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Thermal and Mechanical Properties of Polymeric Films Based on PLA / PBAT and Corn Starch and Babassu Mesocarp Starch by Flat Extrusion for Packaging

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Abstract: The influence of different amounts (1, 3 and 5%) of commercial corn starch and of babassu mesocarp starch on a (polylactic acid)/poly (butylene co-terephthalate adipate) (PLA/PBAT) based blend obtained by flat extrusion was ascertained. The thermal and mechanical properties were determined and the results obtained are independent of the type of starch employed but are dependent on its concentration, the nucleating effect of the different starches and on the mobility of the polymer chains that make up the blend. Thermogravimetric analysis indicated the presence of two defined stages of mass loss for all films under investigation. Tensile testing shows that films containing starch had similar behavior to that of PLA in the PLA/PBAT blend, presenting high values of tensile strength, elastic modulus and tensile strength and low values of strain at break. The results suggest that babassu mesocarp starch is viable alternatives to the production of packaging films.

Keywords: Starch; Babassu mesocarp; Corn; Films; Packaging.

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1. Introduction

The thermomechanical behavior of polymeric materials is closely related to the spatial arrangement, orientation and conformation of their long chains [1,2]. Unarranged polymeric substrates inhibit complete relaxation of the chains in processing and result in significant thermal mismatches between the filler and the polymeric matrix. The study of thermomechanical properties is used to understand the morphology of chain networks and the effect of the type of charge on the polymeric film during processing [3–5].

PLA has high transparency, good tensile strength, excellent surface quality and printability compared to many polymers. However, for packaging it has a relatively high permeability to gases and vapors, which limits its application to short-lived packaged products [6,7]. PBAT is a synthetic biodegradable aliphatic-aromatic polyester which exhibits elastic behavior and has a lower melting point than PLA [8,9].

PLA and PBAT polymers are more promising materials, with thermomechanical properties close to those of polyethylene, when combined with each other or with other materials to form blends or polymeric composites [10–13].

Conventional corn starch has long been used in mixtures with PLA and PBAT for the development of films for food packaging, due to its renewable, cheap, ecological, biodegradable and biocompatible characteristics [14–16]. Several botanical sources have been investigated to develop packaging, the native starch of babassu mesocarp appears as a potential candidate for future investigations, since it is widely cultivated in Brazil [17–21].

During use, handling and disposal, plastic containers are exposed to mechanical demands, chemical interference and temperature variations, which prompts studies on their thermomechanical and barrier properties under real or simulated conditions [22–24]. Although thermal degradation may occur during processing and it is a concern, extrusion is the most used technology for hot processing films from starch-based PLA/PBAT blends. By studying these mixtures, it was possible to obtain stronger, thermal resistant films [25–28].

Taking into account this scenery, this work aimed to develop and study the termomechanical behavior of PLA/PBAT flat extrusion films containing 1, 3 or 5 % of commercial corn starch or native starch derived from the mesocarp of babassu coconut aiming at packaging applications.

2. Materials and methods

2.1 Materials

Babassu mesocarp starch (BMS) donated by the Laboratory of Biodiesel Plants at the Federal University of Piauí (UFPI). Corn starch (CS) marketed by the ADRAM industry. The polymeric matrix used was a biodegradable commercial blend produced by BASF with 55% w/w of poly PBAT (adipate-co-butylene terephthalate) and 45% w/w of poly (lactic acid) - PLA.

2.2 Starch extraction from babassu mesocarp

The process for starch extraction from babassu mesocarp was adapted from the methodology reported by Rodrigues, Silva, Carvalho, Alves, & Barbosa [18], performed at the Polymer and Conjugated Materials Laboratory (LAPCON) at the Federal University of Piauí (UFPI).

2.3 Preparation of PLA/PBAT/Starch blends films

The films were obtained using single-screw extruded in an AX Plastics Lab model 16. Three steps were performed: (1) extrusion — PLA/PBAT/Starch preparation (pellets), (2) Pelletization — preparation of PLA/PBAT/Starch blends (pellets) and (3) extrusion—blend films according to Figure 1, the process of preparing films as described in Rodrigues et al. [17]. Table 1 shows the composition and identity of the films manufactured.

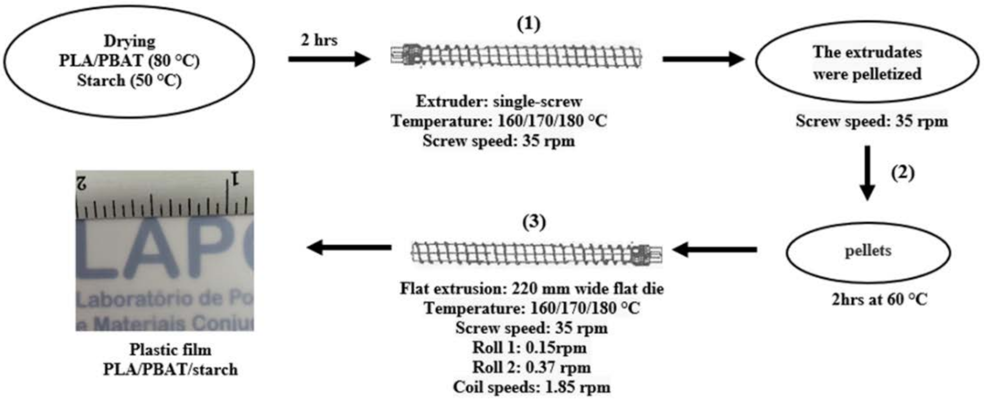

Figure 1. PLA/PBAT/Starch film production process.

Table 1. Identity and composition of PLA/PBAT/Starch films described in Rodrigues et al. [17].

Films	Blend	Babassu mesocarp starch	Corn starch
	PLA / PBAT (%)	**BMS (%)**	**CS (%)**
PLA / PBAT	100	0	0
PLA / PBAT / CS1	99	0	1
PLA / PBAT / CS3	97	0	3
PLA / PBAT / CS5	95	0	5
PLA / PBAT / BMS1	99	1	0
PLA / PBAT / BMS3	97	3	0
PLA / PBAT / BMS5	95	5	0

2.4 Film characterization

2.4.1 Thermal properties

1)Thermogravimetry and differential scanning calorimetry (TG / DSC)

Thermogravimetric and differential scanning calorimetric (TG-DSC) analyzes were carried out to study the thermal properties of film on an SDT Q600 V20.9 Build 20 equipment from TA instrument. The samples were heated from 30 to 500 °C at 10 °C.min $^{-1}$ under argon gas flow (100 mL.min $^{-1}$). The degree of crystallization ($\varDelta X_{c(sample)}$) of the samples was calculated using the following eqs (1) and (2) [29–31].

$$X_{c(polymer)} = \frac{\Delta H_m}{\Delta H_{100\%}} \times 100 \tag{1}$$

$$\varDelta X_{c(\text{sample})} = X_{c\,PLA} \times 100\%_{\,PLA} + X_{cPBAT} \times 100\%_{cPBAT} \tag{2}$$

where, $X_{c(polymer)}$ is the degree of crystallinity (%) of polymer, ΔH_m is the observed melting enthalpy of PLA and PBAT determined from the DSC heating scan and $\Delta H_{100\%}$ is the melting enthalpy for a 100 % crystalline polymer. $\Delta H_{100\%}$ values used for PBAT and PLA were, respectively, 114 J.g $^{-1}$ and 93 .6 Jg $^{-1}$ [29,31].

2) Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) was carried out in a 3-point static flexural mode using a Shimadzu dynamic mechanical analyzer (Model TMA-50, TA Instruments). The measurements were dynamic time sweep tests starting from T = 25 °C to 150 °C at a heating rate of 10 °C.min $^{-1}$ and frequency of 1 Hz. The storage modulus (E'), loss modulus (E''), and loss factor (tan δ) of the samples were measured. The peak temperature of tan δ was taken as the glass transition temperatures (Tg).

2.4.2 Mechanical properties

Mechanical properties of 125 mm × 12.5 mm filmstrips were measured according to D882-01 (ASTM. 2001), using an Emic DL-3000 Universal Testing Machine with a load cell of 100 N, initial grip separation of 100 mm, and crosshead speed of 12.5 mm/min. The films (with ten replicates) were obtained by extrusion with thickness between 200 to 250 µm and kept for 48 hours before analysis, under controlled temperature and relative humidity conditions (22.2 ± 1.37 °C and 48.78 ± 2.49 %).

2.4.3 Statistical analysis

The results obtained were evaluated by analysis of variance (ANOVA) and the average of the samples were compared by the Tukey's test at a 5 % significance level using the Statistics software, version 6 (GraphPad Prism).

3. Results and discussions

3.1 Thermal properties

3.1.1 Thermogravimetric analysis

The TG / DTG curves shown in Figure 2 show two defined stages of mass loss for all films investigated. The first peak ($T_{\text{peak 1MAX}}$) appears at around 350 °C and is associated with the mass loss of PLA chains and the second peak ($T_{\text{peak 2MAX}}$) close to 400 °C corresponding to thermal degradation of PBAT chains which make the Ecovio blend [30].

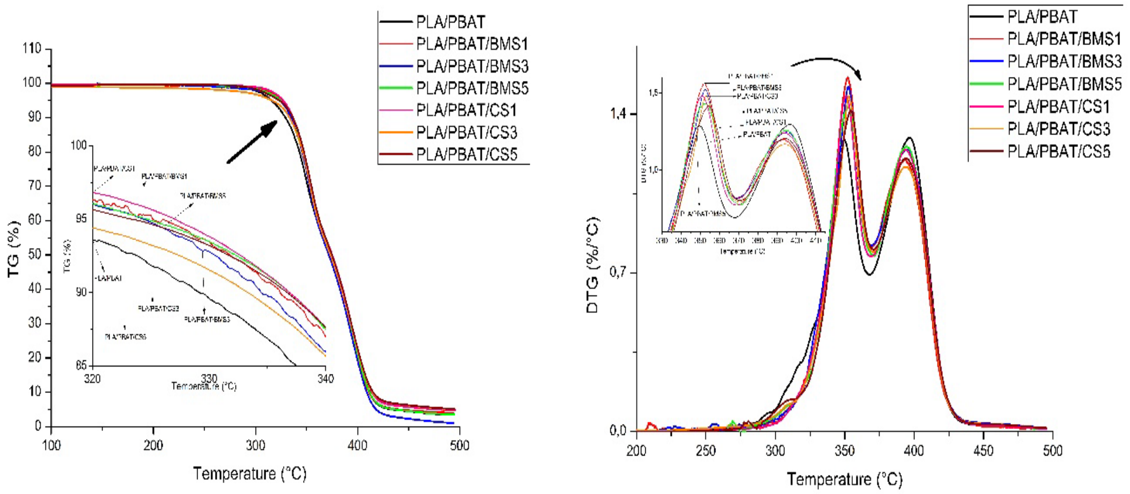

Figure 2. TG (a) and DTG (b) curves of PLA/PBAT/Starch films.

Data shown in Table 2, indicates that the addition of 1, 3 and 5 % BMS or CS in the PLA/PBAT matrix resulted in a linear increase of the PLA peak temperature values ($T_{peak\ 1MAX}$) and a decrease the peak temperature value of PBAT ($T_{peak\ 2MAX}$). According to Subramaniam [32], in compatible polymer blends, the components interpenetrate resulting in thermal properties with intermediate values. Since starch addition led to an increase in peak temperature of PLA, one concludes that films containing starch were more thermally stable than PLA alone.

In the studies on thermal properties of PLA/PBAT films conducted by Homklin and Hongsriphan [33] and Moustafa, El Kissi, Abou-Kandil, Abdel-Aziz and Dufresne [34] showed a more marked decrease in peak temperature associated with PLA decomposition, according to Li *et al.* [35] a higher thermal stability for the PBAT which was attributed to the presence of the benzene ring in PBAT structure making it more thermally stable.

The increases in the $T_{peak1MAX}$ values in films with starch, either from BMS or CS, are associated with improved interactions between the incorporated starches and the PLA chains in the blend. Despite the incompatibility of the hydrophilic starch and hydrophobic PLA, studies such as those by Reul *et al.* [36], Khan, Niazi, Samin and Jahan [37] and Prabhu and Prashantha [38], show that the granular structure of starch and processing conditions, can promote its bonding with PLA chains, accelerating nucleation and crystallization. These bonds must have played an important role in improving film thermal stability, which is noticeable in the values of T_{onset} (extrapolated to the beginning of thermal decomposition) that were closer to the temperature values of $T_{peak1MAX}$.

Table 2. Summary of TG/DTG degradation temperatures of PLA/PBAT/Starch films.

	$T_{peak\ 1MAX}$ (°C)	$T_{p\ eak\ 2MAX}$ (°C)	T_{onset}	Residue (%)
PLA / PBAT	349.24	397.06	339.63	3.42
PLA / PBAT / BMS1	351.53	392.76	333.54	4.13
PLA / PBAT / BMS3	352.58	394.67	332.26	1.25
PLA / PBAT / BMS5	352.58	394.67	333.92	4.14
PLA / PBAT / CS1	351.15	393.71	333.15	5.07
PLA / PBAT / CS 3	352.58	393.24	334.41	5.34
PLA / PBAT / CS 5	354.02	393.24	334.38	5.14

Mano, Koniarova and Reis [39], Nofar *et al.* [40] and Ai *et al.* [41] showed that PLA/PBAT composite films with thermal characteristics closer to PLA are good materials to replace various petroleum-based polymers in packaging applications.

The residual mass of the samples was also calculated and presented in Table 2. Our data shows that, except for the PLA/PBAT/BMS3 blend, all films containing starch had higher residual mass values than that of the neat PLA/PBAT blend and that, in general, samples with CS displayed higher residual mass than those containing BMS.

3.1.2 Differential scanning calorimetry analysis

Figure 3 shows the presence of three small peaks in the ranges of 100 - 150 °C, 150 - 250 °C and 370 – 400 °C and a sharp peak in the range of 325 to 370 °C for all films manufactured.

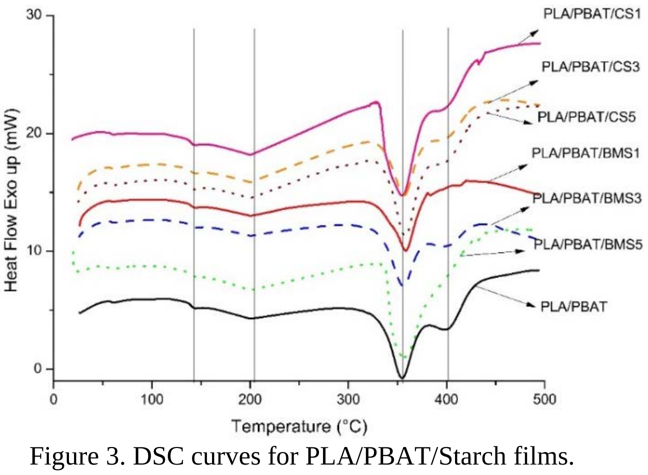

Figure 3. DSC curves for PLA/PBAT/Starch films.

Table 3. DSC data obtained from heating for PLA/PBAT/Starch films.

PLA / PBAT	**T_m (°C)**	**ΔH_m (Jg^{-1})**	**ΔXc (100%)**	**T_d (°C)**	**ΔH_d (Jg^{-1})**
PLA	200.60	24.13	26.0	354.49	141.7
PBAT	143.21	4.897	4.0	400.22	16.68
PLA / PBAT / BMS1	**T_m (°C)**	**ΔH_m (Jg^{-1})**	**ΔXc (100%)**	**T_d (°C)**	**ΔH_d (Jg^{-1})**
PLA	200.49	35.78	38.0	358.30	199.4
PBAT	143.07	5.989	5.0	383.80	1.791
PLA / PBAT / BMS3	**T_m (°C)**	**ΔH_m (Jg^{-1})**	**ΔXc (100%)**	**T_d (°C)**	**ΔH_d (Jg^{-1})**
PLA	200.59	31.06	33.0	355.57	179.2
PBAT	143.15	5.895	5.0	399.18	13.59
PLA / PBAT / BMS5	**T_m (°C)**	**ΔH_m (Jg^{-1})**	**ΔXc (100%)**	**T_d (°C)**	**ΔH_d (Jg^{-1})**
PLA	200.60	46.97	50.0	352.93	285.10
PBAT	143.24	5.278	5.0	401.64	4.053
PLA / PBAT / CS1	**T_m (°C)**	**ΔH_m (Jg^{-1})**	**ΔXc (100%)**	**T_d (°C)**	**ΔH_d (Jg^{-1})**
PLA	200.35	44.11	47.0	354.38	270.1
PBAT	143.11	5.798	5.0	398.27	13.42
PLA / PBAT / CS3	**T_m (°C)**	**ΔH_m (Jg^{-1})**	**ΔXc (100%)**	**T_d (°C)**	**ΔH_d (Jg^{-1})**
PLA	200.43	49.54	43.0	356.64	164.3
PBAT	143.18	5.641	5.0	399.42	11.52
PLA / PBAT / CS5	**T_m (°C)**	**ΔH_m (Jg^{-1})**	**ΔXc (100%)**	**T_d (°C)**	**ΔH_d (Jg^{-1})**
PLA	200.66	38.47	41.0	357.44	162.0
PBAT	143.55	5.848	5.0	399.91	10.75

* T_m = melting temperature, T_d = degradation temperature, DH_m = melting enthalpy DH_d = Enthalpy degradation and ΔX_c = e index of crystallinity.

In all curves, there was a peak around 143 °C attributed to melting of the less crystalline PBAT polyester and another, around 200 °C, associated with melting of PLA [42,43]. It is worth noticing that both these temperatures remained essentially unchanged with BMS or CS incorporation to the PLA/PBAT blend.

Two extra endothermic events associated with the degradation temperature (T_d) of PLA and PBAT, respectively were observed by DSC. A strong endothermic peak around 354 °C was attributed to decomposition PLA while another much less intense peak, near 400 °C was attributed to the decomposition of PBAT [44,45].

DSC thermal data shown in Table 3 indicates that neither the incorporation of BMS nor of CS to the PLA/PBAT blend caused significant changes in the melting pattern or on the degradation of PLA and PBAT in the films.

The small displacements in the temperature values are only a result of the small mobility of the segments of the polymer chain that constitute the matrix, generally induced by deformation, by the stress of the melting process, these displacements are prerequisites for the reorganization of the system during heating [44–46].

The data on Table 3 also shows that addition of either BMS or CS to the blend led to an average 25 % increase in PBAT crystallinity for all films under investigation compared to that of PBAT in the pure blend.

The increase in PLA crystallinity caused by the incorporation of BMS or CS starches to the PLA/PBAT blend was much more significant, ranging from 46 - 92 % with respect to that of PLA in the pure blend ($Xc = 26$ %) were achieved, with starch incorporation. The increase in PLA and PBAT phase crystallinity in PLA/PBAT/Starch blends is attributed to a nucleating effect of the starches on the matrix polymers, especially PLA.

In other words, starch incorporation led to increased crystallinity of the PLA phase in the blend, but no clear trend was observed for the effect of starch identity and content on the degree of crystallinity of the PLA phase in the PLA/PBAT blend. Our data may indicate a tendency for it to be higher for the systems containing CS and to decrease with increasing starch content, but in order to unequivocally state that this is indeed the case, replicate studies need to be made.

It was also observed that films with starch needed to absorb more energy for the PBAT chains to undergo fusion (ΔH_m) and for the PLA chains to go through the process of fusion (ΔH_m) and degradation (ΔH_d).

Analyzing the studies by Falcão *et al.* [29], Mohapatra, Mohanty and Nayak [46] and Nayak [47], it is reasonable to ensure that the investigated starches acted as a thermal barrier, hindering the movement of PLA chains and increasing the its stability in the matrix. The films needed higher temperatures for the degradation of the polyester phase, as starches act as seeds and can increase the rate of crystallization of the films, under these conditions the matrix polymers will have more difficulty, will take a longer time to organize, or that is, to crystallize.

Differently from what happened in the PLA chains, starches promoted a decrease in the enthalpy of degradation (ΔH_d) values for PBAT in all composite films, this shows that despite the nucleating effect of starch for the PBAT segments as well as for the of PLA, somehow there was favoring the diffusion of water molecules through this way in the system, probably the main responsible for this permissiveness are the carbonyl groups located near the PBAT benzene rings, facilitating this degradation event in the films.

The values of the melting and degradation temperatures of the PLA and PBAT in the blend and in the composites containing starch are similar. According to Rodrigues *et al.* [18], the gelatinization temperature of BMS is at around 60 °C and that of CS around 70 °C and their degradation temperatures are approximately 274 °C and 277 °C, respectively. Thus, since the films investigated have the same matrix and of the crystals of the starches used are similar in quality, gelatinize and melt in near temperatures, it is reasonable that the films containing starch displayed a similar thermal behavior.

3.1.3 Dynamic mechanical analysis

Table 4 lists the peak values obtained from DMA curves obtained for all systems investigated. Tan δ values were taken to represent Tg.

Table 4. DMA analysis for PLA/PBAT and PLA/PBAT/Starch films.

Films	E´ (10^9 MPa)	Tan δ	
	(94.5 ° C)	T_g	T_g
PLA / PBAT	3.68	-24.3 ° C	59.55 ° C
PLA / PBAT / BMS1	1.74	-24.3 ° C	58.15 ° C
PLA / PBAT / BMS3	3.50	-26.5 ° C	62.15 ° C
PLA / PBAT / BMS5	3.87	-28.7 ° C	59.55 ° C
PLA / PBAT / CS1	3.90	-24.3 ° C	59.55 ° C
PLA / PBAT / CS3	3.87	-23.2 ° C	59.55 ° C
PLA / PBAT / CS5	3.87	-23.2 ° C	58.15 ° C

Table 4 showed that the storage modulus of all samples decreased with increasing temperature and that all starch films, with the exception of PLA/PBAT/BMS1 and PLA/PBAT/BMS3 had E' value greater than 3.7×10^9 MPa at - 94.5 °C. This result indicates that the incorporation of 1, 3 and 5 % CS and 5 % BMS contributed to the films becoming less viscoelastic, more rigid and, consequently, more brittle. Interestingly, while the PLA/PBAT/CS1 film had the highest stiffness at all temperatures and the PLA/PBAT/BMS1 film exhibited the lowest stiffness.

Nayak [47], Arruda *et al.* [48] and Signori, Coltelli and Bronco [49] showed that the increased tenacity in films after addition of starch is due to the polar incompatibility of the polysaccharide with the biodegradable polymer matrix.

Two peaks were highlighted, both associated with the glass transitions of the polymers that make up the PLA/PBAT blend. The first peak is associated with the glass transition PBAT around - 24 ° C and the second peak, near 60 °C refers to that of PLA. Similar values were found by Signori, Coltelli and Bronco [49], Kumar, Mohanty, Nayak and Parvaiz, *et al.* [50] , Sis, Ibrahim and Yunus [51] , Weng *et al.* [52] , Díez-Pascual and Díez-Vicente [53] , Mallegni, Phuong, Coltelli, Cinelli, and Lazzeri [54] and Carbonell-Verdu *et al.* [55] when studying binary PLA/PBAT blends.

It is observed in Table 4 that 3 and 5 % addition of BMS to the led to, approximately, 9 and 18 % decreases in the glass transition temperature of the PBAT phase in the blend. By contrast, the incorporation of 3 and 5 % CS contributed to a 4.5 % increase in the glass transition temperature of PBAT in the blend, for both compositions. The glass transition temperature of PLA in PLA/PBAT films containing starch, decreased by 2.35 % in samples containing 1 and 5 % BMS and a 4.41 % increase for the film with 3 % BMS (PLA/PBAT/BMS3).

Both DMA and simultaneous TG/DSC data show that variations in the glass transition temperatures of the polymers present in the blend under study do not seem to depend on starch identity and content but rather seems to be associated with the nucleating effect of these starches and the mobility of the PLA and PBAT chains. The amounts of starch used seem to alter the mobility of the chains, but not enough to modify their thermomechanical behavior.

3.2 Mechanical properties

The average values of maximum tensile strength (σ_{max}), strain at maximum force ($\mathbf{e}_{\mathbf{max}}$), stress at break ($\sigma_{\mathbf{rup}}$), strain at break ($\epsilon_{\mathbf{rup}}$) and elastic modulus (E), obtained from the mechanical tests performed in the films are detailed in Table 5. These properties are the most commonly evaluated when studying materials for the production of packaging.

Table 5. Average values of the mechanical properties of the PLA/PBAT and PLA/PBAT/Starch films.

Films	σ (MPa)	e_{max} (%)	σ_{rup} (MPa)	ϵ_{rup} (%)	E (MPa)
PLA/PBAT	15.9 ± 1.39 ^{a}	13.93 ± 1.60 ^{a}	14.94 ± 1.49 ^{a}	21.72 ± 1.97 ^{a}	593.50 ± 52.98 ^{a}
PLA/PBAT/BM1	19.27 ± 0.99 ^{b}	7.00 ± 1.00 ^{b}	14.70 ± 1.19 ^{a}	17.98 ± 1.73 ^{a}	807.08 ± 27.03 ^{b}
PLA/PBAT/BM3	19.23 ± 1.12 ^{b}	5.08 ± 0.51 ^{c}	10.87 ± 3.79 ^{b}	28.86 ± 5.50 ^{c}	850.47 ± 44.18 ^{b}
PLA/PBAT/BM5	18.10 ± 1.70 ^{b}	5.18 ± 0.84 ^{c}	16.02 ± 1.75 ^{a}	9.47 ± 1.94 ^{d}	784.65 ± 75.67 ^{b}
PLA/PBAT/CS1	18.14 ± 0.57 ^{b}	7.00 ± 1.00 ^{b}	14.14 ± 2.54 ^{a}	18.54 ± 3.13 ^{a}	756.94 ± 25.80 ^{b}
PLA/PBAT/C3	17.47 ± 0.26 ^{a}	5.77 ± 0.81 ^{c}	15.03 ± 1.02 ^{a}	20.38 ± 3.28 ^{a}	752.68 ± 41.02 ^{b}
PLA/PBAT/CS5	19.14 ± 1.97 ^{b}	4.79 ± 0.55 ^{c}	15.35 ± 3.33 ^{a}	17.06 ± 2.78 ^{and}	817.14 ± 107.51 ^{b}

* Same letters in the same column show no significant difference between averages obtained, $^{a, b, c, d, and}$ different letters indicate significant differences between the systems, using the Tukey test ($p \leq 0.05$).

Table 5 shows that starch incorporation (BMS or CS) to the blend led to increases in tensile strength and elastic modulus of all composite films in relation to the sample without starch (PLA/PBAT). The PLA/PBAT/BMS1 film exhibits higher tensile strength and PLA/PBAT/BMS3 showed a higher elastic modulus compared to PLA/PBAT. Starches were also responsible for increasing the breaking strength values in most of the films, but not significantly ($p \leq 0.05$), with the exception of the PLA/PBAT/BMS3 film which presented a 27.34 % decrease in the value of this property in relation to the control film.

The data obtained on the maximum tensile strength and tensile strength at break for the films with starch did not follow the expected trend, i.e., a decrease with starch incorporation. It was expected that, since starches are more hydrophilic than both polymers present in the matrix, a weak interface would result and cause the final composition to have lower mechanical properties. Starch usually is used with additives such as compatibilizers and plasticizers in most polymer blends to improve adhesion between polymeric constituents [56].

Although there is a consensus that the mechanical properties that starch based films are too low for several applications, there are studies such as those by Markarian [57] , Hu [58] and Pilla, Kim, Auer, Gong and Park [59] showing several polymer blends containing starch, such as those of PLA/PBAT, have good processability and mechanical characteristics that render them useful for many applications.

The results of tensile strength illustrated in Table 5 show that by proper choice of matrix, processing conditions and starch content, it is possible to develop compatibilizer-free starch-based films with a good set of mechanical properties. All extruded films obtained herds showed tensile strength values in the range of 15–20 MPa, which is comparable to commercial oil-derived polymers used for the production of high-quality plastic films such as low-density polyethylene (PELD). According to Siegenthaler, Künkel, Skupin and Yamamoto [60], Molenveld, Van den Oever and Bos. [61] and Jeevahan and Chandrasekaran [62], although there is not a specific legislation, a conventional requirement for food packaging films is to have tensile strength of at least 3.5 MPa.

Unlike the maximum tensile strength, tensile strength at break and elastic modulus of all the films containing starches, which were slightly higher than those of the matrix, their elongation at maximum stress and elongation at break tended to be lower than those exhibited by the neat blend film, with the exception of PLA/PBAT/BMS3.

The results obtained indicated that we were able to develop starch-based films with higher elastic modulus and tensile strength than that of the matrix. The increase in tensile strength, elastic modulus and the decrease in elongation at break is certainly related to the presence of non-gelatinized grains in the matrix. The observed increase in stiffness in the composite films is in agreement with the DMA results.

It is believed that the increase in tensile strength is due to an increase in cross-links in the polymeric network, making the films more rigid [63]. The increase in bonds promotes satisfactory interfacial adhesion between the particles of starches and the PLA/PBAT blend even with differences in polarity. If the adhesion is insufficient, there is a high probability of failure arise are which can lead to the material to rupture at the interfacial region [64].

Although the two starches used were different, i.e. commercial corn starch and native starch from the mesocarp of babassu coconut, the thermal and mechanical profile of the PLA/PBAT films they were added to showed no significant differences, which suggests and the extraction method and gelatinization BMS was efficient.

According to Larotonda, Matsui, Sobral and Laurindo [65] and Shirai *et al.* [66] when the native starch gelatinization process takes place, new groups such as carbonyls and esters are introduced with structures that make it less hydrophilic, and these new groups are potentially reactive points for cross-links that promote compatibility between polymer molecules and generates stronger films.

Films based on PLA polyester are fairly brittle, but with reasonable tensile strength and high elastic modulus, while those based on PBAT have high flexibility and elongation at break, but low elastic modulus and tensile strength [67–70].

Therefore, a proper combination of these two polymers could lead to a material with a good balance between strength, modulus and flexibility. Mechanical and thermal analysis have shown that starch addition to the PLA/PBAT blend led to films with mechanical behavior closer to the mechanical performance of the PLA with high elastic modulus, high tensile strength and higher elongation at break than that of the PLA/PBAT blend alone.

4. Conclusion

This study dealt with the thermal and mechanical properties of extruded films containing 1, 3 and 5 % of commercial corn starch or native starch from babassu mesocarp aimed at packaging applications.

As for the thermal properties, the TG, DSC and DMA curves indicated for all films a system with the presence of two degradation, melting and glass transition peaks, respectively, one attributed to PLA and another to PBAT polymers constituents of the blend.

Although the starches used come from different sources analysis of TG, DSC and DMA revealed that the incorporation of these, in the films did not significantly affect the thermal profile of the PLA/PBAT blend, that is, the thermal behavior of the films did not show but it seemed to be associated with the nucleant effect of starches in the matrix and the mobility of the polymer chains that make up the blend.

Starch incorporation led to a 25 % increase in PBAT of crystallinity and an increase higher than 46 % in PLA crystallinity in all of the compounds compared to the film without starch. This explains the high values of enthalpy involved in the melting and degradation of PLA in the films containing starch.

Tensile test results indicate that all films displayed ductile behavior and that starch incorporation (BMS or CS) led to increased tensile strength, elastic modulus and strength at break and a decrease in the values of strain at maximum strength and strain at break.

The results of the thermal and mechanical properties showed that the films with starch exhibited similar behavior to the PLA phase of the PLA/PBAT blends. When comparing the effect of the two starches, it was found that the films with commercial starch suffered less thermal-mechanical alterations than the films with native babassu starch.

This research comprises the first steps in the literature in the development of polymeric films from babassu mesocarp starch by the extrusion process. There is need for further characterizations for effective applications of babassu starch in the development of biodegradable films.

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