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ORIGINAL ARTICLE

Development of mulch films from biodegradable polymer and agro-industrial waste

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Abstract

Plasticulture improves crop quality and yield through polymeric films, but their improper disposal harms the environment due to humidity and contamination. This study aimed to develop biodegradable mulch films using soybean and peanut hulls and poly (butylene-adipate-co-terephthalate) (PBAT). The residues were characterized by thermogravimetric analysis and mulch films were evaluated by water absorption, contact angle and mechanical properties. The thermal behavior of the residues indicated stability below 200ºC. The agro-waste improved hydrophobicity but increased the water absorption values of the films by up to 18.5x (PBAT/SH5 after 14 days). Micrographs obtained by scanning electron microscopy indicated an important distribution of residue particles and formation of agglomerates, leading to lower mechanical performance. The study found that agro-industrial residues in powder form can be added to the polymeric matrix to produce biodegradable mulch films through traditional processing techniques. This approach has the potential to contribute to a more sustainable production system.

Keywords: *PBAT, peanut, plasticulture, soybean, waste.*

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1. Introduction

As population growth accelerates, the demand for food crop production is expected to rise dramatically. However, water resources are becoming increasingly scarce, making it challenging to meet this growing demand[1]. Agriculture plays a crucial role in the global food supply and should be enhanced by adopting better management practices that promote the conservation of natural resources, while also embracing an ecological approach[2].

The expansion of agricultural production faces challenges due to suboptimal soil conditions, including limited water and nutrient availability, unfavorable temperatures, and weed infestations. These factors contribute to a worldwide struggle in sustaining production, particularly for seasonal products[3]. To control these parameters, one simple and effective strategy to improve soil properties and increase crop production is the use of polymeric films as soil cover. This technique, commonly referred to as plasticulture, enables the control of crucial parameters such as water and nutrient availability, while also aiding in the prevention of weed infestations[4].

According to American Society of Plasticulture, the term Plasticulture refers to the "use of plastics in agriculture" for the production of plants, including plastic cover, drip irrigation, row covers, low tunnels, high tunnels, among others[5,6]. The mulching technique is a highly effective agricultural practice that involves covering the soil surface around plants with organic or synthetic materials. This creates ideal conditions for plant growth and development, resulting in increased efficiency and higher crop yields[6].

Some of these films are even biodegradable, making them an eco-friendly option for farmers. By using this technique, farmers can reduce soil erosion, conserve water, and suppress weed growth, all while improving the overall health and productivity of their crops[7,8]. In this context, mulch is a crucial component in conditions of excessive rainfall, as it possesses the ability to reduce the occurrence of fungal diseases and the need for fungicide applications. This can greatly influence microclimatic conditions by increasing the temperature and reducing wind speed, which in turn decreases heat loss due to less air movement[9].

In recent years, the use of biodegradable polymers as an alternative to synthetic materials to cover films has been seen as a sustainable solution, since they can degrade in the field, thus reducing removal and disposal costs[10]. Given this scenario, it is crucial to make changes in the profile of polymeric material usage[11], to add sustainable value to the development of mulch films, and the addition of agro-industrial residues has demonstrated significant viability[12,13].

In this line of thought, Mo et al.[14] evaluated the use of biodegradable polymers (BDPs) as mulch film and found that the degradation of BDPs varies depending on soil conditions. This study also noted that degradation of BDPs can lead to the release of microplastics and polymer additives. The authors concluded that the use of BDPs in agricultural soil ecosystems can have both positive and negative impacts. While biodegradable polymers can improve soil quality and promote plant growth, the study also found that the degradation of these plastics in soil can lead to the release of microplastics and nanoplastics, which can have negative environmental impacts. The authors recommended that more research is needed to fully understand the environmental fate and impacts of biodegradable polymers on agricultural soil ecosystems.

Furthermore, Candlen et al.[15] found that biodegradable mulch films produced from soybean-filled polymeric resins, including poly(butylene adipate-co-terephthalate) (PBAT) and poly(lactic acid) (PLA), have promising performance in plasticulture, with similar or better results compared to conventional plastic films. The authors have reached the conclusion that the utilization of biodegradable films represents a viable and sustainable alternative to conventional plastic films. Nevertheless, further investigations are imperative to enhance their performance and mitigate potential environmental repercussions that might impede their biodecomposition.

This work aimed to develop mulch films using biodegradable polymer additived with natural residues of soybean hulls and peanut hulls, and to assess their feasibility for use in plasticulture. It is believed that the results of this research have the potential to make a significant contribution to the mulch film industry by producing a biodegradable product that utilizes readily available renewable resources.

2. Materials and methods

2.1 Materials

Biopolymer PBAT Ecoflex® FC1200 from BASF (melt flow index: 2.7-4.9 g.10min^{-1} at 2.16 Kg/190 °C - ISO 1133) was used as polymeric matrix. As fillers, agro-industrial residues of soybean and peanut hulls were used.

2.2 Treatment of agro-industrial waste

Prior to their incorporation into the polymer, the peanut hulls (PH) and soybean hulls (SH) residues were crushed using a knife mill. Afterward, the crushed material was passed through a 100-mesh sieve and PBAT were then dried in an oven at 60°C for 24h.

2.3 Preparation of the systems composition

Subsequent to the preparing the agro-industrial waste, polymer/waste systems were initially prepared with 2.5% and 5% by weight to the polymer mass, resulting in the formation of four systems: PBAT/PH2.5, PBAT/PH5, PBAT/SH2.5, and PBAT/SH5. The residues were incorporated into the polymeric matrix by melting them in a single screw extruder (Ax-Plásticos Lab 16) with a temperature profile in the three zones (140,145, and 145°C), and screw speed of 50 rpm.

2.4 Preparation of films

All previously described systems obtained were dried in an oven at 60 °C for 24 h, before being processed into flat films using a single-screw extruder (Lab 16 by Ax-Plásticos) with a temperature profile (140, 155, and 160 °C), screw speed of 50 rpm, and pulling system operating at speeds: roller 1 (15 rpm), roller 2 (15rpm), puller (19 rpm), and winder (18 rpm).

2.5 Characterizations of agro-industrial residues and films

2.5.1 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was conducted using a TA Instruments SDT Q600 analyzer to evaluate the thermal stability of agro-industrial residues. The test was performed under a synthetic air atmosphere, from room temperature to 500 °C, at rate of 10 °C.min^{-1}.

2.5.2 Water absorption test

Water absorption tests of the mulch films were carried out following ASTM 570 standard. The samples were then weighed at 1, 7, 12, and 28 days after immersion in water.

2.5.3 Water contact angle

To evaluate the hydrophilicity of the mulch films, contact angle measurements were conducted following the ASTM D5725 standard. Through the images captured by the digital camera, the contact angle is determined using SURFTENS – an image processing software.

2.5.4 Scanning electron microscopy

The morphology of the films was observed using a scanning electron microscope FEI Quanta FEG 250, with an accelerating voltage from 1 to 30 kV. Prior to analysis, the surface of the samples was sputter-coated with gold.

2.5.5 Mechanical properties

Tensile strength and elongation at break were carried out in a Universal Testing Machine Emic DL 30000 according to ASTM D882 standard with a speed of 50 mm/min and at room temperature. A minimum of eight samples were tested.

2.5.6 Statistical analysis

All measurements were reported as mean ± standard deviation. One-way analysis of variance (ANOVA) was applied using Excel Microsoft Office (Professional Plus 2019 version), and the Tukey's test was used to evaluate the significant difference between samples. The confidence level was 95%.

3. Results and Discussions

3.1 Thermogravimetric analysis

TG/DTG thermograms of peanut hull are shown in Figure 1. Note that decomposition occurred in three events, according previous works[16-18]. The first event in the temperature range of 24.0 to 121.1°C, maximum rate of decomposition at 37.4°C, and resulting in a mass lass of 9.20%, corresponds to moisture loss zone. This indicates the evaporation of moisture and the removal of highly volatile compounds.

The second event in the range of 142.7 to 358.2°C, with maximum decomposition rate at 277.5°C, showed a mass loss of 61.4% attributed to the decomposition of organic compounds. According to Varma et al.[18], this region corresponds to the zone of active pyrolysis where hemicellulose, cellulose and lignin bonds are rapidly destroyed. Within this temperature range, devolatilization actively occurs, with the rate increasing sharply as temperature increases. The authors reported peak values between 316 and 342°C, along with a mass loss of 82.0%, depending on the applied heating rate.

The third event was seen in the range between 370.0 and 482.0°C, with a peak temperature of 434.7°C, being associated with the decomposition of cellulose and lignin, with a mass loss of 24.6%. According to Suriapparao and Vinu[19], this event corresponds to the final degradation of cellulose up to 400°C, and above 350°C the decomposition of lignin begins, which goes up to 900°C.

TG/DTG thermograms of soybean hull (Figure 1) also indicated the presence of three thermal events[20,21]. The first event corresponds to the loss of moisture in the sample and occurs in a range of 24 and 156.8°C with a mass reduction of 12.2% and maximum decomposition rate at 47.5°C. The second event occurs between 156.8 and 370.0°C with a mass reduction of 50.2%, that is related to the degradation of organic matter composed of hemicellulose and cellulose. Finally, the third event is associated with the thermal decomposition of cellulose followed by lignin that occurs in the range from 374.5 to 490.5°C with maximum rate at 444.0°C and a mass loss of 25.7%. According to the thermal degradation of lignin and hemicellulose begins around 200°C.

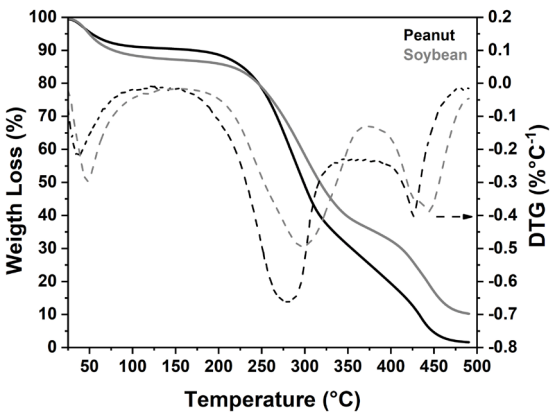

Figure 1. TG/DTG of the peanut hulls and soybean hulls.

Hemicellulose undergoes total pyrolysis at 315°C, while cellulose elimination starts around 300°C to 400°C. Lignin is the last component to be dissipated at 700°C. These data are in agreement with the results previously reported by Toro-Trochez et al.[20] and Fitri et al.[21]. However, Barros et al.[22] and Ikladious et al.[23] observed only two stages of decomposition for peanut shells. The first stage occurred between 27 to 160°C, with a peak at 61.5°C, and a mass loss of only 7.3%. This stage was attributed to the evaporation of water and light volatile components present in hemicellulose and lignin. The second stage occurred between 257 and 394°C, with a peak at 357°C, and a mass loss of only 63%. This stage was attributed to the degradation of the anhydrous material, characteristic of the strong separation between hemicellulose and lignin.

Based on these results, it appears that both fillers exhibit similar levels of thermal stability. Then, they could be used as polymer fillers in traditional processing methods, which typically involve operating temperatures below 200°C. However, it is worth highlighting that extra care must be taken during the drying phase of these fillers, given the hydrophilic nature of cellulosic materials.

3.2 Water absorption test

The results obtained in the water absorption test for pure PBAT and the PBAT/PH2.5, PBAT/SH2.5, PBAT/PH5 and PBAT/SH5 systems are shown in Table 1. The pure PBAT film was used as a reference for the other fillers PBAT systems. It is notable that in the absence of fillers, the percentage of water absorption of the PBAT showed slight changes throughout the analysis, a decrease from 0.42% on the first day to 0.32% after 28 days. As mentioned by Camani et al.[24], neat PABT has low water absorption values (<1%) due to its hydrophobic nature.

Results indicated that increasing filler content resulted in a slight increase in water absorption. This was due to the hydrophilic nature of the natural waste, which is responsible for water absorption in composites due to the presence of abundant hydroxyl groups. Consequently, a higher filler content results in a higher amount of absorbed water, as reported by Obasi[25], who suggested that water molecules can easily penetrate the void spaces of polymer/natural waste systems, increasing the absorbed water content, even in a short period of exposure. No saturation point was observed, suggesting that the exposure time was short.

Table 1. Water absorption measurements for all films.

Films	Water Absorption (%)			
	1st day	7th day	14th day	28th day
Neat PBAT	0.4266 ± 0.0141^{c}	0.3603 ± 0.0223^{e}	0.3370 ± 0.0276^{c}	0.3164 ± 0.0259^{b}
PBAT/PH2.5	2.0036 ± 0.0303^{b}	2.1365 ± 0.0452^{d}	2.7526 ± 0.1235^{b}	4.2366 ± 0.4836^{a}
PBAT/PH5	2.2784 ± 0.0403^{a}	$2.5503 \pm 0.0592^{b,d}$	2.9054 ± 0.1519^{b}	4.8102 ± 0.5592^{a}
PBAT/SH2.5	2.0366 ± 0.0542^{b}	$2.9065 \pm 0.4965^{a,b}$	6.1026 ± 0.3565^{a}	4.2465 ± 0.2456^{a}
PBAT/SH5	2.3635 ± 0.0645^{a}	3.1361 ± 0.5542^{a}	6.2419 ± 0.3793^{a}	4.7186 ± 0.2810^{a}

Results expressed as mean ± standard deviation; different letters (a, b, c, d, and e) in the same column indicate a significant difference between the treatments by Tukey's test ($p < 0.05$).

It is notable that the PBAT/PH2.5 and PBAT/SH2.5 systems show an increase in the degree of water absorption within 24 hours of testing compared to pure PBAT, exhibiting initial values of approximately 2.10 and 2.15%, respectively. Analogously, with a discrete dynamic within 24 hours, the PBAT/PH5 and PBAT/SH5 systems absorbed about 2.28 and 2.36%, respectively. However, the systems show different behaviors as the test continues. For the systems with the addition of peanut hull: PBAT/PH2.5 and PBAT/PH5, a gradual increase in absorption was observed. However, for the PBAT/SH2.5 and PBAT/SH5 systems, there was a relevant increase after 7 days of evaluation, reaching a peak close to 6.0 and 6.24%, respectively, followed by a decline that at the end of the evaluation with 28 days they obtained an approximate absorption value of 4.35 and 4.72%, in that order.

In this context, the behavior of increasing the water absorption index can be attributed to the presence of vegetable residues that have a hydrophilic character due to the presence of polar groups characteristic of hemicellulose and lignin, which, although presenting a hydrophobic macromolecule, has ramifications of alcohols aromatic in its formation[26,27], allowing the attraction of water molecules. The systems with the addition of peanut hull which, according to Castro et al.[28] have values in their constitution on average of 16% lignin and 36% hemicellulose, may present polar groups in their structure and through these hydroxyl groups hydrogen bonds are established with water molecules, thus influencing the increase in absorption[23,25]. It is described by several researchers[23,25,29] that it is even plausible to relate the fact of increased water absorption with the reason for the differences in particularities between the matrix and the filler, where there is a hydrophobic characteristic for the PBAT matrix and a hydrophilic one for the natural filler, producing an inadequate compatibility, which consequently causes a weak adhesion between the phases, causing voids and cracks that consequently allow the penetration of water.

The presence of the chosen fillers causes a change in the amount of water absorbed from the pure PBAT film and from the other evaluated materials. According to the ANOVA analyses, significant differences ($p<0.05$) were found between all water absorption measurements performed at each specified time interval. The results of the average values show that the time considered has an impact on how the water is absorbed.

According to Tukey's test, the average values of water absorptions for the first 24 hours (1st day) suggest that the content behavior of each filler influences in a similar way, with notable increases shown in comparison with the pure PBAT film. Measurements taken on the seventh day indicate that each type of filler produced similar absorption with increases of up to 7.1x (PBAT/PH5) and 8.7x (PBAT/SH5) over pure PBT. The PBAT/PH5 and PBAT/SH2.5 compositions show ambiguous behavior to the PBAT/PH2.5 and PBAT/SH5 films, respectively. For the 14th day, it was observed that the water absorption was similar regardless of the filler content. Compared to pure PBAT, absorption was increased by up to 8.6x (PBAT/PH5) and 18.5x (PBAT/SH5). Finally, on the 28th day, it was found that all films containing residues resulted in similar mean water absorption values, regardless of the type of filler applied. Compared to pure PBAT, absorption increased from 13.4x (PBAT/PH2.5) to 15.2x (PBAT/PH5).

3.3 Water contact angle

The results referring to the measurements of the water contact angle of the films based on neat PBAT and the respective systems are presented in Table 2. It is possible to visualize that the pure PBAT presents an angle of $50.90 \pm 0.59°$, confirming hydrophilic feature. However, higher values (72.0 to 76.6°) were previously reported for PBAT films[30,31].

The contact angle values of systems containing peanut hull were found to be higher than those containing soybean hull. Particularly, the contact angle values of the PBAT/PH2.5 and PBAT/PH5 films were $59.56 \pm 1.33°$ and $57.56 \pm 2.15°$, respectively, showing a minor decline in values with increasing filler content. On the other hand, when the filler amount grew, the contact angle of the soybean husk filler with the water increased. Water contact angle measurements for the PBAT/SH2.5 and PBAT/SH5 films were $54.44 \pm 1.21°$ and $55.66 \pm 1.98°$, respectively.

This angular growth behavior when compared to pure PBAT is characterized by an increase in surface hydrophobicity. This increase can be explained by the composition of plant residues, which have lignin in their structure, a complex macromolecule with a high concentration of aromatic groups, with less hydrophobicity than cellulose[32,33]. As observed in the results of TG/DTG (Figure 1), where it was verified that the soybean hull presents a mass loss corresponding to the decomposition of the lignin slightly higher than the peanut hull.

According to Bauli et al.[33], in general, these facts are justified, as natural fibers vary in cross-section, dimensions and physical properties and have rough surfaces. During contact angle measurements, liquid is often absorbed by natural fibers. Therefore, the addition of filler also influences through the roughness on the film surfaces, since a rough surface presents greater wetting of the solid.

Table 2. Water contact angle measurements for all films.

Film	Water Contact Angle (°)
Neat PBAT	50.09 ± 0.84^{c}
PBAT/PH2.5	59.56 ± 1.33^{a}
PBAT/PH5	$57.56 \pm 2.15^{a,b}$
PBAT/SH2.5	54.44 ± 1.21^{b}
PBAT/SH5	$55.66 \pm 1.98^{a,b}$

Results expressed as mean ± standard deviation; different letters (a, b, and c) in the same column indicate a significant difference between the treatments by Tukey's test ($p<0.05$).

Ultimately, according to the ANOVA analyses, there were significant differences ($p<0.05$) in the water contact angles between the films indicating that a major impact is caused by the presence of fillers in these components. The average results show, however, that there is no statistically significant difference between the contents of each filler from the standpoint of the Tukey's test. However, when compared to pure PBAT film, its impact can be seen proving that the surface structure of the films is statistically altered by the presence of natural residues, enhancing their hydrophobicity.

3.4 Scanning electron microscopy

Behavior for pure PBAT with a smoother, more homogeneous and uniform surface morphology was previously reported[34-36]. SEM micrographs of PBAT films with peanut hull and soybean hull at 10,000x magnification are shown in Figure 2.

When particulate fillers are added to a PBAT matrix, the morphology generally tends to present an irregular and rough surface that allows a granular phase to be seen. The filler incorporated into the polymeric matrix is represented by this phase. These characteristics can be observed in films containing 5% by weight of both residues (Figure 2). However, the soybean hull residue (PBAT/SH5 - Figure 2d) showed particles slightly larger and more uniform than those present in the peanut hull film (PBAT/PH5 - Figure 2b). The presence of granular surfaces and the reduction in tensile strength corroborate previous works[35,37,38]. Films with contents of 2.5wt% showed a similar surface. The presence of isolated granules was observed only for PBAT/2.5SH, possibly due to the greater size distribution among the granules[39].

In general, the images show that in both types of fillers (PH and SH), the increase in the filler content provided the formation of a granular and rough surface, which would be expected due to the higher content of material added to the matrix of the PBAT. The presence of granules associated with increased filler content was previously identified and reported[40-43].

3.5 Mechanical properties

Mechanical properties of all films containing 2.5, and 5wt% of both fillers are show in Table 3. PBAT's mechanical properties are highly flexible, similar to those of LDPE, making it a promising material for various applications[40]. It is possible to verify that the tensile strength of the PBAT film was 18.89 ± 1.00 MPa and that there was no rupture of the any film. According to Jian et al.[40] the tensile strength and elongation found were 21.0 MPa and 670%, respectively. On the other hand, according to Moustafa et al.[41], pure PBAT presents low tensile strength close to 14.0 MPa and high elongation at break (>1.500%).

Both tensile strength and elongation at break at break significantly changed when peanut hull fillers were added to the PBAT. For filler contents of 2.5% and 5.0% by weight, respectively, the tensile strength reduced to 12.59 ± 0.55 MPa and 8.96 ± 0.71 MPa, while the elongation at break at break decreased to 473.5 ± 28.06% and 666.5 ± 38.42%.

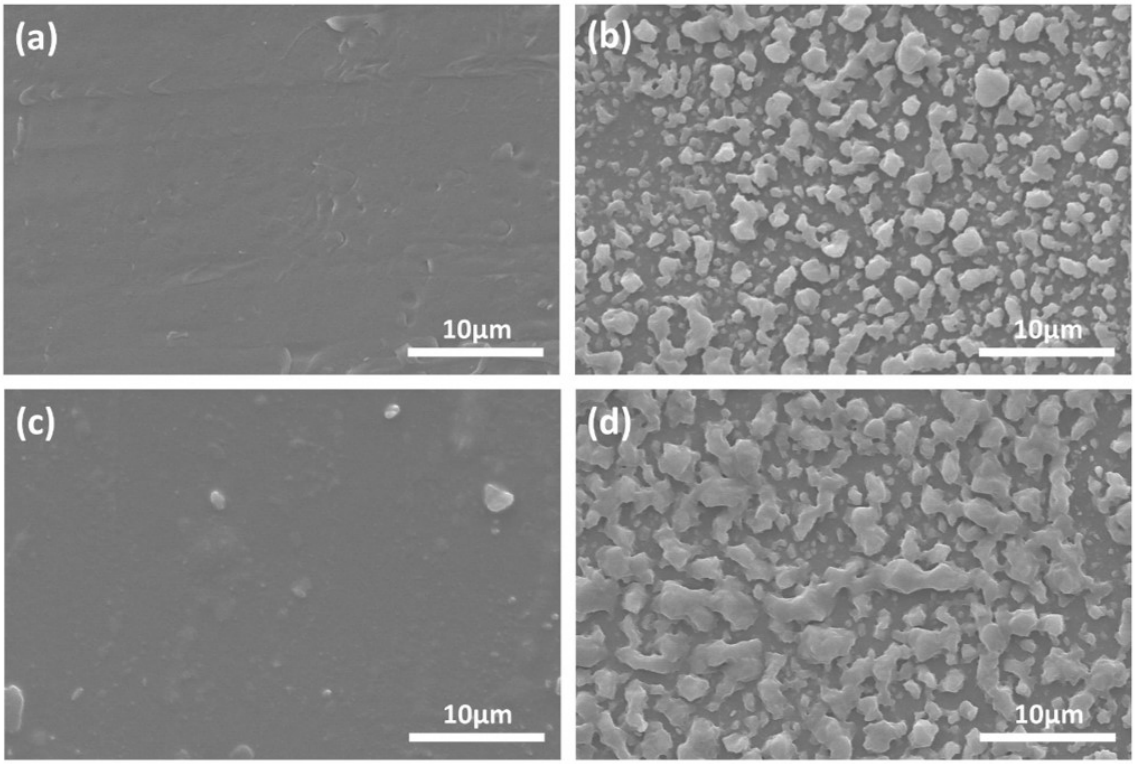

Figure 2. SEM micrographs of PBAT films with peanut hull (PH) and soybean hull (SH) at 10,000x magnification: (a) PBAT/PH2.5, (b) PBAT/PH5, (c) PBAT/SH2.5, and (d) PBAT/SH5.

Table 3. Mechanical properties (tensile strength and elongation at break) for all films.

Film	Tensile Strength (MPa)	Elongation at break at Break (%)
Neat PBAT	18.89 ± 1.00^{a}	– *
PBAT/PH2.5	12.59 ± 0.55^{b}	473.5 ± 28.06^{b}
PBAT/PH5	8.96 ± 0.71^{d}	666.5 ± 38.42^{a}
PBAT/SH2.5	8.43 ± 0.79^{d}	497.3 ± 41.06^{b}
PBAT/SH5	11.07 ± 0.97^{c}	701.3 ± 41.95^{a}

Results expressed as mean ± standard deviation; different letters (a, b, c, and d) in the same column indicate a significant difference between the treatments by Tukey's test ($p < 0.05$). *The neat PBAT films did not break during the tensile test

As cellulosic fibers have a lower elongation at break[42] than PBAT, they may be responsible for these changes. It is clear that these natural residues had an impact on the quality of the films.

Similarly, incorporating soybean hulls into PBAT also led to changes in the tensile strength and elongation at break at break of the resulting films. Specifically, at filler contents of 2% and 5% by weight, the tensile strength and elongation at break values were 8.43 ± 0.79 MPA and 497.3 ± 41.06%, and 11.07 ± 0.97 MPa and 701.30 ± 41.95%, respectively.

It was observed by Al-Oql et al.[42] observed that the tensile strength decreased when the cellulosic fiber filler content was increased. This is due to the fact that, as the filler content increases, the interfacial area between the filler and the polymeric matrix also increases. Voids are formed at this interface and potentially decrease the tensile strength even further, especially when stiffer and inert fillers than the polymeric matrix are applied. In general, more rigid and less resilient materials are created when hard fillers are added to polymer matrices.

The mixture of natural fibers with polysaccharides improves some of the mechanical properties of the matrix. The low resistance observed in the systems may be the result of failures in the interface, caused by the weak interaction of the constituents. Thus, both the stiffness of the fibers and the low affinity between polyesters (such as PBAT) and cellulosic fibers lead to significantly lower elongation at break, despite maintaining or increasing tensile strength and increasing the modulus of elasticity of the composite relative to the matrix. This affinity can be improved through chemical modification of fibers surface[43-46].

Analysis of variance (ANOVA) applied to the mechanical properties shown in Table 3 revealed a significant difference in the values obtained ($p < 0.05$), confirming that the fillers used had an impact on the mechanical properties of the PBAT. Tukey's test showed that each filler generated a statistically significant difference in terms of tensile strength. Only the PBAT/PH5 and PBAT/SH2.5 compositions showed no significant difference between their mean values. In terms of elongation at break at break, a similar mean value was observed for each content (2.5 or 5 wt%). Notably, PBAT/PH2.5 and PBAT/SH5 films exhibited the best mechanical properties of tensile strength and elongation at break at break, respectively, when compared to films with the same type of filler. Therefore, in the selection process, it is important to consider the economically viable profile of each batch for the production of films on an industrial scale.

4. Conclusions

The films were developed from pure PBAT and PBAT systems with 2.5 and 5% by weight of peanut hull and soybean hull. Based on the results obtained, the increase in hydrophobicity and water absorption was caused by the cellulosic components that are the main constituents of the evaluated residues. According to the micrographs, the increase in the content of both fillers provided the formation of a greater number of granules with good distribution and dispersion for peanut hull and an irregular distribution for low content of soybean hull. Filled composites showed, in general, lower expected mechanical performance, due to the increased area and formation of interfacial defects between the filler and the polymeric matrix. However, the fillers added relevant properties such as low cost and better recycling. The findings from this research have the potential to make a significant contribution to the mulch film industry by producing a biodegradable product that utilizes readily available renewable resources.

5. Author's Contribution

- **Conceptualization –** Railha Antunes de França.
- **Data curation –** Railha Antunes de França.
- **Formal analysis –** Cristiano José de Farias Braz.
- **Funding acquisition –** Renata Barbosa; Tatianny Soares Alves.
- **Investigation –** Railha Antunes de França; Cristiano José de Farias Braz.
- **Methodology –** Railha Antunes de França; Ana Carolina Ferreira dos Santos Rosa.
- **Project administration –** Tatianny Soares Alves.
- **Resources –** Renata Barbosa; Tatianny Soares Alves.
- **Software –** Cristiano José de Farias Braz.
- **Supervision –** Renata Barbosa; Tatianny Soares Alves.
- **Validation –** Cristiano José de Farias Braz.
- **Visualization –** Railha Antunes de França; Cristiano José de Farias Braz.
- **Writing – original draft –** Railha Antunes de França.
- **Writing – review & editing –** Cristiano José de Farias Braz; Renata Barbosa; Tatianny Soares Alves.

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