# Extruded/Injection-Molded Composites Containing Unripe Plantain Flour, Ethylene–Vinyl Alcohol, and Glycerol: Evaluation of Mechanical Property, Storage Conditions, Biodegradability, and Color\*

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ABSTRACT: Extruded/injection-molded composites of excellent mechanical property were produced from plantain flour (PF) blended with ethylene-vinyl alcohol (ÊVA) and glycerol. Scanning electron microscopy (SEM) revealed that composites had a smooth surface, indicative of an excellent compatibility between PF, EVA, and glycerol. Generally, tensile strength (TS), elongation at break (%E), and the displacement (DM), all decreased with increased PF content in the composite accompanied by an increase in Young's modulus (M). The composites with higher PF contents (60% or higher) had more stable mechanical properties. Selected composites (60% PF content) stored at  $-20^{\circ}$ C and  $4^{\circ}$ C for  $40^{\circ}$  h showed only minor changes in mechanical properties compared with controls (23°C). However, samples stored for a similar period at 80°C were drastically altered in their mechanical

# **INTRODUCTION**

Plantain (*Musa paradisiacal* L.) is the largest herbaceous plant in the world and is grown abundantly in many developing countries. It is considered to be one of the most important sources of energy for people living in humid regions and is the fourth on the list of the developing world's most important food crops, after rice, wheat and maize.<sup>1</sup> Plantain is a seasonal and highly perishable fruit, and surplus quantities are often available year around, necessitating the need to seek other alternatives for utilization of properties resulting in huge increases in TS and *M* and a 10-fold decrease in the %E. Samples prestored at various relative humidities (RHs) for 40 h exhibited only slight decrease in TS and *M* and a concomitant increase in the %E with increased RH. Interestingly, sample prestored at both  $-20^{\circ}$ C and  $80^{\circ}$ C exhibited significantly higher rates and extents of degradation. SEM analysis of samples left in compost for 8 weeks showed a rapid surface erosion and material deterioration with time. Evaluation of the color produced during heat processing of starch in PF as a result of Maillard reaction showed an increase in the values of luminosity (*L*\*), chroma (*C*\*), and hue angle (*h*\*) with decreased PF content in the composite. © 2011 Wiley Periodicals, Inc.<sup>+</sup> J Appl Polym Sci 124: 2632–2639, 2012

Key words: plantain flour; EVA; composite; biodegradation

this raw material. Beside their fruit, plantains have been used for the production of a low-cost plantain flour (PF) ingredient and for the starch production. Starch represents over 70% of the dry weight of plantain. Due to its high starch content, surplus plantain crops are mostly processed to produce flour and starch for use in foods and other industrial applications.<sup>2–4</sup> Blending of flour or starch derived from plantain with synthetic polymers has been proposed,<sup>5</sup> but their use in nonfood applications is almost nonexistent. In recent years, there has been significant interest in developing biodegradable materials from blends of natural and synthetic polymers.<sup>6,7</sup> Particularly, naturally biodegradable polymers have been used as low-cost fillers in composite materials. In this regard, binary or hybrid blends have been prepared containing natural polymer (such as cellulose, starch, and protein) in combination with synthetic polymers to create functionalized product.<sup>8-12</sup> For example, starch or cellulose when blended with a biodegradable synthetic polymer such as ethylene-vinyl alcohol (EVA), produced a multi-layered extruded composite where EVA

<sup>\*</sup>Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may be suitable.

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migrated toward the external surface sandwiching the starch or cellulose in between.<sup>13</sup> Both starch and cellulose, being highly hydrophilic polymers, are susceptible to moisture. However, being trapped between mostly hydrophobic but slowly biodegradable EVA layers, yielded a biodegradable composite with much improved water resistance and mechanical properties.

If the synthetic polymer in the blend is not a biodegradable polymer, the resulting product will have different properties. For example, gelatinized cornstarch processed with high-density polyethylene (HDPE) and subjected to injection molding, yielded composites of excellent mechanical property where starch was essentially encapsulated within the polyethylene (PE) matrix, thus, making composites highly resistant to microbial enzymes.<sup>14</sup> In this regard, it has been shown recently that an incorporation of an oxidative additive in the HDPE film formulation leads to its chain scission and the release of low molecular-weight compounds that can be readily degraded by soil microbes. For blend to be useful in single-use applications, it is essential that it degrades either chemically or biologically under aerobic or anaerobic conditions.<sup>15</sup> If processed blends have reasonable strength and successfully retain their ability to degrade in the environment, they can be utilized in a wide range of disposable products and could also help alleviate the disposal problem created by the many nondegradable plastics.<sup>16–18</sup>

The uses of natural renewable polymers in blends offer many advantages and are considered quite attractive due to their low density, low-cost, renewability, and sustained biodegradability characteristics. Bio-based polymeric blends have been the subject of study by several investigators.<sup>19–23</sup> However, no report exists on the use of starch from plantain source in bioblends.

The use of extrusion technology has been recently considered for the processing of natural polymers in combination with synthetic polymers to develop novel value-added consumer products. In this study, the use of PF with EVA and glycerol to produce extruded/injection-molded composites was examined. Formulations were prepared and evaluated for their mechanical properties. Studies were also conducted to assess the impact of concentration of the PF, relative humidity (RH), and temperature conditions on the mechanical property and microstructure of the produced composites as well as their biodegradation behavior in compost environment.

# EXPERIMENTAL

America (Pasadena, TX) under the trade name

# Materials

EVA was purchased from the EVAL Company of

TABLE I Formulations of Blends Containing PF, EVA, and Glycerol (% Wet-Weight Basis)

Formulation	PF	EVA	Glycerol
1	70	15	15
2	65	20	15
3	60	25	15
4	55	30	15
5	50	35	15
6	40	45	15

EVAL-E105. EVAL is an EVA copolymer that is characterized by copolymerization ratio of ethylene and vinyl alcohol. Specifically, EVAL grade E-150 has high ethylene content (44 mol %), density of 1.14 g/cm<sup>3</sup>,  $T_m$  of 165°C,  $T_g$  of 55°C, and oxygen transmission rate of 1.5 cc–20 µm/m<sup>2</sup> day atm. EVAL with high ethylene content offers greater flexibility and easier processing. The glycerol was obtained from  $\sigma$ -Aldrich Corp. (St. Louis, MO). Unripe plantains of Chiquita brand were purchased from a local supermarket (Ranch 99, Richmond, CA).

#### Methods

#### Plantain processing

Unripe plantains (*M. paradisiacal* L.) were peeled and cut into 3 mm thick slices and dipped into 3% sodium sulfate solution for 1 min to avoid enzymatic browning of the PF mediated by phenol-oxidases. Slices were placed in a forced-air oven to dry (Proctor Schwartz, Horsham, PA) at 100°C for 2.5 h or until the moisture was reduced to <5%. The dried plantain slices were initially crushed in a commercial blender yielding a coarse material (approx. 5–10 mm particle size), which was subsequently milled into flour (UDY-Mill equipped with 50 µm sieve; UDY Corp., Fort Collins, CO). The recovered flour was transferred into a zip-lock bag and stored (50% RH, 23°C) for subsequent use.

#### Extrusion and injection molding

Formulations of the blends prepared from PF, EVA, and glycerol are provided in Table I. Premeasured amount of flour and EVA were mixed by shaking in a zip-lock plastic bag ( $30 \times 30$  cm) for several min until the mixture was homogeneous. The powder mix was subjected to extrusion in a corotating twinscrew melt-extruder (Leistritz Micro 18, Germany). The extruder has six heating zones with the first five cooled by water. The temperatures for each zone were set at 80, 90, 100, 110, 110, and 100°C from feed to die. The screws have a diameter of 18 mm, and the barrel has a length to diameter ratio of 30 : 1. A Bran + Luebbe N-P31 metering pump

was used to control the liquid (deionized water and glycerol) feed rate. Extrusion was carried out at a screw speed of 60 rpm, with a torque of 27% and a pressure of 300 psi. Glycerol (15% wt/wt) mixed with the deionized water was pumped (Bran + Luebbe N-P31 metering pump) directly into the barrel just before the first temperature zone (6 g/min). The powder mix was fed into the extruder (12 g/min) using a K-Tron Soder T-20 (American Pitman, NJ) loss-in-weight feeder. The resulting extrudate was in the form of a flexible rod and had a smooth texture. After drying, the extruded rods were pelletized for injection molding.

Injection molding was accomplished in a Boy 15S (Compression Boy 15S; Internationale Gröbe 42-22) equipped with three zones all set at the same temperature (150°C). The pellets were injected (110 psi for 30 s) to produce type IV dog-bone films (ASTM D-638).

# **Color evaluation**

Color evaluation was done to determine any changes in color of the extruded material due to the extrusion processing, particularly, as the concentration of PF increased in the formulations. The color production is attributed to the brown products generated during the course of Maillard reactions. The colorimeter, a Minolta Chroma-Meter CR-200 (Minolta, Ramsey, NJ), equipped with a xenon lamp in the  $L^*$ ,  $a^*$ , and  $b^*$  system was calibrated with a white tile  $(L^* = 94.4000; a^* = 0.3134; b^* = 0.3205).$ Color measurements were taken holding the sensing head in direct contact with the surface of the dried flours. Triplicate measurements were taken at random locations on each sample. The  $L^*$ ,  $a^*$ , and  $b^*$  readings obtained directly from the instrument provided measures of lightness, redness, and yellowness, respectively. These readings were converted to the  $L^*C^*H^*$  system using  $a^*$  and  $b^*$  to calculate values of chroma ( $C^*_{ab}$ ), color saturation (vividness or dullness), and hue  $(h^{\circ}_{ab})$  using the following equations<sup>24</sup> (X-Rite, 1993):

$$C^* = \sqrt{(a^*)^2 + (b^*)^2}$$
  
Hue angle = arctan  $(b^*/a^*)$  or  $h^0 = \tan^{-1}(b^*/a^*)$ 

### Mechanical testing

Samples were conditioned for 40 h at  $50 \pm 5\%$  RH before use. Extruded samples were evaluated for their tensile strength (TS), percent elongation at break (%E), and Young's modulus (*M*) and displacement (DM) according to the ASTM D3039 method under ambient conditions using an Instron 5500R Universal Testing Machine (Instron, Canton, MA).

The Instron was equipped with a 1 kN load cell. The cross head speed was 5 mm/min, the gauge length was 2 cm, and the extension rate was 5 mm/min. Mechanical tests were also performed on composite samples exposed to variable temperatures and RH values.

# **Biodegradability tests**

Samples were milled to fine consistency (average particle size is 25 µm) using a hammer mill under liquid nitrogen environment. About 0.2 g of each sample was mixed with 20 g of compost with 60% moisture content (Garden Basics Topsoil, Swiss Farm Products, Las Vegas, NV) in a 250-mL reaction chamber. Sample chambers were connected to an automated and fully computerized closed-circuit Micro-Oxymax Respirometer System (Columbus Instruments, Columbus, OH) equipped with an expansion interface and a condenser. This system monitors the concentration of gas contained within an enclosed head space (reaction chamber) into which the material being monitored gives off the CO<sub>2</sub> as a breakdown product. Periodic sensing of the gas concentration, along with an equally accurate measurement of the volume of the head space, allows calculations of incremental and accumulated values for the production of CO<sub>2</sub> resulting from the material biodegradation. Experiments were carried out at room temperature (23  $\pm$  0.2°C) over a period of 200 h. The respirometer was programmed to measure CO<sub>2</sub> evolution (mg) from each sample every 8 h as an indicator of biodegradation. Each sample was run in triplicate and averaged (<2% variability). Samples were accompanied by at least three blanks (unsupplemented compost) to measure the background CO<sub>2</sub>.

# Scanning electron microscopy (SEM)

Samples were mounted onto aluminum specimen stubs using double-sided adhesive carbon tabs (Ted Pella, Redding, CA). All specimens were coated with gold–palladium for 45 s in a Denton Desk II sputter coating unit (Denton Vacuum U.S.A, Moorestown, NJ). Specimens were viewed in a Hitachi S4700 field emission scanning electron microscope (Hitachi HTA, Japan) at 2 kV.

# **RESULTS AND DISCUSSION**

The extruded composite had a smooth surface throughout with only few occasional inconsistencies, indicative of excellent compatibility between the PF, EVA, and glycerol [see SEM in Fig. 2(A)] in the formulation. Generally, TS, elongation at break (%E) and DM, all decreased in the composites with increased PF content in the formulations (Table II).

Mechanical Properties of Composites Containing Plantain Flour, EVA, and Glycerol				
Formulation <sup>a</sup>	TS (Mpa)	M (Mpa)	%Е	DM (mm)
1	8.91 ± 0.88a	118.97 ± 7.8c	28.5 ± 5.34a	5.7 ± 1.09a
2	$9.01 \pm 0.31a$	99.18 ± 12.6c	$37.03 \pm 5.73a$	$7.41 \pm 1.15a$
3	$9.79 \pm 0.90a$	$79.55 \pm 6.09b$	$37.57 \pm 5.09a$	$7.51 \pm 1.02a$
4	$12.14 \pm 0.07b$	68.55 ± 6.51a,b	$60.91 \pm 4.90b$	$12.18 \pm 0.98b$
5	$11.66 \pm 0.54b$	$62.13 \pm 6.92a$	$86.95 \pm 7.82c$	$17.39 \pm 1.56c$
6	$12.37 \pm 0.43b$	$63.47 \pm 4.21a$	$200.9 \pm 9.47d$	$40.18 \pm 1.89d$

 TABLE II

 Mechanical Properties of Composites Containing Plantain Flour, EVA, and Glycerol

Each data point is a mean of 6 replicates  $\pm$  standard error. Means in the same column that do not share the same letters are significantly different ( $\alpha = 0.05$ ).

TS, tensile strength; M, Young's modulus; E, elongation at break; DM, displacement.

<sup>a</sup> For sample identification see Table I.

Interestingly, in composites with 60% or higher PF content, the impact on mechanical property was minimal. Mechanical properties in these samples remain stable, and differences were statistically insignificant ( $\alpha = 0.05$ ). The decrease in the TS of the composites due to increased PF content apparently resulted from weak interactions among the constituents of the blends. Particularly, at very high PF concentrations, other nonstarch polysaccharides may increase incompatibility among the constituents and contribute toward the weakness of the overall matrix. Various studies have shown that starch/PE blends with elevated starch content yielded materials with much reduced tensile property.20,25 Addition of nonstarch polysaccharide additive in the formulation has been shown to reduce the interaction between the starch and blended polymer directly impacting the film's mechanical property.<sup>26</sup> The blending of hydrophilic starch in PF with mostly hydrophobic EVA may also be responsible for creating much weaker interactions between these two components, producing discontinuity within the EVA matrix and yielding a composite with lower tensile properties. The %E and DM exhibited a similar trend, and lower FP content blended with EVA yielded a composite that was much more rigid. The modulus of the composites, on the other hand, remained proportional to the amount of PF used.

Increased PF content in the formulation apparently leads to increased toughness in the composites, a behavior quite similar to the one observed in EVA blends with added wood fiber.<sup>23</sup>

Composites containing 60% PF (formulation #3 in Table I) were selected to study the impact of storage temperature and RH. Samples were stored at -20°C, 4.5°C, 23°C, and 80°C for 40 h and evaluated for impact on their mechanical property. The data provided in Table III indicated that both TS and M decreased at lower storage temperature, whereas %E and DM showed a reverse pattern. Little difference in properties was apparent in samples exposed at 4.5°C and -20°C. The highest values for TS and M were found in samples exposed at 80°C which is attributed to the loss of plasticizer at high temperature. This may lead to much reduced mobility provoking interactions among the polymer chains in starch molecules. It has been suggested that under such conditions polymeric chains in the starch molecule can undergo a reorganization causing the composite to harden.<sup>22,27</sup> Mechanical properties in samples exposed at room temperature (23°C) did not change much.

Selected samples of similar formulation (see #3 in Table I) were also exposed at various RH and tested for their impact on mechanical properties (Table IV). The TS and *M* both decreased, whereas %E and DM

TABLE IIIEffect of the Storage Temperature Conditions on the Mechanical Properties ofComposites (Only Formulation with 60% PF; 25% EVA; and 15% Glycerol Was<br/>Tested)<sup>a</sup>

		,		
ST (°C)	TS (Mpa)	M (Mpa)	%Е	DM (mm)
80 23 4.5	$21.64 \pm 1.2$ da $10.18 \pm 0.37$ c $9.28 \pm 0.26$ b	$1414.3 \pm 63.3c$ $171.2 \pm 21.1b$ $142.5 \pm 17.6a$	$3.33 \pm 0.13a$ $37 \pm 3.76b$ $42.37 \pm 3.15c$	$0.67 \pm 0.03a$ 7.31 ± 0.6b 8.47 ± 0.63b,c
-20	$8.15\pm0.53a$	$132.1 \pm 12.9a$	$49.69 \pm 2.69d$	$8.94\pm0.54c$

Each data point is a mean of 6 replicates  $\pm$  standard error. Means in the same column that do not share the same letters are significantly different ( $\alpha = 0.05$ ).

ST, storage temperature; TS, tensile strength; *M*, Young's modulus; E, elongation at break; DM, displacement.

<sup>a</sup> Samples were conditioned (50% RH, 23°C for 40 h) before testing.

		5	
TS (Mpa)	M (Mpa)	%Е	DM (mm)
11.11 ± 0.13d	$160.47 \pm 5.35c$	30.23 ± 1.43a	$6.05 \pm 0.29a$
$10.72 \pm 0.12c$	$150.83 \pm 3.92b$	$34.71 \pm 1.07b$	$6.94 \pm 0.21b$
9.69 ± 0.15b	$149.70 \pm 3.73b$	$35.92 \pm 0.98b$	7.18 ± 0.20b
$8.62 \pm 0.52a$	139.9 ± 6.02a	$41 \pm 3.46c$	$8.20\pm0.69c$
	$\begin{array}{c} 11.11 \pm 0.13d \\ 10.72 \pm 0.12c \\ 9.69 \pm 0.15b \end{array}$	$\begin{array}{c} 11.11 \pm 0.13d \\ 10.72 \pm 0.12c \\ 9.69 \pm 0.15b \end{array} \begin{array}{c} 160.47 \pm 5.35c \\ 150.83 \pm 3.92b \\ 149.70 \pm 3.73b \end{array}$	$11.11 \pm 0.13d$ $160.47 \pm 5.35c$ $30.23 \pm 1.43a$ $10.72 \pm 0.12c$ $150.83 \pm 3.92b$ $34.71 \pm 1.07b$ $9.69 \pm 0.15b$ $149.70 \pm 3.73b$ $35.92 \pm 0.98b$

 TABLE IV

 Effect of Relative Humidity (RH) on the Mechanical Properties in Composite (Only Formulation with 60% PF, 25% EVA, and 15% Glycerol Was Tested)<sup>a</sup>

Each data point is a mean of 6 replicates  $\pm$  standard error. Means in the same column that do not share the same letters are significantly different ( $\alpha = 0.05$ ).

RH, relative humidity; TS, tensile strength; *M*, Young's modulus; E, elongation at break; DM, displacement.

<sup>a</sup> Samples were conditioned (50% RH, 23°C for 40 h) before testing.

increased with increased RH storage conditions. Increased water content in the polymer matrix probably leads to increased mobility of polymeric chains in starch molecules and thus restricting the reorganization of the polymer chains. At highest RH, the composites were softer with higher DM and elongation at break, and these properties could prove useful for certain application such as packaging of fresh meats.

Samples that were preconditioned at the storage temperatures -20 to 4°C, 23°C (room temperature), and 80°C were evaluated to learn the impact of such pretreatments on their biodegradation in compost. Tests also included individual components of the blend. Results presented in Figure 1 indicated that all samples degraded rapidly and the only exception was the EVA, which showed the slowest degradation. The CO<sub>2</sub> production (indicator of biodegradation) was high for the initial 5-6 days, indicating a rapid degradation rates in this period; thereafter, the CO<sub>2</sub> production and the rate of degradation progressed steadily for most samples. Samples tested for 12 days showed degradation in the following order: EVA < glycerol < composite conditioned at  $23^{\circ}C$  < PF < composite conditioned at  $-20^{\circ}C$  < composite conditioned at 80°C. Samples conditioned at -20°C and 80°C exhibited twice as much degradation compared with sample conditioned at room temperature (23°C) or individual components of the blend during the 12 days of testing. Higher degradation in samples pre-exposed at elevated temperature was hardly surprising as prolonged exposure could lead to depolymerization of starch resulting from its decreased crystallinity and reduced molar mass. This can facilitate the breakdown of the matrix making, it more accessible and prone to degradation by microbes and their hydrolytic enzymes.28,29 More recently, investigators have shown that oxobiodegradable PE mulch film pre-exposed to elevated temperature followed by exposure to sun-light deteriorated the film matrix to an extent where it was readily biodegraded by soil microbes.<sup>18</sup> Similarly,

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samples exposed at  $-20^{\circ}$ C showed higher degradation rate and extent due to freezing and thawing of the matrix. In this case, ice crystals assist in the breakdown of biological polymers, reducing their molar masses and priming the matrix for rapid microbial degradation. As expected, loss of mechanical properties and much rapid biodegradation rates were also observed in both composites exposed to extreme storage temperatures.

The scanning electron micrographs generally revealed that composites had smooth surface, indicating an excellent compatibility between the EVA and PF with glycerol as a plasticizing agent [Fig. 2(A,B)]. The EVA and starch polymer were indistinguishable even at a higher magnification

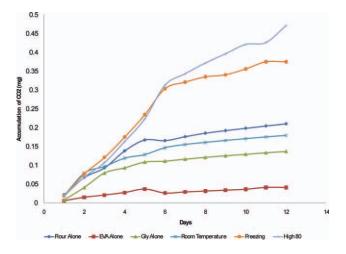
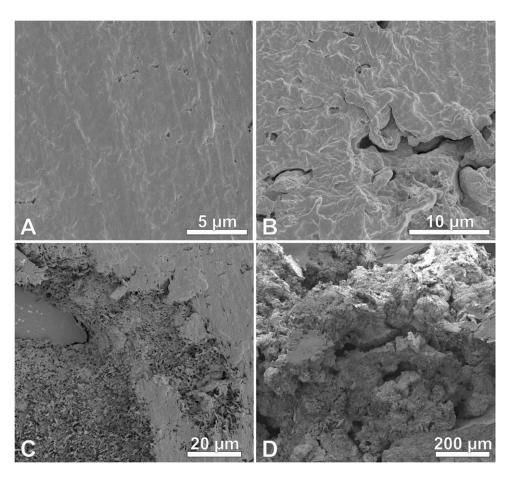


Figure 1 Biodegradation of injection-molded composites measured as a function of CO<sub>2</sub> production in time. Formulation containing 60% plantain flour, 25% EVA and 15% glycerol were subjected to various storage temperature conditions ( $-20^{\circ}$ C,  $23^{\circ}$ C, and  $80^{\circ}$ C) and evaluated for biodegradability along with each additive separately. ×— composite conditioned at room temperature; \*—composite conditioned at -20; ●—composite conditioned at  $80^{\circ}$ C; [♦]—flour plantain; ■—EVA; ▲—glycerol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

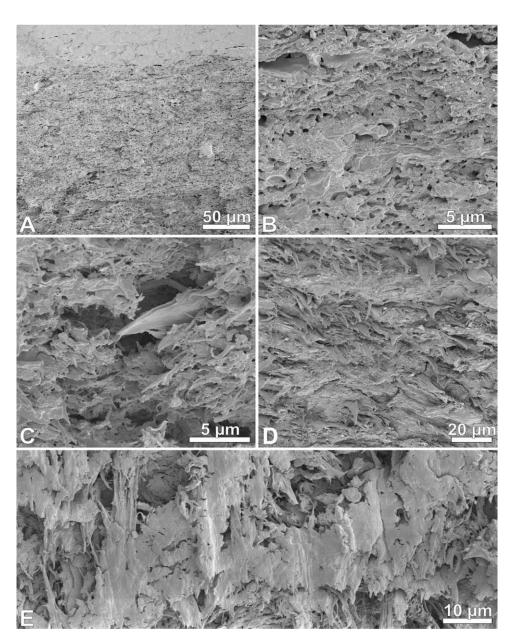


**Figure 2** Scanning electron micrographs depicting the microstructure of the composites (formulation 65% plantain flour). (A) Surface view; (B) surface view at higher magnification; (C) sample exposed for 8 weeks at  $-20^{\circ}$ C; (D) sample exposed to  $80^{\circ}$ C for 8 weeks.

[Fig. 2(B)], indicating that starch was completely gelatinized due to the exposure to high temperatures during the extrusion processing. Composites conditioned for 8 weeks under extreme storage temperatures (-20°C and 80°C) exhibited a rapid deterioration under both conditions [Fig. 2(C,D)]. Surface erosion accompanied by numerous cracks was noted in samples stored at  $-20^{\circ}$ C, which were probably caused by the freezing and thawing of the composite. In samples exposed at 80°C, large clumps or aggregates were apparent throughout the matrix, resulting from long-term desiccation and material degradation. Apart from respirometry tests, samples were also left in compost (23°C, 50% RH) for a period of 8 weeks to observe the impact of composting on the surface of the composite (Fig. 3). Examination of samples drawn at 7 days, 15 days, and 8 weeks showed a significant loss of material (data not shown) with a progressive erosion of the surface indicative of an overall deterioration of the composite [Fig. 3B-E)].

The colorimetric data for parameters of luminosity  $(L^*)$ , chroma  $(C^*)$ , and Hue angle  $(h^*)$  are presented in Table V. The high extrusion and injection-molding temperatures used to process the PF mixes had a

significant effect on the lightness, saturation, and color of the resulted films. The values of lightness (whiteness) significantly ( $\alpha = 0.05$ ) decreased as the concentration of PF increased in the mixes. Similarly, the values of chroma (color saturation) and hue angle (color tonality) decreased with increased PF in the mixes. At the highest PF concentration of 70%, the product had a reddish-brown tone, represented by the lowest hue values. In general, the progressive decreased on color parameters' values resulted in a chromatic shift to a darker and duller color. PF contains reducing sugars that can react with lysine, under high processing temperature, to promote nonenzymatic browning known as the Maillard reaction.<sup>30-32</sup> Therefore, the observed darkening of the films is attributed to the effect of products generated during the course of the Maillard reaction. It is interesting to observe that the lowest values for TS, %E, and DM (Table II) coincide also with the lowest values of  $L^*$ ,  $C^*$ , and  $h^*$ , represented by the highest PF concentration of 70% in the films; and their values tend to increase in the films made with lower PF concentration. Conversely, the values of Mshowed an inverse relation trend. This observation



**Figure 3** Scanning electron micrographs of the samples left to degrade in compost for 8 weeks (50% RH, 23°C). Unexposed control sample (A); samples exposed for 7 days (B); 15 days (C); 21 days and 8 weeks (D). (E) is the higher magnification of the sample in (D). The control was kept under similar conditions but without compost.

indicates that the selected color parameters of  $L^*$ ,  $C^*$ , and  $h^*$ , could be used as potential indicators of the mechanical properties of films made with PF and other similar natural food materials. More studies are needed to validate these observations.

Decreased physical properties in blends with added PF content was not surprising. Several investigators similarly found that nonstarch polysaccharides, oils, and proteins in PF restricted the interaction between the EVA and starch that led to the decrease in the mechanical property of the extruded films.<sup>33,34</sup> In this regard, Pedrosa and Rosa<sup>25</sup> also reported that the addition of a second phase in the polymeric matrix influenced the mechanical properties in

TABLE V Color Measurement of Composites Prepared from PF, EVA, and Glycerol

		•	
Formulation <sup>a</sup>	Lightness (L*)	CHROMA (C*)	Hue angle ( <i>h</i> *)
1	33.47 ± 0.56a	$0.92 \pm 0.06b$	10.65 ± 2.7a
2	32.77 ± 0.31a	$0.72 \pm 0.03a$	$21.17 \pm 4.3b$
3	34.83 ± 0.54a,b	$2.68 \pm 0.32c$	38.51 ± 2c
4	$33.95 \pm 0.35a$	$2.50 \pm 0.13c$	39.95 ± 2.5c
5	$35.80 \pm 0.57b$	$2.45 \pm 0.15c$	49.13 ± 2.2d
6	$40.25 \pm 0.34c$	$4.61 \pm 0.19d$	$57.03 \pm 0.35e$

Each data point is a mean of 25 replicates  $\pm$  standard error. Means in the same column that do not share the same letters are significantly different ( $\alpha = 0.05$ ).

<sup>a</sup> For sample identification see Table I.

composites. It was observed that the elongation of PF-EVA films improved considerably with increased RH. These results are consistent with earlier findings of Lawton and Fanta,35 who reported that increased PVOH content in starch matrix enhanced elongation of the composite blend under relatively high-humidity conditions. This behavior can be explained taking into consideration that the water behaves as plasticizer for starch and any increase in water content (RH) in the blends results in a greater mobility of both the starch in FP and the EVA macromolecules. Increase of EVA content in blends (Table III), improves its TS, which is probably due to the decrease in the macromolecular chain mobility caused by the presence of the strong intermolecular hydrogen bonds and association between the macromolecular components of the blend.

More studies are needed with respect to PF to evaluate its viability as a raw material for an extruded plastic material. The overall data presented here are encouraging and provided some meaningful information. Some EVA/PF blends were physically strong, offered good storage properties and were also biodegradable, suggesting their usefulness for certain packaging applications. Particularly, for single-use packaging such as food containers, packaging film, etc. However, further improvements in vapor-barrier property, oxygen transmission rate, etc. are needed for successful commercialization of such products.

### CONCLUSIONS

About 60–70% of PF could be used in conjunction with EVA and glycerol to produce injection-molded products of excellent property and surface morphology. Mechanical property of the composites deteriorated rapidly when composites were pre-exposed to extreme storage temperatures and high RH conditions. These samples also degraded at a much faster rate and extent. Composites degraded readily in compost and colored products produced during the Maillard reaction had little impact on the quality of the produced composite. This study shows a promise for surplus plantains biomass to serve as an important source of raw material in developing biodegradable plastic products for consumers.

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# References

1. Anon. Banana INIBAP international network for the improvement of banana and plantain (www.inibap.org), 2000.

- Lei, C. Y.; Chang, S.-M.; Young, Y.-L. J Food Science 1982, 47, 1493.
- Bello-Perez, L. A.; Agama-Acevedo, E.; Sanchez-Hernandez, L.; Paredes-Lopez, O. J Agric Food Chem 1999, 47, 854.
- 4. Bello-Perez, L. A.; Romero-Manilal, R.; Paredes-Lopez, O. Starch 2000, 52, 154.
- 5. Vargas-Torres, A.; Zamudio-Flores, P. B.; Salgado-Delgado, R.; Bello-Pérez, L. A. J Appl Polym Sci 2008, 110, 3464.
- 6. Jiang, Z.; Yunhai, M.; Jian, Z.; Jin, T. J Appl Polym Sci 2009, 112, 99.
- Imam, S. H.; Glenn, G. M.; Chiou, B.-S., Shey, J., Narayan, R., Orts, W. J. In Chiellini, E., Eds. Environmentally Compatible Food Packaging; Woodhead Publishing Limited: Cambridge, UK, 2008; p 29.
- 8. Imam, S. H., Cinelli, P.; Gordon, S. H.; Chiellini, E. J Polym Environ 2005, 13, 47.
- 9. Corradini, E.; Imam, S. H.; Agnelli, J. A. M.; Mattoso, L. H. C. J Polym Environ 2008.
- Imam, S. H.; Chiou, B.-S., Woods, D. F.; Shey, J.; Glenn, G. M.; Orts, W. J.; Narayan, R.; Avena-Bustillos, R. J.; McHugh, T. H.; Pantoja, A.; Bechtel, P. J. BioResources 2008, 3, 758.
- 11. Cinelli, P.; Chiellini, E.; Lawton, J. W.; Imam, S. H. J Polym Res 2006, 13, 107.
- Rosa, M. F.; Chiou, B.; Medeiros, L. S.; Wood, D. F.; Mattoso, L. H. C.; Orts, W. J.; Imam, S. H. J Appl Polym Sci 2009, 111, 612.
- 13. Martin, O.; Averous, L. Polymer 2001, 42, 6209.
- 14. Imam, S. H.; Gordon, S. H.; Thompson, A.R.; Harry-O'kuru; Greene, R. V. Biotechnol Techniq 1993, 7, 791.
- Calmon-Decriaud, A.; Bellon-Maurel, V.; Silvestre, F. Adv Polym Sci 1998, 135, 207.
- Shey, J.; Imam, S. H.; Glenn, G. M.; Orts, W. J. J Ind Crops Prod 2006, 24, 34.
- Medeiros, E. S.; Mattoso, L. H. C.; Ito, E. N.; Gregorski, K. S.; Robertson, G. H.; Offeman, R. D.; Wood, D. F.; Orts, W. J.; Imam, S. H. J Biobased Mater Bioenergy 2008, 2, 1.
- Corti, A.; Muniyasamy, S.; Vitali, M.; Imam, S. H.; Chiellini, E. Polym Degrad Stab 2010, 95, 1106.
- 19. Bhattacharya, M. J Mater Sci 1998, 33, 4131.
- Vargas-Torres, A.; Zamudio-Flores, P. B.; Salgado-Delgado, R.; Bello-Pérez, L. A. J Appl Polym Sci 2007, 106, 3994.
- 21. Prinos, J.; Bikiaris, D.; Theologidis, S.; Panayiotou, C. Polym Eng Sci 1998, 38, 954.
- 22. Ramkumar, D. H. S.; Bhattacharya, M.; Vaidya, R. U. Eur Polym Mater 1997, 33, 729.
- 23. Dikobe, D. G.; Luyt, A. S. J Appl Polym Sci 2007, 103, 3645.
- X-RITE. A guide to understanding color communication. X-Rite Form L10-001 (Rev. 8-90). P/N918-801. X-Rite Inc., Grandville, MI, 1993.
- 25. Pedrosa, A. G.; Rosa, D. S. Carbohydr Polym 2005, 59, 1.
- Ovando, M. M.; Sayago, A. S.; Agama, A.E.; Goni, I.; Bello, P. L. A. Food Chem 2009, 113, 121.
- 27. Trevoy, D. J. Ind Eng Chem 1953, 45, 2367.
- Van Den Einde, R. M.; Akkermans, C.; Van Der Goot, A. J.; Boom, R. M. Carbohydr Polym 2004, 56, 415, 422.
- 29. Liu, H.; Ramsden, L.; Corke, H. Starch/Starke 1999, 51, 249.
- 30. Liu, Q.; Yada, R.; Arul, J. J Food Sci 2002, 67, 560.
- Berrios, J.; De, J.; Wood, D. F.; Whitehand, L.; Pan, J. J Food Process Preserv 2004, 28, 321.
- 32. Bayram, O. A.; Bayram, M.; Tekin, A. R. J Food Eng 2005, 69, 253.
- Rodriguez-Ambriz, S. L.; Islas-Hernandez, J. J.; Agama-Acevedo, E.; Tovar, J.; Bello-Pérez, L. A. Food Chem 2008, 107, 1515.
- Ovando-Martinez, M.; Sayago-Ayerdi, S.; Agama-Acevedo, E.; Goñi, I.; Bello-Pérez, L. A. Food Chem 2009, 113, 121.
- 35. Lawton, W. J.; Fanta, G. F. Carbohydr Polym 1994, 23, 275.