


Effectiveness of modified lignin on poly(butylene adipate-co-terephthalate)/poly(lactic acid) mulch film performance

Janetty J. P. Barros^{1,2} | Rene R. Oliveira³ | Carlos B. B. Luna¹ |
 Renate M. R. Wellen^{1,4}  | Esperidiana A. B. Moura^{1,2}

¹Academic Unit of Materials Engineering, Federal University of Campina Grande, Campina Grande, Brazil

²Centro de Química e Meio Ambiente, Instituto de Pesquisas Energéticas e Nucleares, São Paulo, Brazil

³Centro de Ciências e Tecnologia de Materiais, Instituto de Pesquisas Energéticas e Nucleares, São Paulo, Brazil

⁴Materials Engineering Department, Federal University of Paraíba, João Pessoa, Brazil

Correspondence

Renate M. R. Wellen, Academic Unit of Materials Engineering, Federal University of Campina Grande, Campina Grande 58249-140, Brazil.

Email: wellen.renate@gmail.com

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Abstract

In this work, the biodegradable poly(butylene adipate-co-terephthalate) (PBAT)/poly(lactic acid) (PLA) blend (ECOVIO[®]) and lignin, a renewable and biodegradable natural polymer with high UV absorption and modified by gamma radiation were used to produce agriculture mulch films. Lignin was gamma-irradiated at 30 and 60 kGy. The irradiated and non-irradiated lignin content of 2 wt% was incorporated into PBAT/PLA blend matrix using a twin-screw extruder and extrusion blown film to prepare flexible films. PBAT/PLA/LIGNIN films were characterized by Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), x-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), tensile tests, contact angle, and UV-Vis analysis. FTIR spectra showed partial miscibility between PBAT/PLA and lignin, being intensified in irradiated lignin compounds. The DSC and XRD results confirmed that the degree of crystallinity of the blends was not significantly influenced by lignin addition. FE-SEM images showed better dispersion and miscibility in PBAT/PLA/Irradiated lignin. Miscibility improvement provided by irradiated lignin promoted better mechanical properties, mainly with lignin irradiated at 60 kGy. PBAT/PLA/LIGNIN films containing 2 wt% showed excellent UV-barrier property and greater hydrophobicity. Summing up, incorporation of low contents of irradiated lignin could be an interesting alternative to produce biodegradable UV-blocking agriculture mulch films.

KEYWORDS

gamma radiation, lignin, PBAT/PLA, UV-blocking

1 | INTRODUCTION

Using plastic films for covering agricultural land has increased considerably in recent decades, reaching more

than 1.5 megatons (Mt) annually worldwide.¹ One of the prominent factor is the increase in the global population that has stimulated the use of these films, with the objective of improving the agricultural crops yield, which is a

big challenge especially in regions with little precipitation and low air temperature. In these regions, plastic film roofing has become an important productivity enabler.¹

The most used agricultural mulch films are made from polyethylene (PE), because they are low cost, easily processed, durable, and flexible. However, the widespread use of PE has resulted in serious environmental contamination, leading to the accumulation of remaining film fragments in agricultural soils with negative impacts on productivity and soil composition. A viable strategy to overcome this drawback is to replace the conventional non-biodegradable films by biodegradable films.^{2,3}

Among the biodegradable polymers, poly(butylene adipate-co-terephthalate) (PBAT) is a synthetic aliphatic-aromatic polyester with mechanical properties similar to those of low-density polyethylene (LDPE), PBAT has 30 MPa of tensile strength and 700% of elongation at rupture (related to LDPE). The soil biodegradability character of PBAT is provided by the butylene adipate group; making it a viable option for replacing PE in agricultural mulch applications.⁴ However, PBAT has not achieved the expected industrial success, one of the reasons being its sensitivity to the UV radiation, having a limited shelf life in agricultural film applications and low tensile strength. In order to overcome such limitations, mixing PBAT with other biodegradable polymers such as poly(lactic acid) (PLA) is considered a promising way to extend its shelf life and improve toughness.^{4,5} The literature reports some works based on films of PBAT/PLA blends.^{6,7} The structural difference between PBAT/PLA tends to result in blends with limited miscibility.^{8,9} As a way to improve the UV barrier properties and tensile strength of the PBAT/PLA blend, adding lignin to the system can be an excellent alternative.¹⁰⁻¹²

Lignin is a natural polymer that attracts attention because it is renewable and one of the most abundant polymers on the planet. Lignin is an extremely complex macromolecule consisting of a mixture of aromatic polymers with similar structures. It is composed of methoxylated phenylpropane units, known as syringyl (S), guaiacyl (G), and p-hydroxyphenyl propane (p-H) units.¹³ Lignin can be widely used in the industry, however, its practical use is limited due to its complex, reticulated and branched structure, with a variety of cross-links among the chain units, which makes it highly heterogeneous. With that comes the need for the functionalization of this very promising material.¹⁴⁻¹⁶ An alternative is the use of ionizing radiation for the formation of functional groups and improvement of the interaction in polymeric blends.

Ionizing radiation or high-energy radiation is radiation that carries enough energy to ionize molecules. They are usually electromagnetic radiation, such as radiation emitted by natural or artificial radioactive nuclei, such as gamma rays (γ) or beams of accelerated particles such

as electron beams. Polymers irradiation with ionizing radiation (gamma rays, electron beam) leads to the formation of excited states, that is, reactive intermediate products such as ions and free radicals, several reaction pathways that result in rearrangement and/or formation of new connections and structures.^{17,18} Research has demonstrated the benefits of ionizing radiation in improving the properties of polymeric composites with lignocellulosic fibers, such as improved adhesion between fiber and matrix, aiming at better mechanical properties, improved water resistance, and thermal stability.^{19,20} Ionizing radiation is a promising tool to control polymers properties and an alternative route to functionalize lignin expanding its use in polymeric applications.^{21,22}

PBAT/PLA blends with 10% of the weight of non-irradiated and irradiated lignin at doses of 30, 60 and 90 kGy were investigated in Barros et al.²³ From Fourier transform infrared (FTIR) spectra, partial miscibility among PBAT/PLA and lignin was observed, being intensified in blends with irradiated lignin. Differential scanning calorimetry (DSC) scans showed that irradiated lignin shifted the crystallization peak of PBAT/PLA blend to lower temperatures and decreased the crystallization rate. Kinetic modeling by Friedman and Vyazovkin showed that crystallization in blends with irradiated lignin requires higher activation energy (E_a). Field emission scanning electron microscopy (FESEM) images showed better dispersion and miscibility for irradiated PBAT/PLA/Lignin samples. Overall, the results showed that Kraft lignin irradiation promoted miscibility and compatibility among PBAT/PLA/Lignin.²³

Based on the above information, addition of irradiated lignin in polymeric matrices has great potential to improve compatibility and promote UV barrier.²⁴⁻²⁶ However, studies using the irradiated PBAT/PLA/Lignin system are scarce in the literature, being an excellent route for the development of biodegradable agricultural mulch films, improving sustainability, replacing conventional polymeric films and consequently overcoming the problems of disposal associated with them.

The objective of this work was to produce mulch films for agriculture based on PBAT/PLA incorporated with non-irradiated and irradiated lignin at doses of 30 and 60 kGy; and to analyze the effects of gamma radiation on lignin and its influence on the miscibility and thermal, mechanical, surface and UV barrier properties of the films.

2 | METHODOLOGY

2.1 | Materials

The blend PBAT/PLA (82% PBAT and 18% PLA) trade name Ecovio[®] F2332, supplied by BASF SE (Ludwigshafen,

Germany), with the following properties: melt index (MFI) between 7.0 and 11.0 g/10 min (2.16 kg at 190°C), density 1.24–1.26 g/cm³, melting point between 140 and 155°C and water vapor permeation rate (23°C, 50% RH) equal to 120 cm³/(m² d bar). Lignin obtained by precipitation of black liquor from the kraft pulping process of eucalyptus pulp and paper industry, supplied by Suzano Papel e Celulose S/A (São Paulo, Brazil), (pH: 3.8; solids content: 95%; ash content: 2%).

2.2 | Lignin washing

Kraft Lignin was previously washed to remove residual impurities, filtered, dried in an oven, macerated and granulometrically classified according to the methodology described in our previous work.²³

2.3 | γ -irradiation

Lignin was submitted to gamma radiation at a rate of 5.0 kGy/h at room temperature, obtaining irradiated lignin at absorbed doses of 30 and 60 kGy, using the Cobalt-60 Multipurpose Gamma Irradiator at the Center for Radiation Technology at IPEN, São Paulo.

2.4 | Blends processing and flexible films

PBAT/PLA blend and lignin were initially dried in an oven with air circulation, from Quimis, model Q317M93, at 80 ± 2°C for 24 h to remove moisture before processing. Mixtures of PBAT/PLA with 2% of the weight of irradiated and non-irradiated lignin were obtained by extrusion using a 16 mm Haake Rheomix twin-screw corrodng extruder, L/D = 25 from Thermo Scientific (Germany). The extruder temperature profile was 130/145/150/135/150/145°C, with screw rotation of 14 rpm. The extrudates were air-cooled, pelleted using a pellet machine, dried in an oven with air circulation at 80 ± 2°C for 24 h.

To obtain the flexible films, the pelletized mixtures of PBAT/PLA with 2% of irradiated and non-irradiated lignin were fed to a single screw extruder of tubular film processing system, HAAKE Rheomix, 16 mm, rate L/D = 25 from Thermo Scientific (Germany) and films with a thickness of 0.05 ± 0.02 mm were acquired. The temperature profile used during the films production was 140/140/140/160/160/165°C with the screw rotation of 20 rpm.

2.5 | Characterizations

2.5.1 | Fourier transform infrared spectroscopy measurements

Fourier transform infrared spectroscopy analyses were performed using the Perkin Elmer – Frontier (Llantrisant, UK). Tests carried out in the medium infrared range with wavenumber ranging from 4000 to 650 cm⁻¹, with 16 scans and resolution of 4 cm⁻¹ with the attenuated total reflectance (ATR) accessory.

2.5.2 | Differential scanning calorimetry measurements

Differential scanning calorimetric scans were carried out using a DSC Q10 – TA Instruments (New Castle, DE). Specimens with approximately 4–5 mg were sealed in aluminum crucibles; the purge gas used was nitrogen with a gas flow of 50 mL/min. A four-stage thermal cycle was applied: specimens were heated from 25 to 200°C, remaining at 200°C for 3 min (isotherm), after which the melt was cooled to 25°C (cooling) and reheated to 200°C, it was done in order to analyze the existence of crystallization and melting events. Tests were performed under non-isothermal conditions, at constant heating/cooling rate of 10°C/min.

2.5.3 | X-ray diffraction measurements

X-ray diffraction (XRD) data were collected using a Rigaku multiflex diffractometer, model DMAX 2200 (Tokyo, Japan). These measurements were performed using Cu K α ($\lambda = 15,418 \text{ \AA}$), under the operational conditions of 40 kV and 20 mA, over the 2θ range from 3 to 70°. Crystallinity was calculated as the ratio between the crystalline area (peaks) and amorphous halo, described by Equation (1)²⁷:

$$\%C = \frac{I_c}{I_c + I_a} \times 100 \quad (1)$$

Where %C is the crystalline fraction. I_c is the diffraction peaks area. I_a is the amorphous halo area.²⁷

2.5.4 | Field emission scanning electron microscopy images

PBAT/PLA/Lignin blends were cryofractured under liquid nitrogen and their surfaces' morphology were

analyzed by FESEM using a JEOL, model JSM-6701F (Tokyo, Japan). Prior to SEM analysis, samples were covered with a layer of gold by sputtering.

2.5.5 | Tensile tests

The mechanical tensile strength tests were carried out according to ASTM D 882-91 standard, using a universal testing machine model Instron 5567 (Canton, MA). The test was carried out with the flexible films specimens, in the machine direction, with a displacement rate of 50 mm/min, at room temperature.

2.5.6 | Contact angle

The contact angle with water was determined by means of the sessile drop method, using portable contact angle equipment; model Phoenix-I by Suface Eletro Optics – SEO (South Korea). The drop was deposited on the film surface using a micrometric doser. The captured image was analyzed by the software associated with the equipment, using an interval of 10 seconds to capture each image.

2.5.7 | Spectroscopy in the ultraviolet–visible region (UV–Vis) measurements

The UV–Vis transmittance of the films was evaluated using a Shimadzu UV-2600i spectrophotometer (Kyoto, Japan), with scan range from 220 to 700 nm, in transmission mode (%T) with 0.5 nm resolution.

3 | RESULTS AND DISCUSSION

3.1 | Fourier transform infrared spectroscopy measurements

Figure 1 shows the FTIR spectra of PBAT/PLA blend and PBAT/PLA blends with non-irradiated and irradiated lignin at doses of 30 and 60 kGy. The bands corresponding to 2995 and 2945 cm^{-1} represent, respectively, asymmetric and symmetric stretching vibrations of CH_3 , since the carbonyl groups and vicinal oxygen are electron-withdrawing groups, and the inductive effect of CH_3 provides higher vibration frequency. The 1750 cm^{-1} band represents the carbonyl elongation vibration ($\text{C}=\text{O}$) referring to PLA, since the hydrogen atoms and the carbonyl group in PLA molecules generate a hyperconjugated system, and the hyperconjugation effect raises the

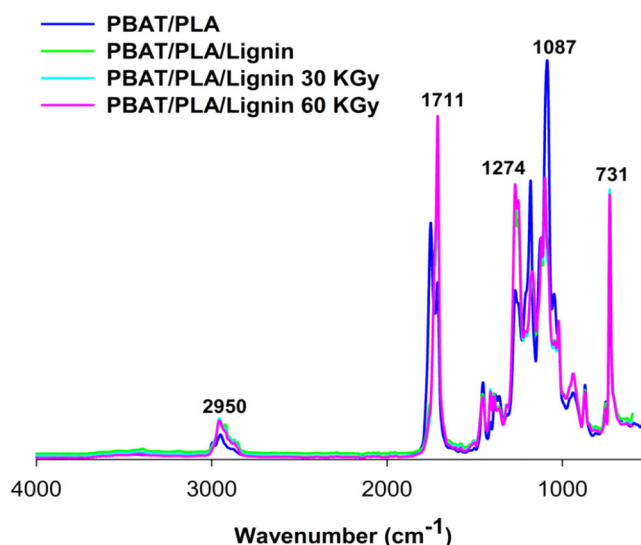


FIGURE 1 Fourier transform infrared spectra of PBAT/PLA, PBAT/PLA/Lignin, PBAT/PLA/Lignin 30 kGy, and PBAT/PLA/Lignin 60 kGy. [Color figure can be viewed at wileyonlinelibrary.com]

elongation vibration frequency of carbonyl group at 1750 cm^{-1} .²⁸ The vibration at 1712 cm^{-1} corresponds to the stretching of carbonyls and ester groups present in PBAT.²⁹ PBAT and PLA present different bands of carbonyl vibration due to the difference in chemical structure.²³ Bands at 1300 and 1015 cm^{-1} refer to ester group stretching ($\text{C}-\text{O}$). The band observed at 725 cm^{-1} can be attributed to the elongation of methylene groups.²⁹

Mixtures based on commercially available PBAT and PLA tend to separate the PBAT phase from the PLA one, that is, they have low miscibility.³⁰ The different vibration bands of carbonyl groups at 1750 and 1712 cm^{-1} observed in PBAT/PLA spectrum without lignin is an indicative of poor miscibility/interaction among the mixture's constituents. Lignin addition can improve the blend miscibility, since lignin is highly functional, has phenolic and aliphatic hydroxyl groups that can be exploited for its modification^{15,31} and thus improve the interaction among the blend's components.

Figure 2a shows the magnified carbonyl vibration region. With lignin addition, changes in the spectrum are observed. The carbonyl band (1750 and 1712 cm^{-1}) is shifted to a shorter wavelength, forming only a peak of greater intensity, at 1711 cm^{-1} , more evident in blends with irradiated lignin, indicating secondary interaction by hydrogen bonds between the carbonyls present in PBAT/PLA with the hydroxyls present in lignin, illustrated in Figure 2b, suggesting that lignin, mainly irradiated at doses of 30 and 60 kGy, promoted greater miscibility and compatibility of the blends. Similar results were reported in Barros, et al.²³ for PBAT/PLA blends

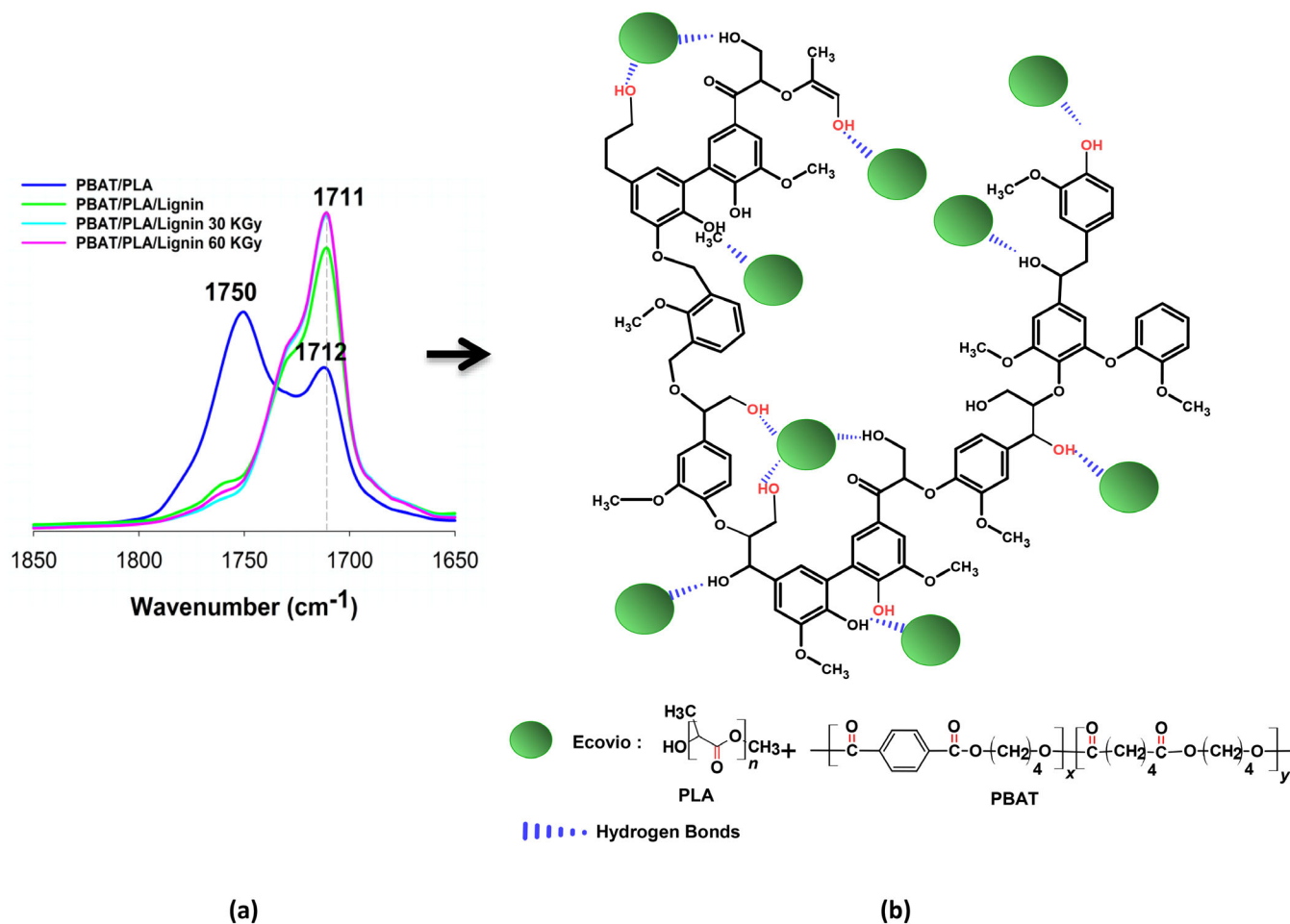


FIGURE 2 (a) Zoomed Fourier transform infrared spectra in the range from 1850 to 1650 cm^{-1} , (b) The schematic process of secondary interaction and miscibility between PBAT/PLA/Lignin. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/polb.254684)]

with 10% non-irradiated and irradiated lignin at doses of 30, 60 and 90 kGy.

3.2 | Differential scanning calorimetry measurements

Figure 3 shows the non-isothermal DSC scans of PBAT/PLA and PBAT/PLA blends with non-irradiated and irradiated lignin at doses of 30 and 60 kGy, acquired during cooling, Figure 3a and during the second heating, Figure 3b.

Cooling is characterized by an exothermic peak characteristic of the melt crystallization of PBAT/PLA. Crystallization parameters of the blends are shown in Table 1. No significant changes are verified in the initial ($T_{0.01}$), final ($T_{0.99}$), and peak (T_p) temperatures, except for the blend with irradiated lignin at a dose of 60 kGy, where T_p displacement is observed for lower temperatures, $\sim 2^\circ\text{C}$, what could be related to the lignin addition subtle hindering PBAT/PLA crystallization, due to the interaction between the carbonyls in PBAT/PLA and the

hydroxyls in irradiated lignin, demanding more energy for ordering the polymeric chains. Similar results for the blend containing 10 wt% (% of the weight) of lignin irradiated with 30 kGy were reported in a previous work.²³ Where a decrease of approximately 11.5°C was observed, and from the kinetic modeling, it was found that at reaching the required E_a , higher crystallization values were obtained for blends with irradiated lignin.

The enthalpy of crystallization and the degree of crystallinity did not change upon lignin addition (Table 1). These results indicate that the presence of lignin did not significantly alter the crystalline structure of PBAT/PLA matrix.³² To corroborate the degree of crystallinity evaluated from the DSC scans, the measurement of the degree of crystallinity was also performed using XRD (%C), acquired data are shown in Table 1. The crystallinity computed by DSC and by XRD showed similar results and trend, with a maximum variation of $\sim 1.7\%$, which it is in the error range, indicating that the results are representative. Similar behavior was observed by Di et al.³³ in the addition of organophilic clay to polymeric matrix.

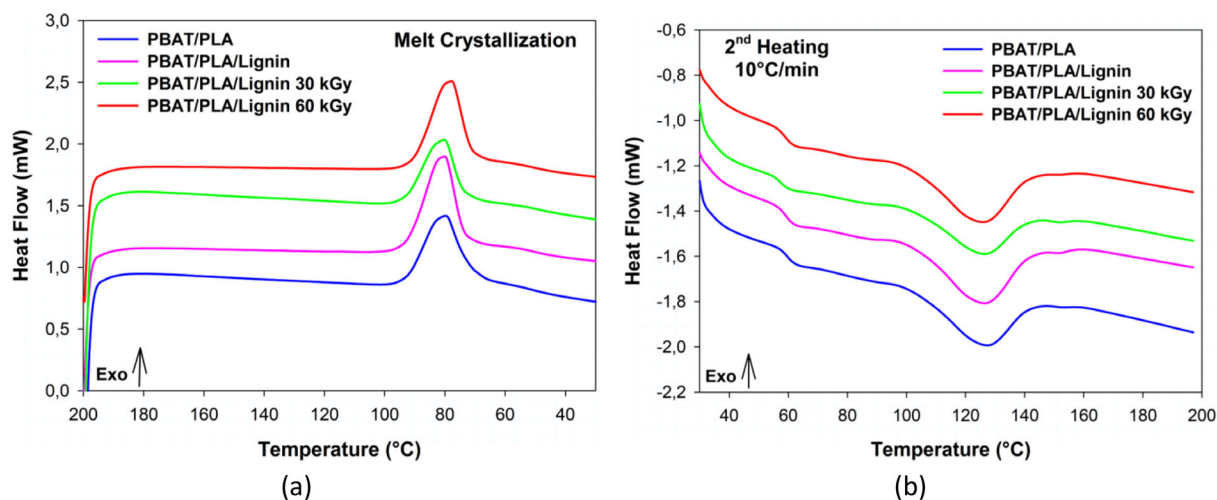


FIGURE 3 Differential scanning calorimetric scans acquired during: (a) cooling and (b) second heating. Heating rates and compounds indicated. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

TABLE 1 Crystallization parameters computed from DSC and XRD scans.

Compound	$T_{0.01}$ (°C)	T_P (°C)	$T_{0.99}$ (°C)	ΔH (J/g)	ΔX_c % - DSC	%C - XRD
PBAT/PLA	96.5	80.0	65.6	12.5	11.7	11.0
PBAT/PLA/Lignin	96.7	80.2	67.6	14.4	13.1	12.5
PBAT/PLA/Lignin 30 kGy	96.8	80.3	66.7	13.5	12.3	11.3
PBAT/PLA/Lignin 60 kGy	94.4	78.0	66.2	14.2	13.0	11.3

Note: $T_{0.01}$: temperature of 1% crystallized fraction (a good estimate of the event initial point). T_P : peak crystallization temperature. $T_{0.99}$: temperature of 99% crystallized fraction (a good estimate of the event final point). ΔH : latent heat of crystallization. ΔX_c : change in crystallinity during the event. %C: degree of crystallinity evaluated from the XRD.

Abbreviations: DSC, differential scanning calorimetry; PBAT, poly(butylene adipate-co-terephthalate); PLA, poly(lactic acid); XRD, x-ray diffraction.

The second heating is characterized by the glass transition temperature (T_g) of PLA $\sim 57.4^\circ\text{C}$. A shift to 56.5°C is observed in the PBAT/PLA/Lignin composition, 55.2°C for PBAT/PLA/Lignin 30 kGy and 56.1°C for PBAT/PLA/Lignin 60 kGy. In the amorphous region of the investigated blends, that is, in the glass transition region, it is supposed to take place intermolecular interactions of hydrogen between the phenolic hydroxyl group of lignin and the carbonyl groups of PLA, as shown in the FTIR section, above presented.³⁴ In the second heating, endothermic peaks are also observed, in the temperature range between 90 and 145°C , which is associated with the melting of PBAT/PLA blend crystals formed during cooling.

3.3 | X-ray diffraction measurements

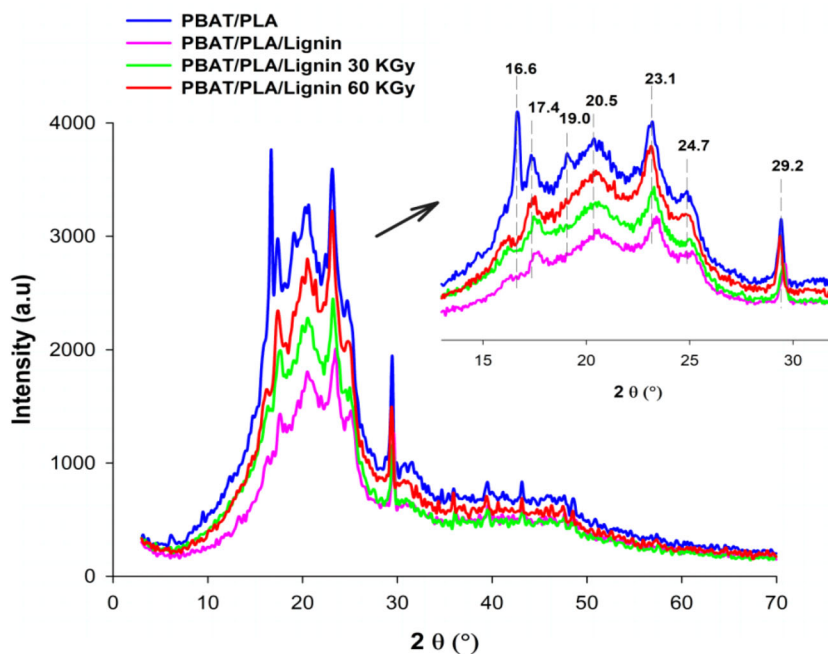
XRD diffractograms are shown in Figure 4. As PBAT/PLA blend has higher weight content of PBAT than PLA, the XRD pattern was predominantly characteristic of PBAT

diffraction peaks. Therefore, the diffraction peaks observed at 16.6 , 17.4 , 20.5 , 23.1 , and 24.7° , correspond to PBAT crystal planes (011), (010), (110), (100), and (111), respectively, indicating triclinic packing in the α -form of PBAT.^{9,35,36} The crystal plane (110) of PLA, generally presents a strong diffraction peak close to 16.0° being superimposed by the diffraction peak of PBAT.³⁷

Upon lignin addition to PBAT/PLA blend, a decrease in the relative intensity and an increase in the peak width is apparently observed. However, from the peaks area integration and with the aid of Equation (1), the percentage of crystallinity was calculated and shown in Table 1, noting that the lignin addition subtly changed the crystallinity of PBAT/PLA, promoting only a quite small increase, which can be considered to be within the error range.

The peak width of a polymer is related to the packing of the crystalline structure, where a narrower peak reflects a tightly packed structure, a wider peak represents a loosely packed crystalline structure, and peak intensity represents the relative crystallinity of the

FIGURE 4 X-ray diffractograms of PBAT/PLA/Lignin blends. [Color figure can be viewed at wileyonlinelibrary.com]



polymer.³⁸ Consequently, the lignin addition might promote heterogeneous nucleation in PBAT/PLA blend. Other researchers have observed lignin acting as a nucleating agent by increasing PLA crystallinity.^{38,39}

3.4 | Field emission scanning electron microscopy images

In Figure 5, the surface micrographs captured by FESEM are presented. In Figure 5a, it is observed that PBAT/PLA specimen presents an immiscible character. PBAT as the main phase in the compound involves PLA, which takes the form of domains in PBAT matrix. It is identified in the domains the poor adhesion with the matrix, in addition to a well-defined interface and pores on the surface. This is due to reduced interaction and different surface tension between PBAT and PLA. Similar results were reported.^{23,40} These factors are directly related to the blends' mechanical properties reduction.

The FESEM micrographs, Figure 5b–d of PBAT/PLA/Lignin blends showed large particles formed by self-aggregation of lignin. In addition, in the composition with non-irradiated lignin, Figure 5b one observes well-defined domains, presence of pores, loose particles and space between interfaces, indicating the weak interaction between the constituents.

After irradiation, the intermolecular interaction among the lignin macromolecules was weakened and the lignin clusters decreased in the irradiated PBAT/PLA/Lignin blends, mainly in the composition with irradiated lignin at a dose of 60 kGy, Figure 5d, observing a more

homogeneous surface, with better dispersion, interfacial adhesion, that is, there was less phase segregation and greater interaction among the blend constituents. Gamma irradiation promotes the formation of greater amounts of functional groups available to react with PBAT/PLA, explaining the greater interaction, miscibility and compatibility promoted by irradiated lignin, corroborating the FTIR results, where it was seen that the carbonyls present in PBAT and PLA interact with the hydroxyls present in lignin. Similar results were reported by Xiong et al.,⁴¹ it was observed that lignin methylation promoted greater interaction between PBAT/Lignin and decreased the agglomerates formation of PBAT surface.

3.5 | Tensile tests

Tensile tests were carried out to investigate the effect of non-irradiated and irradiated lignin on the mechanical properties of PBAT/PLA blend. Figure 6 shows the stress–strain plots for PBAT/PLA films and upon addition of 2% of the weight of non-irradiated and irradiated lignin at 30 and 60 kGy. The mean values for yield stress, tensile strength at break, modulus of elasticity and elongation at break, acquired in the tensile tests are shown in Table 2.

The stress versus strain plots, Figure 6, show that PBAT/PLA films and those containing non-irradiated lignin showed lower tensile strength at break and elongation at break. These results are confirmed by the mean values of the tensile properties presented in Table 2, which shows a reduction in the values of yield stress,

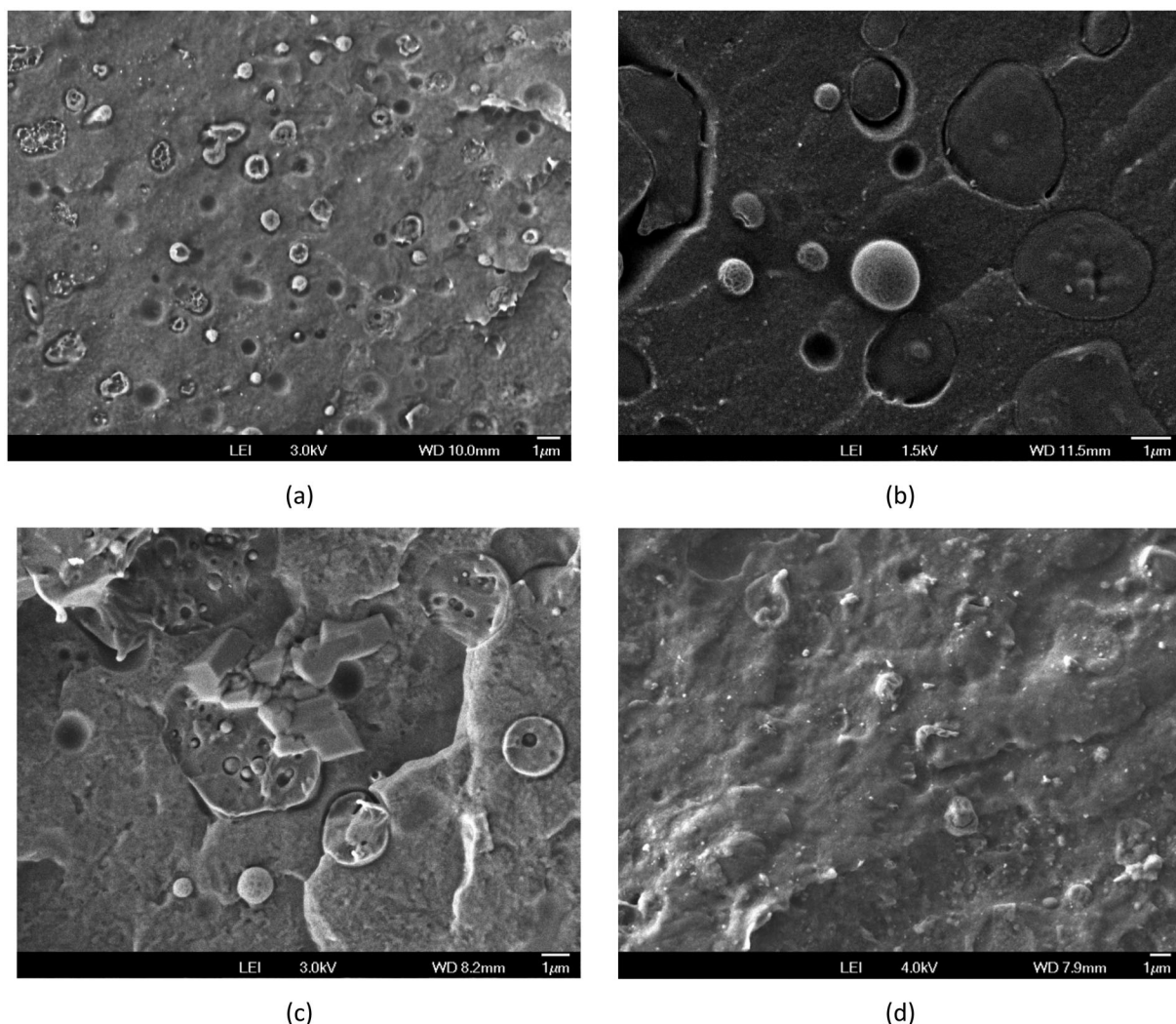


FIGURE 5 Field emission scanning electron microscopic images of fracture surfaces (a) PBAT/PLA, (b) PBAT/PLA/Lignin, (c) PBAT/PLA/Lignin 30 kGy, and (d) PBAT/PLA/Lignin 60 kGy.

tensile strength at break and elongation at break for the films with addition of non-irradiated lignin, when compared to that of PBAT/PLA film and films containing irradiated lignin. Young's modulus showed a slight increase upon non-irradiated lignin addition. Previous studies have reported a decrease in the mechanical properties of PLA and PBAT with the lignin addition.^{34,42} On the other hand, the addition of irradiated lignin led to gains in the average values of the film's tensile properties, mainly in relation to tensile strength at break and elongation at break. This is due to the miscibility and better interfacial interaction between the irradiated lignin with PBAT/PLA matrix, as observed in the FTIR and FESEM section.

Comparing the tensile strength at break of the films containing lignin in relation to PBAT/PLA film, it is observed that PBAT/PLA/Lignin 30 kGy presented a gain of 10.6% and the composition PBAT/PLA/Lignin 60 kGy, a gain of 13%, whereas the composition with non-

irradiated lignin showed a reduction of 5.8% in the original tensile strength at break of PBAT/PLA blend.

Regarding the elongation at break, addition of irradiated lignin promoted a gain of 138.81% for PBAT/PLA/Lignin 30 kGy and 153.4% for PBAT/PLA/Lignin 60 kGy, compared to PBAT/Lignin 60 kGy film; whereas the composition with non-irradiated lignin showed a reduction of 39.4% compared to PBAT/PLA film.

The relatively lower values of tensile strength presented by PBAT/PLA films, when compared to those of films containing irradiated lignin, can be correlated with the reduced interaction and different surface tension between PBAT and PLA as verified in FESEM analysis, where it was observed that PBAT/PLA blend presents biphasic morphology typical of immiscible systems, with spheroidal PLA domains dispersed in the PBAT matrix.

The inferior performance of PBAT/PLA films containing non-irradiated lignin can be explained due to the

formation of lignin clusters, the lack of strong interfacial interactions and the reduction in the continuous region of PBAT/PLA matrix.⁴¹

The addition of irradiated lignin promotes greater interaction and compatibility due to the more reactive functional groups that are more likely to interact with PBAT/PLA, as is the case with the greater availability of hydroxyls present in lignin that interact with the carbonyl groups present in PBAT/PLA, forming secondary hydrogen bonds, as seen in FTIR analysis, supporting the better results observed in the mechanical properties.

For the Young's Modulus, no significant change was observed in the acquired data for PBAT/PLA film and for the films with irradiated lignin at doses of 30 and 60 kGy, considering the standard deviation, whereas the film with non-irradiated lignin showed an increase of 11.7%, this may be associated with the fact that the Young's modulus is measured in the linear deformation region of the material called elastic deformation and depends on the forces and interatomic bonds, that is, it strongly depends on the chemical composition of the material.⁴³⁻⁴⁵ It is suggested that in non-irradiated PBAT/PLA/Lignin films, lignin

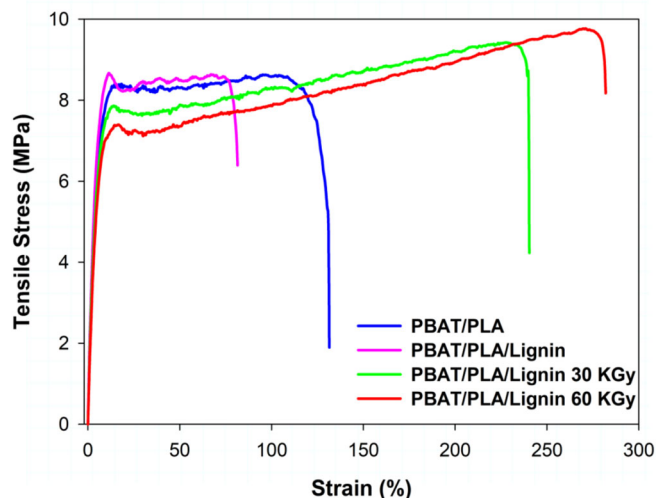


FIGURE 6 Tensile stress–strain plots for films of PBAT/PLA, PBAT/PLA/Lignin, PBAT/PLA/Lignin 30 kGy, and PBAT/PLA/Lignin 60 kGy. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

TABLE 2 Tensile tests results for PBAT/PLA, PBAT/PLA/Lignin, and PBAT/PLA/Lignin 30 e 60 kGy.

Test	PBAT/PLA	PBAT/PLA/lignin	PBAT/PLA/lignin 30 kGy	PBAT/PLA/lignin 60 kGy
Tensile stress at yield (MPa)	8.3 ± 0.1	7.9 ± 0.5	8.5 ± 0.6	8.7 ± 1.3
Tensile strength at break (MPa)	8.5 ± 0.2	8.0 ± 0.4	9.4 ± 0.2	9.6 ± 0.9
Young's modulus (MPa)	127.6 ± 20.7	142.5 ± 23.7	128.0 ± 3.7	124.8 ± 15.8
Elongation at break (%)	102.8 ± 16.7	62.3 ± 11.6	245.5 ± 14.9	260.5 ± 37.1

Abbreviations: PBAT, poly(butylene adipate-co-terephthalate); PLA, poly(lactic acid).

influences the Young's modulus more clearly, since the particles size and the intermolecular interaction among lignin macromolecules is greater before irradiation, as seen in the FESEM analysis. For the tensile stress at yield no significant changes were observed. Similar results were reported by Kumar, et al.²⁴ it was applied electron beam radiation to make PBAT/Lignin blend compatible in the presence of 3 phr triallyl isocyanurate (TAIC). It was observed that lignin irradiation promoted blend compatibility, resulting in a significant improvement in mechanical properties.

3.6 | Contact angle

Hydrophobicity is an important property to agriculture mulch films, as one of the main films functions is to maintain soil moisture, reducing the rate of water evaporation. Therefore, it is recommended that the films have a hydrophobic character, with low moisture absorption and water resistance in order to preserve their structural integrity so that they perform the insulating function and provide the benefits for agricultural production.^{46,47} To investigate the effect of lignin on the surface properties and to characterize the hydrophilicity/hydrophobicity of the films, measurements of the contact angle with water were performed and are shown in Figure 7.

The contact angle of PBAT/PLA film was 62.4°, confirming the hydrophilic character, since the surface is considered hydrophilic if the contact angle is lower than 90°, while the surface is hydrophobic if contact angle is higher than 90°.^{48,49}

Lignin addition provided higher hydrophobicity to the films, as the contact angle average increased to 71.4° upon non-irradiated lignin addition. Irradiated lignin addition at doses of 30 and 60 kGy promoted an increase in the contact angle to 72.2 and 72.7°, respectively. Literature reported that lignin addition promoted an increase in the hydrophobicity of PLA.^{50,51}

The increase in the contact angle can be provided by the hydrophobicity of lignin, which is considered a hydrophobic natural polymer due to its aromatic structure.⁵² In addition to the predominant aromatic structure that makes it more hydrophobic, lignin also has polar

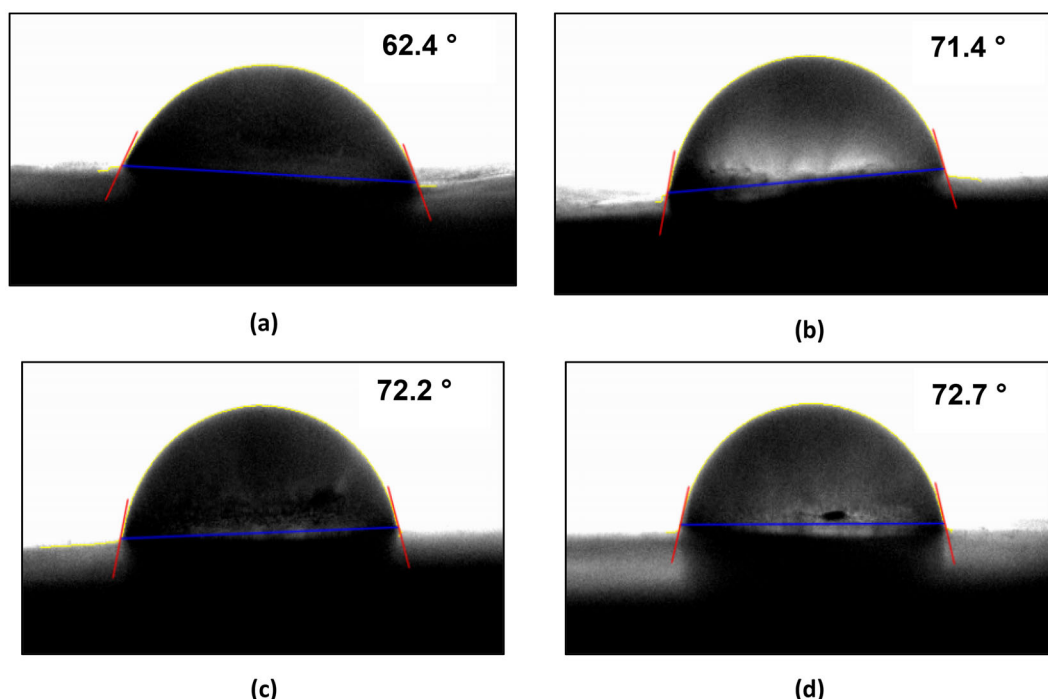


FIGURE 7 Contact angle of (a) PBAT/PLA, (b) PBAT/PLA/Lignin, (c) PBAT/PLA/Lignin 30 kGy, (d) PBAT/PLA/Lignin 60 kGy. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.54684)]

functionalities, such as hydroxyl, phenol and carboxylic acid.^{53,54} Phenolic hydroxyls are among the main reactive groups of lignin⁴⁹ and as shown in the FTIR results, Figure 2, the hydroxyls present in lignin tend to interact with the carbonyls present in PBAT/PLA blend, thus improving the films hydrophobic character.

3.7 | Spectroscopy in the ultraviolet-visible region (UV-Vis) measurements

PBAT/PLA and PBAT/PLA films with non-irradiated and irradiated lignin were analyzed by UV-Vis spectroscopy in the UV-B (280–320 nm), UV-A (320–400 nm) and visible light (400–700 nm), in order to evaluate the influence of lignin on the UV blocking properties of PBAT/PLA blend. The spectra are shown in Figure 8.

In the UV-B region, PBAT/PLA films showed maximum transmittance of 5.8%, that is, they absorbed around 94.2% of UV-B rays up to 302 nm, linearly increasing the transmittance after this wavelength, consequently decreasing absorption.

Lignin addition promoted excellent protection in the entire UV-B range (280–320 nm), with maximum transmittance of 6% (protection of approximately 94%) for PBAT/PLA/Lignin of 6.3% (protection of approximately 93.7%) for compounds with irradiated lignin at doses of 30 and 60 kGy, different from PBAT/PLA film that after 302 nm the absorption of UV-B rays dropped.

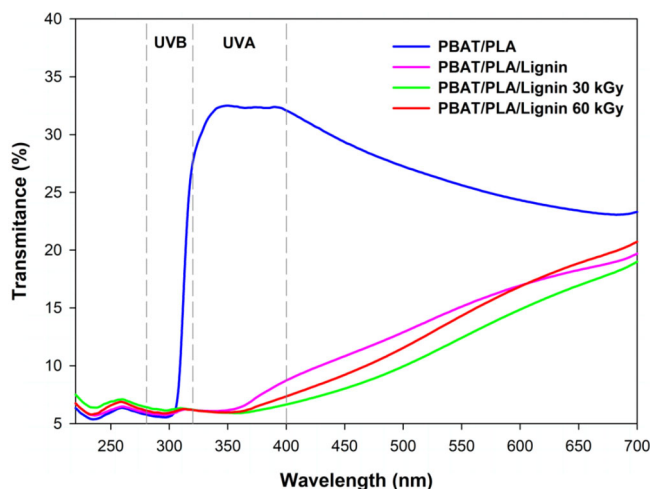


FIGURE 8 Transmittance of PBAT/PLA, PBAT/PLA/Lignin, PBAT/PLA/Lignin 30 kGy, and PBAT/PLA/Lignin 60 kGy. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.54684)]

In the UV-A region, PBAT/PLA films showed inferior UV blocking properties, with a maximum transmittance of 32%, protecting around 68% of UV-A rays. Lignin addition to the blends, mainly irradiated lignin, promoted a considerable increase in UV-A blocking, with an increase of up to $\sim 36.2 \pm 1\%$ of UV-A absorption for compounds with irradiated lignin.

The maximum transmittance reached for the blends in the UV-A region are: 9% (91% absorption) for PBAT/

PLA/Lignin, 6.7% (93.3% absorption) for PBAT/PLA/Lignin 30 kGy, and 7.43% (absorption of 92.6% of UV-A rays) for PBAT/PLA/Lignin 60 kGy.

In the visible light region, it is observed that lignin addition, mainly irradiated lignin, decreased transmittance over the entire wavelength range and consequently improved the light absorption.

The blocking properties of lignin can be explained due to its chemical structure which contains UV chromophore as functional groups, including quinones and methoxy-substituted phenoxy groups, which can be conjugated with double bonds or carbonyl functional groups. Thus, the phenolic structure and the p- π conjugation of hydroxyl and carbonyl phenol in lignin molecule allow it to absorb large amounts of ultraviolet light.^{55,56} The unsaturated functional groups that absorb visible light are the main light absorbers and turn the color of the lignin from brown to black. These groups include conjugated carbonyl groups, aromatic rings, and carbon-carbon double bonds.²⁵ Excellent UV barrier property for PBAT films with 10 wt% lignin modified with biobased oleic and 10-undecenoic acids, having full protection over the entire UV irradiation range (280–400 nm), has been reported in the literature.²⁶

From the presented data, it appears that lignin is a component with high UV absorption, being an excellent alternative to minimize the effects of photodegradation in agriculture mulch films, since, during the films useful life, they are exposed to solar radiation, mainly ultraviolet light, causing photodegradation that compromises the mechanical properties and the films efficiency to protect the soil against the weeds growth, for instance. During this process, both chain scission and cross-linking processes can occur, leading to reduced elongation and tensile strength. In addition, the formation of the gel can hinder the biodegradation process, by preventing the accessibility of microorganisms to the polymeric chains.⁵⁷

4 | CONCLUSION

Flexible films of PBAT/PLA with irradiated and non-irradiated lignin were produced by extrusion. Gamma irradiation of lignin promoted chemical changes in its structure, enabling improvement in the miscibility and compatibility of the blends, through the secondary interaction between the carbonyls present in PBAT/PLA and hydroxyls present in lignin, as observed in FTIR spectra. DSC data showed that lignin addition did not promote significant changes in the blends crystallinity, the results were corroborated by XRD diffractograms. The greater miscibility and compatibility achieved by lignin irradiation was proven in FESEM images, observing from the fracture surface better dispersion and interaction among the mixtures' constituents, providing positive impacts on the mechanical properties, noting that

irradiated lignin addition effectively improved the films' tensile strength properties, mainly tensile strength at break and elongation at break, more evident results for the PBAT/PLA/Lignin 60 kGy. The hydrophobicity, the barrier to UV-B, UV-A and visible light of the films increased upon lignin addition, the most satisfactory results were acquired with irradiated lignin.

This study proves that the incorporation of gamma-modified lignin was effective in conferring property gains to PBAT/PLA films, making them an attractive alternative for application as agriculture mulch films, providing a solution to the problems aroused from the large-scale use of conventional agriculture mulch films.

AUTHOR CONTRIBUTIONS

Janetty J. P. Barros: Formal analysis (lead); investigation (lead); methodology (lead); writing – original draft (lead). **Rene R. Oliveira:** Formal analysis (equal); methodology (equal); validation (equal). **Carlos B. B. Luna:** Formal analysis (equal); investigation (equal); methodology (equal). **Renate M. R. Wellen:** Conceptualization (equal); funding acquisition (equal); supervision (lead); writing – review and editing (lead). **Esperidiana A. B. Moura:** Funding acquisition (equal); supervision (equal); writing – review and editing (equal).

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

Data will be made available on request.

ORCID

Renate M. R. Wellen  <https://orcid.org/0000-0002-3565-7366>

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