Study of Biodegradation Evolution During Composting of Polyethylene-Starch Blends Using Scanning Electron Microscopy

H. Vieyra, M. A. Aguilar-Méndez, E. San Martín-Martínez

Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada del Instituto Politécnico Nacional, Legaria 694. Colonia Irrigación, C.P. 11500, México D. F., México

Correspondence to: E. San Martín-Martínez (E-mail: esanmartin@ipn.mx)

ABSTRACT: The end product of low-density polyethylene–starch was manufactured by injection molding process. Four starch concentrations (10, 25, 40, and 50%) were used for blend preparations, which were injected into the mold of a 250 mL commercial cup. A control sample of neat polyethylene (PE) was also included. Square coupons ($4 \text{ cm} \times 4 \text{ cm}$) of each blend were buried in the middle of a 50 cm pile of compost. Samples were recovered, washed, dried, and weighed after 25, 50, 75, 100, and 125 days beneath the compost. Scanning electron microscopy (SEM) analysis was performed on the samples to track the biodegradability evolution. A SEM scandium analyzer was used to measure the size and number of pores and the eroded area. Weight loss measurements were conducted to validate the SEM observations. Total biodegradation time was determined by mathematical analysis and graphical extrapolation. SEM analysis revealed the formation of pores, cavities, discontinuities, and cracks resulting from the time beneath the compost. Pore measurements revealed that the specimen composed of 40% starch and submerged for 125 days experienced up to 25% eroded area. Pure PE remained practically unchanged for the 125-day period. Fourier transform infrared spectroscopy studies also demonstrated the biodegradation of PE in PE–starch blends. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: polyethylene; biodegradable; starch; extrusion; microstructure

Received 5 April 2011; accepted 27 March 2012; published online **DOI: 10.1002/app.37818**

INTRODUCTION

Solid waste management is an issue of enormous concern all over the world because of factors that include oil consumption and CO₂ production.^{1,2} In developing countries, additional factors like poverty, overpopulation, urbanization, and lack of government funding amplify the problem.3 Because plastics are considered an ecological problem, the design and development of biodegradable materials are being explored.⁴ Polyolefins such as polyethylene (PE), polypropylene, and polystyrene are synthetic polymer materials that are not biodegradable, but they have become essential in our everyday life. Starch is a natural polymer commonly used in thermoplastic applications because of its biodegradability, abundant availability, and generally low cost.⁵ Thus, the polysaccharide blend of amylose and amylopectin is ideal for blending with synthetic polymers, and it is reported that such blends increases biodegradability.^{6,7} The origin of starch is very important to prepare materials with different properties due to the content of amylose and the granule size. The content of amylose was found to be an important parameter in plasticized films.⁸ In this study, commercial corn starch has been used. Commercial starches contain 25–30% amylose and the granule size is about 15–20 μ m. Starches and modified starches from corn, wheat, rice, potato, and banana have been successfully blended with low-density PE (LDPE)^{9,10} to produce biodegradable plastics.

Traditional disposal methods include recycling, incineration, and burial in landfills. Because synthetic polymers do not easily degrade in landfills, the need for degradable polyolefins has become a major topic of research to manage such environmental problems. The number of patents secured by scientists who work in the field of degradable plastics is growing; however, caution is advised because the impact of the degradation products on the environment is not clearly known.¹¹

PE is believed to be an inert polymer with strong resistance to microbial attack.⁶ It has been shown that PE buried in soil does not degrade for at least 32 years. At such slow rates, it would take \sim 300 years for 60 μ m LDPE films to degrade completely

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in soil.¹² PE–starch blends degrade faster than pure PE in soil. Soil contains extensive microbial diversity¹³ and multiple microorganisms have been reported to degrade PE: *Brevibacillus borstelensis*,¹⁴ *Rhodococcus rubber*,¹⁵ and *Penicillium simplicissimun YK*.¹⁶ In addition, the microorganisms *Aspergillus niger*, *Penicillium funiculosm*, and *Phanerochaete chrysosporium*¹⁷ have been reported as capable of degrading LDPE–starch blends.

LDPE–starch blends are biodegradable because the starch moiety is a carbon source that is consumable by microorganisms. Besides, starch is considered a feeding stimulant for insects possessing specific amylase digestive enzymes.¹⁸ In fact, there are insects and macroorganisms capable to masticate and digest the plastic.¹⁹ Subsequently, the remaining synthetic polymer matrix experiences attack by natural elements such as thermal oxidation and ultraviolet photodegradation.²⁰ The degradation rate of PE–starch materials has been obtained by thermal gravimetric analysis²¹ and also it has typically been controlled by manipulating the physicochemical properties of the materials (crystallinity, molecular weight, chemical composition, hydrophilicity, and surface area).²²

This material can be used for plastic items requiring molding injection,²³ extrusion, blowing injection, and rotomolding processes. The use of biodegradable materials is practically restricted to bags and coverings. However, PE-starch materials can be used for the injection of any kind of home and light industrial plastic containers, bottles, dishes, glasses, and cups as it was done in this work. Noteworthy, for any product, there should be a specific starch concentration due to particular needs of mechanical, thermal, and water resistance properties, among others. When two polymers are present in a film, one of them will serve as a structural component depending on its strength, its microstructural arrangement in the continuous phase and its interaction with nearby polymeric domains.⁵ LDPE is the structural component in PE-starch blends. When attacked by microorganisms, the structural modifications are likely to take place at two levels: (1) simple hydrolysis breaks down the starch fraction without affecting the PE dry weight and (2) starch is degraded by microbial enzymes at the surface level, generating smaller fragments of the polymer blend that enable PE assimilation by soil microorganisms.²⁴

LDPE-starch is just one alternative to solve the ecological problems presented by polyolefins. There are currently other solutions, but these are expensive and protected under registered patents.

An analysis by response surface methodology of mechanical properties (tensile resistance, elongation to break and yield point), thermal properties, microstructure characteristics, and accelerated intemperism of an LDPE–starch polymer for thick applications has already been conducted.²³ The objective of this article is to show chronologically scanning electron microscopy (SEM) images to study the change in surface morphology resulting from the biodegradation of LDPE–starch blends over a short period. Besides, as a new tool, Scandium SEM software was used to quantitatively measure the degradation process. Thus, we analyzed LDPE–starch samples left under compost for 125 days and estimated the total biodegradation time.

MATERIALS AND METHODS

Materials

Food grade corn starch containing 25% amylose was purchased from Corn Product International Ingredients (Mexico, D.F., Mexico), and LDPE was acquired from Certene Polyethylene (Mexico, D.F., Mexico). LDPE has a melt mass-flow rate (190° C/2.16 kg, ASTM D1238) of 0.75 g/10 min and a density of 0.922 g/cm³ (ASTM D1505).

LDPE-Starch Blend Preparation

Starch was conditioned to 15% humidity, determined by the American Association of Cereal Chemists approved method 44-15A²⁵ and then allowed to stand for 24 h. Samples of 3 kg were prepared by mixing PE and starch at different concentrations (0, 10, 25, 40, and 50%) in an inner mixer (Teledyne Readco, York, PA). The blends were extruded in a single-screw extruder (CICATA-IPN, Mexico City, Mexico) with a length to diameter ratio of 15.8 : 1. The extruder contained three independent heating/cooling zones. The compression ratio of the screw was 2.5 : 1, and the diameter of the die was 10 mm. Temperatures of the three barrel zones and die were 80, 120, 160, and 180°C, respectively. Temperatures were monitored with thermocouples. The mass flow of the product was set at 110 g/min, which was controlled by a Baldor Electric feeder (GGP7454 MDF, FT Smith, AR). The extruder was controlled by frequency converters (Hitachi SJ-100, NY) and was operated at 30 rpm.

Mold Injection

LDPE–starch blends were processed in an industrial mill with a 3-mm riddle. Blends were injected into an Engel 93 model injector (Schwartzberg, Austria) with 55 tons of pressure and a single mold cavity for a 250 mL cup. The optimal temperature for injection was 150°C. All tests and further analyses were performed on the end product.

Composting

PE–starch blend samples (4 cm \times 4 cm) were obtained from the cups. Samples were fixed in a plastic mesh with a 1.5 cm \times 1.5 cm grid to facilitate further localization. The samples were buried between two layers of Organodel compost (Agroformuladora Delta, Mexico) a 50-cm lower layer and a 30-cm upper layer. The compost contained organic matter, humus, and humic acids and was supplemented with N, P, K, Ca and conditioned to 50% humidity. After 25, 50, 75, 100, and 125 days beneath the compost, samples were removed and analyzed.⁷ Samples were retrieved from the mesh and washed with deionized water. Next, the samples were dried for 8 h at 60°C and were then allowed to rest for 3 h at room temperature before being weighed. The percentage weight loss was calculated to complement microstructural and Fourier transform infrared (FTIR) analyses.

Characterization of Biodegradation Evolution by SEM Analysis

All the samples were arranged chronologically to observe their evolution under compost at 0, 25, 50, 75, 100, and 125 days. Samples (3 mm \times 3 mm) were mounted on brass stubs with double-sided graphite-filled tape and were vacuum coated with gold by sputtering (Desk IV, Denton Vacuum). SEM micrographs were obtained at magnifications of 500 \times and 1000 \times (JSM-6390LV, JEOL, Japan). SEM images at 1000 \times magnification for samples retrieved after 125 days under compost were selected to measure the size and number of surface deterioration indicators

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Starch content (%)	Day 0	Day 25	Day 50	Day 75	Day 100	Day 125	Weight loss rate (% per day)
10	0	0.66	1.14	1.24	1.59	1.45	0.0138
25	0	2.17	4.08	3.78	5.39	4.46	0.0448
40	0	1.69	5.04	5.24	11.33	13.03	0.1013
50	0	0.55	2.75	2.75	4.05	2.71	0.0304
0	0	0.16	0.24	0.33	0.23	0.25	0.0025

Table I. Weight Loss Percentage

using the Scandium software. The free-hand tool was used to delimitate the eroded area to measure the perimeter, area, and number of erosion indicators.

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y_{\rm b}({\rm residual \ polymer}) = y_{\rm a}
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ya − [weight loss rate neat PE × days × starch concentration factor]

Residual Polymer Extrapolation

Weight loss rate was determined by the linear regression of weight loss percentage at each time point. To estimate total biodegradation, a weight loss rate graphical extrapolation was performed. Because starch is the first carbon source consumed by microorganisms, the weight loss rate associated with starch content was plotted first.

 y_a (residual polymer) = 100% – [weight loss rate × days].

After the starch is expended, only a PE surface exposed to enzymatic attack remains, and the weight loss rate of the pure PE is expected to increase as much as sixfold (50% starch), depending on the starch concentration.¹⁸ Extrapolation continued until only pure PE consumption was predicted to be occurring.

Fourier transform Infrared Spectroscopy Analysis

The FTIR spectra of starch, PE, and LDPE–starch blends after degradation were obtained using an attenuated total reflectance–FTIR spectrophotometer (Spectrum One, Perkin Elmer). The tested wavelength range was from 500 to 4000 cm⁻¹. The samples were pressed against the objective lens and analyzed directly.

RESULTS AND DISCUSSION

The Process of Biodegradation Evolution

Biodegradation of synthetic polymers and starch blends is believed to occur in three phases. The first stage is a superficial erosion process that results from microbial attack to the amorphous polymeric-starch chain, which is when weight loss begins. In the second stage, there is a deeper microbial invasion that,



Figure 1. Evolution of biodegradation of the samples under compost by SEM (×500). Evaluated in a 25 days periods, from 0 to 125 days.

Table II	Microstructure	Qualitative	Analysis	of Polymer	Degradation	Throughout the	125 Days Period
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Starch content						
(%)	Day 0	Day 25	Day 50	Day 75	Day 100	Day 125
10	Injection flux, smooth surface	Injection flux, irregular surface and starch cumulus	Few holes by starch disintegration	A few holes	Pores, holes, discontinuities and some dirt particles	A large pore in a smooth surface.
25	Injection flux, rough surface, and starch cumulus	Few small holes	Cavities and holes	Pores, holes and large cracks	Injection flux, discontinuities and superficial cavities	Accumulated pores and holes
40	Injection flux, rough surface, and starch cumulus	Few superficial pores	Visible flux breaches and cavities	A deep fracture	A long fracture pores and holes	Accumulated holes and cavities
50	Injection flux, rough surface, and starch cumulus	Injection flux, rough surface, and starch cumulus	Few cracks, small cavities and holes	Some pores, holes and few cavities	Pores, holes, cavities, discontinuities and breaches	Discontinuities, holes, pores, and superficial deterioration
0	Injection flux and smooth surface	Injection flux, smooth surface	Smooth surface and a single pore	Intact surface and dirt particles	Intact surface and dirt particles	Irregular surface

along with the humidity, leads to the extensive degradation of the material. In the last phase, the reduction of starch leads to a decrease in microorganisms, but depending on the starch concentration, the newly generated surface can accelerate degradation up to six times.²⁶ Most of the studies performed to characterize biodegradation have been performed on thin films.

In this study, we followed the evolution of the biodegradation of an end product (cups), which were manufactured with LDPE-starch blends and subjected to composting. The analysis of the first stage included the assessment of weight loss evolution of each sample during the 125 days of composting (Table I). In most cases, weight loss increased with starch content and time. As expected, the beginning of surface erosion was accompanied with weight loss. The samples containing 25 and 40% starch lost additional weight after the 125-day composting treatment. This weight loss at the end of treatment proved that LDPE-starch blends with these starch concentrations are highly biodegradable. Remarkably, the blend with 50% starch, which was expected to lose more weight because of its higher starch content, lost only 2.71%. In contrast, the sample with 40% starch lost much more weight despite its lower starch content. Single samples of 4 cm \times 4 cm were placed under compost. Although these 4 cm \times 4 cm coupons have the same concentration, starch could not be distributed homogeneously. So, the 100-days samples could have had starch cumuli that were taken first by microorganism. This effect occurs because we are evaluating a short period of time, but in a long-term scenario, the weight loss would correlate with the time under compost; for this reason, we decided to measure the weight loss rate (% per day). In LDPE-starch blends, weight loss may result from leaching or dispersion of additives into the compost. Carbon dioxide production might result from the degradation of starch and other low molecular weight fractions, with no degradation of large molecular weight polymer chains.²⁷ Additives were not added to the blends in this work; therefore, the degradation of starch in the 50% concentration is smaller than expected because of inhomogeneous mixing in the extruder,

1 1 1 1	Table	III.	Erosion	Measurement	of Samples wi	th Varying	Starch	Contents	After	125	Days of	Compost
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Erosion measurement	10%	25%	40%	50%	0%
Pore counts	14	4	17	17	nvse ^a
Mean (μm²)	73.18	419.29	150.47	59.92	nvse
Minimum (μm²)	9.74	37.44	12.72	3.86	nvse
Maximum (μm²)	187.21	1472.68	446.26	211.65	nvse
Total eroded area (μm ²)	1024.49	1677.14	2557.98	1018.63	nvse
Total sample area (μm^2)	10,660	10,660	10,660	10,660	nvse

^anvse: not visible superficial degradation





Neat polyethylene



Figure 2. Pore measurement after 125 days under compost.

which can cause the starch to be covered by PE at the material surface. From SEM study (Figure 1) also, it can be noticed in the surface material that a larger amounts of starch, homogeneity decreased. Zero days images revealed a smooth surface in sample without starch to a not continuous rough surface for 50% starch sample. Homogeneity can be improved by placing dispersion and distribution head screw in the extruder. In a similar study, films of high density PE (HDPE) and 5% starch



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Figure 3. Total biodegradation by weight loss extrapolation.

lost 0.79% of their weight after 150 days in soil.²⁸ The time and starch concentration-weight loss ratio for the HDPE study may be similar to this work, but the important difference in this investigation is that the end product thickness is greater than that of a film.

Scanning Electron Microscopy Study

The PE-starch degradation process during composting has the advantage of permitting microscopic studies from the initial to the final phases of biodegradation.²⁸ The second stage in the degradation of the blends, which initially consists of vast surface degradation, was evaluated using electron microscopy.

From SEM observations (Figure 1) and microstructural analysis (Table II), it can be concluded that samples containing 10, 25, 40, and 50% starch entered the second stage by day 50 of the composting treatment. Erosion indicators such as fractures, breaches, cavities, and holes were present in the PE–starch samples and continued to increase throughout the treatment. In contrast, neat PE was practically intact after 125 days under compost, and there was an absence of degradation indicators, as confirmed by the weight loss data and SEM analysis.

The accelerated degradation that characterizes the third stage of biodegradation was also observed with SEM analysis from day 75 to day 125. As erosion increases, the holes and pores begin to accumulate and create biodegradation blocks, as seen in the column labeled "125 days" in Figure 1. The biodegradation blocks also depend on the degree of dispersion and distribution of starch in the LDPE matrix. Because of the incompatibility of LDPE and corn starch, it is necessary to improve the blending process, especially when no additives are included. An inappropriate blending process can thus promote the starch cumulus that could accelerate biodegradation initially but delay it later in the process.

Pore Measurement

In this study, SEM was paired with the Scandium software to perform additional quantitative analysis of degradation to investigate erosion and microstructural changes. It was possible to reveal the starch distribution by SEM images. Scandium software allowed us to survey the total eroded area by counting

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the number, examining the size and the dispersion of pores (Table III). This approach is of relevance because the investigated LDPE–starch blends are not intended to be used as disposable products such as bags or packaging materials, or experimentation films (25–60 μ m thickness),²⁹ which have a degradation time between two and five years.^{4,10} Rather, the blends are intended to be used for a variety of industrial purposes; hence, the reason for using an industrial production process (injection molding). In addition, there were significant effects on the final product that small-scale laboratory approaches would have been unable to distinguish.³⁰

Pores can be generated by starch cumulus biodegradation. An increased number of holes, fractures, branches, and cavities are expected to be generated by a blend with a higher starch concentration. These structural damages allow microorganisms to penetrate into deeper layers of the material.³¹ Fungi secrete organic acids during their metabolism that can react with components of the PE–starch material and increase erosion of the surface and consequently the rate of biodegradation.³² The degradation process for neat PE is very slow. On the basis of assumption that biodegradation begins with an erosion process,³³ along with the qualitative biodegradation evolution assessed by SEM, the plastic material degradation was evaluated quantitatively by measuring pore size and superficial erosion (Figure 2). Table III summarizes these observations.

The percentage of eroded surface area correlated with weight loss. The greatest amount of erosion was observed in the sample containing 40% starch, which also registered the greatest weight loss. Within an observed area of 10,660 μ m², an area of 2557.98 μm^2 was eroded. This data indicates that the biodegradation was evenly distributed in the material and was not localized, as was observed in the other blends. Similar SEM results were obtained for PE films that were buried in soil for 17 months.³⁴ For the current conditions, it was expected that the 50% starch blend would exhibit the largest surface erosion, but that sample experienced the same level of erosion as the blend with 10% starch, which did display the predicted correlation between starch percentage and weight loss. This unexpected result is probably because at this extrusion temperature this decreased amount of LDPE (50%) promotes a better melting and its motility increased. The starch was dextrinized as a consequence of the cutting effect of extrusion; in such settings, the blend resulted in a more uniform entanglement of the two polymers, where the LDPE covered the starch and prevented the microbial dependent hydrolysis of the starch fraction. Samples with lower starch contents (10 and 25%) experienced less weight loss, but there was evidence of numerous and sizable pores, indicating an acceptable biodegradability even though the blends were under the compost for only 125 days. The sample of neat PE was not evaluated by the Scandium software because signs of deterioration were completely absent. This observation can be corroborated by the weight loss data.

Residual Polymer

Among other techniques, analytical formulae obtained for the degradation of organic carbon are used for measuring the rate

Wave number		
(cm ⁻¹)	Starch	LDPE
3423	Stretching (—O—H)	
2932-2860	Symmetric and antisymmetric stretching (– CH_2)	Symmetric and antisymmetric stretching (–CH $_3$ and CH $_2$)
1650 ± 10	Hemiacetalic stretching (-C-O-C-)	
1460-1440	Scissors symmetric bend (CH ₂)	Symmetric and antisymmetric bend (CH $_{\rm 3}$ and CH $_{\rm 2}$)
1435-1420	Flexion (—OH)	
1385		Umbrella symmetric bend (CH_3)
1081	Antisymmetric stretching (O—C—C)	
1016	Stretching of cyclic (-C-C-)	Aliphatic stretching of –C–C–
730		Aliphatic chain vibration of CH ₂

Table IV. Wave Number Tentative Assignation from Starch and LDPE FTIR Spectrum

of biodegradation of plastics and to estimate total biodegradation time. $^{\rm 35}$

Because of the long periods required for plastic degradation, a graphical model can help to establish an approximate biodegradation rate for new materials. In this study, all samples were predicted to follow the same pattern for longer periods until complete degradation. To calculate the complete degradation time, the weight loss rate was extrapolated. Figure 3, initially showed pronounced negative slopes, indicating the fast consumption of starch by the microorganisms in the materials. Then, softer, descending slopes mark the slow biodegradation of the remaining PE. Only one negative slope was observed for neat PE, indicating a relative absence of degradation.

According to Figure 3, a solid end product injected from the blend containing 40% starch is expected to last 4375 days (11.98 years) before complete degradation. Although this period

of time seems long for a biodegradable material in a composting process, the end product analyzed in this study is of interest in the industrial arena. Therefore, this 3-mm thick end product with no additives must have a degradation rate that is different from that of films that use a pro-oxidant,³⁶ which in most cases reach a thickness of 1 mm.^{37–39} The sample containing 50% starch is expected to degrade in 5000 days (13.69 years). The sample with 25% starch needs 10,559 days (28.92 years), and the sample with 10% starch needs 30,611 days (83.86 years) to reach complete degradation. Neat PE requires 40,000 days (109.58 years) to degrade. It was expected that the sample with 50% starch would be the first to degrade, but because of its weight loss rate, the blend containing 40% starch reached total biodegradation first. We suggest that the blend with the lowest predicted biodegradation time (11.98 years) is suitable for industrial use because its degradation rate is advantageous over that of neat PE.



Figure 4. FTIR (a) starch, (b) neat PE, and (c) PE-starch blends after 125 days under compost.



Fourier Transform Infrared Spectroscopy Analysis

FTIR spectroscopy is widely used to study the degradation of polymers.⁹ Characteristic bond vibrations for starch and LDPE are shown in Table IV. Figure 4 shows the FTIR spectra in the range of 4000–500 cm⁻¹ of corn starch, pure PE, and PE–starch blends after 125 days in compost. The bond vibrations changed after blending and extrusion of starch and LDPE. Either attenuation or weaknesses in individual bond vibrations were observed in polymer blends as starch content increased. Thus, vibration of the group —OH (3423 cm⁻¹) in the 10% starch blend remained a broad peak, but when the starch content was increased to 50%, the vibration intensity of this —OH group diminished.

The symmetric and antisymmetric stretching bond vibrations of the groups --CH₂ and CH₃ in LDPE (2970-2860 cm⁻¹) exhibited a peak intensity reduction compared with pure LDPE in the blend containing 10% starch [Figure 4(c)], and continued to lessen with starch content. Hemiacetal bonds of starch (1650 cm^{-1}) and $-CH_2$ stretching (1460–1440 cm^{-1}) remained unaffected, as is characteristic for oxidation synthetic polymers. However, the sharpness and intensity of vibration peak (1010 cm^{-1}) belonging to the cyclic -C-C- of the glucose in the starch were reduced as the starch content increased in the extruded materials. These changes were probably due to starch biodegradation in the polymer blend. It was observed that there was no absorbance modification at 10% starch concentration, possibly because LDPE protected the starch from being biodegraded. As the starch contents increased (40 and 50%), the absorbance of the groups -OH, C-O-C and -C-C- was reduced proportionally, induced by higher biodegradation. This result suggests that a higher polysaccharide concentration stimulates PE biodegradation.⁴⁰ Although this could be inconsistent with the weight loss analysis performed on 4 cm \times 4 cm coupons. To achieve a FTIR analysis, the samples need to be milled and homogenized before the test; this should yield more accurate results than a weight loss analysis.

CONCLUSIONS

Here, we investigated the surface structure and erosion characteristics during biodegradation of a plastic end product of industrial interest. Starch biodegradation generates erosion, which facilitates microorganism entrance and enzymatic attack of the residual synthetic polymer. Except for the 50% starch content sample, weight loss increased with starch content and time. SEM micrographs evaluated every 25 days display biodegradation evolution in samples obtained from an end product that was subjected to a compost process. SEM chronological images showed biodegradation indicators such as fractures, breaches, cavities, and holes. The number and size of the superficial pores indicated the total erosion in a specific area, which provided information about the biodegradation state at the time of evaluation. Scandium software allowed us the measurement of the pores in the eroded surface versus total observed area. The greatest amount of erosion was observed in the sample containing 40% starch, which also registered the greatest weight loss. Measurement of pores can be used as an additional tool to determine biodegradation under compost. FTIR studies also showed the biodegradation of LDPE in LDPE-starch blends.

On the basis of objective and techniques used in this work, 40% starch was the ideal concentration for blending with PE for an end product without additives. For the sample that contained 40% starch, it was expected that about 12 years would be required for complete degradation. Even though this is a long time for biodegradable materials, it is realistic for end products with possible applications extending far beyond disposable materials or films.

ACKNOWLEDGMENTS

The authors thank SIP-IPN and Maquimtra S.A. for the injection equipment facilities. H. Vieyra thanks COFAA-IPN and The National Council of Sciences and Technology of Mexico (CONACYT) for the scholarship received.

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