %
Cladosporium no. 9	A_2	0	0	0
	B_5	0	0	−6
	C_2	0	−13	−27
Nocardia no. 13	A_2	0	0	0
	B_5	0	0	0
	C_2	0	−33	−27
Rhodococcus no. 28	A_2	0	0	0
	B_5	0	−3	−15
	C_2	−4	−5	−11

and a decrease of thickness was observed after 2 months of incubation with *Rhodococcus* and 4 months with *Cladosporium* and *Nocardia*.

CONCLUSIONS

LDPE-based photodegradable systems should be considered to be photo(bio)-degradable. They undergo abiotic degradation which can be programmed and predicted from artificial aging experiments. After fragmentation, the heavily oxidized particles have erodibility in the presence of several selected strains in starving mineral media where the degraded polymer is the only carbon source. This result contrasts with those obtained in nonstarving media.

REFERENCES

[1] J. E. Guillet, US Patents 3,753,952, 3,811,931, 3,860,538, and 3,878,169.
[2] G. Scott, in *Polymers and Ecological Problems* (J. Guillet, Ed.), Plenum, 1973, p. 27.
[3] G. J. L. Griffin, in *Proceedings of the Symposium on Degradable Plastics*, SPI, Washington, D.C., 1987, p. 49.
[4] M. H. Amin, G. Scott and L. M. K. Tillikeraine, *Eur. Polym. J., 11*, 85 (1975).
[5] R. Arnaud, J. Y. Moisan, and J. Lemaire, *Macromolecules, 17*, 332 (1984).
[6] R. J. Statz and M. C. Dorris, in *Proceedings of the Symposium on Degradable Plastics*, SPI, Washington, D.C., 1987, p. 51.
[7] G. Scott, *Polym. Degrad. Stab., 29*, 135 (1990).
[8] A. C. Albertsson, S. O. Andersson, and S. Karlsson, *Ibid., 18*, 73 (1987).
[9] A. C. Albertsson, *J. Macromol. Sci.—Pure Appl. Chem., A30*, 757 (1993).

Downloaded At: 15:38 24 January 2011