CHARACTERIZATION OF BIODEGRADABLE MULCH BLACK FILMS INCORPORATED WITH ORGANICS FERTILIZERS AND RICE HUSK ASH

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CHARACTERIZATION OF BIODEGRADABLE MULCH BLACK FILMS INCORPORATED WITH ORGANICS FERTILIZERS AND RICE HUSK ASH

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Abstract

The effects of organic fertilizer, rice husk ash, both from renewable resources, were evaluated. Both of them were incorporated in biodegradable black mulch films. Morphological, mechanical and thermal properties based on PBAT/PLA composites with 2 % wt. of carbon black were investigated. In addition, the formulations were prepared with 1 % wt. to 2 % wt. rice husk ash and 2 % wt. to 4 % wt. % organic fertilizer The samples were produced by melt extrusion process, using a twin screw extruder machine and blown film extrusion process. As can be seen the properties of biodegradable mulch film samples were investigated by tensile tests, XRD, FTIR, TG, MEV analyses. Correlation between properties were discussed. According to the results it is possible to apply this composite as film for agricultural protection.

Keywords: Biodegradable Films, Organic Fertilizers,Carbon Black, PBAT/PLA

Introduction

Increasing interest in new materials based on blends of two or more polymers has been observed during the last decades. Conventional thermoplastic polymers have good mechanical properties and thermal stability, much better than the biodegradable ones. Biopolymers have advantages over the conventional polymers; biopolymers are from renewable materials and can be biodegradable. There is also a limitation in the performance and application of biopolymers in comparison to conventional thermoplastics. Therefore, the extensive application of these biopolymers is still challenged by one or more of their possible inherent limitations, such as poor processability, brittleness, hydrophilicity, poor moisture and gas barrier, inferior compatibility, poor electrical, thermal and mechanical properties [1, 2]. Blends of conventional plastics (petroleum-derived polymers) and biopolymer can form a new class of materials with improved mechanical properties compared with those of single components. Polymer blending offers possibility of adjusting the cost-performance balance and tailoring the technology to make products for specific end-use applications; extends engineering resinsperformance; improves specific properties or solvent resistance and provides means for industrial and consumer plastics waste recycling [3].

Combination of polymer blends with micro or nanofillers appears quite promising based on balanced performance of biopolymer, to provide better thermal and mechanical properties, to improve service temperature, moisture resistance, gas barrier effect, and in some cases to reduce the cost of biodegradable thermoplastic polymers. Incorporation of micro and nanoparticles into polymer materials has increased their properties[1]. Inorganic materials due to their ability in harsh process conditions, such as metal or metal oxideshave attracted a great deal of attraction recently. Carbon Black among the inorganic and organic materials have particularly interesting due to the both safe for animals and human and stable under harsh condition processes [4, 5].

The synthesis of inorganic-biopolymer micro and nanocomposites has been intensely studied due to their unique combination of properties and widespread potential applications. These generations of biocomposites have more desirable functional properties, such as good mechanical strength, and low water vapor permeability. Lately, researchers have reported the improvements of biopolymer properties by incorporation of micro and nanoparticles, such as clay, silicon dioxide, layered silicate nanoparticles, calcium carbonate, zinc oxide and titanium dioxide. In general, these researchers have reported that the incorporation of micro and nanoparticles improve mechanical properties, as well as barrier and antimicrobial properties of biopolymers [6,7].

The aim of this study was to process and investigate the changes in the mechanical, morphological and environmental UV protection of the biodegradable PBAT/PLA/carbon black composite due to the incorporation of renewable resources: silicon dioxide from rice husk ash and organic fertilizers from composting units.

Material and Methods

Material

The materials used in this work were biodegradable aliphatic-aromatic copolyester (PBAT) with biodegradable poly(lactic acid) (PLA), producing a blend PLA/PBAT and incorporated Brazilian carbon black (CB) nanoparticles., rice husk ash (silicon dioxide (SiO_2)) and organic fertilizers (OF), both from renewable resources [8, 9, 10].

Preparation of blend and composite

PLA, PBAT, carbon black nanoparticle, rice husk ash and organic fertilizers were dried at 60 ± 2 ºC for 4 h to reduce its moisture content to less than 2wt.%. The PLA/PBAT blend based on 2wt.% of carbon black with rice husk ash based on 1 to 2wt.%, organic fertilizer addition, blend based on 2 to 4wt.% , were prepared according Table 1. The formulations were prepared by melting extrusion process, using a co-rotating twin-screw, with 20 mm of diameter, HaakeRheomex P 332 extruder. The temperature profile was 135/145/148/150/150/150 ºC. Screw speed was 180 rpm. The extrudates coming out of the extruder were cooled down in air for a better dimensional stability, pelletized by a pelletizer, dried again at 60 ± 2 ºC for 4 h and fed into extrusion blown film, single screw machine with 25 mm diameter, Carnevalli maker. Test samples were obtained.

Table 1.Samples composition for PLA/PBAT blends with carbon black, rice husk ash and organic fertilizers.

SamplesComposition (wt.%)	A1	A6	A7	A8
PLA	34.3	33.2	32.2	32.9
PBAT	63.6	61.7	59.7	61.0
CB (carbon black)	2	2	2	2
SiO_2 (rice husk ash)	-	1	2	1
OF (organic fertilizer)	-	2	4	3
Anti UV	0.1	0.1	0.1	0.1

Characterization

Mechanical tests

Tensile tests (ASTM D 638) were performed at INSTRON 5900 with 500kgf load cell and 10mm.min^{-1} in order to evaluate the mechanical behavior of the materials studied.

X-rays diffraction (XRD) tests

X-rays diffraction (XRD) were recorded on a BRUKER, Focus-D8 diffractometer operated at 40 kV and 40 mA, with CuKα radiation (λ= 15.4 Å).

Thermogravimetry

Thermogravimetry was performed using an appliance STA 449 F3 Jupiter by Netzch with analysis from 25 to 1000°C under a rate of 10°C.min^{-1} in an atmosphere of N_2.

Differential scanning calorimetry (DSC)

DSC were carried out using a Mettler Toledo DSC 822 from 25 to 200°C at a heating rate of 10 °C.min^{-1}under oxygen atmosphere.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analyses were carried out using a spectroscopy Thermo Nicolet Nexus 4700, with 400 to the 4000 cm^{-1} sweep and 64 scans using an accessory for specimen holder.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) analyses were carried out using a Jeol microscope (JSM 6360LV) in increments at 500 and 5000x with beam 25 keV. aceleration voltage. The samples were cryo-fractured under liquid nitrogen, and then the fractured surface was coated with a fine layer of gold and observed by scanning electron microscopy.

RESULTS AND DISCUSSION

Mechanical tests results

Tensile test results

Figure 1 shows the ultimate tensile strength for the PBAT/PLA/carbon blackcomposite (A1) with PBAT/PLA/carbon black, rice husk ash/ organic fertilizers composites (A6, A7 and A8). These results shown (Table 2) the average values calculated from the data obtained in tests presenting Young's Modulus (*E*) strength stress (σ_{rup}) and rupture strain (ε_{rup}).

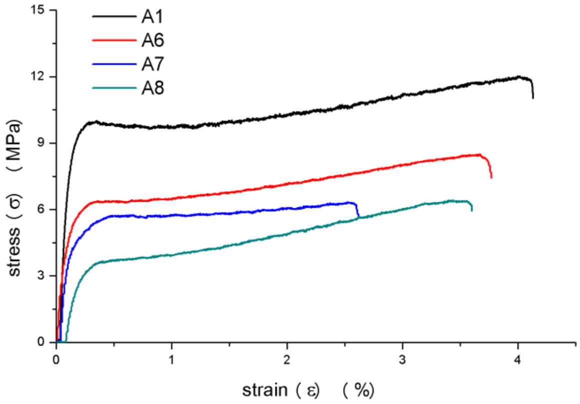

Figure 1. Stress x strain curves for the PBAT/PLA/carbon blackcomposite(A1) and its composites with rice husk ash and organic fertilizers (A6, A7 andA8).

Table 2. Young´s modulus, ultimate tensile tensile strength and elongation-to-fracture for sampled comoposites.

Samples	*E* (MPa)	σ_{rup} (MPa)	ε_{rup}(%)
A1	78 ± 9	12 ± 1	415 ± 14
A6	28 ± 12	9 ± 1	381 ± 7
A7	27 ± 7	7 ± 1	291 ± 36
A8	13 ± 2	6 ± 1	367 ± 18

As it can be seen from Figure (1) the addition of rice husk ash and organic fertilizer in PBAT/PLA carbon black composite decreases the ultimate strength (around 50 %), and elongation-to-fracture (around 30 %). The improve of tensile properties in PLA due to carbon black has been reported in the literature by Chivrac, et al. [11] and Luduena, et al.[12]. These authors suggested that carbon black could be acting as nucleating agent improving the crystallinity of PLA.

PBAT/PLA/carbon black composite (A1) and PBAT/PLA/carbon black/rice husk ash/organic fertilizers composites (A6, A7 and A8). Addition of rice husk ash and organic fertilizers in PBAT/PLA/carbon black composite has great influence in mechanical properties, because of this influence it has maximum limit to incorporate.

It is possible to observe that the behavior of micro and nanocomposites are perfectly elastic, the stress increases linearly with strain. However rice husk ash and organic fertilizer addition caused a significant decrease on tensile strength and elongation of composites.

X-rays diffraction (XRD) analysis results

The XRD patterns of PBAT/PLA/carbon black composite (A1) and PBAT/PLA/carbon black/rice husk ash/organic fertilizers composites (A6, A7 and A8) are shown in Figure 2.

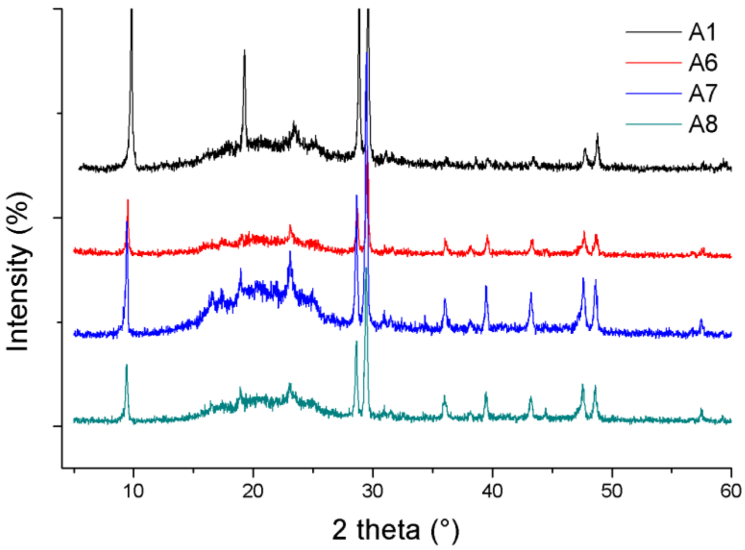

Figure2. XRD diffraction curves for the PBAT/PLA/carbon blackcomposite (A1) and PBAT/PLA/carbon black/rice husk ash/organic fertilizers composites (A6, A7 and A8).

The Figure 2 shows that the blend of PLA / PBAT with carbon black incorporation is low crystallinity and characteristic peaks carbon black (θ = 8.9 °) and polymer (θ = 19.1 °, 29.4 °) [8]. The incorporation of rice hull ash (silica) shows variation characteristic peak (θ = 22.5 °) to change the amorphous halo low intensity between 15 and 30 °. This result is typical of silica obtained from carbonized rice husk. The most adding of organic fertilizer increased the amorphous region of the curve (A7) and the growth of θ peaks at 47.5 ° and 48.7 °, these values may still be typical oxides and carbonates present in fertilizer and soil amendment.

Thermogravimetry (TG)

Thermogravimetry curves for the PBAT/PLA/carbon blackcomposite (A1) and PBAT/PLA/carbon black/rice husk ash/organic fertilizers composites (A6, A7 and A8) can be seen in the Figure 3 and Table 3 represents initial degradation temperature ($T_{10\%}$) and ash values.

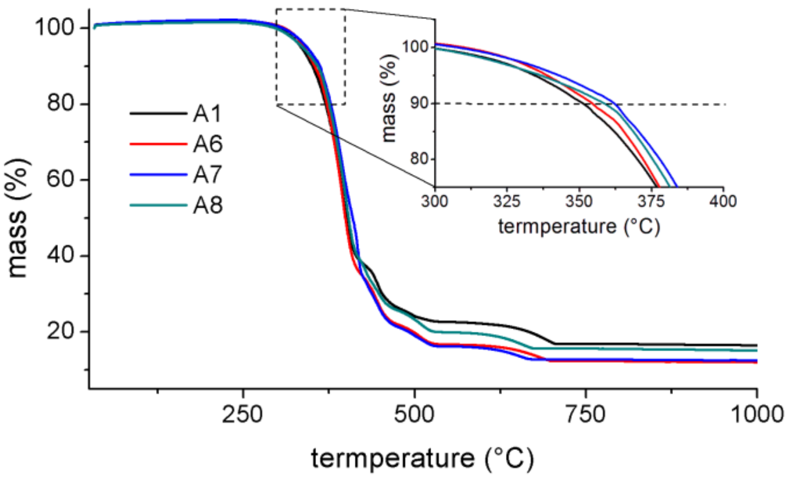

Figure 3. TG analysis for the PBAT/PLA/carbon black composite (A1) and PBAT/PLA/carbon black/rice husk ash/organic fertilizers composites (A6, A7 and A8).

Table 3. Thermal results of initial degradation temperature ($T_{10\%}$) and ash values (%)..

Samples	$T_{10\%}$(°C)	$T_{500°C}$ (wt.%)	Ash(wt.%)
A1	351.3	24.0	16.5
A6	354.4	19.6	12.0
A7	362.1	18.8	12.5
A8	358.6	23.1	15.1

According to Figure 3 and Table 3 that of PBAT/PLA/carbon black composite (A1) and of PBAT/PLA/carbon black/rice husk ash/organic fertilizercomposites (A6, A7 and A8),addition of organic fertilizer composites reduced the degradation temperature of PBAT/PLA/carbon blackcomposite. The thermal stability is around 300 °C which can be considered enough for this application [9].

Differential Scanning Calorimetry (DSC)

DSC curves for the PBAT/PLA/ carbon blackcomposite(A1)and PBAT/PLA/carbon black/rice husk ash/organic fertilizer composites (A6, A7 and A8) its can be seen in the Figure 4 and the average values of first and second melting temperatures (T_m) are presents in the Table 4.

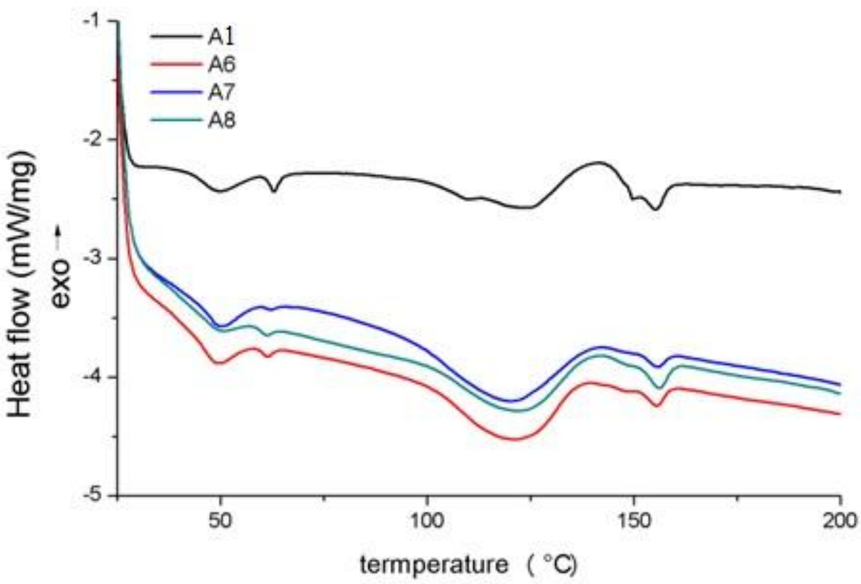

Figure 4.DSC analyses for the PBAT/PLA/carbon black composite (A1) and PBAT/PLA/carbon black /rice husk ash/organic fertilizer composites (A6, A7and A8).

Table 4.Thermal results of first and second melting temperatures (T_m).

Samples	T_{m1}(°C)	T_{m2}(°C)
A1	123	154
A6	120	156
A7	119	157
A8	121	158

In Figure 4 and Table 4, it can be observed two melting temperatures (T_{m1} and T_{m2}), which are near of the melting temperatures of PBAT and PLA respectively[13, 14].This means that rice husk ashand organic fertilizer can be incorporate without change significativelly melting temperature .

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra presented in the Figure 5 for the PBAT/PLA/carbon blackcomposite and PBAT/PLA/carbon black/rice husk ash/organic fertilizer composites (A6, A7 and A8),

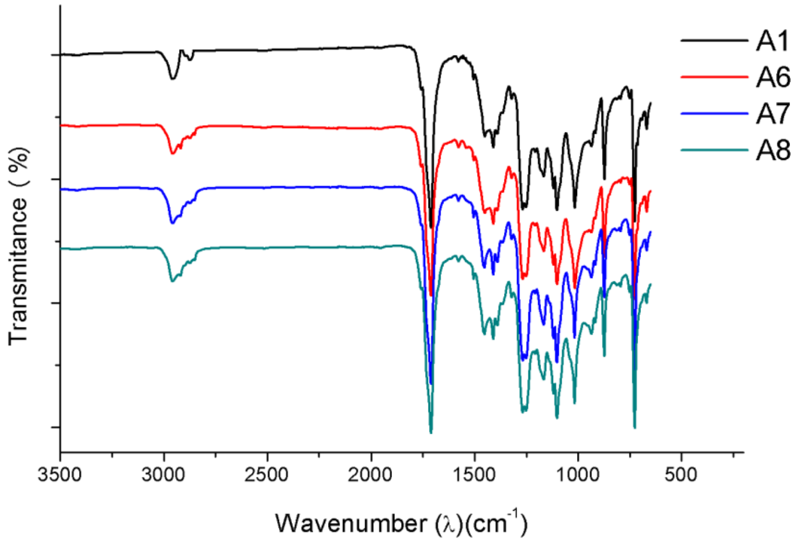

Figure 5.FTIRspectra for the PBAT/PLA/carbon black composite (A1) and PBAT/PLA/carbon black / rice husk ash /organic fertilizer composites (A6, A7 and A8)

The results presented in Figure 5 show little spectral variation between the PLA/PBAT blend with carbon black and theircomposites containing rice husk ash and organic fertilizer. The main peaks around 2950cm^{-1} (C-H groups), 1720cm^{-1} (C=O) and 1280cm^{-1} (C= O) are due to the composition of sample A1. Samples containing rice husk ash and organic fertilizer showed little variation of 800cm^{-1} and 1090cm^{-1} peaks (Si-O bonds); and 875cm^{-1} and 1475cm^{-1} (Ca-O) [15, 16].

Scanning Electron Microscopy (SEM)

The Figure 6 presents the SEM at 500 and 5000x for the PBAT/PLA/carbon blackcomposite (A1) and PBAT/PLA/carbon black/rice husk ash/organic fertilizer composites (A6, A7 and A8).

SEM of PBAT/PLA/carbon black composite (A1) and PBAT/PLA/carbon black/rice husk ash/organic fertilizer (A6, A7 and A8) in different magnifications is showed in Figure 6. The Figure 6 shows micrographs with 500X and 5.000X of magnifications, for the samples of composites. It can be seen that there are several carbon black nanoparticle and rice husk ash/organic fertilizer agglomerates in the surface of the composites.

This result suggests that part of particles were not well dispersed in the PBAT/PLA carbon black composite and PBAT/PLA/carbon black/rice husk ash/organic fertilizer composites.

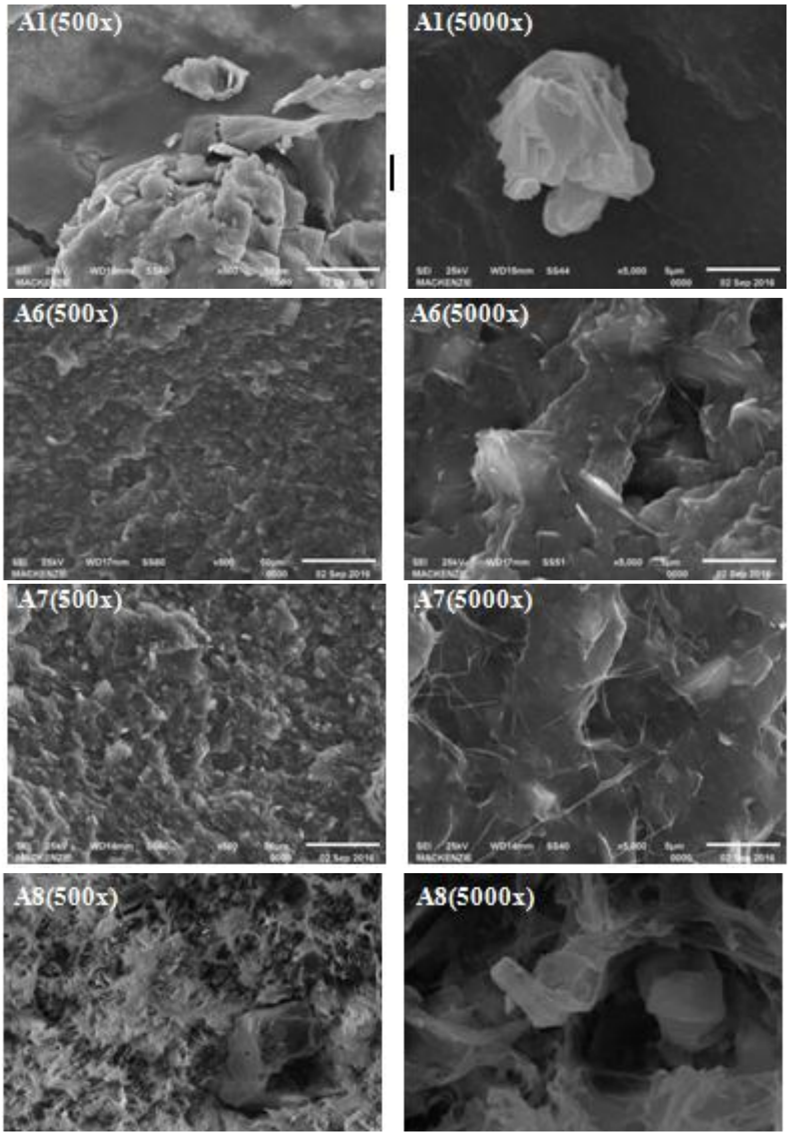

Figure 6.Scanning electron microscopy (500 and 500x) for the PBAT/PLA/carbon black composite (A1) andPBAT/PLA/carbon black/rice husk ash/organic fertilizer composites (A6, A7and A8).

CONCLUSIONS

Although mechanical properties of the PBAT/PLA blend to have increased with the addition of carbon black the results showed that with the addition of rice husk ash/organic fertilizerin the PBAT/PLA/carbon black composite(A1)decreased the mechanical properties of the composite (A1).
The DSC analysis results indicated that PBAT/PLA/carbon black compositewith the addition of rice husk ash/organic fertilizer decreased the melting enthalpy of PBAT/PLA blend, and consequently, increased the crystallinity percentage. The SEMmicrographs results showed that there were several carbon black nanoparticle and rice husk ash/ organic fertilizeragglomerates in the surface of the composites.
The results indicated that the addition of particle of rice husk ash/organic fertilizer in the PBAT/PLA/carbon black composite matrix allows to use this composite as biodegradable with suitable properties, even in the presence of agglomerates, in several agricultural applications.

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