# Effect of Starch Addition on Compression-Molded Poly(3-hydroxybutyrate)/Starch Blends

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**ABSTRACT:** Because of their biocompatibility and total biodegradability, poly(3-hydroxybutyrate) (PHB) and starch have attracted attention as promising raw materials for manufacture of single-use plastic items and biomaterials. PHB/maize starch blends with starch contents in the range of 0–50 wt % were processed in an internal mixer, and their compression-molded films were characterized by tensile tests, X-ray diffraction, thermogravimetric analysis, wettability measurements, and scanning electron microscopy. Water and glycerol were used as plasticizers. The results indicated that the thermal degradation behavior of the blends were similar to that of pure PHB films. All the blends showed heterogeneous morphology, wherein starch granules were dispersed in continuous PHB-rich matrix. Despite the decrease in elongation at break and tensile strength, starch incorporation of up to 30 wt % into PHB matrix resulted in materials as hard as pure PHB films, but exhibiting less crystallinity and more hydrophilic character, which might lead to a higher biodegradation rate. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4338–4347, 2006

**Key words:** poly(3-hydroxybutyrate); thermoplastic starch; blends; microstructure; mechanical properties

## INTRODUCTION

In the recent years, there has been an increasing concern over the harmful effects of synthetic plastic materials in the environment. This ecological awareness impelled the development of new biodegradable materials, especially for single-use plastic items. Poly(hydroxyalkanoates) (PHAs) have attracted much attention as biocompatible and biodegradable thermoplastics with potential application in agricultural, marine, and medical fields.[1] These biopolymers are polyesters of various hydrocarboxylic acids, which are accumulated as an energy/carbon storage or reducing power material by numerous microorganisms under unfavorable growth conditions in the presence of excess carbon source.[2] PHAs exhibit material properties similar to various synthetic thermoplastics and elastomers currently in use, from polypropylene to synthetic rubber. Besides, upon disposal, they are completely degraded to water and carbon dioxide (and methane under anaerobic conditions) by microorganisms in various environments such as soil, sea, lakes, and sewage.[3]

Poly(3-hydroxybutyrate) (PHB) is a homopolymer of 3-hydroxybutyrate, partially crystalline, and is one of the most widely investigated members of PHA family. PHB has attracted industrial attention because of its complete biodegradability and biocompatibility. In addition, PHB possesses mechanical properties like Young's modulus and tensile strength close to those of isotactic polypropylene, although its elongation at break is markedly lower.[4] However, wider scale application of PHB has been hampered owing to its instability in molten state, with a narrow thermal processing window,[5] excessive brittleness upon storage,[6] low biodegradation rate due to its crystallinity,[7] and high production cost as compared with synthetic plastic.

Blending of PHB with other polymers is an interesting approach to overcome these drawbacks. Numerous works have been published in this field,[8–10] including blends with biodegradable polymers such as poly(vinyl alcohol), poly(ε-caprolactone), and polysaccharides. As starch is inexpensive, totally biodegradable, and is produced in abundance beyond available market,[11] it is expected that the use of starch in blends with PHB can result in completely biodegradable material, which can have desired physical properties with concomitant reduction in cost.

Native starch is composed of two polymers—amylose and amylopectin, both of them composed of $\alpha$-D-glucose repeating units. Amylose is mostly linear, while amylopectin is highly branched. Thermoplastic starch (TPS) is obtained after disruption and plasticization of native starch when submitted to thermal and mechanical treatments. Blends with good water resistance and mechanical properties have been developed by different associations between TPS and other biodegradable polymers.[12–14]

Some attempts have been made to produce PHB/starch blends with improved physical properties. Up to now, the blends of PHB were prepared either by conventional solvent-casting techniques usually from chloroform solution, or by melt-mixing technique. Godbole et al.[12] studied the thermal and mechanical properties of solvent-cast blends of bacterial PHB and starch. The researchers reported that blends containing up to 30 wt % starch were obtained, with cost reduction and better properties, when compared with the virgin PHB. Other researchers investigated injection-molded blends of PHB with starch and starch derivatives.[15] They observed that blends containing natural starches and starch adipate resulted in brittle materials. Best results were obtained with grafted starch–urethane blends.

In general, however, it is known that the miscibility and the biodegradability are dependent on the history and methodology of blend preparations. Zhang et al.[16] reported different miscibility behavior of PHB/poly(D,L-lactide) (PLA) blends depending on whether they are solution cast or melt blended. They suggest that PHB/PLA blends prepared by casting a film from a common solvent at room temperature were immiscible over the range of compositions studied, while the melt-blended sample prepared at high temperature showed some evidence of greater miscibility. The thermal history caused a depression of the melting temperature and a decrease in the crystallinity of PHB in the blends.

In the present work, compression molding was used to prepare different compositions of PHB/starch blends. The blends were characterized by X-ray diffraction, tensile tests, thermal analysis, contact angle measurements, and scanning electron microscopy.

## EXPERIMENTAL

### Materials

Food-grade maize starch, composed of 26–30% amylose and 74–70% amylopectin, and with less than 0.5% gluten, was supplied by Corn Products Brazil (São Paulo, Brazil). Poly(3-hydroxybutyrate) (PHB), in the form of a white powder and with an average molecular weight (Mw) of 524,000 Da, was supplied by PHB Industrial S/A (São Paulo, Brazil). Glycerol P.A. was purchased from Vetec Química Fina Ltda. (Rio de Janeiro, Brazil).

### Preparation of films

Compositions of PHB and starch with starch content that varied between 0 and 50 wt % were processed according to the method described in the work of Ramsay et al.[17] Raw PHB was processed in a Rheomix 600 internal mixer equipped with roller-like rotors (Haake, Karlsruhe, Germany) at 165°C and 20 rpm for 10 min. A mixture of starch, water (15 wt %), and glycerol (15 wt %) was added and mixing was continued at 60 rpm for 30 min. Samples were then hot pressed at 160°C and 69 MPa for 30 min to form sheets with a thickness of 1.5 ± 0.2 mm, in average. Compositions with 100 wt % starch were also processed and were called pure thermoplastic starch (TPS). In these cases, compositions were processed at 60°C and 20 rpm for 20 min. The mixed blends were hot pressed at a lower temperature, 90°C.

Dumbbell-shaped specimens were prepared according to ASTM D 638–91 and were allowed to age in an environmental chamber (model MSM-012; Rio de Janeiro, Brazil) at 28°C and 68% relative humidity (RH) for at least 15 days before testing.

### Tensile tests

Tensile properties were evaluated according to ASTM D 638–91 method on dumbbell-shaped specimens, using an Instron Universal Testing Machine (model 4204; Canton, USA) at a rate of 1 mm/min. Five replicated samples were used and the median values were considered.

### Thermal analysis

The thermal stability of the different blends was determined by using ground dumbbell specimens stored at 68% RH for 15 days. The thermogravimetric analysis (TGA) was carried out with a PerkinElmer TGA-7 analyzer (Norwalk, USA), under nitrogen atmosphere. The mass of each sample was 7–9 mg. The thermogravimetric curves were recorded in the course of heating from ambient temperature to 700°C at a rate of 20°C/min. The software Pyris (PerkinElmer) was used to analyze the data obtained.

### X-ray diffraction

X-ray diffraction diagrams of raw PHB, native maize starch, and compression molded PHB/starch blends were obtained with a Miniflex diffractometer (Rigaku Corp., Osaka, Japan) operating at CuK$\alpha$ wavelength of 1.542 Å. The samples were exposed to the X-ray beam with the X-ray generator running at 30 kV and 15 mA.

Scattered radiation was detected at ambient temperature in the angular region ($2\theta$) of 2–40° at a rate of 2° per min and a step size of 0.05°. Diffractograms were smoothed (Savitsky-Golay, polynome = 2, points = 7) and the baseline was corrected by drawing a straight line at an angle of 5°. The total crystallinity was determined by dividing the integrated area of the diffraction peaks (crystalline component) by the integrated area of the whole diffractogram (amorphous and crystalline components).

### Contact angle analysis

The contact angle formed between a water droplet placed at the surface of material and the kinetics of spreading is related to the hydrophobicity of the material. The wettability of PHB/starch films was evaluated by water contact angle measurements with an NRL A-100–00 Ramé-Hart Goniometer (Mountain Lakes, USA). A 2.5-mL droplet of water was applied on the surface of the films. The contact angles were measured on both sides of the drop and averaged. The evolution of the droplet shape was recorded every 15 s by a CCD video camera; an image analysis software was used to determine the contact angle evolution.

### Scanning electron microscopy

The morphology of the PHB/starch films was observed under a Jeol JSM electron microscope (model 5610LV; Akishima-shi, Japan) at an acceleration voltage of 10 kV. Micrographs were taken on an Au/Pd-coated fractured surface of the dumbbell specimens. The samples that were fractured during tensile tests were used for this analysis.

### RESULTS AND DISCUSSION

### Tensile properties

The influence of starch content on the tensile properties of compression-molded PHB/starch blends after conditioning for 15 days at 68% RH can be visualized in Figure 1. Pure PHB films are hard and brittle materials. The Young's modulus [Fig. 1(a)] observed is in agreement with data reported in the literature, around 1.5 GPa.[4,10] Tensile strength [Fig. 1(b)] and elongation at break [Fig. 1(c)] values ranging from 10 to 43 MPa and from 1 to 10%, respectively, were reported. These values are in agreement with the measurements in this work, but it is well known that the tensile behavior greatly depends on the experimental conditions, such as strain rate and temperature. On the contrary, it can be observed that pure TPS film is very weak and soft, having low Young's modulus [Fig. 1(a)] and tensile strength [Fig. 1(b)] and moderate elongation at break [Fig. 1(c)].
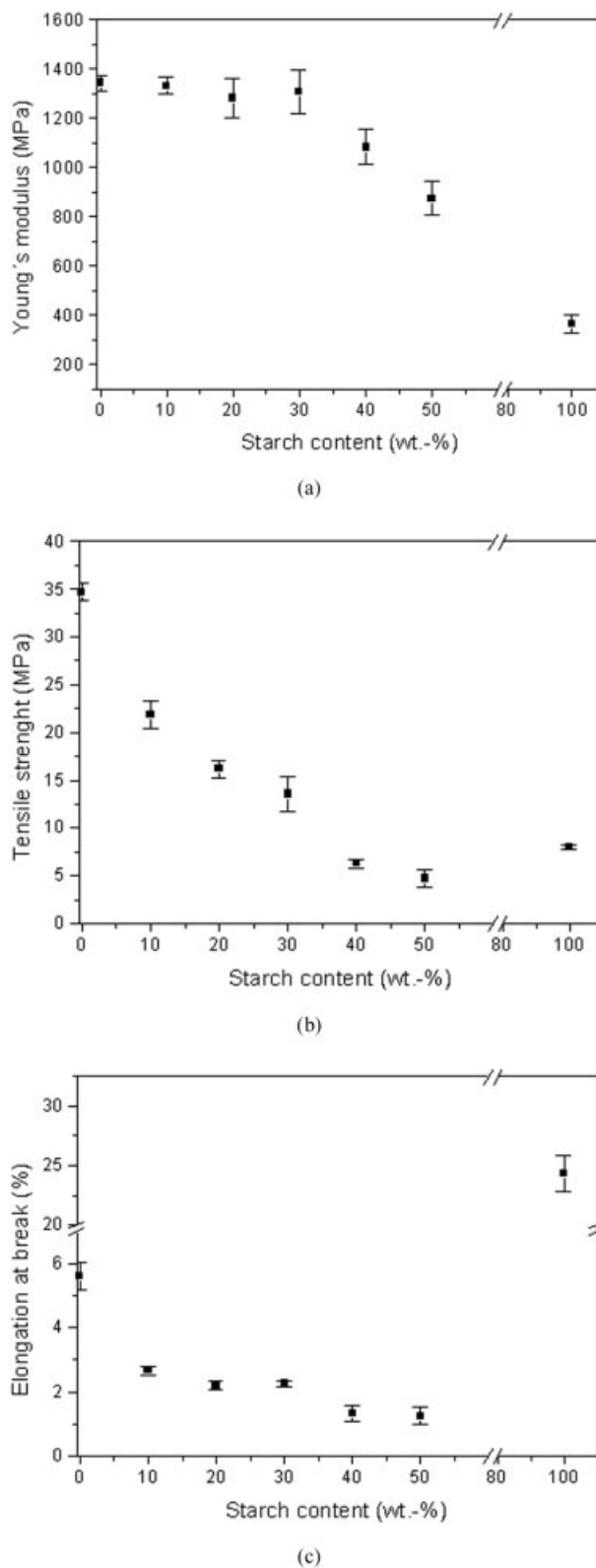


**Figure 1** Tensile properties of compression-molded PHB/starch blends as a function of starch contents in blends: (a) Young's modulus, (b) tensile strength, (c) elongation at break. Samples were stored at 68% RH for 15 days.

In Figure 1(a), it can be observed that Young's modulus remains almost constant for blends up to 30 wt % starch. As starch content is increased, modulus rapidly decreases from 1317 MPa, in average, to 366 MPa, resulting in more flexible materials. This result was expected due to the intrinsic rigidity of PHB macromolecules.

Tensile strength values also decrease in PHB/starch blends with increasing starch content [Fig. 1(b)]. When 10 wt % starch is added to PHB, tensile strength decreases. The value of 18.7 MPa, in average, is maintained for blends containing 20 and 30 wt % starch. As starch content increases from 30 to 40 wt %, tensile strength presents a large drop, showing values close to those in pure TPS films. A decrease of ~66% can be observed in this property. All the blends are less resistant to tensile strength than pure PHB are. However, PHB/starch blends with starch contents up to 30 wt % are more resistant than pure TPS films.

The elongation at break data [Fig. 1(c)] displays similar behavior. There are two drops; when 10 wt % starch is added, the elongation at break decreases from 5.20 to 2.62%, in average. As starch content increases from 30 to 40 wt %, another significant drop is observed, from 2.62 to 1.25%. In this case, all blends are less flexible than pure PHB and TPS films, since they present lower values for elongation at break. This fact probably indicates a lack of interfacial adhesion between PHB and starch, since this property may be related to the interfacial state of material.[18]

Mechanical properties are dependent on such factors as filler volume, filler particle size and shape, and the degree of adhesion of the filler to the polymer matrix.[19] Thus these results are probably because hydrophobic PHB is not compatible with hydrophilic starch. It is a general trend that the better the dispersion of the starch in the thermoplastic matrix, the better the mechanical properties.

## Thermogravimetric analysis

The TGA results of the grounded samples stored at 68% RH after 15 days are shown in Figure 2. The results are separated into two groups. In Figure 2(a), the mass plots of pure PHB (0 wt %) and PHB/starch blends with starch contents up to 20 wt % are shown, and in Figure 2(b), the corresponding derivative of the data (differential thermogravimetry, DTG) are shown. The same kind of plots are presented in Figure 2(c) and 2(d) for the set of blends with starch content in the range of 30–50 wt % and pure TPS (100 wt %). The starch content in each film is indicated in the graphics.

The TGA curve of pure PHB exhibits a single degradation step with onset temperature at 273.2°C [Fig. 2(a), 0 wt % starch]. After thermal treatment up to 700°C, no carbonaceous residue was left. A single peak observed in DTG curve confirms this degrada-

tion profile and indicates that the maximum rate of mass loss was achieved at 291.6°C [Fig. 2(c)]. Thermal degradation of PHB was studied by many researchers.[5,20] Thermogravimetric analysis and pyrolysis coupled with GC/MS suggested that PHB is degraded almost exclusively by a nonradical random chain scission reaction (cis-elimination) involving a six-membered ring transition state.

For pure TPS films (100 wt % starch), the TGA and DTG curves [Fig. 2(b) and 2(d)] suggest the occurrence of two weight loss processes: one occurring at ~100°C and another with onset temperature at 319.7°C. The initial weight loss process corresponds to the loss of water absorbed by starch structure. The total moisture content in pure TPS films was calculated as 4.3%.

The second process is much more intense and may be attributed to the degradation of starch molecules. Degradation step of starch component at 280–350°C was also observed in thermoplastic blends of maize starch with poly(ε-caprolactone), cellulose acetate, poly(lactic acid), and ethylene-vinyl alcohol copolymer.[21] The chemical structure and thermal reaction pathway of native and modified starch samples after being heated up to 600°C have been examined by ^{13}C high-resolution solid-state NMR spectroscopy.[22] It was observed that the chemical reactions for the samples started around 300°C to generate ether and ethylene segments via thermal condensation and dehydration mechanisms. At higher temperatures, aromatic and even crosslinked structures are formed. In general, these reactions lead to a carbonaceous residue. Its composition and quantity depend on starch source. In this work, thermal degradation of pure TPS film yields a residue that corresponds to 7.77% of the initial mass.

The shoulder in the starch degradation DTG peak (indicated by an arrow) was also observed by other researchers[21] and may be due to the different degradation rate of amylose and amylopectin. It can be supposed that amylose molecules degrade at a temperature lower than that of amylopectin because of its mostly linear structure. As expected, the onset temperatures of degradation indicate that compression-molded TPS films are thermally more stable than pure PHB films obtained by the same technique.

PHB/starch blends with 10 and 20 wt % starch show only one degradation step, starting at 279.0 and 274.55°C, respectively, [Fig. 2(a) and 2(c)]. Because of the temperature range in which the weight loss process occurs and the small quantity of starch in the blends, this process may be related mainly to the degradation of PHB. Similar to pure PHB film, water absorption was not observed in these blends, indicating that no water (or almost none) was absorbed by the PHB/starch blends during storage.

For blends with starch content higher than 20 wt %, TGA curves show three degradation steps: at around
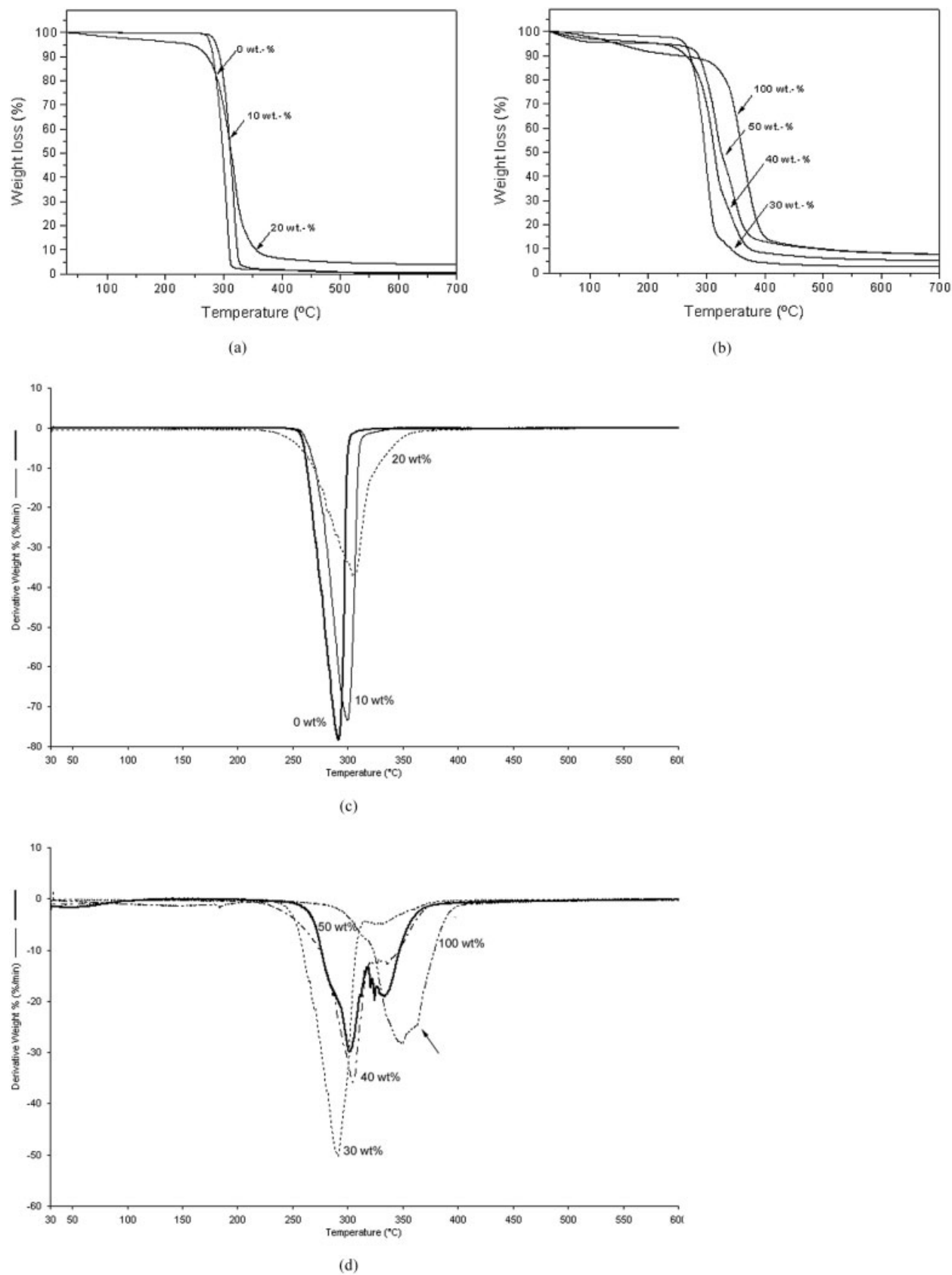
**Figure 2** Thermogravimetric results on pure PHB and PHB/starch blends with starch content up to 20 wt %: (a) weight loss plots; (b) DTG plots. Thermogravimetric results on pure thermoplastic starch and PHB/starch blends with starch content in the range of 30–50 wt %: (c) weight loss plots; (d) DTG plots. The starch content in each film is indicated in the graphics.

100°C, between 200 and 310°C, and above 310°C [Fig. 2(b)]. These weight loss transitions can be better visualized by means of peaks of maximum rate of mass loss in DTG curves [Fig. 2(d)]. As discussed earlier, the first stage, which occurs around 100°C, may be associated to water desorption. The second transition, which occurs in the temperature range of 200–310°C, can be related mainly to the weight loss process of PHB. The latter stage presents the onset temperature above 310°C and the temperature of maximum rate for all blends occurs at ~330°C. This weight loss transition can be attributed mainly to the degradation of starch, which is the most thermally stable component of the blend.

The temperature of maximum rate of weight loss ($T_{max}$) and the onset temperature ($T_{onset}$) of the two latter degradation mechanisms in all the blends studied are presented in Table I. For blends with starch content higher than 30 wt %, it was not possible to determine accurately the onset of starch degradation ($T > 310$°C). Then, the $T_{onset}$ for this process was considered as the temperature in which there was better resolution between the two peaks. The PHB/starch blends showed $T_{onset}$ of 274.5°C, in average, and a deviation of only 2%. The increase in $T_{max}$ value for the blends was also slightly significant: a 5% increase in relation to pure PHB film was observed. The maximum value was obtained for blend with 20 wt % starch. It can be observed that the addition of starch did not have a significant effect on the thermal degradation process of PHB.

The percentage of weight loss during the degradation process in the range of 200–310°C gives a direct indication of the PHB content in the blends. The degradation extent in PHB/starch films containing 70 wt %, 60 wt %, and 50 wt % PHB yield 74.11%, 66.67%, and 50.79%, respectively, which is similar to its nominal content in the blends.

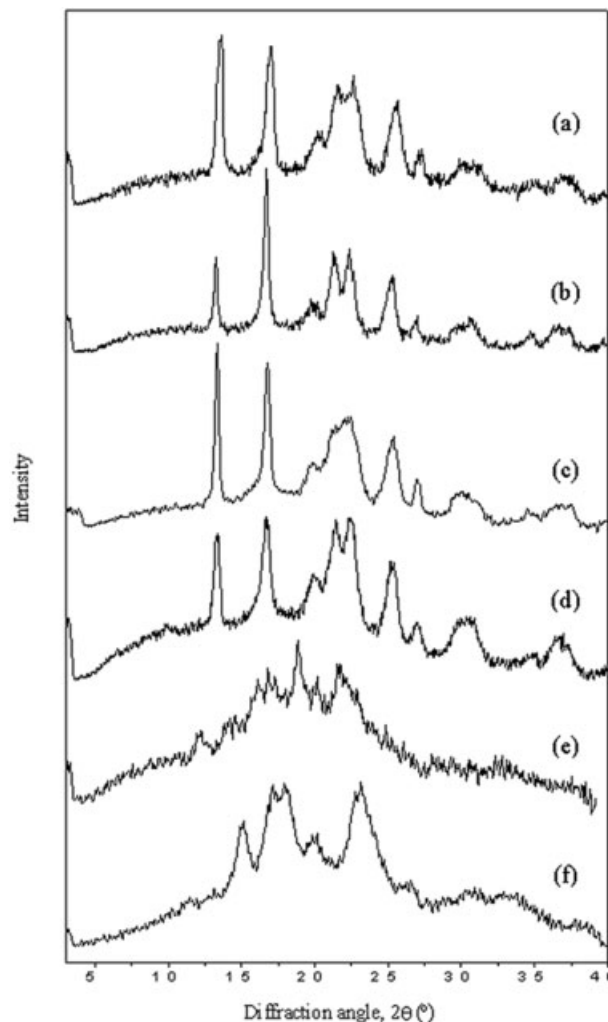The residue obtained after the thermal degradation of the blends varied according to starch content. The



**Figure 3**  X-ray diffractograms of raw PHB (a), native maize starch (f), and compression-molded PHB/starch blends with varied starch contents (wt %): (b) 0, (c) 20, (d) 30, (e) 100, after conditioning at 68% RH for 15 days.

amount of residue obtained was 0.55–7.63% of the initial mass for blends with 10–50 wt % starch, respectively.

## X-ray diffraction

X-ray diffraction patterns of raw PHB, native maize starch, and PHB/starch blends conditioned at 68% RH for 15 days are presented in Figure 3. The diffraction profile of the raw PHB sample exhibits well-defined peaks ($2\theta$) at 13.6, 17.1, 21.7, 22.7, and 25.6° (trace a), which correspond to the 020, 110, 101, and 121 reflections of the orthorhombic PHB crystalline lattice, respectively. This profile was also obtained by other researchers.[8,23] It can be observed that the peak positions remain practically unchanged for compression-molded PHB (trace b). Therefore, the processing induced a decrease in the intensity of the diffraction

### TABLE I
**Onset Temperature of Degradation Process ($T_{onset}$) and Temperature of Maximum Rate of Weight Loss ($T_{max}$) in the Two Main Degradation Mechanisms Observed in Compression-Molded PHB/Starch Blends**

| Starch content (wt %) | 200–310°C | | >310°C | |
|---|---|---|---|---|
| | $T_{onset}$ (°C) | $T_{max}$ (°C) | $T_{onset}$ (°C) | $T_{max}$ (°C) |
| 0 | 273.2 | 291.6 | — | — |
| 10 | 279.0 | 299.4 | — | — |
| 20 | 274.6 | 305.2 | — | — |
| 30 | 267.2 | 291.1 | 316 | 331.7 |
| 40 | 274.9 | 304.4 | 324 | 334.9 |
| 50 | 276.8 | 302.1 | 318 | 331.7 |
| 100 | — | — | 319.7 | 348.5 |

peak at $2\theta = 17.1°$, while the diffraction peak at $2\theta = 13.6°$ appeared more pronounced.

A typical A-type crystallinity pattern of native maize starch with peaks ($2\theta$) at 15.0, 17.1, 18.0, and 23.1° (trace f) is not retained in compression-molded TPS obtained by the experimental conditions employed in this work (trace e). Traces of B-type crystalline pattern characterized by peaks with angular locations at $2\theta = 17.1$ and 22.0° are detected in TPS diffractogram (trace e). It is worth noting that the former diffraction peak is coincident with one of the PHB characteristic reflection. The conversion of native starch into thermoplastic material leads to the loss of natural organization of starch molecules because of gelatinization and/or melting of the granules. Therefore, on storage, amylose and amylopectin molecules recrystallize or retrograde into B-type crystalline structures.[24] This crystalline structure was shown to occur in compression molded glycerol-plasticized starches and to vary in amount by changing processing parameters, such as temperature and water content. The total amount of B-type crystallinity was considered as a summation of residual amylopectin crystallinity, recrystallization of amylose and amylopectin, and partial cocrystallization of both polymers.[25] In the X-ray diffractogram of TPS film (trace e), the peak located at $2\theta = 19.5°$, accompanied by another less intense peak located at $2\theta = 12.5°$, evidences the development of the $V_h$-type crystallinity. This type of crystallinity is attributed to the precipitation of amylase–lipid complexes, which are formed after starch gelatinization. In the crystalline precipitate, amylose adopts a left-handed, single helical conformation.[24]

The development of the crystalline phase of PHB in the PHB/starch molded blends is evidenced by the appearance of its characteristic peaks located at $2\theta = 13$ and 17°, approximately. In a similar way, the diffraction peaks related to B-type crystallinity of starch are also detected for all blends. No additional reflection is observed in the diffractograms of blends. These facts suggest that the PHB crystalline lattice do not change appreciably in the presence of starch. Thus, probably, separated crystalline lattices are formed and there is no cocrystallization between the molecules of blend components. On the contrary, the presence of PHB apparently interferes with the development of $V_h$-type crystallinity of starch, since the less intense characteristic peak located at $2\theta = 12.5°$ is not observed in PHB/starch blends. Because of the similarity of the position of the diffraction peaks of PHB and starch, it was not possible to establish a relation between the intensity of main reflections of the components and the starch content in the blends.

Table II shows the total crystallinity of the samples determined on the basis of the X-ray diffractograms shown in Figure 3. It can be observed that the total crystallinity of raw PHB is reduced because of pro-

**TABLE II**
**Total Crystallinity of Raw PHB, Native Maize Starch, and Compression-Molded PHB/Starch Blends, after Conditioning at 68% RH for 15 Days**

|  | Total crystallinity (%) |
|---|---|
| Starch content (wt %) | |
| 0 | 51.1 |
| 20 | 48.7 |
| 30 | 32.3 |
| 100 | 22.7 |
| Raw PHB | 44.9 |
| Native starch | 23.9 |

cessing, while the compression-molded TPS exhibits the same crystallinity as native starch. The total crystallinity of PHB/starch blends is diminished with starch composition in the samples. The blend with 30 wt % starch shows a decrease of 37% in total crystallinity in relation to pure compression-molded PHB. These results are coherent with the diffractogram profiles of the blends (Fig. 3), since they evidenced an increase in the halo of amorphous phase as higher amounts of starch were added to the blends.

The decrease in crystallinity of PHB/starch blends observed in the present work, in relation to pure PHB film, disagrees with the results obtained by Koller and Owen.[26] These researchers investigated the structure and the mechanical properties of melt-pressed sheets of PHB filled with different amounts of maize starch granules without addition of any other component. According to their results, PHB/starch sheets became more brittle and more crystalline than did PHB sheets. Differences in processing, particularly those related to the thermomechanical treatment used in the present work, may explain the divergence of results.

## Contact angle measurements

Figure 4 shows the evolution of contact angle of water for compression-molded PHB/starch blends with varied starch contents. The blends behaviors are quantitatively illustrated by measurement of the initial values of contact angle just after deposition of the water droplet and by the value of the slope at the origin (Table III).

The hydrophobic character and intrinsic rigidity of PHB film are evidenced by the highest value of initial contact angle and by the slower and more constant evolution of contact angle with time. On the contrary, the lower initial contact angle of pure TPS film rapidly decreases because of its water absorption tendency. This is one of the drawbacks for the most extensive use of TPS.[13]

For the PHB/starch blends, the value of slope at the origin is intermediate to those observed for pure components. The water absorption rate increases as a func-

tion of starch content; an improvement of wettability is observed for the blends in relation to pure PHB. When 20 wt % starch is added, the blend presents an initial contact angle value similar to that of pure PHB. However, the slope at the origin is slightly increased. Blends with starch content higher than 30 wt % showed initial contact angle very close to that of pure TPS. However, a more significant increase in water absorption rate is observed only for the blend with 40 wt % starch. After 1 min of analysis, a linear relation between contact angle and starch content is observed.

An interesting fact of these results is that the introduction of up to 30 wt % starch leads to an increase in the hydrophilic nature of the blend, but the water absorption rate is not increased to a detrimental level. As fastest hydrolytic degradation would be expected for more hydrophilic materials,[16] this result may be an indicative that the biodegradation rate of PHB film might be improved by the presence of starch.

### Fractured surfaces

The morphology of PHB/starch blends was investigated by scanning electron microscopy (SEM). Micrographs of fractured surfaces obtained after tensile tests are shown in Figure 6. The fractured surface of pure PHB film presents a relatively smooth topography, indicating a brittle fracture [Fig. 6(a)]. Several cracks and voids can be observed. On the contrary, the rough topography and the presence of deformed starch granules are an indicative that pure TPS films present more ductile behavior during tensile deformation [Fig. 6(g)]. The process of ductile fracture involves the formation
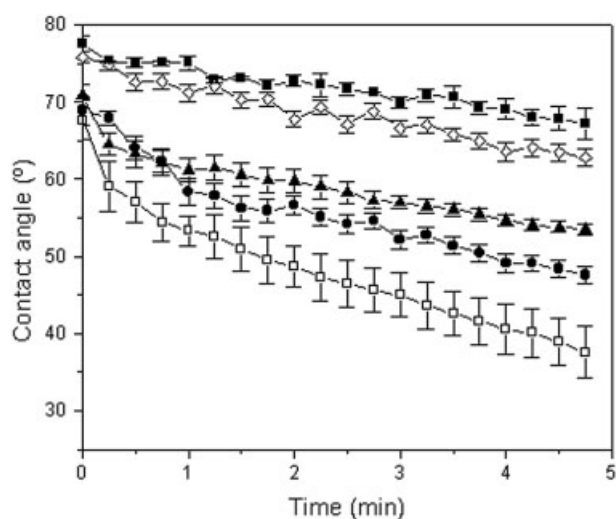
**Figure 4** Evolution of contact angle of water for compression-molded PHB/starch blends with varied starch contents (wt %): 0 (pure PHB) (■), 20 (◇), 30 (▲), 40 (●), 100 (pure TPS) (□).

**TABLE III**
**Contact Angle Measurements of Compression-Moulded PHB/Starch Blends after Conditioning at 68% RH for at Least 15 Days**

| Starch content (wt %) | Initial value (°) | Slope at the origin (°/min) |
|---|---|---|
| 0 | (77.6 ± 1.0) | −1.87 |
| 20 | (75.8 ± 0.7) | −2.56 |
| 30 | (70.8 ± 1.5) | −2.74 |
| 40 | (68.9 ± 1.8) | −4.00 |
| 100 | (67.7 ± 2.5) | −5.06 |

of crazes and its surface shows, in general, regions of plastic deformation associated with voids and fibrils.[27]

Figure 6(b)–6(f) indicates clearly the heterogeneous morphology of the blends. The fractured surfaces of the blends consisted of a continuous matrix with several features of dimensions varying from 4.3 to 25.9 μm in major axis. It was previously reported that maize starch granules are polygonal in shape, with a broad numerical distribution of particles from 2 to 27 μm, in equivalent spherical diameter, with a peak near 13 μm and a shoulder at 7.5 μm.[28] It seems reasonable to conclude that the surface features visualized in Figure 6(b)–6(f) consist of starch granules that were not destructured during processing. These granules are dispersed in the continuous PHB-rich matrix and are loosely adhering to it. In the blend with 10 wt % starch, a void (indicated by an arrow) can be observed, which probably resulted from the ejection of a granule during tensile test. The interfacial adhesion between PHB matrix and starch granules was not sufficient to withstand interfacial stresses generated during tensile deformation. These observations confirm the assumption discussed earlier under Tensile Properties that the poor mechanical properties of the PHB/starch blends (Fig. 1) may be a result of the lack of adhesion between the components.

Blends of wheat starch and poly(β-hydroxybutyrate-co-β-hydroxyvalerate) were obtained by casting and compression-molding techniques.[17] Poor interfacial interaction between the two materials was also visualized by SEM micrographs of freeze-fractured samples. Since the size of dispersed starch granules was the same after heating processing, it was concluded that starch did not melt during blending. The material was characterized as a suspension of rigid particles in polymeric matrices or composites. Similar results were obtained for starch/low-density polyethylene and starch/aliphatic polyester blends.[29]
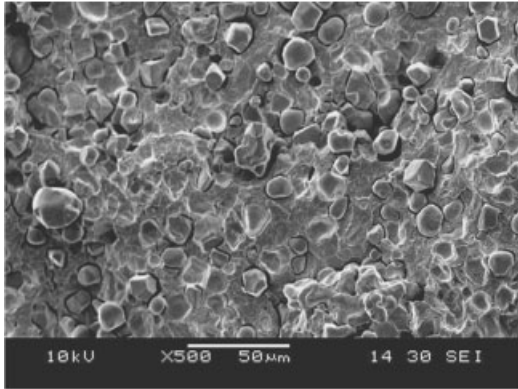
For PHB/starch blends with lower starch contents, the granules are well dispersed throughout the matrix, while at higher starch contents, the granules may be present as agglomerates. In the blend with 50 wt % starch, they are grouped together in clearly demarcated domains. Besides interfacial adhesion between
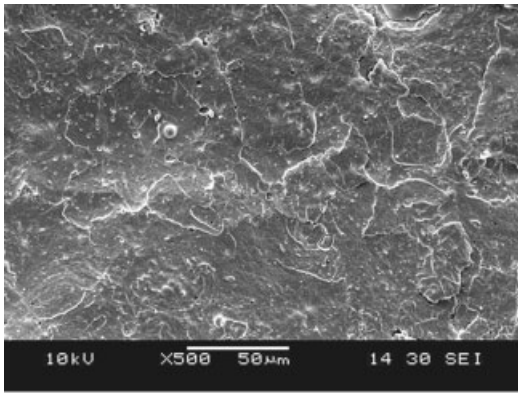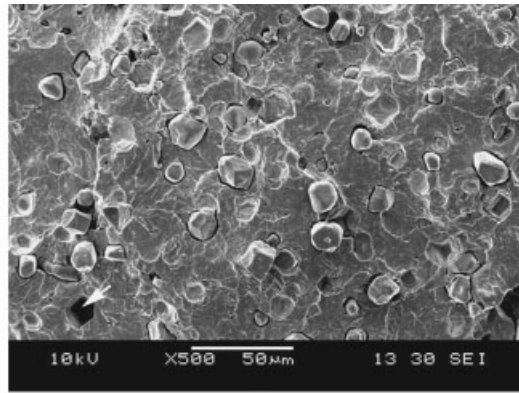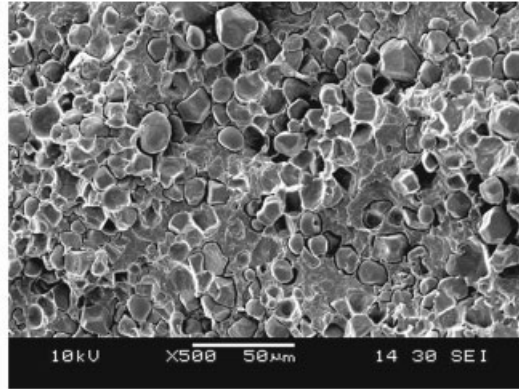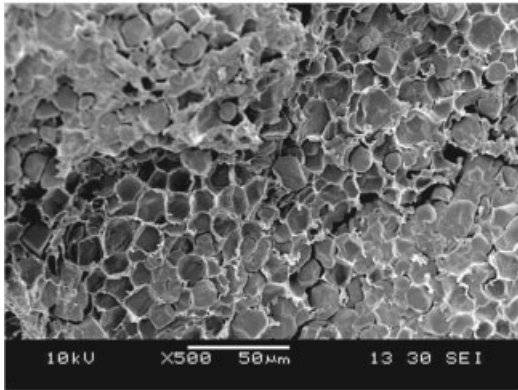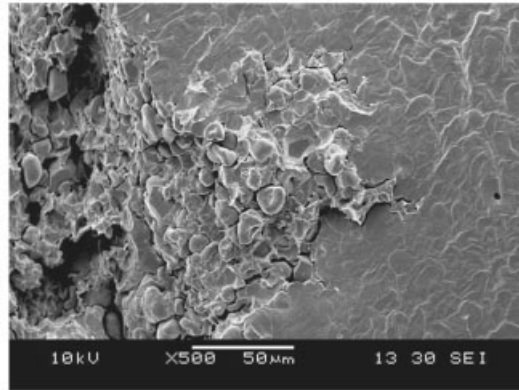
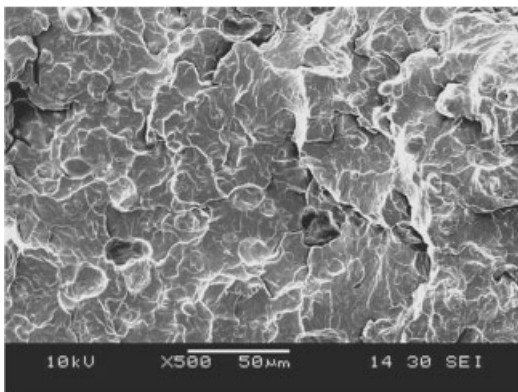**Figure 5** Scanning electron micrographs of PHB/starch blends' fractured surfaces with varied starch contents (wt %): (a) 0 (pure PHB), (b) 10, (c) 20, (d) 30, (e) 40, (f) 50, (g) 100 (pure TPS).

filler and matrix, the size and dispersion of particles are also reflected in the mechanical properties.[30] Probably, the formation of these agglomerates also contributed to poor mechanical properties, as shown in Figure 1.

## CONCLUSION

Compression-molded PHB/starch blends with starch content up to 30 wt % showed values of Young's modulus similar to those of pure PHB films. For blends with higher starch content, this parameter decreased significantly, resulting in softer materials. Elongation at break and tensile strength also decreased for PHB/starch blends in all compositions tested. It was observed that higher starch contents led to poorer mechanical properties. These results may be explained by the lack of interfacial adhesion between starch and PHB and by the heterogeneous dispersion of starch granules over PHB-rich matrix, as evidenced by SEM micrographs of fractured surfaces. Despite SEM micrographs having shown that the physical structure of starch granules were maintained after processing, B-type crystallinity detected in X-ray diffraction profile of the blends revealed that the granules were melted and amylose molecules were leached from the granules. Thus it can be concluded that starch and PHB were processed at very light conditions, which prevent the degradation of starch molecules. Results from X-ray diffraction also suggested that addition of starch decreased the degree of crystallinity without affecting PHB crystalline lattice. The incorporation of starch did not affect appreciably the thermal stability of PHB. Blends with starch content up to 30 wt % presented higher hydrophilic character than pure PHB films did, as determined by contact angle measurements, but the water absorption rate remained in a useful range.

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