

Influence of Carnauba Wax on Films of Poly (Butylene Adipate Co-Terephthalate) and Sugarcane Residue for Application in Soil Cover (Mulching)

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The population increase, urbanization and climatic change adversely affect the agricultural production have prompted actions to improve the means of production without affecting the environment. One of the actions to make the production of food more efficient and sustainable is the use of plastics in protection of crops, soils and packaging, for example. Therefore, the aim of this work was to develop flat extruded mulch films of poly (butylene adipate-co-terephthalate)/2.5 and 5.0% sugar cane residue/2.0% carnauba wax for application in soil cover and characterize them as to their chemical structure, morphology and transmittance. The FTIR results suggest that there was no chemical interaction between the components of the mulch films. SEM images and optical microscopy showed that the polymer matrix was able to cover sugarcane residues and that the carnauba wax dispersed well in the PBAT matrix. In addition, carnauba wax addition increased the transmittance of these mulch films.

Keywords: Biodegradable polymers, plasticulture, composite, transmittance.

1. Introduction

According to the Association of Plastics Manufacturers in Europe, the world production of plastics in 2016 was 335 million tons, and 3.3 % of these plastics made in Europe are destined to plasticulture. The plastics used in this sector are used for energy conservation, water management, grain storage and protection of crops and soils, either by their application in drip irrigation tapes, silage bags, tunnel of low and high forced cultivation or ground cover films (mulch films)^{1,2}.

Soil covering (mulching) may be performed with organic materials such as agricultural residues, animal waste (manure), industrial waste (sawdust) or inorganic materials including artificially obtained materials such as films of synthetic polymers and some bio and photodegradable polymer films³. Mulching is a method used to manipulate cultivation environment that increases crop yields and improves product quality by controlling soil temperature and humidity, as well as weed growth.

Polyethylene (PE) is among the most used synthetic polymers in mulching applications. When applied to the cultivation crops, PE helps to increase root growth resulting in better nutrient uptake before plant maturation, which results in higher fruit yield, better fruit quality, and a lower incidence of viral diseases^{1,2}.

However, waste plastics used in soil cover can accumulate in the field and cause serious agronomic and environmental problems, since mulch film residues can block the transfer of water, nutrients and heat and thus decrease soil quality and reduce crop production⁴. Briassoulis et al.⁵ when analyzing the long-term degradation behavior of PE mulch films with pro-oxidant, under real conditions of biodegradation in the soil for a period of 8.5 years, observed that the films showed no signs of disintegration and were recovered almost intact.

The recovery of non-degradable plastic films after the end of the harvest period, requires time, labor, and is economically expensive. Consequently, the use of biodegradable polymers rises as a sustainable alternative to reduce the costs for mulching applications. Poly (butylene adipate co-terephthalate) (PBAT) is one of the biodegradable matrices that have been used as the basis for producing mulch films to replace conventional plastics such as PE. Bilck et al.⁶ developed black and white films of PBAT/thermoplastic starch blends for use as a mulching film in strawberry cultivation. They observed growth of weeds in the soil covered with white films and that, after 8 weeks in the soil, all the films became brittle, showing an increase in elastic modulus and a decrease in maximum tensile strength and elongation at break. Touchaleaume et al.⁷ evaluated four commercial biodegradable PBAT films to replace PE in mulching applications.

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The authors observed that the mechanical performance of the films decreased after five months of testing, but the films still allowed a good fruit production during the cultivation, even when compared those covered with polyethylene films.

Another alternative used to make agricultural practices more sustainable is the development of mulch film reinforced with natural fillers. The advantages of this type of filler are the low cost, biodegradability, low abrasiveness for the thermoplastic processing equipment, besides being non-toxic. Among the natural fillers used, lignocellulosics are those derived from wood or plants and are mainly composed of cellulose, hemicellulose, and lignin.

The literature reports work that have succeeded in incorporating lignocellulosic fillers into the PBAT matrix. Pinheiro et al.⁸ produced a PBAT biocomposite reinforced with Munguba fiber (*Pachira aquatica*); the authors showed that the addition of the fiber promoted an increase in the crystallization temperature of PBAT, indicating that the fiber acted as a nucleating agent for this matrix, as well as an increase of the modulus of elasticity of the biocomposites. Wu⁹ evaluated the biodegradability, mechanical properties and morphology of PBAT biocomposites reinforced with peanut bark. He found that composites containing PBAT grafted with maleic anhydride exhibited better mechanical properties as maleic anhydride not only improved the compatibility between the components of the biocomposites but also aided the dispersion of the filler in the matrix. In addition, after 60 days of biodegradation, the composite films presented erosion and cracks in their structure.

Although, the literature on composite PBAT films with natural fibers is very scarce on, some work was found on the incorporation of natural fibers in biodegradable films. Finkenstadt and Tisserat¹⁰, prepared a composite of PLA containing 10 and 25% of Osage Orange (OO) wood fiber (*Maclura pomifera*) with different granulometry, for application as mulch films. The composites were first processed in an industrial mixer and then in a single screw extruder with four heating zones. The authors stated that PLA / OO composites can be used as agricultural cover films with several advantages over existing products, including biodegradability, growth promotion and controlled release of organic compounds. Ludueña, Vázquez and Alvarez¹¹ produced composites based on polycaprolactone with 5 and 15 wt% of cotton (CO); cellulose (CE) and hydrolyzed-cellulose (HCE). An intensive mixer was used to incorporate the lignocellulosic filler into the polymer matrix, and after mixing, samples were compression molded in a hydraulic press. The authors reported weak interfacial interaction, demonstrated by fiber displacement during fracture, when evaluating the fracture surface of the composites.

The residue generated during the production of sugarcane is an excellent alternative among lignocellulosic fillers for manufacturing of biocomposites. According to the National Supply Company¹², Brazil is the world's largest producer of sugarcane with an estimated production during the 2016/17 crop of 73.27 kg/ha. Some studies have reported the use of these residues to reinforce thermoplastic polymers.

Agunsoye and Aigbodion¹³ produced recycled PE composites reinforced with sugarcane bagasse by compression molding and reported a uniform distribution of the bagasse particles in the PE matrix and an increase in the tensile strength and the flexural strength of the composites. Paula et al.¹⁴ evaluated the thermal behavior of polypropylene (PP) and sugarcane bagasse composites with and without alkaline treatment. The results indicated that the alkaline treatment improved the thermal stability of the composites.

One of the difficulties for the development of mulch films with biocomposites reinforced with natural fillers is the hydrophilic character of these raw materials, since the soil moisture conservation capacity is a determining property to indicate the efficiency of mulch films¹⁵.

Thus, in this work, carnauba wax was used as additive to reduce the water vapor permeability of polymeric films. Rodrigues et al.¹⁶ prepared composites from cassava starch, cashew tree gum, and carnauba wax and reported that carnauba wax promotes a decrease in the water vapor permeability of the composites. Chiumarelli and Hubinger¹⁷ produced edible films for food coating and the results showed that the formulation containing 3% cassava starch, 1.5% glycerol 0.2% carnauba wax and 0.8% stearic acid has better moisture barrier and gas exchange (CO₂ and O₂) properties.

Therefore, in order further improve the quality of the PBAT films in soil coverages, in this work, carnauba wax was used as a waterproofing agent.

The aim of this work is to develop PBAT films containing carnauba wax and sugarcane residue for mulching applications and to characterize and investigate possible chemical interactions between the components of the biocomposites.

2. Experimental

2.1 Materials

The polymer matrix used for the production of mulch films was poly(butylene adipate-co-terephthalate) – PBAT – trade name Ecoflex® F Blend C1200, produced by BASF (Germany), with melting point range of 110-120 °C and melt flow index of 2.7-4.9 g.10⁻¹ min (190 °C, 2.16 Kg - ISO 1133).

The sugar cane residue (SR) used as filler was donated by COMVAP and the Type 1 carnauba wax (CW) was donated by Salustiano wax factory. According to the manufacturer, the melting temperature range of the carnauba wax was 82-86 °C and its moisture content was 0.5%.

3. Methods

The sugar cane residue was dried in an oven at 60 °C for 24 hours before being shredded and sieved through 100 mesh. According to the treatment carried out on the sugar cane bagasse, the powder was characterized by optical microscopy and scanning electron microscopy, and it was verified that the mean particle size was reported in the range of 0.2-0.4 mm.

Prior to extrusion, the polymer matrix and the shredded and sieved residue were dried in an oven at 60 °C for 4 and 21 hours, respectively. The moisture content of the sugarcane residue after drying was 2%. First, different contents of the additives were incorporated into the polymeric matrix (as described in Table 1) and the mixtures were single screw extruded in an AX Plásticos Lab 16 model extruder, operating with a temperature profile of 140 °C, 145 °C and 145 °C, and screw speed of 50 rpm. The extruded material was chilled, pelletized and dried according to the conditions described in Table 2. The drying times after the first extrusion were determined experimentally so as to allow pelletization of the material.

Table 1. Compositions of PBAT, sugar cane residue and carnauba wax used for producing biodegradable mulch films.

Samples	PBAT (%)	RC (%)	CC (%)*
pure PBAT	100	0.0	0.0
PBAT/SR - 2.5	97.5	2.5	0.0
PBAT/SR - 5.0	95	5.0	0.0
PBAT/SR/CW - 2.5	97.5	2.5	2.0
PBAT/SR/CW - 5.0	95	5.0	2.0

Table 2. Drying conditions after the first extrusion step.

Samples	Time (h) (60°C)
pure PBAT	24:00
PBAT/SR - 2.5	24:00
PBAT/SR - 5.0	05:00
PBAT/SR/CW - 2.5	02:40
PBAT/SR/CW - 5.0	02:40

The extruded materials described above were then used to prepare mulch films in an AX Plásticos Lab 16 model single screw extruder fitted with a 220mm wide flat film die, operating with a temperature profile of 145 °C, 155 °C and 160 °C, and screw speed of 46 rpm. The gear pumps had their rolls speed individually (Table 3) defined for each composition to ensure mulch films with homogeneous thicknesses (approx. 300 µm).

Table 3. Speed of the cooling rollers, puller and winder.

Samples	Roll 1 (rpm)	Roll 2 (rpm)	Puller (rpm)	Winder (rpm)
pure PBAT	0.12	0.12	0.15	0.15
PBAT/SR - 2.5	0.14	0.14	0.19	0.19
PBAT/SR - 5.0	0.15	0.15	0.19	0.18
PBAT/SR/CW - 2.5	0.12	0.12	0.16	0.24
PBAT/SR/CW - 5.0	0.12	0.12	0.17	0.21

4. Characterization of Carnauba Wax, Sugarcane Residue, and Mulch Films

Fourier-Transform Infrared Spectroscopy of the sugarcane residue, carnauba wax and mulching films.

Fourier-Transform Infrared Spectroscopy was used to detect possible changes in the chemical structure of mulch films before and after their application in soil. The analysis was performed on a Bruker Vertex 70v apparatus operating in the wavelength range of 4000-400 cm⁻¹.

Scanning Electron Microscopy – SEM

The surface morphology of cryogenically fractured mulch films was analyzed by scanning electron microscopy, on a FEI, Quanta FEG 250 microscope, with accelerating voltage of 10 kV. The samples were coated in gold in a Quorum, Q150R coater, for 30s, at 20 mA, and plasma generated in argon atmosphere.

As a complementary technique, optical microscopy (OM) was used to evaluate the morphology of the sugarcane residue and surface of the mulch films. The images were captured with a Leica Microsystems, model MD500 optical microscope operating in reflection mode and the images captured with an ICC50E camera.

UV-Vis Spectroscopy

Transmittance (T%) of a film is defined as the total percentage of light transmitted through the material and can be calculated according to Beer's law, by Equation 1¹⁸:

$$T\% = \left(\frac{I}{I_0}\right) \times 100\% \quad \text{Eq. (1)}$$

Where I corresponds to the transmitted light intensity and I_0 is the incident light intensity. The percentage of light transmittance was attained as per Kijchavengkul et al.¹⁹ by using a Cary 60 – UV-Vis spectrophotometer, Agilent Technologies. For each composition, three 300µm samples were analyzed within the 800-400 cm⁻¹ range.

5. Results and Discussion

Fourier-Transform Infrared Spectroscopy of the sugarcane residue, carnauba wax and mulching films.

The sugarcane residue and the carnauba wax were analyzed by infrared spectroscopy and the corresponding spectra are shown in Figure 1.

The chemical components of sugarcane residue are like those found in the cellular wall of other plants. Among these components are cellulose, lignin, hemicellulose, extractives and ash²⁰. Cellulose is a polysaccharide composed of a crystalline polymer with a regular structure, whose repeating unit is glucose, while hemicellulose is a polysaccharide formed by short branched chains containing pentoses and hexoses.

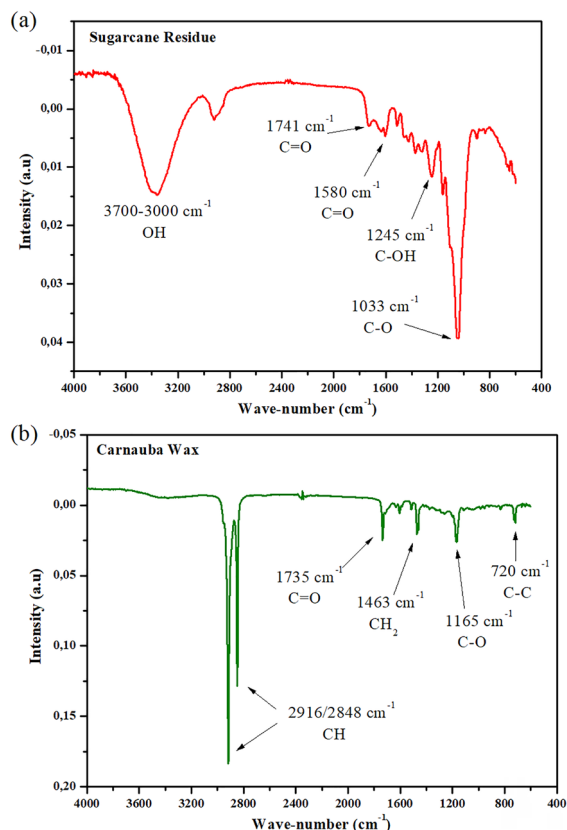


Figure 1. FTIR spectra in the range of 4000-400 cm^{-1} for (a) sugarcane residue and (b) carnauba wax. (colored in the online version)

Lignin is an amorphous resin composed of phenylpropane, the basic unit of the three major lignin precursors, which fills the void space between the polysaccharide fibers¹⁶. The typical functional groups of cellulose, hemicellulose, and lignin are acid, ester, benzene ring, ketone and alcohol²¹.

Figure 1 (a) shows the sugarcane residue spectrum with a broadband at 3700-3000 cm^{-1} associated with the stretching vibration of hydroxyls present in acids and alcohols. The bands at 1741 cm^{-1} and 1580 cm^{-1} correspond to the stretching vibrations of carbonyls present in the esters and ketones and the band at the region of 1245 cm^{-1} can be attributed to the stretching vibration of hydroxyl-bound carbon, while the band at 1033 cm^{-1} corresponds to the vibrational stretches of the CO binding of hemicellulose and lignin^{21,22}. Similar spectra to those found in this work were reported by Zhao, Jiang and Chen²¹ when evaluating the chemical structure of cellulose, hemicellulose, and lignin, also by Simão et al.²² studying the sugarcane residue.

Fei and Wang²³ when describing the composition of carnauba wax reported that it consists of 84% aliphatic and aromatic esters, 3% free fatty acids, 3% free fatty alcohols, 2% hydrocarbons, and 4% resins. The bands of the major functional groups of carnauba wax are identified in Figure 1 (b):

the intense absorption band at 1735 cm^{-1} corresponds to the stretching vibration of the carbonyls present in the esters, at 1165 cm^{-1} the CO bond stretching vibration, the 2848 cm^{-1} and 2916 cm^{-1} vibrations refer to the symmetrical and asymmetrical stretching of carbon-hydrogen bonds, respectively, the absorption at 1463 cm^{-1} corresponds to the stretching vibration attributed to the CH_2 bond and 720 cm^{-1} refers to the stretching vibration of the carbon-carbon bond.

The spectra of the pure PBAT, mulching films and the PBAT band amplification are presented in Figure 2, while Table 4 shows a summary of the wavenumbers and functional groups found in the PBAT spectra, sugarcane residue and carnauba wax.

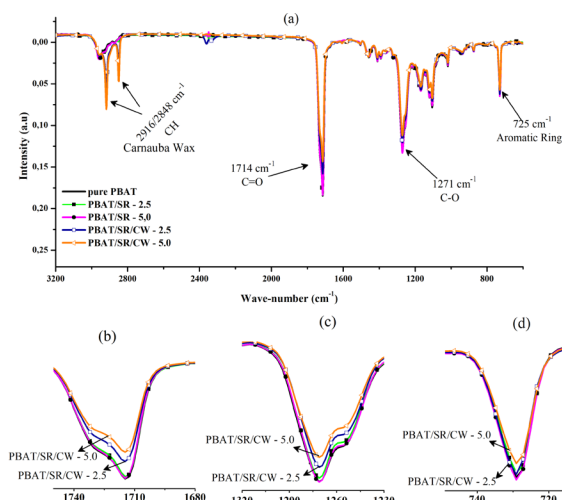


Figure 2. FTIR spectra in the 3200-800 cm^{-1} range of pure PBAT and mulch films (a) and PBAT bands amplifications in (b) 1714 cm^{-1} , (c) 1271 cm^{-1} and (d) 725 cm^{-1} , respectively. (colored in the online version)

Table 4. Wave number and functional groups of PBAT, sugarcane residue, and carnauba wax.

Wave number (cm^{-1})	functional groups
PBAT	
1714	C=O
1271	C-O
725	Aromatic Ring
sugarcane residue	
3700-3000	OH (acids and alcohols)
1741 e 1580	C=O (esters and ketones)
1245	C-OH
carnauba wax	
1735	C=O (esters)
2848 e 2916	C-H
1463	CH_2
1165	C-O
720	C-C

The major PBAT bands identified were the ones corresponding to the stretching vibration absorption of the carbonyl in the ester group located in the 1714 cm^{-1} region; to the stretching vibration of the CO bond directly related to the carbonyl at 1271 cm^{-1} and the band at 725 cm^{-1} is attributed to the out-of-plane deformation of the aromatic ring²⁴.

There were no significant changes on spectra of the mulching films with 2.5 and 5.0% of sugarcane residue without carnauba wax, shown Figure 2, compared to the pure PBAT spectrum. These results indicate there was no chemical interaction between the sugarcane residue and PBAT, probably due to the hydrophilic feature of the residue being incompatible with the PBAT matrix that is hydrophobic.

Wu⁹ evaluated the infrared and the nuclear magnetic resonance spectra of PBAT and PBAT and grafted maleic anhydride (PBAT-g-MA) composites containing 20% peanut shells. They showed that maleic anhydride addition rendered the polymer matrix more hydrophilic and that a condensation reaction between the maleic anhydride and the hydroxyl groups present in the filler took place and led to chemical interactions between the PBAT-g-MA and the peanut shell. This interaction was absent in the composites made with the non-compatibilized matrix (neat PBAT/peanut shell system).

In the present work, the spectra of the mulching films that have the carnauba wax in their composition, besides the feature PBAT bands²⁵, showed bands at 2916 and 2848 cm^{-1} associated to the symmetrical and asymmetrical stretching vibrations of carbon-hydrogen bonds present in the carnauba wax²⁴.

The presence of bands associated with carnauba wax in the mulching films spectra indicates that carnauba wax was not deteriorated during film processing. These results corroborate with the results of the thermogravimetric analyzes, which are not presented in this paper. These analyzes showed that carnauba wax is thermally stable up to temperatures close to $290\text{ }^{\circ}\text{C}$.

Furthermore, in Figure 2 (b-d) it can be observed that although the addition of carnauba wax to the systems did not lead to displacement of PBAT bands, it nevertheless, caused a decrease in the band regions at 1271 cm^{-1} , corresponding to the carbon-oxygen bond stretching vibration, and at 1714 cm^{-1} related to the carbonyl stretching vibration of the ester group. The decrease in these bands is higher for the biocomposite with 5.0% of sugarcane residue. The unchanged positions of the PBAT bands indicated that there was no chemical interaction between the polymer and the wax, while the decrease in the intensity of all feature PBAT bands are attributed to the decreased polymer concentration in the composite systems.

Optical micrographs and scanning electron micrographs of mulch films Figure 3 and 4 show, respectively, optical and scanning electron micrographs of the surfaces of the pure PBAT and of PBAT/SR - 2.5 and PBAT/SR - 5.0 films. The fracture surfaces of pure PBAT and mulching films with 2.5% and 5.0% of sugarcane residue are observed by scanning electron microscopy in Figure 5.

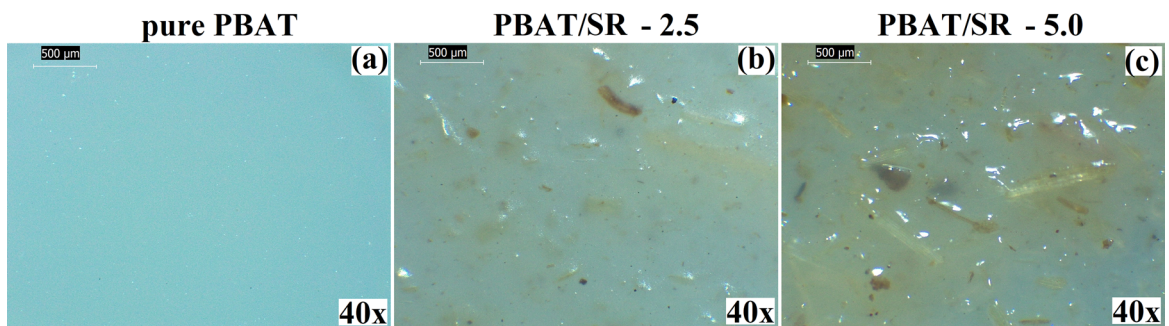


Figure 3. Optical microscopy of the surface: a) pure PBAT and PBAT/SR mulch films without carnauba wax; b) 2.5% SR and c) with 5.0% SR. (colored in the online version)

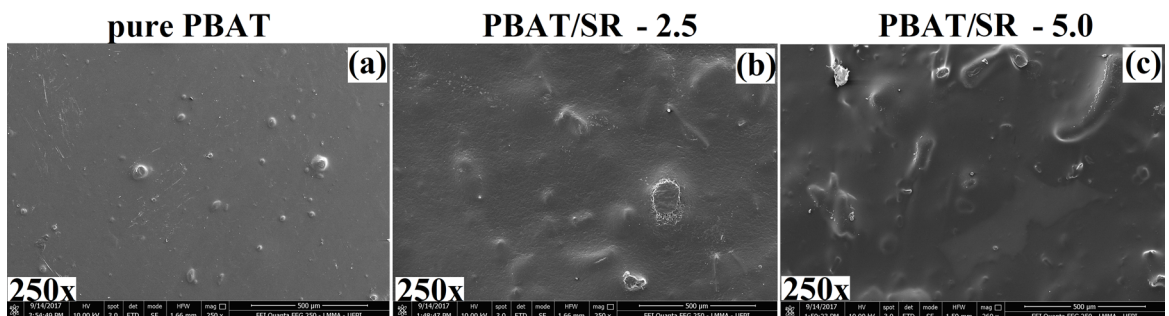


Figure 4. Scanning electron microscopy of the surface: a) pure PBAT and PBAT/SR mulch films without carnauba wax; b) 2.5% and c) with 5.0%. (colored in the online version)

Figure 3 (a) and 4 (a) show, respectively, the OM and SEM images, of the surface of the PBAT film where a smooth and compact appearance is observed. The fracture surface of the same (PBAT) film is shown in Figure 5 (a). It appears homogeneous, with a continuous phase. In addition, regions of plastic deformation, characteristic of ductile fracture (indicated by dashed arrows) are observed.

Optical and Scanning electron microscopy surface images of mulch films containing 2.5% SR are displayed in Figures 3(b) and 4(b) and of those containing 5% SR are shown in Figures 3(c) and 4(c), respectively. The images show that, for both compositions, the sugarcane particles and fibers were coated by the polymer matrix, and that a uniform distribution of the residue in the PBAT matrix was achieved. Filler agglomerates were not detected, indicating that the two-stage processing adopted (extrusion followed by flat film extrusion) was efficient. Figures 4 (b) and (c), show that surface rugosity of the films increased with residue content.

Figure 5 (b) and (c) shows micrographs of the fracture surfaces of mulching films with 2.5% and 5.0% of residue, respectively. It shows that the particles and fibers of the residue were not plucked or peeled off from the polymer matrix and, even though the discontinuous fiber/matrix interface may indicate lack of chemical interaction between the composite components⁹, the presence of PBAT in the residue cavities indicates that there was a mechanical interaction between the system components.

These results differ from those reported in the literature. Studies show that polymer composites reinforced with lignocellulosic fibers usually have low wettability, which causes displacement and fiber extraction during crack propagation, and sometimes it is necessary to use coupling agents or modifications on the filler surfaces or matrices to improve the interface quality of the composites^{9,26}. Ludueña et al.¹¹ when evaluating the fracture surface of the PCL film and lignocellulosic filler, reported weak interfacial interaction demonstrated by fiber displacement during the fracture.

The differences between the results obtained in this work and the ones found in the literature may be associated to the differences in processing as, in order to obtain the mulching films, the composite components were extruded two times (one to mix the components and the other to obtain the films). This double processing may have promoted better filler dispersion and mechanical coupling between the two surfaces, thus filling surface irregularities by the polymer resin favored by the shear stress along the extrusion²⁷.

Figures 6 (a) and 7 (a) show, respectively, the optical and scanning electron micrographs of the surfaces of carnauba wax containing mulching film with 2.5% of sugarcane residue. Similarly, the OM and SEM images of the mulching film with 5.0% sugarcane with carnauba wax are shown in Figure 6 (b) and 7 (b), respectively. The images show that the rugosity of films containing wax was decreased when compared to that of PBAT/SR - 2.5 and PBAT/SR - 5.0 mulching films.

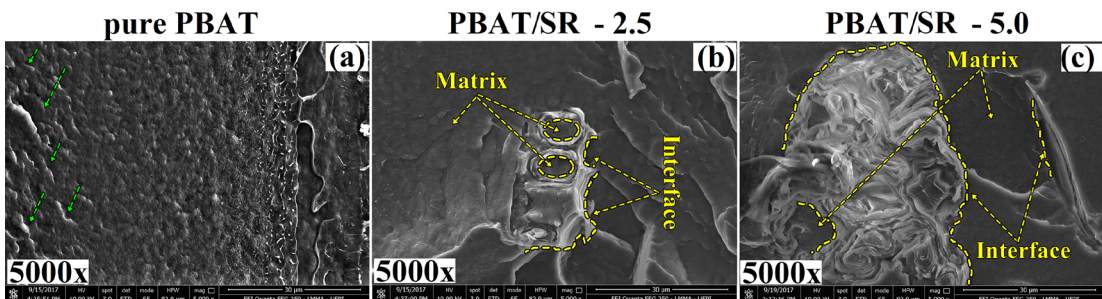


Figure 5. Scanning electron microscopy of fractured surface: a) pure PBAT and PBAT/SR mulch films without carnauba wax; b) 2.5% and c) with 5.0%. (colored in the online version)

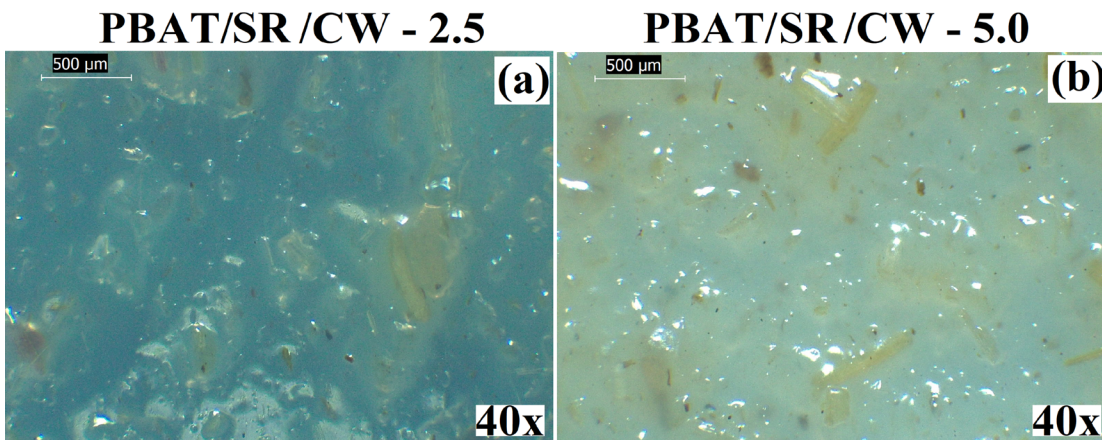


Figure 6. Optical microscopy of the surface: a) PBAT/SR/CW - 2.5 mulch films and b) PBAT/SR/CW - 5.0. (colored in the online version)

PBAT/SR/CW - 2.5

PBAT/SR/CW - 5.0

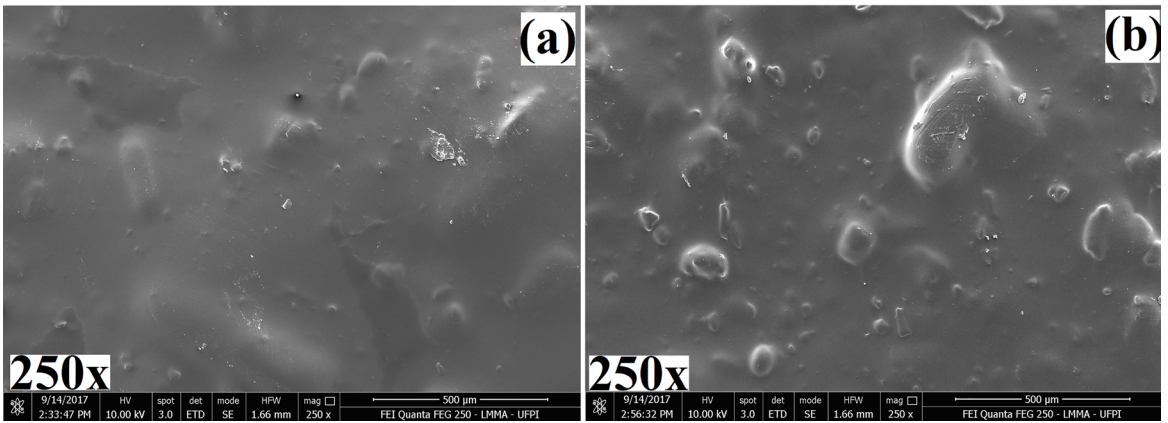


Figure 7. Scanning electron microscopy of fractured surface: a) PBAT/SR/CW - 2.5 and b) with PBAT/SR/CW-5.0. (colored in the online version)

Moreover, the transparency of the wax containing mulching films with 2.5% loading increased compared to the equivalent mulch film without carnauba wax. The opposite effect was observed for the composites with 5.0% of residue.

Figures 8 and 9 show, respectively, the fracture surface images of the mulching films with 2.5% and 5.0% of sugarcane residue in the presence of carnauba wax. These images showed the occurrence of a third phase corresponding to carnauba wax (yellow arrows), a phase rich in fatty acids distributed in the PBAT matrix²³. The images of the carnauba wax phase are in agreement with those reported by Fabra et al.²⁸ and Jiminez et al.²⁹. These authors analyzed the effect of fatty acids and beeswax on the composition of polymeric films and observed that the fatty acids crystallize in successive layers where the hydrocarbon layers are oriented parallel. Figure 8 also shows that the wax particles have smaller sizes with good distribution and no formation of agglomerates in the composition with 2.5% sugarcane residue.



Figure 8. Scanning electron microscopy of the fracture surface of PBAT/SR/CW - 2.5, with a magnification of 5000x. (colored in the online version)

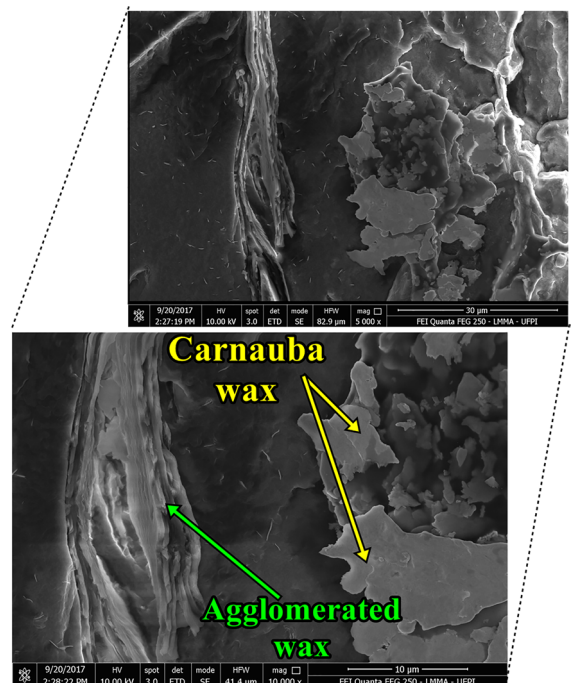


Figure 9. Scanning electron microscopy of the fracture surface of PBAT/SR/CW - 5.0 with a magnification of 10000x (colored in the online version)

However, for the composition with 5.0% of sugarcane residue, the size of the wax particles increases, and wax agglomerates are observed, as shown in Figure 9.

Mulching films transmittance - UV-Vis Spectroscopy Radiation in the range of 400-700 nm is required for photosynthesis and hence for the basic process that controls agricultural production. In addition, the light transmission capacity of the films interferes in the germination and growth stages of invasive plants seeds, and mulching films that allow transmission of light do not prevent the growth of weeds.

Thus, it is necessary to evaluate the films regarding the transmission of light^{15,30}. The UV-vis spectra of the pure PBAT and of the mulching films are shown in Figure 10. The UV-vis spectrum of a commercial mulching film was added for comparison.

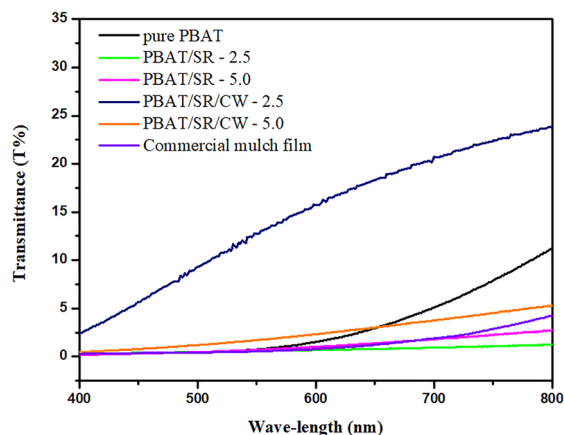


Figure 10. Percentage of light transmitted by pure PBAT and mulch films. (colored in the online version)

Pure PBAT, despite having a greater thickness (~300 μm) than commercial mulching film (25 μm), presented a higher transmittance. This result may influence both soil temperature variation and weed growth during the use of mulching films in the soil.

The pure PBAT film showed a transmittance of up to 11% in the visible region of the spectrum (400–800 nm) and this result is probably associated with the semi-crystalline nature of this material, since light scattering occurs at the boundaries between the crystalline regions and the amorphous due to different refractive indices of the two phases³¹.

The incorporation of the sugarcane residue in the polymer matrix decreased the composites transmittance to 2.74% and 1.22% for the mulching films with 5.0% and 2.5% of residue, respectively, indicating that the vegetable residue works as a light barrier in composites. Transmission reduction with residue incorporation is also associated with light scattering, which will spread through the irregularities of the surface. Similar results were found by Balakrishnan et al.³² by studying the optical properties of thermoplastic starch (TPS) and cellulose films, and by Hietala et al.³³ when evaluating the transparency of TPS and cellulose nanofibrous composites. Both studies explained that the transmittance decrease in the visible region with the cellulose addition is due to light scattering by the filler.

However, the addition of carnauba wax into the PBAT/SR/CW – 2.5 composite increased transmittance to 23.88% and to 5.29% for the PBAT/SR/CW – 5.0 composition. The higher transparency percentage of the films with carnauba wax and 2.5% of the residue can be explained by the good dispersion of the wax particles in the PBAT matrix, as can be visualized by scanning electron micrographs (Figure 8).

The results suggest that the insertion of carnauba wax may have facilitated the dispersion of sugarcane residue and consequently reduced the number of obstacles that prevent the passage of light, thus increasing the transparency of the films. For the composition with 5.0% of residue, the formation of wax agglomerates generated an anisotropic structure where the refractive indices occur at each interface causing intense light scattering, and consequently reducing transparency.

Similar results were found by Cardoso et al.³⁴ when studying the opacity of PBAT/(oregano essential oil) films. They reported an increase in film opacity with increased concentration of the phase fatty acid abundant phase in the PBAT matrix. Jiménez et al.²⁹ when evaluating the effects of fatty acids on the optical properties of films based on hydroxypropylmethylcellulose (HPMC) obtained similar results. Both studies report a reduction in the transparency of the films when the amount of the phase abundant in fatty acid increased, since the presence of the wax modifies the refractive index of the electromagnetic radiation and promotes an intense dispersion of the light.

Opaque mulching films reduce the growth of weeds under the film and hence the commercial mulching film is expected to be more effective in preventing weed growth. Although transparent mulching films cause a higher soil temperature, they are not as efficient against weeds¹⁵. A detailed study on the mechanical properties, biodegradability and thermal degradation of the mulch films manufactured here will be reported in a subsequent paper, as one of the purposes of the use of the sugarcane residue was to increase the system's biodegradability. We can state, however, that although the composites produced here do lose mechanical properties upon exposure, the materials produced still have sufficient mechanical strength to be used as mulch films and the biodegradability of the composites was higher than that of the neat matrix.

6. Conclusion

Biodegradable films of PBAT and sugar cane residue were prepared for mulching. Our results indicate that only mechanical coupling took place between the sugar cane residue and the PBAT matrix. Processing conditions included two extrusion cycles and promoted homogeneous dispersion and distribution of the particles of the vegetable filler, whose insertion led to increased film roughness. Film transparency diminished with the insertion of sugar cane residue into the matrix. Carnauba addition to these compositions, however, led to increased film transparency.

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8. References

- Brown RP. *Polymers in Agriculture and Horticulture. Rapra Review Reports*. Vol. 15. Shawbury, UK: Rapra Technology Limited; 2004. Available from: <http://www.polymerjournals.com/pdfdownload/909982.pdf>
- Kasirajan S, Ngouajio M. Polyethylene and biodegradable mulches for agricultural applications: A review. *Agronomy for Sustainable Development*. 2012;32(2):501-29.
- Kader MA, Senge M, Mojid MA, Ito K. Recent advances in mulching materials and methods for modifying soil environment. *Soil and Tillage Research*. 2017;168:155-66. Available from: <http://dx.doi.org/10.1016/j.still.2017.01.001>
- Zhang D, Liu HB, Hu WL, Qin XH, Ma XW, Yan CR, et al. The status and distribution characteristics of residual mulching film in Xinjiang, China. *Journal of Integrative Agriculture*. 2016;15(11):2639-46. Available from: [http://dx.doi.org/10.1016/S2095-3119\(15\)61240-0](http://dx.doi.org/10.1016/S2095-3119(15)61240-0)
- Briassoulis D, Babou E, Hiskakis M, Kyrikou I. Analysis of long-term degradation behaviour of polyethylene mulching films with pro-oxidants under real cultivation and soil burial conditions. *Environmental Science and Pollution Research*. 2015;22(4):2584-98. Available from: <http://link.springer.com/10.1007/s11356-014-3464-9>
- Bilck AP, Grossmann MVE, Yamashita F. Biodegradable mulch films for strawberry production. *Polymer Testing*. 2010;29(4):471-6. Available from: <http://dx.doi.org/10.1016/j.polymertesting.2010.02.007>
- Touchaleaume F, Martin-Closas L, Angellier-Coussy H, Chevillard A, Cesar G, Gontard N, et al. Performance and environmental impact of biodegradable polymers as agricultural mulching films. *Chemosphere*. 2016;144:433-9.
- Pinheiro IF, Morales AR, Mei LH. Polymeric biocomposites of poly (butylene adipate-co-terephthalate) reinforced with natural Munguba fibers. *Cellulose*. 2014;21(6):4381-4391.
- Wu CS. Utilization of peanut husks as a filler in aliphatic-aromatic polyesters: Preparation, characterization, and biodegradability. *Polymer Degradation and Stability*. 2012;97(11):2388-95. Available from: <http://dx.doi.org/10.1016/j.polymdegradstab.2012.07.027>
- Finkenstadt VL, Tisserat B. Poly(lactic acid) and Osage Orange wood fiber composites for agricultural mulch films. *Industrial Crops and Products*. 2010;31(2):316-20.
- Ludueña L, Vázquez A, Alvarez VA. Effect of lignocellulosic filler type and content on the behavior of polycaprolactone based eco-composites for packaging applications. *Carbohydrate Polymers*. 2012;87(1):411-21.
- Companhia Nacional de Abastecimento (CONAB). Acompanhamento da safra brasileira de cana-de-açúcar. Monitoramento agrícola – Cana-de-açúcar. Vol. 18. Brasília (DF): CONAB; 2017/2018. Available from: http://www.conab.gov.br/OlalaCMS/uploads/arquivos/17_04_20_14_04_31_boletim_cana_portugues_-_1o_lev_-_17-18.pdf
- Agunsoye JO, Aigbodion VS. Bagasse filled recycled polyethylene bio-composites: Morphological and mechanical properties study. *Results in Physics*. 2013;3:187-94. Available from: <http://dx.doi.org/10.1016/j.rinp.2013.09.003>
- Paula PG, Rodriguez RJS, Duarte LPR, Candido VS, Monteiro SN. Formulation and characterization of polypropylene composites alkali treated bagasse fiber. *Materials Science Forum*. 2014;775-776:319-24. Available from: <http://www.scopus.com/inward/record.url?eid=2-s2.0-84892892884&partnerID=tZOTx3y1>
- Adhikari R, Bristow KL, Casey PS, Freischmidt G, Hornbuckle JW, Adhikari B. Preformed and sprayable polymeric mulch film to improve agricultural water use efficiency. *Agricultural Water Management*. 2016;169:1-13. Available from: <http://dx.doi.org/10.1016/j.agwat.2016.02.006>
- Rodrigues DC, Caceres CA, Ribeiro HL, Abreu RFA, Cunha AP, Azeredo HMC. Influence of cassava starch and carnauba wax on physical properties of cashew tree gum-based films. *Food Hydrocolloids*. 2014;38:147-51. Available from: <http://dx.doi.org/10.1016/j.foodhyd.2013.12.010>
- Chiumarelli M, Hubinger MD. Evaluation of edible films and coatings formulated with cassava starch, glycerol, carnauba wax and stearic acid. *Food Hydrocolloids*. 2014;38:20-7.
- Skoog DA, West DM, Holler FJ. *Fundamentos de química analítica*. Vol. 2. São Paulo: Reverte S.A.; 1997.
- Kijchavengkul T, Auras R, Rubino M, Ngouajio M, Fernandez RT. Assessment of aliphatic-aromatic copolyester biodegradable mulch films. Part II: laboratory simulated conditions. *Chemosphere*. 2008;71(9):1607-16.
- Faruk O, Sain M. *Lignin in polymer composites*. Norwich, NY: William Andrew; 2016.
- Zhao C, Jiang E, Chen A. Volatile production from pyrolysis of cellulose, hemicellulose and lignin. *Journal of the Energy Institute*. 2017;90(6):902-13. Available from: <https://doi.org/10.1016/j.joei.2016.08.004>
- Simão JA, Carmona VB, Marconcini JM, Mattoso LHC, Barsberg ST, Sanadi AR. Effect of Fiber Treatment Condition and Coupling Agent on the Mechanical and Thermal Properties in Highly Filled Composites of Sugarcane Bagasse Fiber/PP. *Materials Research*. 2016;19(4):746-51. Available from: http://www.scielo.br/scielo.php?script=sci_arttext&pid=S1516-14392016000400746&lng=en&tlng=en
- Fei T, Wang T. A review of recent development of sustainable waxes derived from vegetable oils. *Current Opinion in Food Science*. 2017;16:7-14.
- Lozhechnikova A, Bellanger H, Michen B, Burgert I, Österberg M. Surfactant-free carnauba wax dispersion and its use for layer-by-layer assembled protective surface coatings on wood. *Applied Surface Science*. 2017;396:1273-81. Available from: <http://dx.doi.org/10.1016/j.apsusc.2016.11.132>
- Oliveira TA, Oliveira RR, Barbosa R, Azevedo JB, Alves TS. Effect of reprocessing cycles on the degradation of PP/PBAT-thermoplastic starch blends. *Carbohydrate Polymers*. 2017;168:52-60. Available from: <http://dx.doi.org/10.1016/j.carbpol.2017.03.054>

26. Silva JSP, Silva JMF, Soares BG, Livi S. Fully biodegradable composites based on poly(butylene adipate-co-terephthalate)/peach palm trees fiber. *Composites Part B Engineering*. 2017;129:117-23. Available from: <http://dx.doi.org/10.1016/j.compositesb.2017.07.088>
27. Hull D, Clyne TW. *An introduction to composite materials*. Cambridge: Cambridge University Press; 1996.
28. Fabra MJ, Jiménez A, Atarés L, Talens P, Chiralt A. Effect of fatty acids and beeswax addition on properties of sodium caseinate dispersions and films. *Biomacromolecules*. 2009;10(6):1500-7.
29. Jiménez A, Fabra MJ, Talens P, Chiralt A. Effect of lipid self-association on the microstructure and physical properties of hydroxypropyl-methylcellulose edible films containing fatty acids. *Carbohydrate Polymers*. 2010;82(3):585-93.
30. Ngouajio M, Ernest J. Light transmission through colored polyethylene mulches affects weed populations. *HortScience*. 2004;39(6):1302-4.
31. Brydson JA. *Plastic materials*. 7th ed. Oxford: Butterworth-Heinemann; 1999.
32. Balakrishnan P, Gopi S, Sreekala MS, Thomas S. UV resistant transparent bionanocomposite films based on potato starch/cellulose for sustainable packaging. *Starch/Staerke*. 2018;70(1-2):1-13.
33. Hietala M, Mathew AP, Oksman K. Bionanocomposites of thermoplastic starch and cellulose nanofibers manufactured using twin-screw extrusion. *European Polymer Journal*. 2013;49(4):950-6. Available from: <http://dx.doi.org/10.1016/j.eurpolymj.2012.10.016>
34. Cardoso LG, Santos JCP, Camilloto GP, Miranda AL, Druzian JI, Guimarães AG. Development of active films poly (butylene adipate co-terephthalate) – PBAT incorporated with oregano essential oil and application in fish fillet preservation. *Industrial Crops and Products*. 2017;108:388-97. Available from: <http://dx.doi.org/10.1016/j.indcrop.2017.06.058>