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Short communication

Development of biodegradable flexible films of starch and poly(lactic acid) plasticized with adipate or citrate esters

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ABSTRACT

Biodegradable films were produced from blends contained a high amount of thermoplastic starch (TPS) and poly(lactic acid) (PLA) plasticized with different adipate or citrate esters. It was not possible to obtain pellets for the production of films using only glycerol as a plasticizer. The plasticization of the PLA with the esters and mixture stages added through extrusion was critical to achieve a blend capable of producing films by blow extrusion. Adipate esters were the most effective plasticizers because they interacted best with the PLA and yielded films with appropriate mechanical properties.

1. Introduction

The environmental problems caused by discarding non-biodegradable materials have led to the research and development of biodegradable materials with characteristics that allow for their use in the production of packaging on a commercial scale. In this context, the use of poly(lactic acid) (PLA) and starch blends is a promising option because in addition to being biodegradable, these materials are derived from renewable source.

Starch is an attractive biopolymer because of its abundance, low cost, and potential application in the production of biodegradable films in the form of thermoplastic starch (TPS). However, TPS film is limited due to its hydrophilic nature, which results in changes to its mechanical properties when exposure to high relative humidity (Avella et al., 2005; Kalambur & Rizvi, 2006; Zullo & Iannace, 2009).

PLA is an aliphatic, biodegradable, and hydrophobic polyester produced from the polymerization of lactic acid molecules and has properties comparable to those of plastics made from petroleum, such as transparency, good processability, and mechanical properties (Garlotta, 2001; Martin & Averous, 2001). In general, PLA-based materials are rigid and brittle; thus, their properties must be modified to produce flexible films. For this purpose, both adding plasticizers and blending with other biodegradable polymers has been examined (Coltelli et al., 2008).

Plasticizers, such as glycerol and sorbitol, have been researched to increase the flexibility and improve the processability of starch/PLA blends; however, no significant improvement in the mechanical properties has been observed (Li & Huneault, 2011; Martin & Averous, 2001).

Several studies compared the plasticizing effect of different adipate and citrate esters and found that these substances efficiently reduced the glass transition temperature (T_g) and improved the mechanical properties of PLA by reducing the elastic modulus and the tensile strength and increasing the elongation, thus making it possible to obtain flexible films (Labrecque, Kumar, Dave, Gross, & Mccarthy, 1997; Ljungberg, Andersson, & Wesslén, 2003; Martino, Jiménez, & Ruseckaite, 2009; Zhang & Sun, 2004).

The objective of this study was to produce TPS films by blow extrusion and evaluate the effect of adding PLA plasticized with adipate or citrate esters in the blend.

2. Materials and methods

2.1. Materials

This study used PLA Ingeo 3251D (Natureworks LLC, Cargill, USA), cassava starch (Indemil, Brazil), and commercial glycerol (Dinâmica, Brazil) as plasticizing for the starch; diisodecyl adipate (426.67 g/mol), diethyl adipate (202.25 g/mol), acetyl triethyl citrate (318 g/mol), acetyl tributyl citrate (402.49 g/mol), and tributyl citrate (360.44 g/mol) (Sigma–Aldrich, Germany) were used as plasticizing for the PLA.

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Table 1
Composition of the TPS and PLA films plasticized with citrate or adipate esters.

Formulation	Starch (%)	Glycerol (%)	PLA (%)	Adipate ester (%)[a]	Citrate ester (%)[b]
C1	69.7	24	6.3	–	–
C2	69.7	24.3	6.0	–	–
DEA1/DIA1	69.7	23.3	6.3	0.7	–
DEA2/DIA2	69.7	23.3	6.0	1.0	–
ATE1/ATB1/TBC1	69.7	23.3	6.3	–	0.7
ATE2/ATB2/TBC2	69.7	23.3	6.0	–	1.0

C1 and C2 = control.
[a] Diethyl adipate or diisodecyl adipate.
[b] Acethyl triethyl citrate or acethyl tributyl citrate or tributyl citrate.

2.2. Production of pellets and films

The pellets were produced in two stages. In the first stage, mixtures containing 30% (w/w) of TPS and 70% (w/w) of PLA and plasticizer were extruded in a twin-screw extruder (BGM, D-20 model, Brazil) using the following processing conditions: a screw diameter of 20 mm, a screw speed of 120 rpm, a feeder speed of 40 rpm, and a temperature profile of 100/150/150/150/150 °C. The concentrations of the plasticizers were 33 g glycerol/100 g starch and either 11 g or 18 g of adipate or citrate ester/100 g PLA. In the control formula, the ester was substituted with glycerol. The extruded cylindrical profiles were chilled in a water bath at room temperature and were pelletized.

In the next step, the pellets produced in the first stage were mixed at a proportion of 10% (w/w) pellets and 90% (w/w) TPS (33 g glycerol/100 g starch) and were extruded in a twin-screw extruder, using a screw speed of 150 rpm, a feeder speed of 50 rpm, and a temperature profile of 100/140/140/140/140 °C. The cylindrical profiles were pelletized and were extruded in a single-screw extruder (BGM, EL-25 model, Brazil) to produce films by blow extrusion under the following conditions: a screw diameter of 25 mm, a screw speed of 35 rpm and a temperature profile of 100/150/150/100 °C. The final composition of each film is presented in Table 1.

2.3. Mechanical properties

The tensile strength tests were performed with a texture analyzer (Stable Micro Systems, TA XTplus model, England) based on the American Society for Testing and Material standards (ASTM, 2002). The samples were previously conditioned at 23 ± 2 °C and 53 ± 2% RH for 48 h. The properties measured were tensile strength (MPa), elongation at break (%), and Young's modulus (MPa).

2.4. Apparent opacity

The apparent opacity (Y_{ap}) was determined using a colorimeter (BYK Gardner, USA), and was calculated based on the ratio of the luminosity (L^* – CIELab system) of the system, which was measured with a black background (L^*_B) and with a white background (L^*_W), divided by the thickness of the film (φ). The results were expressed on an arbitrary scale (0–100% μm^{-1}) according to Eq. (1):

$$Y_{ap} = \left[\frac{L^*_B/L^*_W}{\varphi}\right] \times 100 \quad (1)$$

2.5. Scanning electron microscopy (SEM)

The microstructure of the fractured films was analyzed with a scanning electron microscope (Philips, XL-30 model, Holland) with electron source of tungsten and detectors of secondary and backscattered electrons. The films were immersed in liquid nitrogen and then broken. The samples were coated with gold using a sputter coater (BALTEC, SCD 005 model, Switzerland). All the samples were examined using an accelerating voltage of 10 kV.

2.6. Fourier transform infrared spectroscopy (FT-IR)

The spectra were obtained with an FT-IR spectrophotometer (Shimatzu, IR-Prestige 21 model, Japan) equipped with a diffuse reflectance accessory. A resolution of 4 cm^{-1} was used for each spectrum, with 20 scans between 4000 and 700 cm^{-1}.

2.7. Statistical analysis

The obtained results were evaluated using analysis of variance (ANOVA), and treatment means were compared using Tukey's test at the 5% significance level ($p < 0.05$) with Statistica 7.0 software (Stat-Soft, Tulsa, OK, USA).

3. Results and discussion

3.1. Production of the films

To produce the pellets of the blends of starch and PLA, two stages of mixture were necessary, due to the difficulty in preliminary tests

Table 2
The thickness, mechanical and opacity properties of the TPS and PLA films plasticized with citrate or adipate esters.

Formulation[a]	YM (MPa)	T (MPa)	ε (%)	φ (μm)	Y_{ap} (% μm^{-1})
F-DEA1	3.8 ± 1.0^{a}	0.9 ± 0.1^{a}	126 ± 17^{d,e}	246 ± 30^{a}	0.19 ± 0.01^{c}
F-DEA2	3.6 ± 0.6^{a}	0.8 ± 0.1^{a}	146 ± 18^{e}	492 ± 104^{b}	0.08 ± 0.02^{a,b}
F-DIA1	1.6 ± 0.4^{a}	0.6 ± 0.1^{a}	148 ± 24^{e}	332 ± 76^{a}	0.16 ± 0.04^{b,c}
F-DIA2	2.9 ± 0.6^{a}	0.7 ± 0.1^{a}	120 ± 15^{c,d,e}	923 ± 163^{c}	0.05 ± 0.01^{a}
F-ATEC1	9.7 ± 1.8^{b,c}	1.2 ± 0.2^{b}	109 ± 17^{b,c,d}	621 ± 129^{b}	0.13 ± 0.03^{a,b,c}
F-ATEC2	8.2 ± 2.4^{b,c}	1.1 ± 0.2^{b}	98 ± 15^{a,b,c,d}	534 ± 175^{b}	0.11 ± 0.05^{a,b,c}
F-ATB1	10.8 ± 3.2^{c}	1.3 ± 0.2^{b}	92 ± 18^{a,b,c}	342 ± 71^{a}	0.16 ± 0.03^{b,c}
F-ATB2	10.6 ± 2.5^{c}	1.1 ± 0.1^{b}	86 ± 16^{a,b}	562 ± 139^{b}	0.11 ± 0.05^{a,b,c}
F-TBC1	7.0 ± 2.3^{b}	0.9 ± 0.2^{a}	72 ± 11^{a}	276 ± 38^{a}	0.20 ± 0.06^{c}
F-TBC2	6.8 ± 2.8^{b}	1.1 ± 0.2^{b}	103 ± 19^{b,c,d}	303 ± 101^{a}	0.15 ± 0.03^{a,b,c}

YM = Young's modulus; T = tensile strength; ε = elongation; φ = thickness; Yap = apparent opacity.
a, b, c, d, e: The means followed by the same letters in the same column do not exhibit differences at the 5% significance level according to Tukey's test.
[a] The control formulations (F-C1 and F-C2) did not form films.

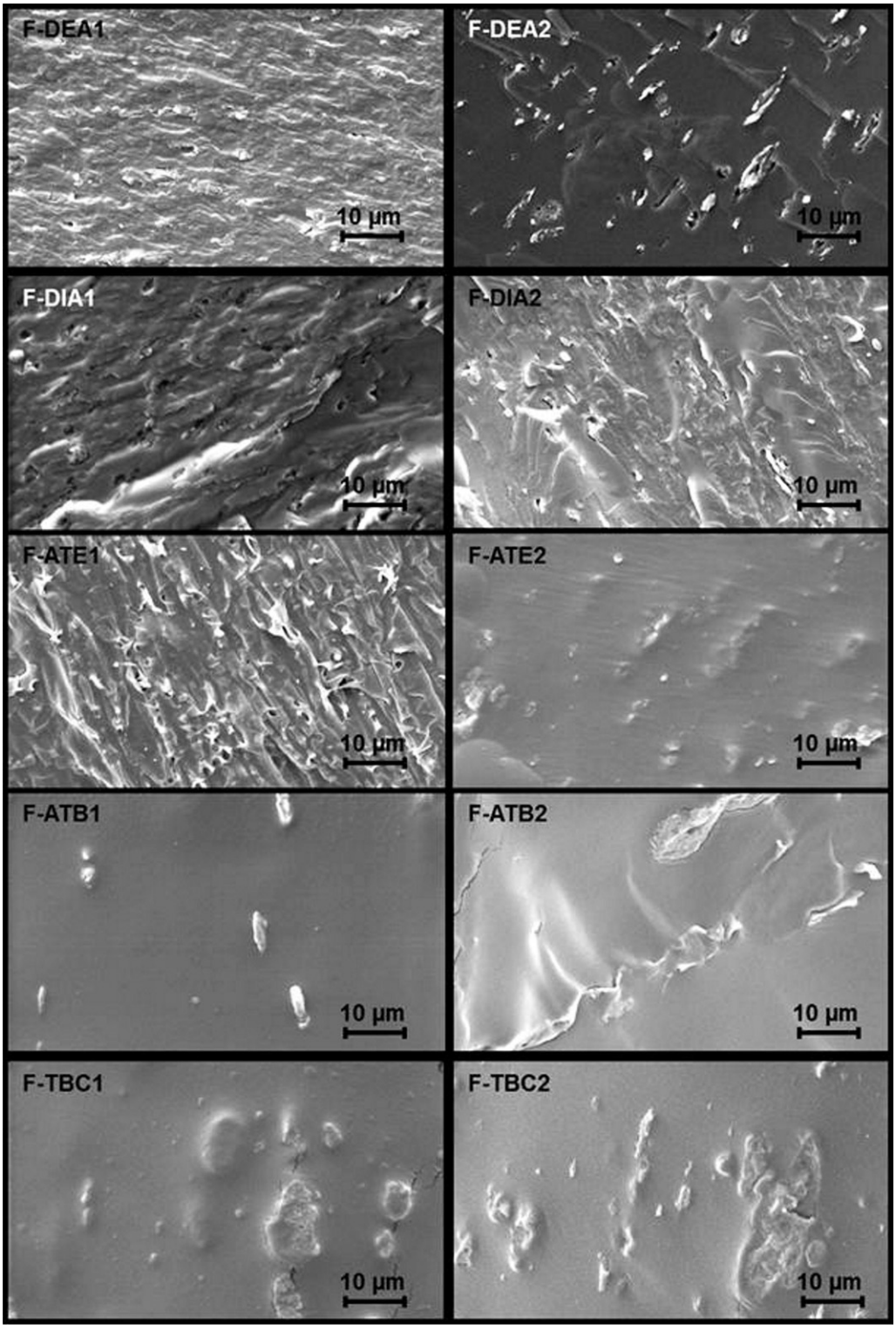

Fig. 1. Micrographs of the fracture (1600×) of the TPS and PLA films plasticized with citrate or adipate esters.

in obtaining a homogenous blend by exclusively extruding all components together.

In general, all of the formulations displayed similar behavior during the film processing step without significant variations in the amperage (~8.0 A) of the extruder. The formulations displayed similar behavior because a majority of the film is composed of thermoplastic starch and an elevated amount of glycerol.

It was not possible to form the extruded profiles into pellets in the control formulation (Table 1) because the material was not homogenous, and after cooling, it became rigid, brittle, and sticky, which indicates that glycerol is not a good plasticizer for PLA, even though it is a good plasticizer for starch. The adipate and citrate esters plasticized the PLA and allowed homogenous pellets to be obtained for the production of films by blow extrusion.

The obtained films had a yellow surface, were homogenous, had irregularities in some spots, and were slightly sticky due to excess glycerol.

3.2. Mechanical and optical properties

The concentration and the type of ester plasticizer, either adipate or citrate, did not have a significant effect on the mechanical properties of the films produced from starch + PLA blends (Table 2). The films with adipate esters were characterized by greater elongation (120–148%), less tensile strength (0.6–0.9 MPa), and a lower Young's modulus (1.6–3.8 MPa) than the films made with citrate esters. The linear structure of these compounds probably facilitated the interaction with PLA, which led to efficient plasticization. The similarity of the chemical structures and the compatibility between the plasticizer and the polymer determine the plasticization efficiency. From a molecular perspective, the plasticizer should be miscible and should have solubility close to that of the polymer, thus requiring less energy to merge or solvate (Murariu, Ferreira, Alexandre, & Dubois, 2008).

Cassava TPS films (20 g glycerol/100 g starch) produced by blow extrusion (Costa, 2008) had a tensile strength of 13 MPa, an elongation of 13%, and a Young's modulus of 134 MPa. According to Martino et al. (2009), PLA films produced by injection molding exhibit reduced tensile strength and increased elongation when plasticized with 20% adipate ester (MW = 2565 g/mol). A PLA–starch blend (55:45) made with maleic anhydride as compatibilizer and plasticized with acetyl triethyl citrate elongated approximately 130% (Zhang & Sun, 2004).

In blow extrusion, thickness is mainly controlled by winding speed and airflow in the balloon matrix. The variation of thickness resulted from the differences in the formulation and processability of the blends.

The increase in the concentration of DEA, DIA, and ATB increased the thickness of the films without altering the mechanical properties. The thickness also increased with the molecular mass of the esters used (DEA2 < ATB2 < DIA2), probably due to the increase in density. A similar pattern was observed in pea starch films plasticized with different monosaccharides and polyols (Zhang & Han, 2006).

Increasing the concentration of adipate esters significantly decreased the opacity of the films, possibly due to the increased free volume resulting from the greater mobility of PLA chains and to the decrease in crystallinity. For the citrate esters, varying the concentration and type of plasticizer did not significantly alter opacity.

3.3. Scanning electron microscopy (MEV)

From the fracture micrographs of the films (Fig. 1), there was no phase separation between the TPS and PLA plasticized with citrate or adipate esters, probably because of the small concentration of PLA relative to TPS. For the films containing adipate esters, particles on the surface, which were non-gelatinized starch granules or PLA droplets dispersed in the matrix, and micropores were observed.

The micrographs support the conclusion that the mixture stages by extrusion used in this study were efficient, both in the plastification of the starch and in the plastification of PLA.

3.4. Fourier transform infrared spectroscopy (FT-IR)

The FT-IR spectra (not shown) reveal that all of the samples displayed peaks of absorption in the same regions but no bands that could indicate interactions between the starch and the PLA.

Absorption bands were observed at approximately 1020 and 995 cm^{-1}, which were related to the C—O fracture strain of the C—O—C group in the anhydroglucose ring that developed because of the starch. A broad band was observed at approximately 3300 cm^{-1}, which is related to the hydrogen interactions due to the presence of hydroxyl groups in the ends of the PLA chain, in the glycerol and in the starch.

A low-intensity absorption peak was observed at approximately 1750 cm^{-1}, which corresponds to the vibration of the C=O bond of PLA and of the adipate and citrate esters as a result of the presence of the ester. This spike was not intense because the concentration of PLA and of the esters in the formulation was low (7%).

4. Conclusion

The plasticization of PLA with citrate or adipate esters, the high concentration of glycerol in the TPS, and the inclusion of mixture stages with twin-screw extrusion allowed the production of TPS + PLA films with low PLA concentration using blow extrusion.

Adipate esters at a low concentration, in particular DEA, which has a linear structure and the smallest molecular weight, were the best plasticizers for PLA. It was possible to produce films with mechanical properties that are appropriate for various types of applications.

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