

# Morphological, Thermal, and Mechanical Studies of Film Elaborated with the Blend Low-Density Polyethylene and Chemical-Modified Banana Starch

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**ABSTRACT:** Films were prepared by extrusion acetylated and oxidized banana starches at different concentration mixed with low-density polyethylene. Morphological, mechanical, and thermal characteristics of the films were tested. Irregularities in the films prepared with native and oxidized banana starches were observed by scanning electron microscopy. This pattern is maybe due to the incompatibility between both polymers. However, films elaborated with acetylated banana starch showed a smooth surface. The tensile strength and elongation at break decreased when starch level in the blend increased. An inverse pattern was showed for elastic module. The effect on mechanical properties was more notorious in those films elaborated with the acetylated and oxidized banana

starches. Two thermal transitions were observed by differential scanning calorimetry, the principal transition at  $\sim 111^\circ\text{C}$  was due to disorganization of the low-density polyethylene. Enthalpy value associated to that principal transition was higher in the films elaborated with acetylated banana starch, showing higher compatibility between both polymers. The use of biodegradable polymers such as chemically modified banana starch might be feasible for elaboration of films with adequate mechanical properties. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3994–3999, 2007

**Key words:** films; mechanical properties; differential scanning calorimetry; extrusion

## INTRODUCTION

The increase of population in the world has diverse problems such as the generation of solid residues and their final disposition. Because of the great interest in the environment preservation, the government agencies have been developing strategies for the elaboration of new biodegradable polymers.<sup>1,2</sup> The use of biodegradable materials based in natural, renewable, and economic polymers such as protein and starch have been subjected to considerable effort of research.<sup>3,4</sup> However, the properties of the synthetic materials are very difficult to overlap by the natural degradable polymers.

Starch can be blended with synthetic polymers to increase the degradability of the materials elaborated using thermoplastic technology such as bags, films, forks, tablespoons, garden containers, etc.<sup>3,5</sup> When the starch dispersion with high water content (up to 70%, w/w) is heated, swelling of granules is carried

by hydrogen bonding formation among adjacent chains of glucose units. However, if the heating is prolonged, breaking of those linkages is produced. This process is named as gelatinization.<sup>6</sup> Thermal process, like an extrusion, is an effective unit operation to obtain the gelatinized starch. Gelatinized starch has the property of film formation and those films present transparency, flexibility and tensile strength.<sup>7</sup> The workability of films prepared with starch is improved when added of plasticizer agents. The blend of gelatinized starch and plasticizer, processed under controlled high pressure and temperature is a thermoplastic starch that has the property to flow.<sup>8–10</sup> In this same sense, the blend of thermoplastic starch and the synthetic polymer have similar properties to those showed by the conventional synthetic polymers. However, the starch type plays an important role in this behavior, since it was reported that when the thermoplastic starch content increases in the blend with low-density polyethylene, the film showed a decrease in value in the tensile strength.<sup>11</sup> This pattern was due to the incompatibility between the polyethylene and the thermoplastic starch used, and that incompatibility can be improved whether the starch is chemically modified<sup>12</sup> and by chemical treatment of polyethylene.<sup>13</sup>

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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                       |

The aim of this study was to determine the effect of the chemical modification and concentration of starch in the blend with low-density polyethylene on the morphological and mechanical properties of films elaborated by extrusion.

## EXPERIMENTAL

### Materials

Low-density polyethylene (LDPE 20020P; IF = 2 g/10 min) was purchased at PEMEX (Coatzacoalcos, Ver., México).

### Starch isolation

Unripe bananas (*Musa paradisiaca*) was purchased in the local market of Cuautla, Morelos, México. The starch was isolated using a pilot scale procedure.<sup>14</sup> The powder was ground to pass a US No. 100 sieve and stored at room temperature (25°C) in a glass container.

### Preparation of oxidized starch

The oxidized banana starch was prepared using the procedure reported by Sánchez-Rivera et al.<sup>15</sup> In brief, 200 g of starch (dry basis) was mixed with 500 g of distilled water. The starch slurry was maintained at 35°C by occasionally turning off the heating power, 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<sub>2</sub>SO<sub>4</sub>, passed to 1-L flask to precipitate and decant the reaction mix and wash with several volume deionized water and dry in a convection oven at 50°C for 48 h. Carboxyl and carbonyl content were determined with the methodology reported by Chattopadhyay et al.<sup>16</sup> and Smith,<sup>17</sup> respectively.

### Preparation of acetylated starch

Slurry of banana starch was prepared mixed 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), anhydride acetic, and NaOH (3%, w/w) were added drop at drop, the last for maintaining the pH between 8.0 and 8.4. When the addition of anhydride acetic was complete, the pH was adjusted at 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 times more. The starch was drying in a convection oven at 50°C for 24 h. Substitution degree was assessed by the method of Wuzburg.<sup>18</sup>

### Film preparation

Films were prepared using diverse blends of banana starch, glycerol, and low density polyethylene (LDPE) (Table I). Twin-screw extruder (C.W. Brabender Instruments, So Hackensack, NJ) was used for film elaboration. The machine has three heating zones and additionally the temperature of the die (diameter 3 mm and length 60 mm), with temperatures of 145, 160, 175, and 150°C, respectively. The screw speed was 15 rpm and the ratio length/diameter ( $L/D$ ) was 25/1.

### Scanning electron microscopy

A JEOL JSMP 100 (Japan) electron microscope was used. Film pieces were mounted on aluminum stubs using a double-sided tape and then coated with a layer of gold (40–50 nm), allowing surface and cross section visualization. All samples were examined using an accelerating voltage of 5 kV.

### Mechanical properties

The mechanical measurements consisted of tests to determine the load tensile strength (TS), percent

elongation at break (%  $E$ ), and elastic modulus (EM). Maximum breaking force ( $N$ ), deformation at break (extension at the moment of rupture, mm), and elastic modulus were obtained from the force versus deformation curves using a (ASTM D 638M-93) Texture Analyser (TA-XT2i) (Stable Micro Systems, Hasler-nere, 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>19</sup> and they were maintained for at least 3 days in a desiccator containing a saturated saline solution of NaBr (57% RH). Separation among gauges was 5 cm. The ends of the film were fixed in each of the subjection gauge. The speed of deformation was 0.9 mm/min.

### Differential scanning calorimetry

Thermal analysis was done using a differential scanning calorimeter 2010 (TA Instruments, New Castle, NJ) previously calibrated with indium. The transition temperature was evaluated by the method proposed by Paredes-Lopez et al.<sup>20</sup> The film (10–15 mg) was weighed (dry basis,  $n = 3$ ) on aluminum pan. The pan was sealed tightly. An empty aluminum pan was used as a reference. The sample was subjected to a heating program over a range of temperature from 20 to 180°C and a heating rate of 10°C/min. The peak temperature ( $T_m$ ) and the transition enthalpy ( $\Delta H$ ) were obtained directly from the analysis of the software TA Instruments Universal Analysis 2000 for windows 3.2B.

## RESULTS AND DISCUSSION

### Degree of substitution of chemical modified banana starch

The acetyl group content and degree substitution assessed in the acetylated banana starch were 1.19% and 0.04%, respectively. These values are considered for acetylated starches with low degree substitution. The acetylating of starch might have increased its adhesion with the polyethylene, because this chemical modification changes the functional groups of starch molecule of hydrophilic to hydrophobic. Acetylated banana starch was prepared with the idea of food used, and the acetyl group content was 1.1%.<sup>21</sup> However, acetylated starches were prepared with two procedures using *Canavalia ensiformis* starch, and the acetyl group level were 0.94 and 2.48%.<sup>22</sup> The oxidation of banana starch was tested with the carbonyl (0.09%) and carboxyl (0.12%) groups. The amount of carboxyl groups was higher than carbonyl groups, since the oxidation was carried out with alkaline conditions (pH 9.5) and under this parameter of the reaction higher amount of carboxyl groups

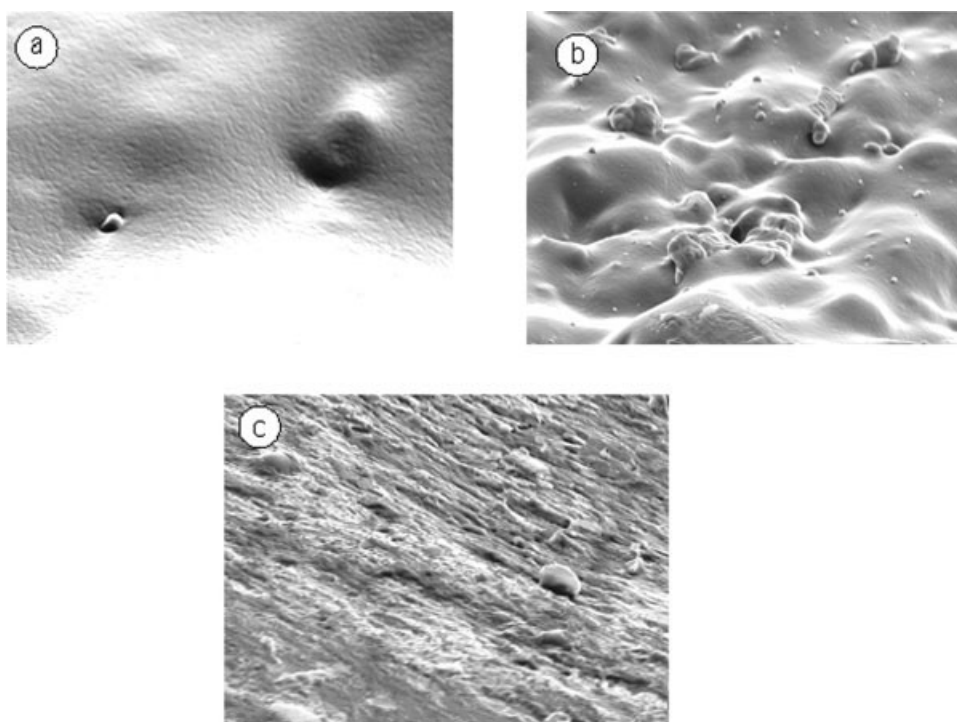
are obtained than in acid conditions or using peroxide of hydrogen.<sup>23,24</sup> Similar values were reported in oxidized maize starch with 2% of NaOCl for carbonyl (0.06%) and carboxyl (0.14%) groups.<sup>25</sup>

### Scanning electron microscopy

The morphology of films prepared with the blend containing 40% of starch is shown in Figure 1. We took this blend as an example due to that low amount of starch in the film is better dispersed in the mixture. The films prepared with acetylated starch [Fig. 1(a)] presented higher dispersion of the components, due to the smooth surface of the films, showing that the acetylated starch was introduced in the network produced by the polyethylene. The films elaborated with oxidized and native banana starches showed lower dispersion than those prepared with acetylated starch due to the irregularities observed in the film with oxidized starch [Fig. 1(b)] and the fissures or cavities on the surface of the film [Fig. 1(c)] prepared with native banana starch. The surface of the films with oxidized and native starches might be due to the low interfacial adhesion of the components present in the blend and this characteristic can decrease the mechanical properties. Additionally, higher starch level in the film might produce poor mechanical properties because the interaction between starch chains are weaker than those between polyethylene chains.<sup>26</sup>

### Mechanical properties

In general, when starch level in the film increased the tensile strength decreased, except in the films elaborated with native and acetylated banana starches at 20 and 30% (Table II), where statistical differences ( $P < 0.05$ ) were not shown. When a second phase is added at the matrix of a synthetic polymer, some immiscible degree is obtained as shown in the microphotography and produced a decrease in the mechanical property. It was reported in films elaborated with low-density polyethylene/starch that tensile strength decreased with the increasing starch content in the blend, indicating that corn starch behaves as a nonreinforcing filler.<sup>26</sup> When tensile strength values of the films with 20% of starch are compared, the film added with the acetylated starch showed higher values than those prepared with the native and oxidized banana starches. This pattern might be related with the introduction of functional groups during the acetylation of the starch that produce an increase in the hydrophobic character improving the compatibility between the starch and polyethylene. The effect of the hydrophobic character of starch films elaborated with modified starch (acetylated) on tensile strength showed



**Figure 1** Micrographics of starch/LDPE blends: (a) AS40/glycerol/LDPE; (b) OS40/glycerol/LDPE; (c) NS40/glycerol/LDPE.  $\times 500$ . For sample identification see Table I.

an increase of this parameter when the  $R\text{-COO-R}'$  groups increased.<sup>27</sup> When the films elaborated with the three starches at 30% are compared, the tensile strength did not change. In general, the films with 40% of starch in the blend had similar pattern than that showed by the films with 30% of starch. This pattern might be due to that when starch concentration in the film increase, the tensile strength is

affected by this parameter more than the chemical modification of starch.<sup>12</sup>

The elastic modules presented an inverse pattern that tensile strength because the values increased when starch concentration in the film increased (Table II). This pattern can be explained by three factors: starch crystallinity, hydrogen bonding, and stiffening effect of the starch granules.<sup>28</sup> In films ela-

**TABLE II**  
Mechanical Properties of Films Elaborated with Native or Modified Banana Starch Mixed with Low-Density Polyethylene\*

| Sample** | Tensile strength (MPa)  | Elastic module (MPa)    | Elongation at break (%) |
|----------|-------------------------|-------------------------|-------------------------|
| NS20     | $8.44 \pm 0.80^{a,A}$   | $190 \pm 25.00^{a,A}$   | $46.73 \pm 2.41^{a,A}$  |
| NS30     | $8.54 \pm 0.28^{a,c,A}$ | $261 \pm 10.90^{c,B}$   | $15.99 \pm 1.11^{d,B}$  |
| NS40     | $7.76 \pm 0.39^{a,B}$   | $326 \pm 16.90^{e,C}$   | $12.67 \pm 0.19^{f,C}$  |
| AS20     | $9.95 \pm 0.36^{b,C}$   | $210 \pm 27.90^{a,D}$   | $61.28 \pm 2.58^{b,D}$  |
| AS30     | $9.10 \pm 0.85^{c,C}$   | $294 \pm 31.20^{d,c,E}$ | $10.61 \pm 0.60^{e,E}$  |
| AS40     | $6.23 \pm 0.67^{e,D}$   | $417 \pm 40.40^{f,F}$   | $8.97 \pm 1.49^{g,F}$   |
| OS20     | $9.27 \pm 1.32^{b,A}$   | $106 \pm 38.30^{b,G}$   | $66.46 \pm 2.80^{c,G}$  |
| OS30     | $8.86 \pm 0.31^{c,E}$   | $327 \pm 24.90^{d,H}$   | $10.62 \pm 1.94^{e,H}$  |
| OS40     | $7.74 \pm 0.42^{d,F}$   | $564 \pm 35.00^{g,I}$   | $6.46 \pm 0.10^{h,I}$   |

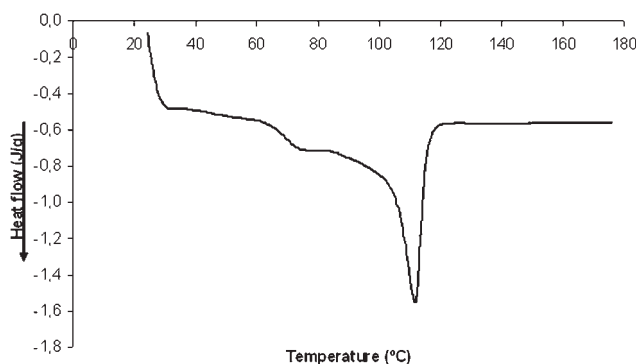
\*Means of 6 replicates  $\pm$  standard error. Lowercase letters represent the effect of the modification of the starch. Uppercase letters represent the effect of the concentration of starch.

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 ( $\alpha = 0.05$ ).

\*\*For sample identification see Table I.





**Figure 2** Typical thermogram obtained by differential scanning calorimetry of film elaborated with 20% native banana starch, glycerol and low-density polyethylene.

borated with low-density polyethylene/corn starch and low-density polyethylene/modified corn starch, the modulus decreases when starch in the blend increased, mentioning that the crystallinity of starch and hydrogen bonding plays an important role in this behavior.<sup>29</sup> The increase in the elastic modulus when starch concentration increases was higher in the films prepared with the modified banana starch because these starches are more susceptible to produce more hydrogen bonding with polyethylene chains, because it was found that the crystallinity in the oxidized banana starch was not different from its native counterpart.<sup>30</sup>

Elongation values decreased when starch concentration in the film increased (Table II). The higher effect was showed in the films prepared with 20 and 30% of starch, because the difference between those two elongation values was more notorious. This effect might be related with the stiffening effect

of the starch granules and with the discontinuity created by the addition of starch granules to low-density polyethylene and by the poor interfacial interaction between starch and low-density polyethylene matrix.<sup>31</sup> Films elaborated with the modified starch at 20% had the highest elongation values and it was reported that the starch concentration higher than 20% produced a negative effect on elongation.<sup>32</sup> Additionally, the chemical modification of starch increases the hydrophobic property of the starch promoted compatibility of starch and polyethylene in the film.<sup>31</sup>

### Differential scanning calorimetry study

A typical thermogram of the films analyzed showed two transitions to  $\sim 70$  and  $111^\circ\text{C}$  is shown in Figure 2. The small peak to low temperature (Table III) was not different ( $P < 0.05$ ) from the films prepared with the same starch type to different concentration, and, in general, the films elaborated with the same starch concentration and different starch were similar. The enthalpy values associated with this transition were lower than that for the second transition and they were not different for the films elaborated with the same starch type at different concentration. Slight differences in enthalpy values were found in the films prepared with different starch at the same concentration. The transition to low temperature is due to that starch not joined to the polyethylene showing a peak due to the glass transition.<sup>33</sup> The large peak of second transition produced to  $\sim 111^\circ\text{C}$  is due to the low-density polyethylene, since it was reported that this kind of polyethylene has a melting temperature about  $110^\circ\text{C}$ .<sup>26</sup> The starch concentration

**TABLE III**  
Thermal Characteristics of Films Elaborated with Native or Modified Banana Starch Mixed with Low-Density Polyethylene Assessed by Differential Scanning Calorimetry\*

| Sample** | $T_{m1}$ ( $^\circ\text{C}$ ) | $\Delta H_{m1}$ (J/g)  | $T_{m2}$ ( $^\circ\text{C}$ ) | $\Delta H_{m2}$ (J/g)  |
|----------|-------------------------------|------------------------|-------------------------------|------------------------|
| NS20     | $71.71 \pm 0.54^{a,A}$        | $0.649 \pm 0.02^{a,A}$ | $111.89 \pm 0.32^{a,A}$       | $22.14 \pm 0.80^{a,A}$ |
| NS30     | $71.26 \pm 0.64^{b,A}$        | $0.634 \pm 0.02^{d,A}$ | $112.67 \pm 1.18^{b,A}$       | $22.14 \pm 0.61^{c,A}$ |
| NS40     | $71.20 \pm 0.73^{e,A}$        | $0.652 \pm 0.01^{g,A}$ | $111.98 \pm 1.00^{c,A}$       | $21.75 \pm 0.24^{e,A}$ |
| AS20     | $72.70 \pm 0.11^{a,B}$        | $0.833 \pm 0.11^{b,B}$ | $112.49 \pm 0.69^{a,B}$       | $24.56 \pm 0.52^{b,B}$ |
| AS30     | $73.30 \pm 0.14^{d,C}$        | $0.872 \pm 0.03^{e,B}$ | $112.93 \pm 0.37^{b,B}$       | $25.03 \pm 0.82^{d,B}$ |
| AS40     | $72.67 \pm 0.19^{g,C,B}$      | $0.853 \pm 0.01^{h,B}$ | $112.03 \pm 0.69^{c,B}$       | $22.84 \pm 0.17^{e,C}$ |
| OS20     | $72.45 \pm 0.14^{a,D}$        | $0.746 \pm 0.01^{c,C}$ | $111.86 \pm 0.18^{a,C}$       | $21.55 \pm 0.23^{a,D}$ |
| OS30     | $73.35 \pm 0.20^{d,D,E}$      | $0.771 \pm 0.02^{f,C}$ | $112.4 \pm 0.25^{b,C}$        | $21.00 \pm 0.85^{c,D}$ |
| OS40     | $73.78 \pm 1.20^{g,E}$        | $0.739 \pm 0.02^{i,C}$ | $111.78 \pm 0.40^{c,C}$       | $20.92 \pm 0.82^{e,D}$ |

\*Means of 6 replicates  $\pm$  standard error. Lowercase letters represent the effect of the modification of the starch. Uppercase letters represent the effect of the concentration of starch.

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 ( $\alpha = 0.05$ ).

\*\*For sample identification see Table I.

in the film did not affect the melting temperature of the second transition and noneffect of the starch type was showed in this melting temperature. Similar pattern of starch concentration was showed for enthalpy values, but differences were presented for the starch type, because those films elaborated with acetylated starch had enthalpy values higher than those prepared with native and oxidized starches. Studies of films elaborated by the blend starch-polyethylene presented only one transition (like the second transition of this study), but not enthalpy values were provided.<sup>26,34</sup>

### CONCLUSIONS

Scanning electron microscopy showed difference among the films analyzed because the film prepared with acetylated starch presented higher dispersion of the components hence producing a film with smooth surface. The mechanical properties of the films were affected by the starch concentration in the blend because the tensile strength and elongation at break decreased, and the elastic module increased when starch concentration in the film increased. Differences in the mechanical properties were found with the starch type used in the blend due to the hydrophilic or hydrophobic character of the starches used. Two transitions by differential scanning calorimetry were determined; the first one (glass transition) due to low temperature because starch that was not joined to polyethylene and the second one due to disorganization of the polyethylene. The use of chemically modified banana starch might be an alternative for the elaboration of films with adequate mechanical properties.

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