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Thermoplastic starch films with vegetable oils of Brazilian Cerrado

Thermal characterization

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Abstract Starch is one of the most promising natural polymers to be abundant, cheap and biodegradable. To get thermoplastic starch (TPS) is necessary mechanical shake, high temperature and use of plasticizers. In this work, TPS films were prepared by casting from cassava starch and three different vegetable oils of Brazilian Cerrado as plasticizer: buriti, macauba and pequi. The materials were analyzed by TG, DSC and TMA. Thermal properties of oils depend on their chemical structures. Starch and vegetable oils are natural resources that can be used how alternative to producing materials that cause minor environmental impact.

Keywords DSC · Plasticizers · Thermoplastic starch · TG · TMA

Introduction

Biodegradable polymers from renewable resources have attracted much attention in recent years. These materials offer a possible alternative to the traditional non-biodegradable polymers, especially in short life-time application and when their recycling is difficult and/or not economical. Huge amounts of plastics produced mostly from fossil fuels, are consumed and discarded into the environment, ending up as wastes that do not degrade spontaneously. Their disposal by incineration produces large amounts of carbon dioxide, and contributes to global warming, some even releasing toxic gases [1]. For these reasons, there is an urgent need for the development of green polymeric materials.

Among the biomaterials present today in the market, those derived from renewable resources such as starch-based products are the most widespread and economic biomaterials. Starch is one of the most promising natural polymers because of its inherent biodegradability in soil and water, overwhelming abundance and possibility of production on a large scale, a low cost. It is mainly used as an enhancement and/or as blends with conventional or biodegradable synthetic polymers [2]. Today, starch is used in a variety of applications, like packaging materials and one-off plastic bags and cups.

Starch is a semicrystalline polymer and it is composed of two polymers with repeating α-D-glucopyranosyl units. These substances are amylase and amylopectin, a linear and a highly branched polysaccharide, respectively. The repeating units in amylase are linked by α (1–4) linkages. The amylopectin has an α (1–4) linked backbone and about 5% α (1–6) linked branches [3]. The thermoplastic starch (TPS) or plasticized starch is obtained after disruption and plasticization of native starch, by temperature and in presence of water and another plasticizer.

However, native starch has several disadvantages such as poor processability and solubility in common organic solvents which limit its wide applications. Modification of starch, physically or chemically, has been extensively studied. Chemical modifications of starch including esterification are efficacious methods to improve the properties of starch. Acetylated starch is a starch ester that has been extensively studied over the last two decades. In modified starch, part of hydroxyl groups in anhydroglucose units have been converted to acetyl groups. A low degree of substitution (DS) with 0.01–0.2 acetylated starch has been

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applied in many areas, such as film forming, binding, adhesion, thickening, stabilizing and texturing [4, 5].

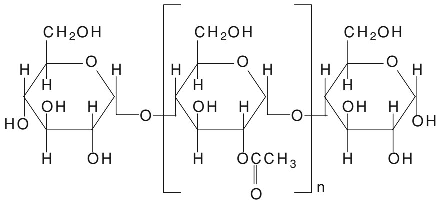
Various plasticizers have been used with starch to convert it into TPS, mainly water and glycerol. Preliminary studies [6] in the modification of starch with a derivate of fatty acid (C18:1, *Z*) have shown that the incorporation of unsaturated side chains onto the polymer has a significant impact on the plasticity of the material [7, 8]. Oils are formed by triglycerides, the most frequent lipids in nature. Brazilian Cerrado is a unique biome of the Midwest center of the country and shows an enormous variety of oil-rich vegetable species that can offer new perspectives for sustainable development of this region.

In this work, we investigated novel and natural plasticizers for acetylated starch: Buriti (*Mauritia flexuosa*), macauba (*Acrocomia aculeata)* and pequi (*Caryocar brasiliense*) oils, vegetable oils of the Brazilian Cerrado's. The Brazilian Cerrado is a biome that shows a unique variety of plant species rich in oil that offer new perspectives for sustainable development of the region. The aim of this paper is the evaluation of the thermal properties of TPS films prepared with different plasticizers by thermogravimetry (TG)/derivative thermogravimetry (DTG), differential scanning calorimetry (DSC) and thermomechanical analyses (TMA).

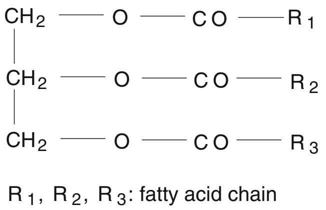
Experimental

Acetylated cassava (*Manihot esculenta Crantz*) starch (Scheme 1) was kindly provided by AVEBE, Brasil S.A. Buriti oil was supplied by Dr. S. G. C. Moreira from Universidade Federal do Pará (UFPA), Brazil. Macauba oil and Pequi oil were supplied by Cocal Brasil and Buriti Comercial Ltda., respectively. Scheme 2 shows the triglyceride chain containing three fatty acid chains joined by a glycerol center. The concentrations of some fatty acids present in oils, obtained by gas chromatography, according to the supplier, are described in Table 1.

Thermoplastic starch was obtained by mixing starch powder, water and vegetable oil (5 mass%) according to Famá et al. [9], with some modifications. The contents were mixed for 1 h to obtain a paste that was transformed into TPS by heating at 368 K in water bath with continuous stirring for 30 min. TPS films were prepared by casting the starch paste in polystyrene Petri dishes. The films were allowed to dry for at least 24 h at 325 K and vacuum (between 6.6 × 10^2 and 13.2 × 10^2 Pa). The obtained films were easily removed from the dishes.



Scheme 1 Acetylated starch structure



Scheme 2 A triglyceride molecule

Table 1 Fatty acids composition (% mass/mass) of buriti, macauba and pequi oil

Free fatty acids composition (%)					
	Palmitic (C16:0)	Stearic (C18:0)	Oleic (C18:1)	Linoleic (C18:2)	Linolenic (C18:3)
Buriti oil	17.34–19.20	2.00	73.30–78.73	2.40–3.93	2.20
Macauba oil	13.20	2.00	76.10	7.10	0.49
Pequi oil	40.20	2.30	53.90	1.50	0.70

Thermogravimetry analyses (TG) was carried out in a TGA-50/Shimadzu from room temperature to 873 K, at a heating rate of 283 K min^{-1}, under helium flow (50 mL min^{-1}). TG curves were used to determine the percentage of mass loss and decomposition temperature (T_d) of the blends was calculated by derivative thermogravimetric curves (DTG).

Differential scanning calorimetry measures were performed in a DSC-50/Shimadzu under helium flow (50 mL min^{-1}). About 6.0 mg of the samples were placed in aluminum pans, sealed and cooled with liquid nitrogen until 173 K. Then, the samples were heated at a rate of 283–473 K min^{-1}. Two scans were obtained for each sample and for the analyses the second scan's resulting curve was used. The temperature at the midpoint of the change in slope of the DSC heat-capacity change was taken as the glass transition temperatures (T_g).

Thermal mechanical analyses were carried out in a TMA-50/Shimadzu, in triplicate with heating rate of 283 K min^{-1}, from room temperature to 443 K with air atmosphere. The analyses were performed in the penetration mode with a load of 100 mN. The softening temperature (T_s) was obtained from the tangent of the first decay of the curve.

Results and discussion

Thermogravimetry analyses and DTG curves gotten for oils are showed in Fig. 1. Buriti and pequi oils presented one decomposition stage at 693 K. Thermal stability of oils depends on their chemical structures [10]. Oils with a high content of unsaturated fatty acids are less stable than the saturated ones. Macauba oil presented two stages of decomposition (523 and 683 K). This can be explained because it has about 7% of linoleic acid (C18:2, *Z*), fatty acid with two unsaturation bonds.

Figure 2 shows TG/DTG curves for acetylated starch. It can be noted basically two main thermal events. The first one is around 373 K and refers to the elimination of the water absorbed by starch. The absorption of water or moisture of the environment by starch is very high because of the hydrogen bonds formed by the hydroxyl of glucose units along its chain. The second step corresponds to the highest stage of decomposition of starch (602 K). According to Aggarwal & Dollimore [11], this step means the elimination of polihidroxilic groups, decomposition and depolymerization of the chains. Products of pyrolytic decomposition of starch and its fractions include carbon monoxide, water, volatile organic compounds and a carbonaceous residue [12].

TG and DTG curves gotten for films (Fig. 3) had presented three decomposition stages. The first step (I) cor-

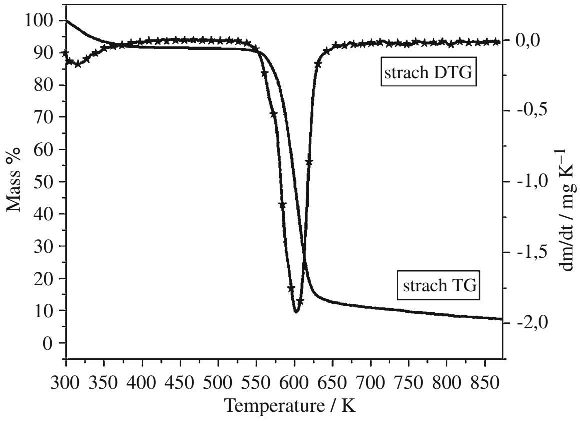


Fig. 2 TG/DTG curves for starch

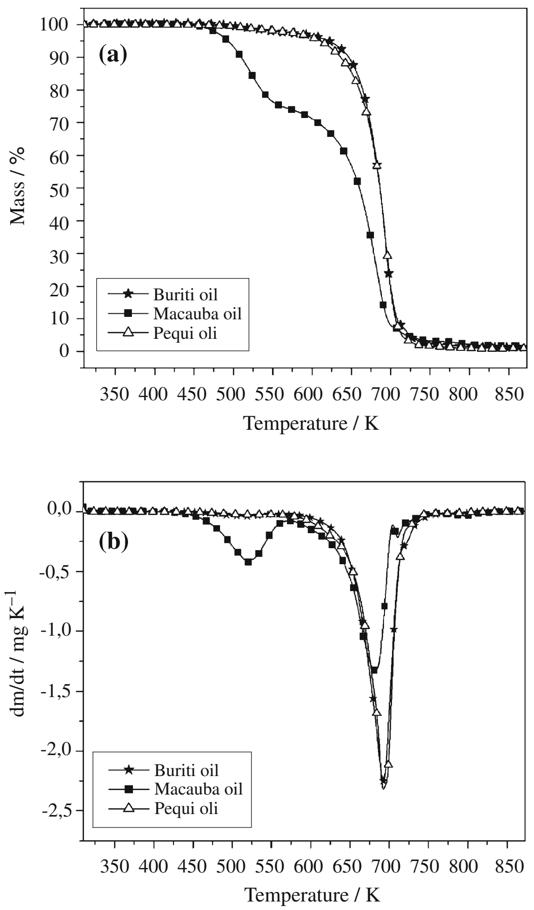


Fig. 1 **a** TG and **b** DTG curves for buriti, macauba and pequi oils

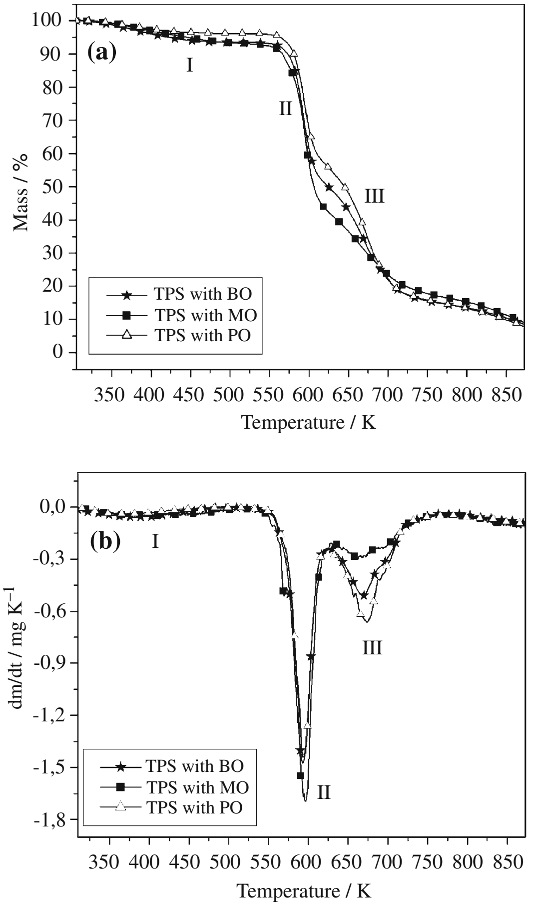


Fig. 3 **a** TG and **b** DTG curves for TPS films with buriti (BO), macauba (MO) and pequi (PO) oils

responds to the water loss. The water absorption of TPS is very high because the water molecules can easily diffuse to H-bonds with OH-groups of glucosyl units along the polymer chains [13]. The second degradation step (II) corresponds to starch decomposition. Films showed a larger proportion of mass loss in the second stage, in comparison to pure starch. The presence of oil into starch matrix may induce a re-organized starch structure with less exposed hydroxyl groups, contributing to the increase of the mass loss in the second step. The third step (III) corresponds to oil decomposition. The films presented the third decomposition step on minor temperatures in relation to pure oils. This is likely due to the weakening of intramolecular interactions in oils and appearance of weak intermolecular interactions starch–oil.

Differential scanning calorimetry is another important technique in thermal analysis. The DSC curves show exothermic and endothermic peaks. These are related to transitions or reactions that occur during analysis, such as glass transition, gelatinization, melting, oxidation and decomposition.

Unlike synthetic thermoplastic polymers, starch exists as semi-crystalline granules with complex internal supramolecular packing [14]. This packed structure gives rise to the characteristic endothermic first order transition known as gelatinization during the transformation of granular starch into TPS [15, 16]. Starch gelatinization can be generally defined as an irreversible order–disorder transition, which involves the disruption of molecular organization within the starch granules upon heating in the presence of plasticizers. To investigate gelatinization starch is generally mixed with water at a ratio of 1:3 and then submitted for analysis. Curves show only one peak of gelatinization, between 323 and 353 K (Fig. 4).

The recognition of starch as partially crystalline polymer led researchers to consider gelatinization as similar to melting process in synthetic semi-crystalline polymers, where the crystallite melting is controlled by pre-requisite plasticization (‘softening’) of the amorphous regions of the native starch granule [16].

The plasticization is a well known phenomenon to synthetic polymers. Compounds or solvents of low molecular mass, acting as external plasticizers, are an integral part of the polymeric system which acts by increasing the flexibility and malleability of the pure polymer. In the materials produced from the starch the plasticizer acting to disrupt the starch–starch hydrogen bonds (between amylopectin helices) and then form starch–plasticizer hydrogen bonds simultaneously. The diffusion and entry of the solvent in the granules is an important preliminary step before the cleavage of starch–starch hydrogen bonds happen [16].

The plasticizers used in this study were analyzed by DSC and the curves obtained are given in Fig. 5. The melting point was below 273 K for all vegetable oils studied. Moreover, buriti and pequi oils had another well defined peak in the same region. For macauba oil these two peaks seem to overlap. This second peak could mean that the melting does not occur at once. The variation of the components concentration with a single or double bonds also determines its thermal behavior. Furthermore, the oleic acid, the major component of all oils studied, shows a solid–solid phase transition, order–disorder type ($\gamma \rightarrow \alpha$) at 270.8 K. This transition of oleic acid indicates that macroscopic properties of oils can be dominated by the properties of oleic acid.

Thermoplastic starch showed almost identical behavior to that of pure oil. Interestingly, the fusion endotherms showed two distinct peaks, as well as the oils. Besides the possible explanations discussed above, some authors have

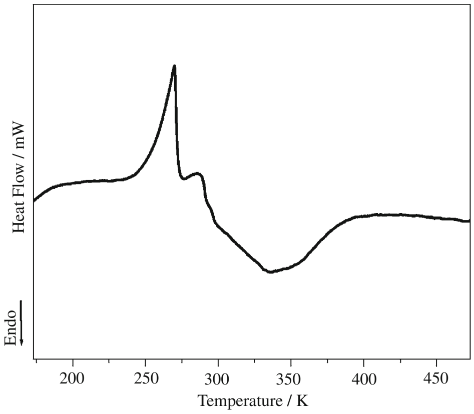


Fig. 4 DSC curve for starch

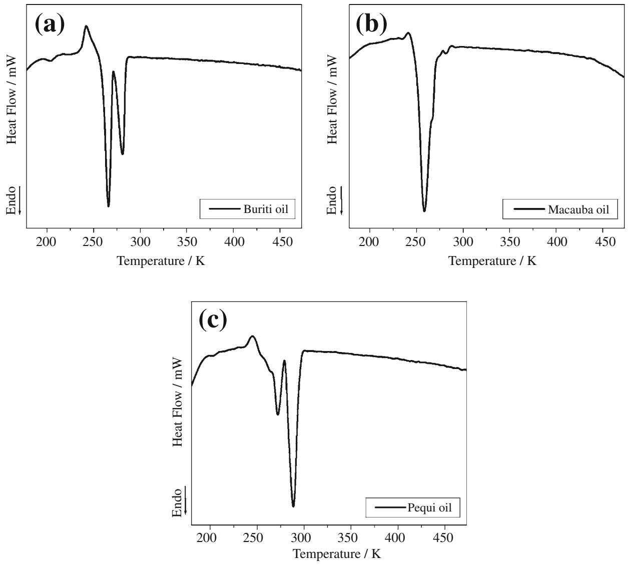


Fig. 5 DSC curves for **a** buriti, **b** macauba and **c** pequi oils

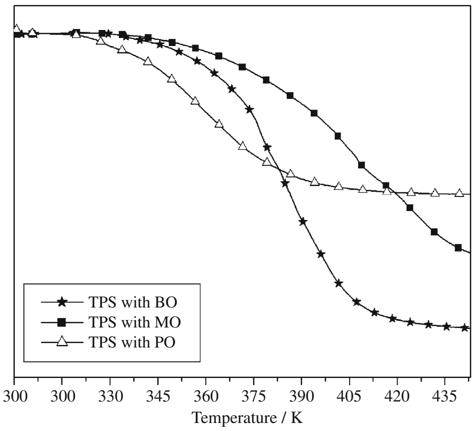


Fig. 6 TMA curves for TPS films with buriti (BO), macauba (MO) and pequi (PO) oils

reported this behavior as a result of lamellar rearrangement during crystallization: a ‘shoulder’ or peak in lower temperature is formed on the melting endotherms of original crystallites [17].

In thermal mechanical analysis, the penetration mode allows the identification of softening point (T_s) that is characterized by quartz probe penetrating material. It could be noticed changes in the mechanical properties of films as respect of resistance to the penetration. When a plasticizer is added to a polymer the intermolecular interactions reduce, so, there are more distances between the chains. Therefore, it could be an association between the T_g and T_s.

Figure 6 shows TMA curves for studied films. TPS film with macauba oil presented the greater resistance to penetration (376 K) in comparison to other oils. TPS with buriti oil was perforated at 368 K and TPS with pequi oil at 347 K. It is important to notice that plasticizer incorporation make polymeric matrix less compact and consequently more permeable. It is assumed that the saturated fatty acids have better diffusion in acetylated starch, favoring the permeability. Thus, in these conditions, pequi oil was better plasticizer for starch, due, probably, to larger amount of saturated fatty acids present in their composition (Table 1).

Conclusions

Preliminary results suggesting that vegetable oils of Brazilian Cerrado are natural resource that can be used how alternative to producing materials that cause minor environmental impact. They presented a good plasticizer effect for cassava starch, with interesting thermal properties.

Cassava starch and vegetable oils are natural, renewable and biodegradable resources. The films obtained from these precursors, were homogeneous and with good properties. Films that were analyzed by TG, DSC and TMA showed that the particular characteristics of different oils used influence the thermal stability of the films, since oils with high concentration of unsaturated fatty acids are less thermal stable. Other characterizations are being made to the properties of materials can be better evaluated.

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