## **Biodegradation of Low-Density Polyethylene-Banana** Starch Films

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Received 5 March 2008; accepted 23 May 2008 DOI 10.1002/app.28938 Published online 15 September 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Films were prepared by extrusion using acetylated and oxidized banana starches at different concentrations mixed with low-density polyethylene, and their biodegradation (buried in soil) at different storage times was studied. Morphological, thermal, and mechanical characteristics of the films after degradation were tested. Films made of acetylated banana starch degraded most rapidly and those prepared with oxidized starch had the slowest degradation time. The type of chemically modified starch plays an important role in degradation of film. Burying the films produced a decrease in degradation temperature at the longest storage time, and there was a longer interval in the films prepared with native banana starch, followed by those made of acetylated starch. The buried in soil films had a broad phase transition and,

#### **INTRODUCTION**

The great variety of physical and chemical properties of the plastics makes them ideal material for a variety of products and applications. Most plastics are widely used and they are considered to be resistant to environmental degradation and their useful lives tend to be short. These facts have led to a significant increase in the volume of residual plastics in recent years. The solution to reduce the problems of plastic waste management is the production and use of environmentally friendly degradable polymers, especially used in packaging applications. The idea of the use and the incorporating a cheap biodegradable additive into otherwise inert polymers was introduced in 1973.<sup>1</sup> The starch inside the matrix of low-density polyethylene (LDPE) acts as degradable filler because it is cheap and can improve its degradconsequently, an increase in enthalpy. This is due to degradation of amorphous starch zones with an increase in the crystallinity. Electron scanning microscopy analysis revealed greater degradation at longer storage time and a more marked effect in the films made of modified banana starch. Mechanical properties of the films were affected by degradation, and these varied depending on the modified banana starch used. The use of biodegradable polymers such as chemically modified banana starch might be feasible for making films with a high rate of degradation. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3464–3472, 2008

**Key words:** oxidized starch; acetylated starch; morphological characteristics; mechanical properties; differential scanning calorimetry; extrusion

ability.<sup>2,3</sup> However, the addition of starch into plastic usually weakens the mechanical strength of films. Therefore, it is necessary to develop a method to improve the mechanical properties of starch-filled plastic. One possible solution is to modify starch chemically. Griffin<sup>1</sup> proposed a process for making a film with improved mechanical strength and biodegradability of plastics.

The granular starch present on the surface of the polymer film is attacked by microorganisms such as fungi and bacteria consume the material,<sup>4</sup> macroorganism degradation in which insects and other macroorganism masticate and digest the plastic,<sup>5</sup> photodegradation in which exposure to ultraviolet radiation produces free radical reaction and chain scission,<sup>4</sup> and chemical degradation in which chemical reactions cleave bonds and reduce the molecular weight of the polymer.<sup>6</sup> The degradation mechanisms will vary depending on the polymer's environment and desired application.

Thermal analysis techniques provide a powerful research tool for obtaining qualitative and quantitative information about the effects of biodegradation on the structure and other important properties of the degraded material.<sup>7</sup> Thermoanalytical and

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Journal of Applied Polymer Science, Vol. 110, 3464–3472 (2008) © 2008 Wiley Periodicals, Inc.

mechanical techniques have been used to investigate the degradation in soil burial for different time periods of blends starch/LDPE.<sup>8,9</sup>

The aim of this study was to determine the biodegradation of the films, elaborated with the blend low-density polyethylene and modified banana starch, assessed by diverse techniques.

#### **EXPERIMENTAL**

#### Materials

LDPE (LDPE 20020P; IF = 2 g/10 min) was purchased from PEMEX (Coatzacoalcos, Ver., México).

#### Starch isolation

Unripe bananas (*Musa paradisiaca*) were purchased in the local market of Cuautla, Morelos, México. The starch was isolated using a pilot scale procedure.<sup>10</sup> The power was ground to pass a US No. 100 sieve and stored at room temperature (25°C) in a glass container.

#### Preparation of modified starch

The oxidation and acetylation of starch was described in an earlier paper.<sup>11</sup> In brief, the starch slurry (200 g of starch in 500 g of distilled water) was maintained at 35°C and the pH was adjusted to 9.5 with 2N NaOH. Sodium hypochlorite with 2% active chlorine w/v was slowly added into the starch slurry over 30 min while maintaining the pH at 9.5 with 1N H<sub>2</sub>SO<sub>4</sub>. After the addition of NaOCl solution, the pH of the slurry was maintained at 9.5 with 1N NaOH for an additional 50 min. The slurry was then adjusted to pH 7.0 with  $1N H_2SO_4$ , passed to 1-L flask to precipitate and decant the reaction mix and washed with several volumes of deionized water and dried in a convection oven at 50°C for 48 h. Acetylated banana starch was prepared mixing 162 g of starch and 220 g of distilled water with magnetic stirrer. The pH was adjusted to 8.0 with NaOH at 3% (w/w), acetic anhydride and NaOH (3%, w/w) were added drop by drop, the last for maintaining the pH between 8.0 and 8.4. When addition of acetic anhydride was complete, the pH was adjusted to 4.5 with HCl 0.5N. The slurry was centrifuged at 1500 rpm for 15 min and the supernatant was eliminated. The solid (bottom) was mixed with distilled water, centrifuged at the same conditions and this step was carried out two more times. The starch was dried in a convection oven at 50°C for 24 h.

#### Film preparation

Films were prepared using diverse blends of banana starch, glycerol, and LDPE. Twin-screw extruder (C.W. Brabender Instruments, So Hackensack, NJ)

 TABLE I

 Blends for Film Preparation by Extrusion (%)

Sample	Native starch	Acetylated starch	Oxidized starch	Glycerol	Low-density polyethylene
NS20	20			10	70
NS30	30			10	60
NS40	40			10	50
AS20		20		10	70
AS30		30		10	60
AS40		40		10	50
OS20			20	10	70
OS30			30	10	60
OS40			40	10	50

was used for film elaboration. The identification of the different films is presented in Table I. The thickness of the films was assessed with a manual micrometer (Mitutoyo, Kobe, Japan) in 12 random positions of the film. The average of these determinations was 1.200  $\pm$  0.045 mm. The appearance of all films was clear and uniform.

#### **Biodegradation process**

The biodegradation process of the film samples was studied during soil burial for 9 months. The samples were prepared using the instructions of the official method ASTM D 638M-93.<sup>12</sup> The study was carried out at environmental conditions (ambient humidity 28.7–61.5% and temperature 26.4–22.7°C). The samples were buried in the soil at a depth of 20 cm from the surface and 5 cm of separation from one another. The rate of biodegradation was studied by measuring the percentage weight loss, thermal analysis, mechanical properties, and morphology of the samples each month. Prior to measuring, samples were washed carefully with distilled water and maintained for 3 days in desiccator containing a saturated saline solution of NaBr (57% RH).

#### Thermal gravimetric analysis

Thermal gravimetric analysis (TGA) were done using an analyzer thermogravimetric Hi-Res 2950 (TA Instruments, New Castle, NJ). In the present study, nitrogen flow was kept at constant rate of about 50 mL/min to prevent thermal oxidation processes of polymer sample. The sample was heated at 10°C/min from 30 to 600°C. The residual starch content in the film was calculated as the change in the slope (see Fig. 1) of the thermogram taking the polyethylene film as reference.

#### Differential scanning calorimetry

The calorimetric study was done using a differential scanning calorimetric 2010 (TA Instruments, New



**Figure 1** Thermogravimetric analysis of loss weight of blends at  $10^{\circ}$ C in a nitrogen atmosphere for an AS30/glycerol/LDPE blends degraded in soil at different times. (a = 0 month; b = 3 month; c = 6 month; d = 9 month). LDPE = low-density polyethylene.

Castle, NJ) previously calibrated with indium. The samples (10–15 mg) were weighed (dry basis, n = 3) on aluminum pan. The pans were sealed and scanned at a heating rate 10°C/min with temperature ranging from 20 to 180°C. The peak temperature ( $T_m$ ) of transition was obtained.

#### Mechanical properties

The mechanical properties measurements consisted of tests to determine the load tensile strength (TS), percent elongation at break (% E), and elastic module (EM). These parameters were obtained from the force versus deformation curves using a (ASTM D 6388 M-93) Texture Analyser (TA-XT2i) (Stable Micro Systems, Haslernere, UK, and Texture Technologies corp., Scarsdale, NY), equipped with 25-kg load cell. The samples were prepared using the instructions of the official method ASTM D 638M-93,<sup>12</sup> and they were maintained for 3 days in a desiccator containing a saturated saline solution of NaBr (57% RH). Separation among gauges was 5 cm. The ends of film were fixed in each of the subjection gauge and the speed of deformation was 0.9 mm/min.

#### Scanning electron microscopy

A scanning electron microscope (JOEL JSMP 100, Japan) was used to study the morphology of the

films samples. Each sample was washed with distilled water and dried at  $40^{\circ}$ C. The scanning electron microscope was operated at 5 kV. The films samples were mounted on aluminum stubs using a double-sided tape and then coated with layer of gold (40–50 nm).

## Statistical analysis

Experiments were arranged in a completely randomized design. An analysis of variance (ANOVA) was carried out with the statistical program Sigma-Stat version 2.03.<sup>13</sup> Media comparison was done by Tukey's multiple test ( $\alpha = 0.05$ ).<sup>14</sup>

### **RESULTS AND DISCUSSION**

## Effect of burying on film starch content

In general, film starch content, assessed by thermogravimetric analysis (Fig. 1), decreased as storage time lengthened (Table II). This is due to degradation of the outer surface starch by microorganisms during the first month, producing fissures on the surface of the film, exposing the inner starch of the material, and accelerating its degradation.<sup>15</sup> This was revealed by the microscopy study which will be discussed below. Degradation rate was higher in the films made of acetylated banana starch: after 3 months 27% residual starch was quantified; this percentage did not increase with longer storage time.<sup>16</sup> The films made of oxidized banana starch were the most resistant to degradation. The difference might be explained by the fact that acetylation of banana starch increases amorphous areas because the hydroxyl groups of native starch are substituted by acetyl groups. Since degradation starts in the amorphous zones of starch present in the film,<sup>17</sup> starch crystallinity decreases, as does starch-starch interaction,<sup>18</sup> while starch degradation increases. Moreover, starch oxidation occurs in the amorphous areas of the starch structure, decreasing the amount of starch and therefore reducing film degradation because of the increase in crystallinity.<sup>19,20</sup> The films prepared with oxidized starch had the lowest rate of degradation, as will be seen in the discussion of the microscopy study below. During the acetylation, the acetyl groups replaced most of the hydroxyl groups on starch and no intermolecular hydrogen bonds were formed, which destroyed the ordered crystalline structures,17 while during the oxidation, starch hydroxyl groups are oxidized to carbonyl groups and then carboxyl groups, this reaction takes place mainly on the amorphous regions, producing more crystalline areas and increasing the resistance to degradation.<sup>19</sup> In films made of a blend of starch and polyethylene, starch content decreased by 10% between 0 and 20 weeks of storage.<sup>21</sup> Another study,

Thermogravimetric Anarysis					
Sample <sup>a</sup>	Duration (month)	Initial starch content (%)	Weight change at 250–350°C (%) <sup>b</sup>	Residual starch after exposure (%)	
NS30	0	$\sim 30$	20.25	100	
NS30	3		16.16	79.80	
NS30	6		15.77	77.87	
NS30	9		13.07	64.54	
AS30	0	$\sim 30$	18.69	100	
AS30	3		5.11	27.34	
AS30	6		5.09	27.23	
AS30	9		5.14	>27.50	
OS30	0	$\sim 30$	20.07	100	
OS30	3		19.82	98.75	
OS30	6		16.32	81.35	
OS30	9		15.92	79.32	

TABLE II
Effect of Burying on Starch Content of Films Assessed by
Thermogravimetric Analysis

<sup>a</sup> Average of three repetitions.

<sup>b</sup> Total weigh change was assumed to be due to complete pyrolysis of starch.

however, found that 25 and 30% of the starch content in the film degraded after 24 weeks of storage.<sup>22</sup> Degradation of the starch in the buried films analyzed might be explained by the percolation theory, which states that environmental conditions make the film components more susceptible to degradation.<sup>23</sup>

#### Effect of burying on thermal stability of the films

Thermograms (Fig. 2) revealed two stages. The first started at ~ 200°C (glycerol evaporation) and continued up to ~ 300°C (thermal degradation of starch component). Degradation at higher temperatures is caused by LDPE that occurs at ~ 430°C. A similar pattern appeared in films made of the blends LDPE/thermoplastic starch<sup>24</sup> and in starch blends buried in soil with degradation temperature between 298 and 339°C.<sup>25</sup>

The temperature at 20% film weight loss was calculated (Fig. 3) and is shown in Table II. The longer the storage time, the higher the degradation temperature, and the more marked was the effect on the films made of acetylated starch, indicating greater thermal stability. This behavior might be explained by the introduction of acetyl groups, which increase the hydrophobic character of starch and, consequently, interfacial adhesion to LDPE. This led to an increase in thermal stability of the film even after 9 months.<sup>17,26</sup> Films prepared with the blend acetylated potato starch/LDPE had higher thermal stability than the film made from native potato starch.<sup>27</sup> Films made from oxidized or native banana starch showed similar thermal stability, suggesting that oxidation did not change their hydrophilic character.<sup>28</sup>

The temperature at which films lost 95% of their weight (LDPE degradation) was calculated (Fig. 2) and is shown in Table III. Burying the films pro-

duced a decrease in temperature as storage time increased, and the widest range (temperature at 9 months—temperature of control sample) was observed in films prepared with native banana starch, followed by acetylated starch. Variation in degradation temperature of synthetic polymer films is due to the increase in its accessibility produced by the degradation of the starch by environmental conditions (temperature, relative humidity) and soil microorganisms.<sup>29</sup> The degradation temperature of polyethylene in the films prepared by blending starch decreased from 504 to 497°C when the films were buried, but a wider range was found in the same film (from 501 to 478°C) exposed to soil for 6 months, demonstrating a greater effect of UV rays



**Figure 2** Thermal diagram for acetylated starch/glycerol/LDPE (30%/10%/40%) respectively; after exposure to soil burial treatment for 9 month. LDPE = low-density polyethylene.

Journal of Applied Polymer Science DOI 10.1002/app



**Figure 3** Thermogravimetric analysis of the effect starch modification on thermal stability of blends (starch 30%/glycerol 10%/LDPE 60%) at different times; a = 0 month; b = 3 month; c = 6 month; d = 9 month. LDPE = low-density polyethylene.

on thermal stability of polyethylene.<sup>30</sup> It is important to mention that environmental changes during the experiment due to changes of season can play an important role in this kind of study.<sup>31</sup>

#### Effect of burying on film crystallinity

A transition phase was observed in the films due to LDPE melting, with similar values of peak tempera-

 
 TABLE III

 Effect of Burying on the Temperature of Decomposition of the Blends Starch/Polyethylene

		5	5
Sample <sup>a</sup>	Time (month)	Temperature (°C) <sup>b</sup> to 20% of loss of weight of the blends	Temperature (°C) <sup>b</sup> to 95% of loss of weight of the blends
NS30	0	299.63	495.07
	3	328.36	486.56
	6	374.41	488.62
	9	392.26	487.06
AS30	0	326.54	497.00
	3	430.60	490.24
	6	437.03	492.75
	9	449.34	491.14
OS30	0	315.17	494.00
	3	328.06	490.38
	6	373.97	491.01
	9	383.98	491.60

<sup>a</sup> Average of three repetitions.

<sup>b</sup> Temperature of decomposition of the blends.



**Figure 4** Effect of buried in soil on crystallinity of polyethylene in blends with oxidized starch assessed by differential scanning calorimetry.

tures (Fig. 4), indicating that chemical modification of the starch used for the film preparation did not affect this parameter.<sup>13</sup> When storage time increased, the peaks were wider and enthalpy increased (Table IV). This pattern is due to an increase in crystallinity of LDPE in the films during storage by the structural reordering of the chains since degradation of the films occurs in the amorphous zones with the concomitant increase in crystallinity, but the storage time used in this study was not long enough for degradation of synthetic polymer.<sup>30,32</sup> The crystallinity level in the stored films made of the blend starch/polyethylene decreased in the first weeks but thereafter increased. This pattern is related to starch degradation with the concomitant increase in crystallinity of the synthetic polymer.33 Films prepared with the blend polypropylene/modified starch

 TABLE IV

 Effect of Burying on the Properties of  $T_m$ ,  $\Delta H_m$ , and

 Crystallinity of Polyethylene in Blends with 40% of

 Native or Modified Banana Starch

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Sample <sup>a</sup>	Time (month)	$T_m$ (°C)	$\Delta H_m$ (J/g)	Crystallinity (%)
NS40	0	112.15	24.34	13.02
	3	112.24	32.79	17.53
	6	112.14	33.64	17.99
	9	112.70	34.72	18.57
AS40	0	112.38	21.77	11.64
	3	112.90	36.23	19.38
	6	113.09	37.12	19.85
	9	113.85	38.52	20.60
OS40	0	112.02	21.60	11.55
	3	112.81	28.55	15.27
	6	112.22	36.06	19.28
	9	112.89	38.97	20.84

<sup>a</sup> Average of three repetitions.



**Figure 5** Scanning electron microscopy ( $\times$ 40) of films elaborated with acetylated banana starch (20% w/w) blending with 10% glycerol and 70 low-density polyethylene. The films were buried in soil at different times. (a) Control sample; (b) 3 months; (c) 9 months.

showed similar melting temperature and enthalpy in the control sample and in those buried in the soil for 20, 120, and 180 days.<sup>30</sup> The temperature pattern was similar to that determined in our study but the pattern for the enthalpy value was different. This difference might be due to the synthetic polymer used for film preparation.<sup>32</sup>

#### Electron scanning microscopy study

After 3 months, the films exhibited degradation because fissures and cavities [see arrows in Fig. 5(b,c)] appeared; this evidence was more notable as storage time lengthened. The films made of acety-lated banana starch showed more degradation than those prepared with oxidized and native banana starch (Fig. 6). This pattern is produced because the acetylation reaction produces more amorphous zones in starch molecules<sup>17</sup> and they are degraded faster by soil microorganisms. The effect was more evident when starch concentration in the film increased, concordant with the results shown in Table II from the thermogravimetric analysis. This

effect might be explained by the percolation theory; when starch levels in the film increase, more granules aggregate into clusters producing more sites for microorganisms and enzymes to move toward the starch molecule.<sup>34</sup>

# Effect of burying films in soil on their mechanical properties

In general, TS decreased when the starch level in the film rose (Table V) due to degradation by soil microorganisms. This may be explained by the percolation theory,<sup>34</sup> as discussed above. In the same sense, when starch level in the film increases, degradation rate is higher, producing a decrease in the TS value over a longer time.<sup>35</sup> No significant effect ( $\alpha = 0.05$ ) of starch type was shown in this mechanical property. When storage time increased for the same film type, a slight change in the TS value was obtained. This pattern suggests that polyethylene is the principal component responsible for this property. Films were prepared with the blend hydroxipropilated potato starch/polyethylene and stored; these films



**Figure 6** Scanning electron microscopy ( $\times$ 40) of films elaborated with different banana starches (30% w/w) blending with 10% glycerol and 60 low-density polyethylene. The films were buried in soil for 6 months. (a) Acetylated banana starch; (b) oxidized banana starch; (c) native banana starch.

had TS values that decreased after 7 weeks, but those films made with the blend native potato starch/polyethylene had longer time (11 weeks), indicating that the former films had a higher degradation rate.<sup>35</sup> Ratanakamnuan and Aht-Ong<sup>35</sup> reported that the blend banana starch/polyethylene showed higher photobiodegradation (defined as a decrease in the TS value) during storage, and that the effect was more marked when storage time was longer and when the starch content in the film increased.

Film elongation to breaking (Table VI) decreased when starch level in the blend increased, concordant with the fact that film degradation rate is higher when the natural polymer is present in larger quantities. With shorter storage time (3 months), there was an effect of starch type (40% starch) on this mechanical parameter of the film. The modified starches (acetylated and oxidized) had higher elongation to breaking point value than native starch. However, at 6 months an inverse pattern was observed; degradation rates were higher in films prepared with modified banana starch. When storage time increased (9 months), the pattern was similar to that of the samples stored for 3 months, but the films with acetylated and oxidized starch had

TABLE VEffect of the Time of Buried in Soil on the TensileStrength (MPa) in the Films Elaborated with Native<br/>or Modified Banana Starch Blending with<br/>Low-Density Polyethylene<sup>a</sup>

		Time (month)	
Sample	3	6	9
NS20 NS30 NS40 AS20 AS30 AS40 OS20 OS30 OS40	$\begin{array}{c} 6.70 \pm 0.37^{a,A,1} \\ 6.16 \pm 0.28^{b,A,2} \\ 3.32 \pm 0.40^{e,B,4} \\ 6.55 \pm 0.39^{a,C,1} \\ 6.68 \pm 0.29^{b,C,3} \\ 3.65 \pm 0.43^{e,D,5} \\ 6.76 \pm 0.35^{a,E,1} \\ 5.84 \pm 0.14^{c,F,3} \\ 3.39 \pm 0.2^{e,G,5} \end{array}$	$\begin{array}{c} 6.65 \pm 0.33^{a,A,1} \\ 5.66 \pm 0.45^{c,A,2} \\ 4.33 \pm 0.29^{e,B,5} \\ 5.94 \pm 0.09^{b,C,2} \\ 4.51 \pm 0.27^{d,D,A} \\ 3.01 \pm 0.37^{f,E,6} \\ 5.79 \pm 0.29^{b,C,2} \\ 4.59 \pm 0.29^{d,D,A} \\ 2.46 \pm 0.58^{f,E,6} \end{array}$	$\begin{array}{c} 6.50 \pm 0.64^{a,A,1} \\ 4.58 \pm 0.47^{b,B,3} \\ \\ & - \\ 5.71 \pm 0.49^2 \\ \\ & - \\ \\ - \\ \\ - \\ \\ - \\ \\ - \\ \\ - \\ \\ - \\ \\ - \\ \\ - \\ \\ - \\ \\ - \\ \\ - \end{array}$

<sup>a</sup> Means of 6 replicates  $\pm$  standard error. Lowercase letters represent the effect of the modification of the starch at the same concentration. Uppercase letters represents the effect of the concentration of starch at the same modification. Number represents effect of the time. Means in the columns that do not share the same lowercase letters are significantly different ( $\alpha = 0.05$ ). Means in the columns that do not share the same uppercase letters are significantly different ( $\alpha = 0.05$ ). Means in the rows that do not share the same number are significantly different ( $\alpha = 0.05$ ).

higher degradation rates, such that they were not analyzed because of the high level of decomposition of the samples. Behavior of the films was variable since biodegradation of the starch-based materials depends on the chemical modification of the natural polymer, and decomposition can increase or decrease depending on the type of chemical modification.<sup>36–38</sup>

The elasticity module increased when starch concentration in the blend rose (Table VII). When starch granules are added to the polyethylene matrix, they act as filler and consequently increase the elasticity module.<sup>39</sup> The films prepared with the modified starches had a lower elasticity module, and the effect was more evident in the film with acetylated starch because of the more hydrophobic character and higher degradation rate of this starch. At longer storage time (6 months) the elasticity module decreased and the effect was greater since some samples were not analyzed because they were too highly degraded.

#### CONCLUSIONS

Degradation of surface or external starch in the film was observed, causing exposure of inner starch and consequently an increase in degradation. Films made of oxidized banana starch were more resistant to degradation. These results are in agreement with the microscopy study. Degradation temperature increased with longer storage time, and the effect

 TABLE VI

 Effect of the Time of Buried in Soil on the Elastic

 Module (MPa) in the Films Elaborated with Native or

 Modified Banana Starch Blending with Low-Density

 Polyethylene<sup>a</sup>

Time (month)	9
	9
Sample 3 6	· · · · ·
NS20 $104.4 \pm 12.0^{a,A,1}$ $97.8 \pm 2.0^{a,A,2}$	$92.8 \pm 15.0^{a,A,3}$
NS30 $143.3 \pm 7.0^{d,B,2}$ $118.4 \pm 8.0^{d,B,3}$	$108.0 \pm 3.0^{a,A,3}$
NS40 $164.4 \pm 9.0^{g,C,4}$ $121.8 \pm 7.0^{g,B,5}$	_
AS20 $56.4 \pm 6.0^{b,D,1}$ $48.3 \pm 2.0^{b,C,2}$	$44.40 \pm 5.0^2$
AS30 $73.0 \pm 6.0^{e,E,3}$ $56.5 \pm 0.6^{e,D,4}$	-
$AS40 \qquad 104.2 \pm 11.0^{h,F,4} \qquad 84.9 \pm 2.0^{h,E,5}$	_
OS20 $66.0 \pm 3.0^{c,G,1}$ $61.2 \pm 2.0^{c,F,2}$	-
OS30 $117.4 \pm 13.0^{f,H,3}$ $60.3 \pm 3.0^{f,F,4}$	-
OS40 $140.0 \pm 16.0^{i,L,5}$ $71.1 \pm 5.0^{i,G,6}$	_

<sup>a</sup> Means of 6 replicates  $\pm$  standard error. Lowercase letters represent the effect of the modification of the starch at the same concentration. Uppercase letters represents the effect of the concentration of starch at the same modification. Number represents effect of the time. Means in the columns that do not share the same lowercase letters are significantly different ( $\alpha = 0.05$ ). Means in the columns that do not share the same uppercase letters are significantly different ( $\alpha = 0.05$ ). Means in the rows that do not share the same number are significantly different ( $\alpha = 0.05$ ).

TABLE VII Effect of the Time of Buried in Soil on the Elongation at Break (%) in the Films Elaborated with Native or Modified Banana Starch Blending with Low-Density Polyethylene<sup>a</sup>

	Time (month)				
Sample	3	6	9		
NS20	$43.93 \pm 3.32^{a,A,1}$	$26.23 \pm 2.53^{a,A,2}$	$14.89 \pm 2.61^{a,A,3}$		
NS30	$14.72 \pm 2.31^{c,B,4}$	$12.46 \pm 2.48^{\mathrm{d,B,4}}$	$10.16 \pm 2.28^{c,B,5}$		
NS40	$4.19 \pm 1.19^{ m e,C,6}$	$3.04 \pm 0.44^{\mathrm{g},\mathrm{C},7}$	_		
AS20	$44.52 \pm 3.11^{a,D,1}$	$19.20 \pm 2.33^{\mathrm{b},\mathrm{D},\mathrm{2}}$	$2.47 \pm 0.01^{3}$		
AS30	$17.04 \pm 2.47^{ m d,E,4}$	$11.09 \pm 1.78^{\mathrm{e,E,5}}$	-		
AS40	$14.11 \pm 0.73^{ m f,F,6}$	$2.21 \pm 0.46^{ m h,F,7}$	_		
OS20	$45.96 \pm 3.26^{a,G,1}$	$13.91 \pm 0.29^{c,G,2}$	-		
OS30	$20.92 \pm 1.92^{c,H,3}$	$13.77 \pm 0.41^{ m f,G,4}$	-		
OS40	$17.99\pm0.93^{g,I,6}$	$2.78\pm0.43^{i,H,7}$	_		

<sup>a</sup> Means of 6 replicates  $\pm$  standard error. Lowercase letters represent the effect of the modification of the starch at the same concentration. Uppercase letters represents the effect of the concentration of starch at the same modification. Number represents effect of the time. Means in the columns that do not share the same lowercase letters are significantly different ( $\alpha = 0.05$ ). Means in the columns that do not share the same uppercase letters are significantly different ( $\alpha = 0.05$ ). Means in the rows that do not share the same number are significantly different ( $\alpha = 0.05$ ).

was more notable in the films made of acetylated starch. The amorphous zones of the starch degraded and thus increased crystalline zones. However, the storage time used in this study was not long enough to show degradation of the synthetic polymer. The mechanical characteristics of the films, such as TS, elongation to breaking, and elasticity modulus, were modified by degradation. The films prepared with the modified starches had a lower elasticity module and the effect was more evident in the film with acetylated starch. The higher degradation rate of chemically modified banana starch makes it a possible alternative for use in biodegradable films. The main advantages of these biodegradable films might be the low cost and the ecological impact.

One of the authors (AVT) acknowledges the scholarship from DGEST-SEP-México.

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