

# Synergistic effect of adding lignin and carbon black in poly(lactic acid)

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## Abstract

Antistatic packaging is a very important sector since the electrostatic discharge of electronic devices can damage and/or disable these products. In addition, it is essential to dispose of this packaging correctly. In this work, the synergistic effect of the addition of lignin and carbon black on the development of antistatic and biodegradable packaging was verified. In this study, PLA was mixed with lignin and carbon black and the composites were prepared using a high-speed thermokinetic homogenizer where the melting of the PLA and the blend with fillers occurred by friction. The composites were characterized by Izod impact tests, scanning electron microscopy, thermal properties, electrical characterization and biodegradation tests in garden soil. The results show that lignin is a great option to accelerate the biodegradation of PLA in the garden soil and the carbon black acts as an antistatic agent reducing the electrical resistivity of the composites.

**Keywords:** *antistatic, biodegradable, poly(lactic acid), lignin, carbon black.*

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## 1. Introduction

Antistatic packaging is used for the protection and storage of electronic boards and sensitive electronic components<sup>[1,2]</sup>. Conductive carbon black is the most commonly used antistatic agent for the production of antistatic packaging and is intended to increase the electrical conductivity (and consequently reduce electrical resistivity) of the packaging so that the electronic devices are not subjected to electrical shocks and are damaged during their transport and storage<sup>[3-5]</sup>. The conductive carbon black has typical values of electrical conductivity of 100 S.cm<sup>-1</sup><sup>[6]</sup>.

Antistatic packaging is generally composed of polyethylenes<sup>[1]</sup>, polystyrene<sup>[7]</sup> or polyethylene terephthalate<sup>[2]</sup>. However, after using these packaging, there is a serious problem of disposal, which generates waste and damages the environment. Several strategies are being carried out to reduce the amount of plastic waste, including the biodegradation process. The biodegradation process consists of physical or chemical modifications, caused by the action of microorganisms, under certain conditions of heat, humidity, light, oxygen and suitable materials nutrients and minerals<sup>[8]</sup>. Another way to help reduce the amount of plastic waste in the environment is the use of biodegradable polymers. Biodegradable polymers are considered a generation of environmentally sustainable polymers. To be considered a biodegradable polymer, it must present, after significant degradation, final products compatible with the environment, such as carbon dioxide, water and microbial biomass<sup>[9]</sup>.

Among the biodegradable polymers, the poly(lactic acid) (PLA) is one of those that has attracted researchers attention due possesses a variety of desirable properties, such as biodegradability, biocompatibility and exhibiting excellent mechanical properties under tensile tests<sup>[10,11]</sup>. As limitations, PLA has a high cost, low mechanical toughness, and degradation that ranges from 6 months to 2 years, depending on the conditions under which the material is submitted<sup>[12,13]</sup>.

In our previous work<sup>[3]</sup>, the authors have shown that the PLA/carbon black composite can be an excellent alternative for the preparation of antistatic packages, but the biodegradation time of these packages is still long (Composites of PLA with 15 wt% carbon blacks lost approximately 0.52% residual mass in 6 months). PLA/carbon black with 5, 10 and 15 wt% carbon black were prepared in a thermokinetic homogenizer. The addition of 15 wt% of carbon black in the PLA matrix increased the electrical conductivity and decreased the electrical resistivity of the composites by 11 and 8 orders of magnitude, respectively. The composites of PLA with the addition of 10 and 15 wt% of carbon black presented values of electrical resistivity that allow its use as antistatic packaging. Furthermore, the authors confirm that the addition of carbon black does not change the time of biodegradation of these composites, but nevertheless are still too long.

Rane et al.<sup>[14]</sup> made a comparative analysis of processing techniques' effect on the strength of carbon black filled poly (lactic acid) composites. Two techniques were used to obtain the specimens, the first was the dispersion of carbon black was prepared by using chloroform in water bath sonication at room temperature and the second using a Haake mixer, followed by pressing. Hardness and Tensile Tests tests were performed. They concluded that both methods were efficient to homogenize the mixtures and there was no significant difference between mechanical property results of the samples made by sonicator and mixer.

One way to reduce the time of biodegradation of PLA/carbon black antistatic packages is through the addition of another phase in the composite. This phase can be composed of organic material of renewable origin, such as lignin<sup>[15]</sup>. Lignin is a compound of plant origin with a high molecular weight and can contribute to the reduction of PLA biodegradation time, as reported by Gordobil et al.<sup>[16]</sup> that prepared PLA/lignin composites with different contents of lignin (0.5, 1, 5, 10 and 20 wt%) by extrusion and demonstrated that the addition of 5 wt% lignin decrease the degree of crystallinity of the PLA and facilitate the degradation of the composite.

Silva et al.<sup>[9]</sup> studied the addition of lignin in PLA. The composites were prepared using a high speed rotary mixer at 3000 rpm, followed by hot pressing. The thermal characterization, biodegradation test and impact resistance test was performed. The results show that lignin is a great option to accelerate PLA biodegradation in garden soil. PLA/lignin compound with a 10% by weight addition of lignin is the best option for the manufacture of biodegradable packaging as it has similar thermal and mechanical properties to clean the PLA and has a higher biodegradation rate.

Thus, this work seeks a synergistic effect of the addition of carbon black and lignin in a PLA matrix. In order to obtain antistatic packaging for storage and transportation of electronic devices it is necessary to add the antistatic agent, in this case, the carbon black, and in order to decrease the biodegradation time of the PLA matrix the lignin was used. The combination of these two fillers (lignin and carbon black) may contribute to accelerate the biodegradation process and to reduce the electrical resistivity of PLA for the preparation of a new technological and sustainable packaging. Another goal is the use of a high-speed mixer to provide a very homogeneous mixture between PLA and the fillers. In this process, the mixing, melting, and homogenization occur by friction between the mixing components and the equipment rotor with a rotation of 3000 rpm that may lead to better dispersion and distribution of lignin and carbon black in PLA matrix. The effect of different contents of lignin and carbon black was also investigated.

## 2. Materials and Methods

### 2.1 Materials

Poly(lactic acid) (PLA) - PLI 005 produced by Nature Plast (France) with a density of 1.25 g/cm<sup>3</sup> and melt flow index of 5-10 g/10 min (235 °C/2.16 kg). Hardwood Kraft lignin was kindly provided in powder by Suzano Papel e Celulose S.A. Corp. (Brazil) with a surface area of 1.56 m<sup>2</sup> g<sup>-1</sup>, a pore

diameter of 47 Å (BET, Quantachrome Instruments, model Nova 4200e) and particle size of 3.76 µm (CILAS analyzer, model 1190 L), and was used as received. Conducted carbon black (VULCAN® XC72R) supplied by CABOT (USA) as a fine powder with a mean particle size of 50 nm and a density of 0.264 g/cm<sup>3</sup>. The electrical conductivity found for this material was 4.5 S cm<sup>-1</sup><sup>[3]</sup>.

### 2.2 Preparation of PLA/lignin/carbon black composites

All materials were dried for a minimum of 24 h in an oven at 80 °C prior to melting processing. PLA/lignin/carbon black composites were prepared using a high-speed mixer (thermokinetic mixer produced by MH Equipamentos Ltda, model MH50-H) rotating at 3000 rpm and mixing chamber with a capacity of 70 g of material. The mixing temperature was monitored using a thermocouple and reached 200 °C in 40 seconds of mixing. This technique were chosen because promote great homogeneity between the polymer matrix (PLA) and the fillers (lignin and carbon black) as observed in our previously works<sup>[1,3,9]</sup>. Composites with 5, 10 and 15 wt% of lignin and 5, 10 and 15 wt% of carbon black were prepared. Table 1 shows the nomenclature and compositions prepared. After 1 min of mixing, the homogenized composites were collected and pressed into 3.2 mm thick plates with standard dimensions for the Izod impact tests in a hydropneumatic press (MH Equipamentos Ltda, model PR8HP) at 200 °C with a pressure of 5 bar for 3 min. All the composition presented great homogeneity and the fillers were completely incorporated in the polymer matrix.

### 2.3 Characterization of PLA/lignin/carbon black composites

#### 2.3.1 Thermal characterization of PLA/lignin/carbon black composites

Thermal characterization of PLA/lignin/carbon black composites was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Thermogravimetric analysis (TGA) of the composites were performed using a Netzsch equipment model TG 209 F1 Iris®, from room temperature to 600 °C at a rate of 20 °C/min, under N<sub>2</sub> atmosphere.

The DSC analyses were performed using a TA Instruments equipment, QS100 model under an N<sub>2</sub> atmosphere with a flow rate of 50 mL.min<sup>-1</sup>. Samples were sealed in an

**Table 1.** Nomenclature and composition of the PLA/lignin/carbon black composites.

Samples	PLA (wt%)	Lignin (wt%)	Carbon Black (wt%)
Neat PLA	100	--	--
90/5/5	90	5	5
85/10/5	85	10	5
80/15/5	80	15	5
85/5/10	85	5	10
80/10/10	80	10	10
75/15/10	75	15	10
80/5/15	80	5	15
75/10/15	75	10	15
70/15/15	70	15	15

aluminum DSC pan and heated from room temperature to 200 °C at 10 °C/min. They were kept at 200 °C during 5 min to eliminate the heat history; subsequently cooled to 0 °C at 10 °C/min to determinate the crystallization temperature ( $T_c$ ). After this, they were heated to 200 °C at 10 °C/min. The degree of crystallinity ( $X_c$ ) was calculated according to Equation 1:

$$X_c(\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \cdot 100(\%) \quad (1)$$

where  $X_c(\%)$  is the degree of crystallinity;  $\Delta H_m$  is the melting enthalpy obtained by DSC;  $\Delta H_c$  is the crystallization enthalpy during heating and  $\Delta H_m^0$  is the theoretical melting heat value for 100% crystalline material (93.7 J/g for PLA<sup>[17]</sup>). The  $\Delta H_m^0$  value for the composites was calculated for each composition considering the mass fraction of the PLA in the composite.

### 2.3.2 Electrical characterization of PLA/lignin/carbon black composites

The surface electrical characterization of all composites was performed by impedance spectroscopy and AC electrical resistivity (alternating current) according Silva et al.<sup>31</sup>. The values of electrical conductivity ( $\sigma$ ) were calculated from the inverse of the resistivity ( $\rho$ ) (Equation 2), which were obtained from the relation between the impedance values ( $Z$ ) and the electrical contact area dimensions of the samples ("A", area and "l", thickness), Equation 3. A thin layer of gold/palladium alloy was deposited by a metallizer (MED020 Bal-tec) on both sides of the samples, in order to form the electrical contact, producing a metal-composite-metal structure.

$$\sigma = \frac{l}{\rho} \quad (2)$$

$$\rho = \frac{Z \cdot A}{l} \quad (3)$$

Impedance measurements were performed on an impedance analyzer (Solartron SI 1260, Impedance/Gain-phase Analyzer) which sends the data to a computer. The measurements were performed at room temperature at a frequency of 1 Hz and voltage amplitude of 0.5 V.

### 2.3.3 Biodegradation test of PLA/lignin/carbon black composites

The soil biodegradation test was carried out according to ASTM G160-98<sup>[18]</sup>. An aquarium apparatus was used containing garden soil (pH 5.92). Figure 1 shows the

apparatus used. Test specimens for Izod impact strength tests of all compositions were buried in the garden soil and kept at room temperature (25 °C) and humidity controlled between 20 and 30%. Samples of all compositions were removed at 0, 30, 60, 90 and 180 days. The samples were removed from the soil at the end of each period and were gently washed with distilled water to remove soil particles. Then the samples were dried at 30 °C for 6 h. After each time interval, the samples were characterized by Izod impact strength, and scanning electron microscopy (SEM) to verify the effect of biodegradation in the samples. The residual mass ( $M_r$ ) in %, was calculated according to Equation 4:

$$M_r(\%) = \left( \frac{M_f}{M_i} \right) \cdot 100 \quad (4)$$

where  $M_f$  is the final mass of the sample after soil exposure and  $M_i$  is the initial mass before soil exposure.

### 2.3.4 Mechanical characterization of PLA/lignin/carbon black composites

Impact strength tests were performed on a CEAST/Instron Izod Impact Test Machine (model 950). The test method adopted was carried out according to ASTM D256-78<sup>[19]</sup>. All the test specimens were notched using a manual notched machine (CEAST/Instron, model 9050) and the tests were performed using a 0.5 J hammer. A minimum of five samples of each composition was tested.

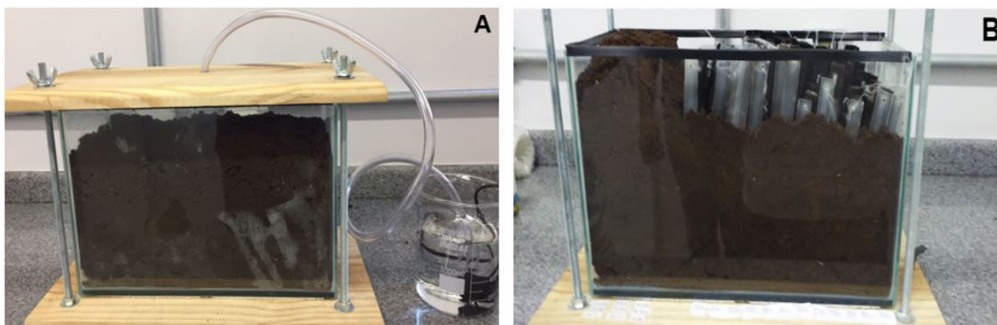
### 2.3.5 Morphological characteristics of PLA/lignin/carbon black composites

SEM images of neat PLA and PLA/lignin/carbon black composites before and after of exposure in garden soil were analyzed using a scanning electron microscope FEI Inspect S50, operating at 7.5 keV. The samples were placed on aluminum stubs and coated with gold.

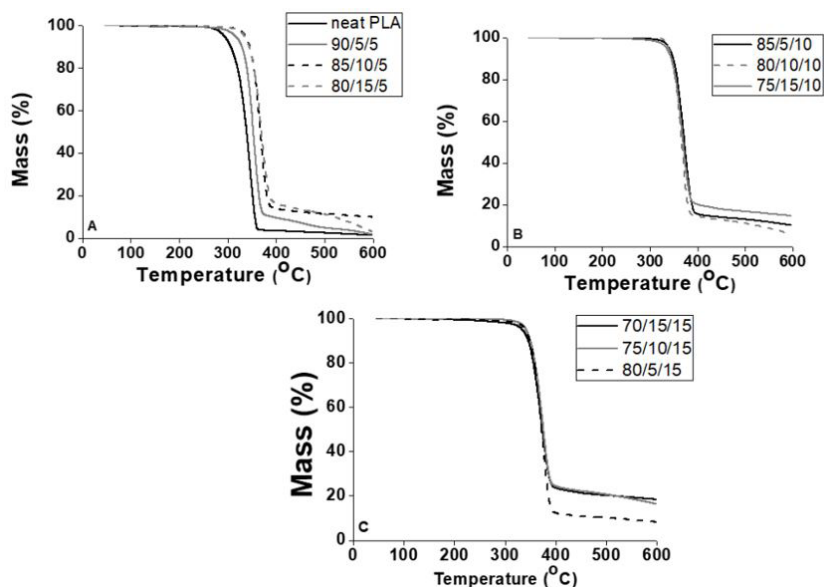
## 3. Results and Discussions

### 3.1 Thermal characterization of PLA/lignin/carbon black composites: TGA and DSC

Figure 2 shows the TGA curves and Table 2 shows the  $T_{onset}$  values for the neat PLA and the PLA/lignin/carbon black composites. It is possible to observe that the temperature of the irreversible thermal degradation ( $T_{onset}$ ) of neat PLA at 324 °C with a mass loss of 98.5% at 600 °C. This event was also observed in the studies of Zhao et al.<sup>[20]</sup>.



**Figure 1.** (A) Apparatus with garden soil used in the biodegradation test; (B) specimens buried in garden soil.



**Figure 2.** TGA curves: (A) neat PLA and PLA/lignin/carbon black composites with 5, 10 and 15 wt% of lignin and 5 wt% of carbon black; (B) PLA/lignin/carbon black composites with 5, 10 and 15 wt% of lignin and 10 wt% of carbon black; and (C) PLA/lignin/carbon black composites with 5, 10 and 15 wt% of lignin and 15 wt% of carbon black.

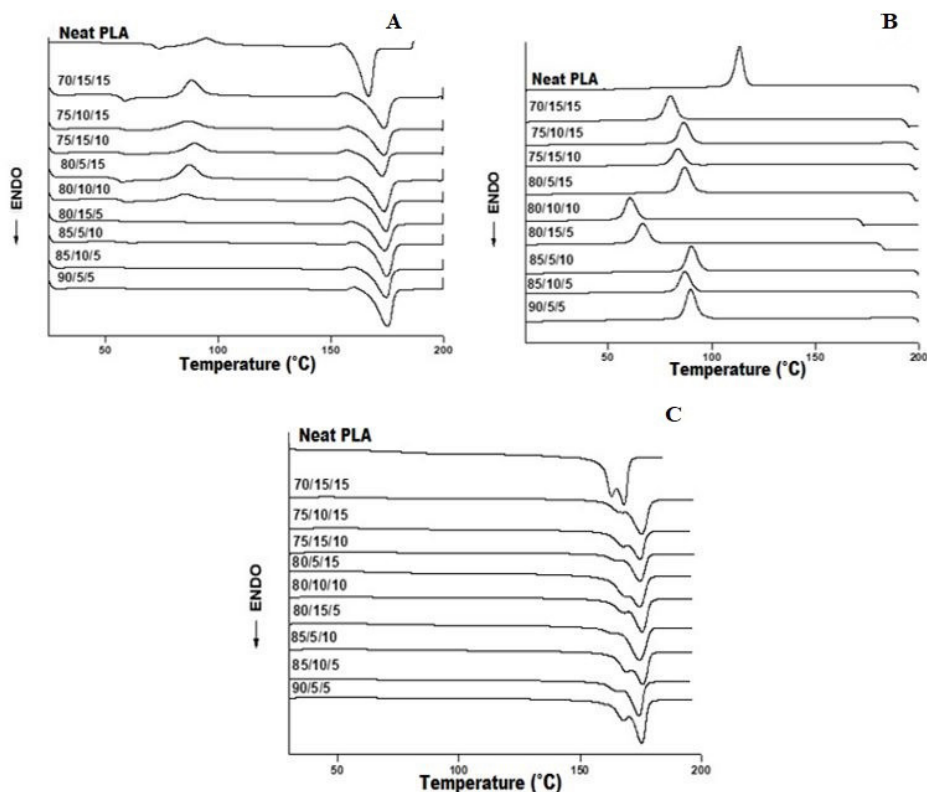
**Table 2.** Values of  $T_{gl}$ ,  $T_{CC1}$ ,  $\Delta H_{CC1}$ ,  $T_{m1}$ ,  $\Delta H_{m1}$ , and  $X_{c1}$  obtained during first scans of heating,  $T_c$  obtained during cooling and  $T_{g2}$ ,  $T_{CC2}$ ,  $\Delta H_{CC2}$ ,  $T_{m2}$ ,  $\Delta H_{m2}$  and  $X_{c2}$  obtained during second heating (DSC) and (*Tonset*) values obtained by TGA for the neat PLA and PLA/lignin/carbon black composites.

	TGA		First heating					Cooling		Second heating				
	$T_{onset}$ (°C)	$T_{gl}$ (°C)	$T_{CC1}$ (°C)	$\Delta H_{CC1}$ (J/g)	$T_{m1}$ (°C)	$\Delta H_{m1}$ (J/g)	$X_{c1}$ (%)	$T_c$ (°C)	$T_{g2}$ (°C)	$T_{CC2}$ (°C)	$\Delta H_{CC2}$ (J/g)	$T_{m2}$ (°C)	$\Delta H_{m2}$ (J/g)	$X_{c2}$ (%)
Neat PLA	324	59	88	9.3	175	56.1	49.9	113	62	--	--	177	50.9	54.3
90/5/5	347	57	-	-	175	47.5	47.8	111	63	--	--	176	51.8	55.3
85/10/5	359	59	-	-	175	53.1	53.7	109	64	--	--	176	52.4	55.9
80/15/5	364	58	-	-	174	52.1	53.1	106	64	--	--	175	53.4	57.0
85/5/10	350	56	-	-	175	49.3	49.6	111	65	--	--	176	52.0	55.5
80/10/10	365	57	85	9.0	175	50.5	37.2	109	66	--	--	176	48.1	51.3
75/15/10	350	58	90	18.0	173	51.8	26.1	108	65	--	--	175	53.5	57.1
80/5/15	355	56	87	19.2	173	52.4	27.2	110	65	--	--	176	52.7	56.2
75/10/15	354	58	86	15.7	174	58.7	36.9	110	65	--	--	176	54.4	58.1
70/15/15	349	57	88	18.7	174	54.8	25.3	107	65	--	--	175	52.6	56.2

$T_g$  is the glass transition temperature obtained during heating scans,  $T_{cc1}$  is cold crystallization temperature obtained during heating scans,  $\Delta H_{CC1}$  is the cold crystallization enthalpy obtained during heating scans,  $T_{m1}$  is crystalline melting temperature obtained during heating scans,  $\Delta H_{m1}$  is the melting enthalpy obtained during heating scans,  $X_{c1}$  is degree of crystallinity obtained during heating scans,  $T_c$  is crystallization temperature,  $T_{g2}$  is the glass transition temperature obtained during second heating scans,  $T_{CC2}$  is cold crystallization temperature obtained during second heating scans,  $\Delta H_{CC2}$  is the cold crystallization enthalpy obtained during second heating scans,  $T_{m2}$  is crystalline melting temperature obtained during second heating scans,  $\Delta H_{m2}$  is the melting enthalpy during second heating scans,  $X_{c2}$  is degree of crystallinity obtained during second heating scans, *Tonset* is start temperature of irreversible thermal degradation, and TGA is thermogravimetric analysis.

The initial temperature of degradation (or initial thermal stability) was altered with the incorporation of lignin and carbon black, just as it is possible to observe a single thermal event. The addition of lignin and carbon black increased the *Tonset* of the composites. There was an increase of about 41 °C in *Tonset* for the PLA/lignin/carbon black composite (80/10/10) compared to the neat PLA. Overall, this was the formulation that obtained a larger increase in the *Tonset*. Thus, a synergism is observed when the two fillers (lignin and carbon black) are added, reaching values higher than neat PLA and PLA/lignin composites<sup>[9,16]</sup> and PLA/carbon black<sup>[3]</sup>.

Figure 3 shows the DSC thermograms of the neat PLA and the PLA/lignin/carbon black composites. For neat PLA, three thermal transitions can be observed in the first heating: the glass transition temperature ( $T_g$ ) at 59 °C, an exothermic event at 88 °C corresponding to the cold crystallization and, the crystalline melting temperature ( $T_m$ ) at 175 °C, results close to those found by Kumar Singla et al.<sup>[21]</sup> and Mosnáčková et al.<sup>[22]</sup>. All thermal parameters obtained by DSC are shown in Table 2. Qin et al.<sup>[23]</sup> showed that PLA exhibits an exothermic event that represents a rate of cold crystallization, with heat gain without phase change, during its  $T_g$ , energy is released with increasing temperature, reorganization occurs in structure until the polymer melts.



**Figure 3.** DSC thermogram for the first (A) heating cycle; (B) cooling; and (C) the second heating cycle for the neat PLA and for the PLA/lignin/carbon black composites with different contents of lignin and carbon black.

The degree of crystallinity ( $X_c$ ) of the compositions was calculated from the enthalpy in the DSC in the first and second heating cycles<sup>[24,25]</sup>. For the first heating, there was a significant change in  $T_g$  and  $T_m$  (Figure 3A), and in the degree of crystallinity for all composites when compared to neat PLA (Table 2).  $X_c$  is strongly affected by the addition of lignin and carbon black. By analyzing the compositions with 5 wt% of carbon black, it is noted that the increase in the lignin content increases the value of the  $X_c$  of the composite. On the other hand, increasing the carbon black values (10 and 15 wt%) shows a decrease in the value of  $X_c$  for all the composites. Thus, it can be inferred that the carbon black is one of the main responsible for the changes in the crystallization of the composites. The reason for the decrease in the degree of crystallinity with increasing of carbon black content in PLA may be that PLA chains have less mobility and crystallize with great difficulty at high temperatures in the presence of carbon black<sup>[26-28]</sup>. The composite 75/15/15 showed  $X_c$  (in the first heating) of 25.3% lower than neat PLA (49.9%).

In Figure 3B it can be seen that there was a decrease in the  $T_m$  during cooling for all PLA/lignin/carbon black composites compared to neat PLA. In the second heating (Figure 3C), it is possible to observe an increase in  $T_g$  and a reduction in  $T_m$ , the PLA/lignin/ carbon black composites also presented a double peak endotherm (melt temperature) between 154 °C and 156 °C, values close to that found by Arruda et al.<sup>[29]</sup> in their study of PLA/PBAT blends. This double peak is common in polyesters, and the literature

justifies its presence by a melt/recrystallization/remelt mechanism<sup>[30,31]</sup>. However, in the second heating, all values of  $X_c$  of the composites were higher than neat PLA, but these values are very close to each other.

Thus, it can be concluded that the effect of processing conditions greatly influence the degree of crystallinity of the composites. The controlled cooling rate facilitated the crystallization of the PLA and, in the second heating, the increase of the carbon black content contributed to a slight increase in the degree of crystallinity of the composites. It is worth mentioning that in order to be applied as antistatic packaging the effect of the first heating is more significant since the packaging will not undergo heat treatments after its production.

### 3.2 Electrical characterization of PLA/lignin/carbon black composites

The results of electrical conductivity and electrical resistivity of the neat PLA and PLA/lignin/carbon black composites were shown in Table 3. It is possible to observe that most of the composites exhibit characteristics of insulating materials (electrical resistivity greater than  $1 \times 10^{11} \Omega \cdot \text{cm}$ )<sup>[2]</sup>, except compositions 80/10/10 and 75/15/10. These compositions exhibit characteristics of dissipative materials, that is, their electrical resistivity is between  $1 \times 10^4 \Omega \cdot \text{cm}$  and  $1 \times 10^{11} \Omega \cdot \text{cm}$ .

Regarding the electrical resistivity of the composites, the addition of lignin significantly reduces this property.

The lignin makes it difficult to form the percolative path between the carbon black particles, which resulted in a significant increase in the electrical resistivity (or decrease in the electrical conductivity) of the composites. Thus, compositions with the addition of 5 wt% carbon black cannot be used for the preparation of antistatic packages. With the increase in black carbon content to 10 wt%, it can be noticed that two compositions (80/10/10 and 75/15/10) presented a reduction in electrical resistivity in 5 decades of magnitude, making possible its use as antistatic packaging. In this case, the decrease in the electrical resistivity was due to the formation of conductive paths between the carbon black in the polymer matrix. As the content of the carbon black is increased the distance between this filler black is reduced and particles began to contact each other to form a continuous conductive pathway.

When 15 wt% of carbon black was used in the composites, an increase in the electrical resistivity of the composites was again noted. In this case, the large content of carbon black and lignin used possibly helped to form agglomerates and aggregates of these fillers in the polymer matrix, contributing to a low dispersion and distribution of these fillers and preventing the formation of electric percolation path. Therefore, it is feasible to use the compositions 80/10/10 and 75/15/10 for the preparation of antistatic packages, since in these compositions the polymer has become less resistive, framing it as dissipative and reaching the values similar to materials already used for the manufacture of these packaging. This feature makes it suitable for packaging and uses in protected ESD areas in order to avoid electric discharges and to avoid damaging electronic components.

**Table 3.** Electrical conductivity (S/cm) and electrical resistivity ( $\Omega\cdot\text{cm}$ ) for neat PLA and PLA/lignin/carbon black composites with different contents of lignin and c carbon black.

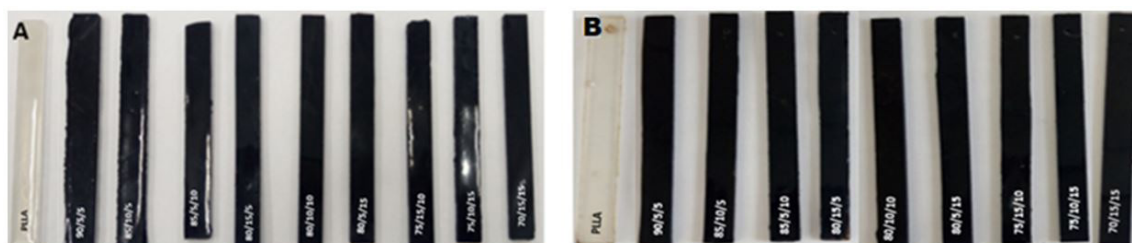
	Electrical Conductivity (S/cm)	Electrical Resistivity ( $\Omega\cdot\text{cm}$ )
Neat PLA	$3.32 \times 10^{-12}$	$3.01 \times 10^{11}$
90/5/5	$3.88 \times 10^{-16}$	$2.58 \times 10^{15}$
85/10/5	$5.50 \times 10^{-16}$	$1.82 \times 10^{15}$
80/15/5	$4.12 \times 10^{-16}$	$2.43 \times 10^{15}$
85/5/10	$1.14 \times 10^{-15}$	$8.79 \times 10^{14}$
80/10/10	$8.29 \times 10^{-07}$	$1.20 \times 10^6$
75/15/10	$3.75 \times 10^{-07}$	$2.66 \times 10^6$
80/5/15	$8.14 \times 10^{-15}$	$1.23 \times 10^{14}$
75/10/15	$8.52 \times 10^{-15}$	$1.17 \times 10^{14}$
70/15/15	$8.59 \times 10^{-16}$	$1.16 \times 10^{15}$

### 3.3 Evaluation of biodegradation tests of PLA/lignin/carbon black composites

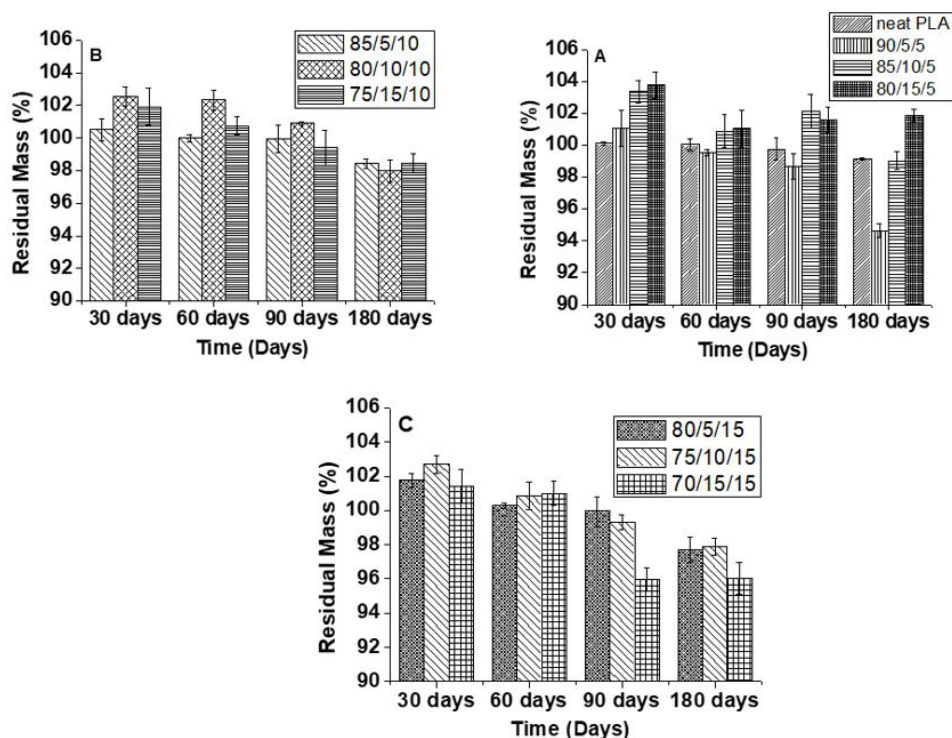
The degradation of polymers is associated with changes in characteristics such as shape, color, surface morphology and mechanical properties of the materials<sup>[32]</sup>. Some works in the literature related that PLA takes a long time to degrade in other media such as photodegradation, laser exposure and accelerated aging test<sup>[33,34]</sup>. Grigull et al.<sup>[34]</sup> performed the accelerated aging test on PLA films. The films were stored in the aging chamber, following the ASTM G154-06 standard, kept at 45 °C, 65% air humidity, and under direct incidence of UV lamp rays. Samples were taken at 0, 30, 60, 90 and 120 days. The results showed that the start of biodegradation occur after 60 days, and only after 120 days did the authors observe more significant changes in mass loss.

Since in the present work impact strength specimens were used for the biodegradation test, the soil biodegradation test was performed. Figure 4 shows the images of the neat PLA and the PLA/lignin/carbon black composites before and after the biodegradation test (180 days). It is possible to observe that neat PLA prior to the biodegradation test has a very smooth and shiny surface and is almost transparent. After 180 days submitted to degradation conditions in garden soil, there are no major modifications to the surface of the samples. The loss of brightness and yellowing being the main changes observed. Our results with neat PLA were consistent with those of other researchers<sup>[27,32]</sup> and show that the biodegradation rate of neat PLA is very slow under garden (natural) soil conditions and room temperature. In the Figure 4, it is also possible to observe that all samples were dark with the addition of lignin and carbon black, predominating the black color of carbon black. After 180 days of exposure in garden soil, the samples lost their brightness and showed no other significant visual changes.

Figure 5 shows the loss of mass obtained in the biodegradation test in garden soil. An increase in the mass of all samples was observed during the first 30 days of the test. This behavior may be due to the hydrophobicity of the PLA. According to several authors<sup>[3,13,35,36]</sup>, the degradation of PLA occurs in two stages: the hydrolysis of the material (to the ester group occurs by the penetration of water in the material that attacks the amorphous phase), followed by the attack of microorganisms to the oligomers of lactic acid. In general, the degradation time in the environment may vary from 6 months to 2 years, depending on the conditions under which the material is subjected<sup>[13]</sup>. As a result of the degradation process, the chains are reduced in smaller and soluble fragments, which leads to a reduction in the mass of the material<sup>[35,36]</sup>.



**Figure 4.** Samples of neat PLA and PLA/lignin/carbon black composites (A) before and (B) after the biodegradation test for 180 days.



**Figure 5.** Residual mass (%) after the biodegradation test for 30, 60, 90 and 180 days of exposure: (A) neat PLA and PLA/lignin/carbon black composites with 5, 10 and 15 wt% of lignin and 5 wt% of carbon black; (B) PLA/lignin/carbon black composites with 5, 10 and 15 wt% of lignin and 10 wt% of carbon black; and (C) PLA/lignin/carbon black composites with 5, 10 and 15 wt% of lignin and 15 wt% of carbon black.

It is possible to observe that all the composites developed had a mass increase in the first 30 days of exposure in garden soil, may be related to the adhesion of the microorganisms in the polymeric material surface. Because, the contact with the microorganism for 30 days leads to the polymer integrity loss, which is proportional to the surface area since the biodegradation, is usually initiated on the polymer surface, ie first adhesion, biofilm formation, followed by biodegradation, resulting in mass loss. Thus, the beginning of mass loss was observed after 60 days<sup>[37]</sup>, of exposure which was more significant for the composition 80/15/5 (2.7%) and after 180 days the largest loss of mass was for composition 90/5/5 (6.4%).

According to the results of mass loss and electrical characterization, it is possible to conclude that PLA/lignin/carbon black composites (80/10/10) and (75/15/10) would be the best options for the manufacture of antistatic and biodegradable packaging. These composites presented characteristics of dissipative materials, which is an option for the production of antistatic packaging and presenting a significant mass loss. The composites 80/10/10 and 75/15/10 lost about 4.6% and 4.8% of the mass, respectively, after 180 days of soil biodegradation test, being a good option for the production of biodegradable packaging.

In our previous work, we studied the biodegradation and electrical characterization of PLA/lignin<sup>[9]</sup> and PLA/carbon black<sup>[3]</sup> composites. We observed that the PLA/lignin composition with 10% lignin showed higher biodegradation, while the PLA/carbon black compounds had a minor loss,

showing that lignin aids degradation and carbon black does not accelerate, but also does not interfere with PLA degradation. However, the PLA/carbon black composition 15% increased the electrical conductivity and decreased the electrical resistivity of the composites by 11 and 8 orders of magnitude, respectively, allowing their use as antistatic packaging. And the PLA/lignin composites, as expected, presented characteristics of insulating materials. Thus, this work shows the synergistic effect of the addition of lignin and carbon black in the PLA matrix. The compositions 80/10/10 and 75/15/10 presented characteristics of dissipative materials, which is an option for the production of antistatic packaging and present a significant mass loss after 180 days of exposure in garden soil, is a good option for the production of biodegradable packaging.

### 3.4 Mechanical characterization of PLA/lignin/carbon black composites

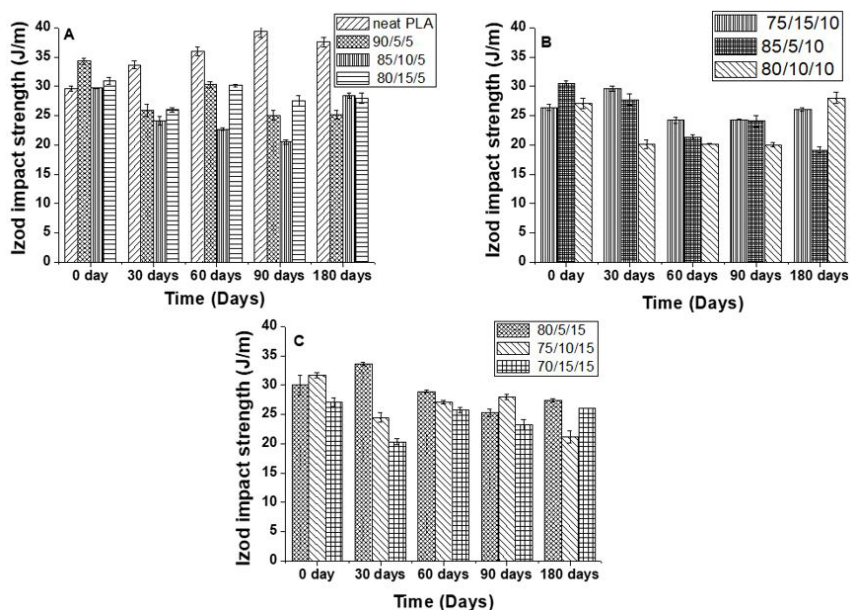
Figure 6 presents the results of Izod impact strength tests of notched specimens for all compositions, before and after biodegradation tests in garden soil. It is possible to observe that the Izod impact strength decreased after the exposure of the samples in garden soil, including neat PLA, and this fact may be indicative of the biological degradation of the material. Neat PLA lost about 4.7% of its impact strength after the biodegradation test on garden soil after 180 days.

Recalling that lignin and carbon black have not been added to improve impact strength, they are not reinforcing agents. Lignin was added to aid in the acceleration of the

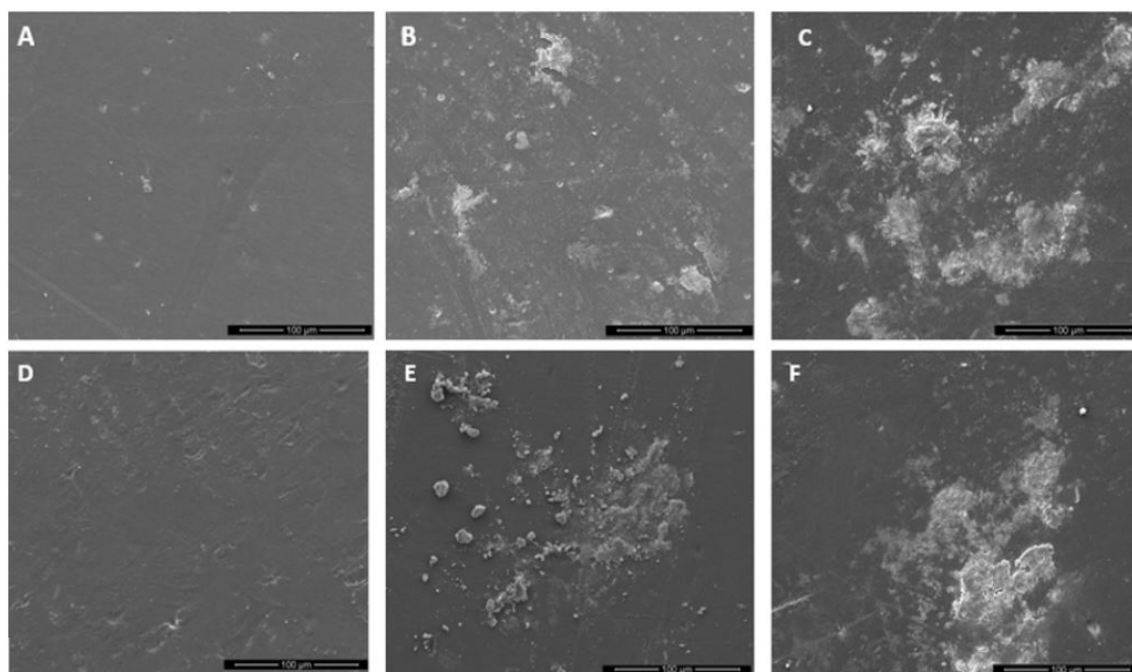
biodegradation process of PLA and carbon black to decrease the electrical resistivity of PLA. When lignin and carbon black were added to the PLA, the composite 75/15/10 decreased 10.8% impact strength, while the composite 90/5/5 had a 15.7% increase in impact strength. Lignin actually improved the biodegradation, and thus notably had a reduction in impact resistance. It is noted that after 180 days of exposure

in garden soil, the PLA/lignin/carbon black composite in composition 90/5/5 was the most lost in impact strength, about 66% and composition 80/10/10 was the one that lost the least impact resistance, about 44%.

3.5 Morphological characterization using scanning electron microscopy (SEM) of PLA/lignin/carbon black composites



**Figure 6.** Impact resistance of PLA/lignin/carbon black compositions according to the biodegradation time: (A) neat PLA and PLA/lignin/carbon black composites with 5, 10 and 15 wt% of lignin and 5 wt% of carbon black; (B) PLA/lignin/carbon black composites with 5, 10 and 15 wt% of lignin and 10 wt% of carbon black; and (C) PLA/lignin/carbon black composites with 5, 10 and 15 wt% of lignin and 15 wt% of carbon black.



**Figure 7.** SEM images of the PLA/lignin/carbon black 75/15/10 after (A) 0 day, (B) 90 days and (C) 180 days exposure on garden soil and PLA/lignin/carbon black 80/10/10 after (D) 0 day, (E) 90 days and (F) 180 days exposure on garden soil.



Figure 7 shows the surface morphology of the 75/15/10 and 80/10/10 composites after different time intervals (0, 90 and 180 days) of exposure in garden soil. These compositions were chosen because they were the most biodegradable characteristics. In Figures 7A and 7D it is possible to observe a surface with marks resulting from the pressing process. In Figures 7B and 7E, there are the presence of granules on the surface of the samples, these may be biofilm residues that have rested after washing, or some other material adhered or deposited during the analysis<sup>[3,38]</sup>. Figures 7C and 7F show the formation of large spots and some small surface cracks, results similar to those found by previous searches<sup>[27,39,40]</sup>, which may be associated with the formation of biofilms, once the PLA begins to degrade with 180 days. It is possible to observe similar structures of the compositions 75/15/10 and 80/10/10.

#### 4. Conclusions

Antistatic and biodegradable packages based on the poly(lactic acid) matrix were successfully obtained due to the synergy of the addition of lignin that acted as a biodegradation agent and carbon black that acted as an antistatic agent. The addition of 10 wt% of carbon black reduced the electrical resistivity of the composites, allowing the application as antistatic packaging. The addition of lignin was crucial to shortening the biodegradation time of the samples compared to neat PLA. PLA/lignin/carbon black composites (80/10/10) and (75/15/10) are the best alternatives for the manufacture of an antistatic and biodegradable packaging, since these composites presented characteristics of dissipative materials, which is an option for the production of antistatic packaging and present a significant mass loss after 180 days of exposure in garden soil. The composite of PLA/lignin/carbon black (80/10/10) lost about 4.6% of its mass and the composite (75/10/15) lost about 4.8% of its mass after 180 days of exposure in garden soil, is a good option for the production of biodegradable packaging.

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