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Thermal and microscopic analysis of biodegradable laminates made from cassava flour, sorbitol and poly (butylene adipate-co-terephthalate) PBAT

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ABSTRACT. Blends of biodegradable laminated materials were developed using cassava flour as starch and natural fibers source, sorbitol as a plasticizer and PBAT as a biodegradable polyester. After obtaining pellets from three different formulations, high temperature thermopressure was used to form laminates. The characterization was performed by scanning electron microscopy (SEM) and by differential scanning calorimetry (DSC). The amount of sorbitol for the best extrusion process was 15% (weight/weight) and the formulation of the best homogeneity observed by microscopy was 55:40:15 (flour/sorbitol/PBAT). Although fibers were dispersed throughout the surface in the three treatments, scattered areas of fibers could be found among them. As rates of flour increased, an increase in the melting point of the laminates occurred when compared to pure PBAT.

Keywords: starch, extrusion, thermomoulding, SEM, DSC.

Análise térmica e microscópica de laminados biodegradáveis obtidos a partir de farinha de mandioca, sorbitol e poli (butileno adipato co-tereftalato) PBAT

RESUMO. O objetivo deste trabalho foi desenvolver blendas de materiais laminados biodegradáveis, utilizando farinha de mandioca como fonte de amido e fibras naturais, sorbitol como plastificante e PBAT como componente biodegradável. Primeiro obteve-se peletes de três formulações diferentes e a partir destes, utilizou-se a termoprensagem a alta temperatura como alternativa na formação dos laminados. A caracterização foi feita através de microscopia eletrônica de varredura (MEV) e calorimetria diferencial de varredura (DSC). A quantidade se sorbitol que melhor permitiu a extrusão foi a de 15% (peso/peso); a formulação do laminado mais homogêneo, observada pela microscopia, foi de 55:15:40 (farinha/sorbitol/PBAT). As fibras ficaram dispersas por toda a superfície nos três tratamentos estudados, porém, por dentre eles, observaram-se zonas dispersas das fibras. Conforme se aumentou o teor de farinha, houve aumento no ponto de fusão dos laminados em comparação ao PBAT puro.

Palavras-chave: amido, extrusão, termoprensagem, MEV, DSC.

Introduction

Polymer materials, such as plastics, have a mean annual growth index of 10% in Brazil, which is practically unattainable by any other type of synthetic material. The easiness in the improvement and modification of their mechanical and thermal characteristics favors the inclusion of the above-mentioned materials as the most studied and the most promising in the development of new products (REIS, 2010).

Compounds from renewable sources, such as starch and vegetal fibers, have been researched to lower the costs of polymer materials and decrease their impact on the environment.

Cassava (*Manibot utilissima*) has always been salient among the main cultures in Brazil. Production has mainly concentrated on cassava flour and the rest divided between the manufacturing of human and animal meal and starch processing (CEREDA et al., 2003). Cassava flour is obtained by slightly toasting cassava root shavings, previously pealed, washed and free from cyanide, as a starch and vegetal fiber source (RUSIKE et al., 2010). Cassava flour contains approximately 98% starch at dry weight and is formed by two types of polysaccharides: amylase, featuring linear chains of glucose monomers and molecular weight between 1.5 x 10^5 and 1.0 x 10^6 g mol^{-1}, and amylopectin featuring ramified chains and molecular weight between 5.0 x 10^6 and 1.0 x 10^8 g mol^{-1} (SILVA; CABELLO, 2006).

Starch is not a true thermoplastic material. Its semi-crystalline granular structure should be destroyed so that the starch thermal-plastic (STp) characteristics may be acquired. This fact produces a homogeneous essentially amorphous polymer matrix which requires plasticizers (polyols such as sorbitol and glycerol) (MALI et al., 2010) by mechanic and thermal energy, such as in the single- or double-screw extrusion process (LOURDIN et al., 1998). On the other hand, disadvantages may be listed, namely, sensitiveness to water, time-caused changes in mechanical characteristics, crystallization due to plasticization and low mechanical resistance to traction (VAN SOEST, 1999). Several authors (AVEROUS; LE DIGABEL, 2006; CURVELO et al., 2001; MULLER et al., 2009; WOLLERDORFER; BADER, 1998) found that there is a decrease in the permeability of film water vapor as fiber rates increase.

PBAT, trademark Ecoflex®, is a biodegradable synthetic polymer produced by BASF (Germany), with a mean mol mass 6.6 x 10^5 g mol^{-1}, used in film production, reforestation tubes, plastic bags and bags for seedlings (BASF, 2008). It has also been used for starch and vegetal fiber blends (AVEROUS; LE DIGABEL, 2006). According to ASTM, films have been arbitrarily defined as plastics with a nominal thickness of 0.25 mm and thin sheets of up to 1 mm thickness. Laminates may be thus listed under the latter group.

Extrusion is a processing method used on a large scale by transformation industries to manufacture compounds as pellets, films, spaghetti, tubes. It may be associated with lamination processes or film inflation. Thermomoulding or compression moulding, perhaps the oldest and simplest method to mould plastic material, basically consists in the conformation of a thermoplastic sheet by heat (GIRONÈS et al., 2012).

Merging temperature (Mt) is the temperature when the crystalline region disappears and the rubber-like state changes into the viscous state (HA; BROECKER, 2002). Transition is macroscopically reflected by changes in thermodynamic characteristics, such as heat capacity, mechanical, di-electrical and viscoelastic characteristics. The above modifications do not occur at a specific temperature but at a temperature band (YAMAKI et al., 2002). In fact, the factor influences polymer biodegradability. The polymer with the lowest Mt is generally the most sensitive to biodegradation due to the chains' high flexibility (NIKOLIC; DJONLAGIC, 2001). The morphological analysis may provide information on the structure of the material, such as blending, porosity and other micro-structural aspects (FAMA et al., 2007) through SEM. Dominions and adhesions between polymer blend phases may be thus observed.

Current assay provides biodegradable laminates from cassava flour, PBAT and sorbitol by extrusion and thermomoulding processes.

Material and methods

Preparation of samples

Dry, fine, white type 2 cassava flour, provided by Yoki Alimentos S.A.; synthetic biodegradable polymer poly(butylene adipate-co-terephthalate) PBAT, provided by BASF (Germany), trademark Ecoflex®; sorbitol p.a. (Casa Americana) with molar mass 182.17 g mol^{-1}, were used.

Flour characteristics were carried out following instructions by Instituto Adolfo Lutz (IAL, 2008), or rather, amount of crude fiber by acid digestion followed by alkaline digestion, starch by titer with Fehling solutions of sugar reducers into glucose and non-reducing sugars into saccharose.

Extrusion and formation of pellets

A BGM EL-25 laboratory extruder, single screw with diameter 25 and 750 mm long, 5 hp motor, 4 heating areas, matrix with double wire outlet, coupled to a granulator was employed. Temperatures between the first heating area and the matrix were respectively 120, 120, 115 and 110°C, with a screw speed of 35 rpm. Sorbitol was first mixed to the cassava flour at room temperature by an ARNO kitchen mixer at a speed of approximately 780 rpm, for 5 min; polymer PBAT was added later.

Several experiments had to be performed to establish the components' percentage so that pellets could be produced. It was initially evaluated that the amount of sorbitol was the equipment's limiting factor and that 15% concentration (p p^{-1}) was the amount best adapted to the process. This was due to the fact that a homogeneous, non-brittle extruded material, proper for thermomoulding, was obtained within this percentage. The material failed either above (17 and 20%) or very below (10 and 5%) this concentration and pellets could not be produced.

When the amount of sorbitol was kept fixed and the quantity of flour and PBAT was varied, the percentages of each component could be defined. Treatments were codified F20, F40 and F60 (Table 1).

Table 1. Treatments and percentages of starch, fibers and sorbitol to obtain laminates.

Treatments	Cassava flour	PBAT	Sorbitol	Percentage after mixture
F20	20%	65%	15%	(14.42% starch; 0.63% fibers; 1.04 g sorbitol g $starch^{-1}$)
F40	40%	45%	15%	(28.8% starch; 1.27% fibers; 0.52 g sorbitol g $starch^{-1}$)
F60	60%	25%	15%	(43.2% starch; 2.54% fibers; 0.34 g sorbitol g $starch^{-1}$)

Preparation of laminates

A hydraulic monoblock press JOMAQ PHB 200, with maximum pressure 647 MPa, three electric resistance-heated plates, with maximum temperature 300°C, with two spaces at a maximum of 120 mm between them, a manometer and an electrical-electronic panel were used. The heated plates were isolated by a polytetrafluoroethylene Teflon® lining to avoid adherence of blended material and, at the same time, to allow heat transference during molding.

Further, 6.0 g of pellets and 6.89 MPa (1000 psi) pressure applied for 5 minutes, with plates at 120°C were employed for the formation of the laminates.

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry, SHIMADZU DSC-50, with aluminum capsules, temperature ranging between 0 and 200ºC, heating rate at 10ºC min.$^{-1}$, under a nitrogen flow of 50 mL min.$^{-1}$, was used. Two scannings were performed to erase thermal records and to verify blending temperature.

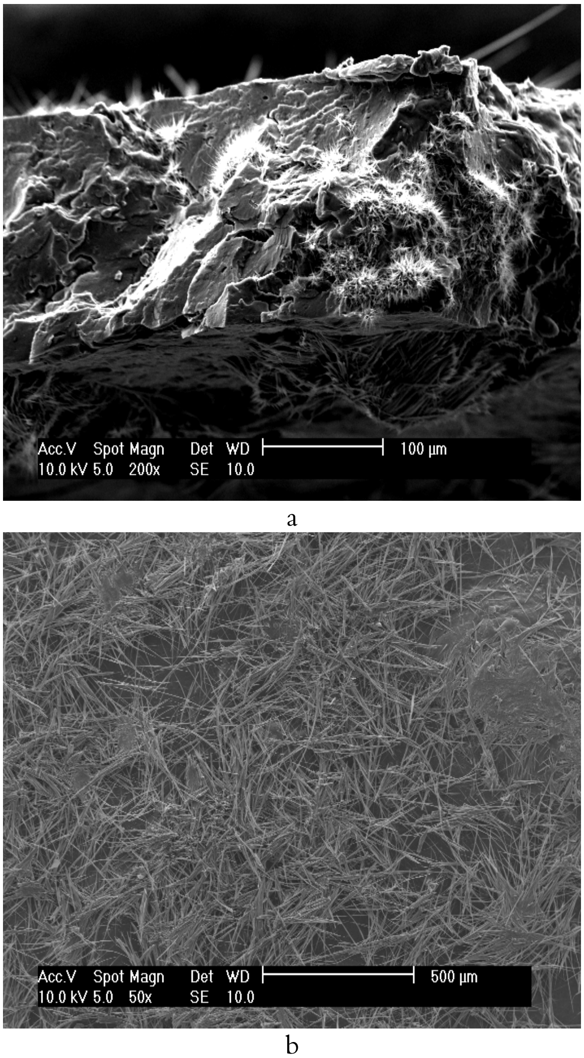
Scanning Electronic Microscopy (SEM)

Samples were immersed into liquid nitrogen and then fractured so that thickness could be observed. In the case of surface and fragments, the samples were covered with a gold layer undertaken by SCD-005 Baltec metalizer and a 10kV electron beam. Scanning microscope Phillips XL-30 was used, with tungsten electron source and secondary back-scattered electron detector.

Results and discussion

Scanning Electronic Microscopy (SEM)

The absence of integral structures of starch granules may be observed in the cryoscopy fractures of Figures 1a, 2a and 3a. This fact shows that granule de-structuring occurred during the lamination process due to the extrusion process or thermomoulding, and the formation of a blend with PBAT. In spite of the visualization of the polymers' homogeneous phase in the three treatments, wrinkles, discontinuities and empty spaces could be seen in the laminates. The homogenous distribution of fibers through surface micrography of the three treatments could be detected (Figures 1b, 2b and 3b), with several agglomerates throughout the surface. The direction parallel to the surface was induced by pressure applied on the pellets' edge during thermomoulding. The overlaying fibers showed that the polymer was blended. Since the latter was denser than the fibers (MULLER et al., 2009), it occupied the spaces between the heated plates and pushed the fibers within the pellets to the external part of the laminate. The great amount of fibers distributed over the surface of the laminate and not on its profile (micrography of fractures) could be observed. Micrographs also suggested that each agglomerated site came from the pellet unit since the fibers were more concentrated around the agglomerate. It may be deduced that fibers moved from the pellets' center to their periphery.



a

b

Figure 1. F20 treatment; micrography of fracture (a), with details of fibers inserted in the polymer matrix; surface micrography (b); details of agglomerates.

F20 and F60 laminates (Figures 1a and 3a) were more wrinkled and unequal when compared to F40 ones which were more homogeneous and compact. Fibers in this treatment (Figure 2a) were spread radially and not longitudinally and could be seen only on surface micrography. The laminate in F60 (Figure 3a) shows a more irregular structure, with greater porosity and heterogeneity, coupled to the presence of certain PBAT dispersed throughout the blend which failed to be compatible, as the arrows show. Since STp rate in this treatment was higher, viscosity was consequently greater too (AVEROUS; FRINGANT, 2001), with less flow and providing greater fiber agglomeration. The latter remained together in large quantities and less dispersed than those in F20 and F40.

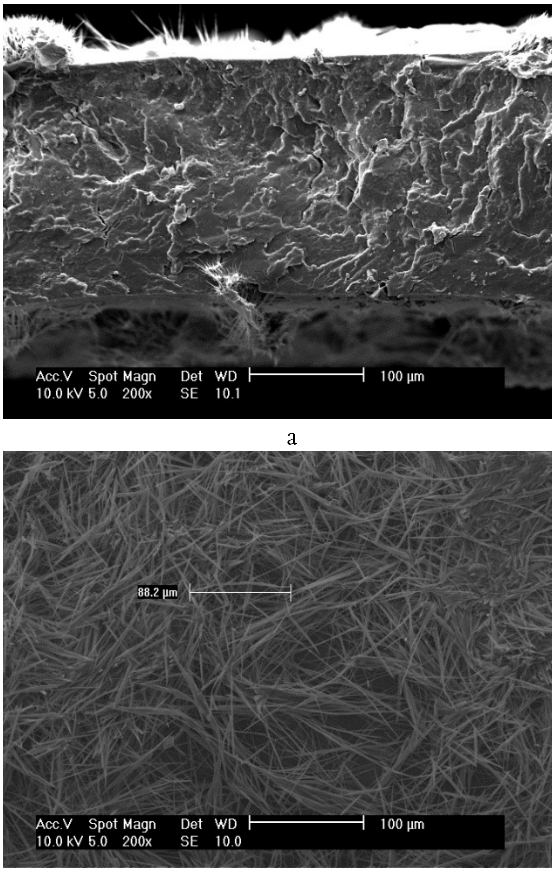


Figure 2. F40 treatment; micrography of fracture (a) and surface (b) with details of fiber size.

Laminate in F20 (Figure 1a) was also compact although a greater number of clefts and many fibers forming concentrated areas could be observed. These internal formations were not observed in F40 (Figure 2a).

Differential Scanning Calorimetry (DSC)

Since there was only one endothermal peak characteristic of blend fusion, the separate fusion of the compounds did not occur. Compatibility of compounds was registered (Figure 4), corroborated by the fracture micrographs in Figures 1a, 2a and 3a.

It may be observed that the melting temperature (Tm) increased (Table 2) in proportion to the quantity of flour added. The treatments demonstrate that when an increase in flour rate occurred, the quantity of fibers increased and sorbitol/STp ratio decreased. Abdorreza et al. (2011) reported that when sorbitol/STp in films decreased, there was an increase in the blend's melting point. The same results were obtained by Bourmaud and Baley (2007) with sisal fibers and PP. Using PBAT and lignocelluloses fibers, Averous and Le Digabel (2006) found that the trend in increase melting point might be due to molecular interactivity between the fiber hydroxyl groups and the carbonilla groups of the PBAT ester.

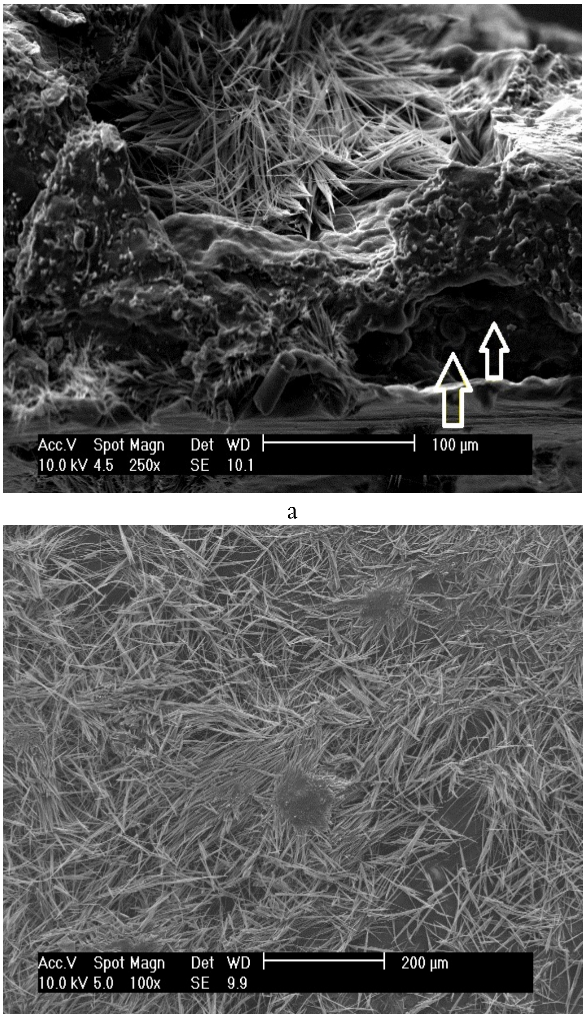


Figure 3. F60 treatment; micrography of fracture (a) showing some PBAT in the blend; surface micrography (b).

These hydrogen bonds probably decreased the polymer's mobility with greater energy for its melting point. A set of factors may be observed, namely, an increase in STp quantity, decrease in the sorbitol/STp ratio and an interactivity of the fibers with PBAT, which increased the blend's melting point.

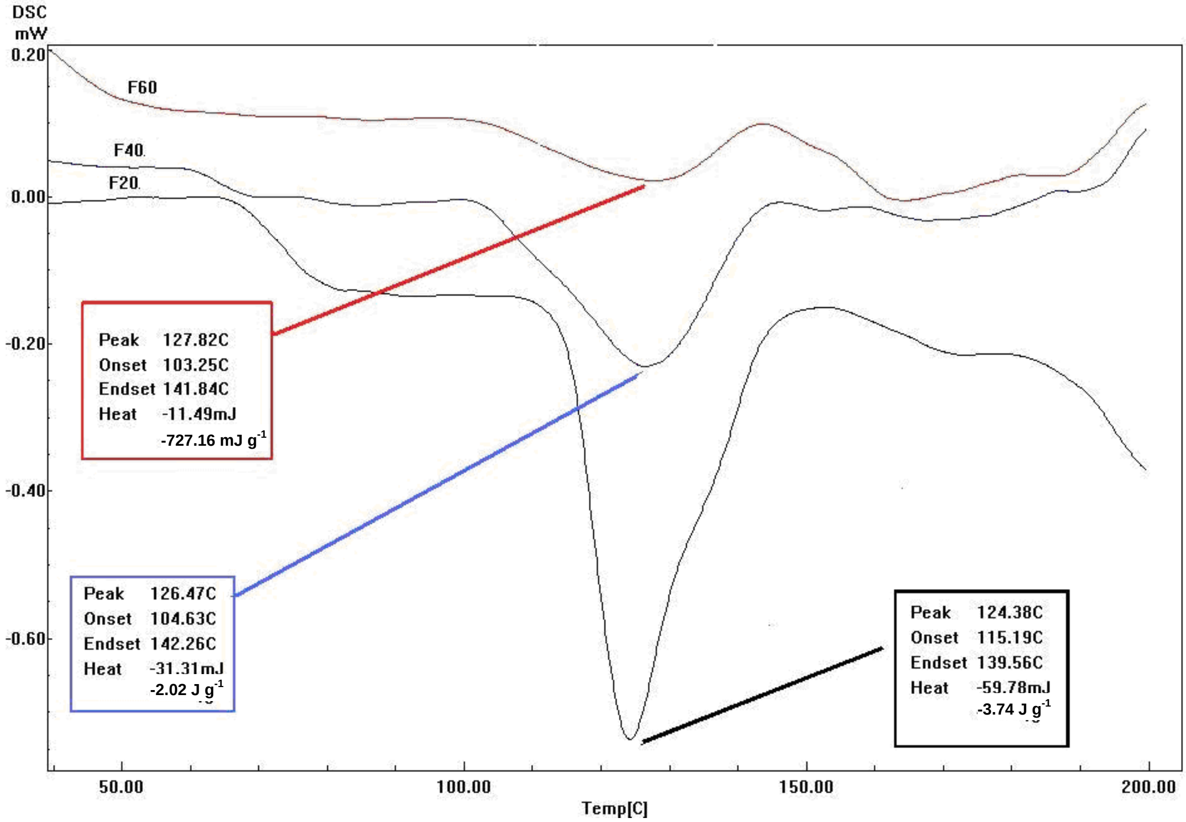


Figure 4. DSC curves of laminates F60, F40 and F20.

Table 2. Melting temperatures (Mt) and melting heat (ΔHf) of laminates.

Treatment	Mt of laminate (°C)	ΔH_f (J g^{-1})
F20	124.38	3.74
F40	126.47	2.02
F60	127.82	0.72

Conclusion

Cassava flour is a good alternative for prime matter in processes that involve high temperatures and pressure such as extrusion and thermomoulding. A blend was obtained by the homogeneous mixture of two different polymer species.

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