

Article

Effect of Different Compatibilizers on the Properties of Green Low-Density Polyethylene Composites Reinforced with Bambusa Vulgaris Bamboo Fibers

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Abstract: Low-density green polyethylene (LDGPE) composites reinforced with 5 wt% of bamboo fiber and 3 wt% of a compatibilizing agent (polyethylene grafted with maleic anhydride and tannin) were processed through extrusion and injection molding. Bamboo fiber, *Bambusa Vulgaris*, was characterized using Fourier-transform infrared spectroscopy (FTIR). The molded specimens were analyzed for their thermal, mechanical, and morphological properties. The estimated concentration was chosen to provide the best mechanical strength to the material studied. FTIR analysis of the fibers revealed the presence of groups characteristic of bamboo fiber and tannin. Differential scanning calorimetry revealed that both compatibilizing agents increased the matrix's degree of crystallinity. However, scanning electron microscopy (SEM) showed that, despite the presence of compatibilizing agents, there was no significant improvement in adhesion between the bamboo fibers and LDGPE.

Keywords: bioeconomy; maleic anhydride; tannin; sustainable composites; natural fibers



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1. Introduction

The demand for more sustainable alternatives in the manufacture of materials has increased in recent decades, aiming to reduce the negative impacts on the environment and overcome the scarcity of non-renewable resources [1]. Several studies are being carried out with the aim of finding solutions to reduce the use of raw fossil materials and reuse of agroindustry residues, such as the development of biobased polymers and the use of lignocellulosic materials to produce composite materials.

Polymer composites can achieve great properties with low density, replacing several conventional materials. They are formed via a matrix and a dispersed phase, present in smaller quantities to enhance their characteristics [2], and widely used for structural purposes in the automotive, civil construction, bioengineering, and aerospace areas [3]. In this context, green polyethylene, a semi-crystalline polyolefin material developed from ethanol extracted from sugar cane, stands out having the advantage of reducing CO₂ emissions in the atmosphere since its precursor is a renewable raw material, and it can be recycled at the end of its consumption cycle [4,5]. In addition to the environmental advantages that this new line of polymers offers, it has similar performance in terms of properties, processability, and applications to petroleum-based polyethylene [6,7].

Natural fibers have been widely used in composite materials as reinforcement because they have a low cost, are a renewable natural resource, have no toxicity, have good mechanical properties, and are biodegradable and recyclable [8,9]. Fibers can be obtained from jute, sisal, coconut, bamboo, etc. [10], and among them, the use of bamboo from the Bambuseae genus must be highlighted as an alternative in replacing structural materials such as steel and concrete [11], presenting good mechanical properties, lightness, versatility, and a low cost, while being applied in various sustainable composites [12,13].

However, there is a crucial parameter for polymer composites reinforced with natural fibers that must be taken into consideration: interfacial adhesion, which is responsible for the load transfer from the matrix to the fibers [14,15]. Since the polymer matrix generally has hydrophobic characteristics, while the fibers have hydrophilicity, it is necessary to use a coupling agent (compatibilizer) to achieve the chemical mediation between the matrix and the reinforcement improving the adhesion without impairing the mechanical properties of the composite [16,17]. Polymers grafted with maleic anhydride, such as polyethylene (PE-g-MA) and polypropylene (PP-g-MA), are the most widely used compatibilizing agents since these copolymers promote good interface adhesion, resulting in satisfactory properties for the composite when compared to those that are non-compatibilized [18,19]. However, besides being manufactured from petrochemical resources, they have a high energy cost during production and a high price compared to natural raw materials. Therefore, researchers investigate natural coupling agents from lignocellulosic sources for composites, such as lignin and tannin, in order to replace synthetic compatibilizers [20–22].

Tannins are water-soluble phenolic compounds found naturally in various parts of plants such as fruits, wood, leaves, bark, and herbs [23]. This compound has antioxidant characteristics and is traditionally used in the leather tanning process and also as flocculants, adhesives, and coatings [24]. Chemically, tannins can be classified as hydrolyzable and condensed, having different applications. Condensed tannins have oligo/polyphenol units containing polar and non-polar parts in their composition, which resembles synthetic compatibilizers, where the apolar aromatic groups have an affinity with the polymer matrix, while the hydroxyl groups interact with the lignocellulosic fibers, anchoring the matrix to the reinforcement agents [25].

In view of the promising properties of tannin for applications as a coupling agent in the production of sustainable composites, this work aims to analyze the compatibilizing effect of polyethylene grafted with maleic anhydride (PE-g-MA) and tannin in bamboo fiber-reinforced, low-density green polyethylene composites.

2. Materials and Methods

2.1. Materials

The polymer matrix was a low-density green polyethylene (LDGPE), commercially known as SLD4004 resin (I'm green™), supplied by Petroquímica Braskem (Triunfo, Brazil), with a melt flow index of $0.2 \text{ g} \cdot \text{min}^{-1}$ ($190 \text{ }^{\circ}\text{C} \cdot 2.16 \text{ kg}^{-1}$) and a density of $0.923 \text{ g} \cdot \text{cm}^{-3}$. The bamboo was collected from a bamboo grove in March 2022. It was then cut, dried in an oven at $50 \text{ }^{\circ}\text{C}$, and subsequently ground in a knife mill, and then a 32-mesh sieve was used to control the granulometry of the resulting fibers (BF). Polyethylene-graft-maleic anhydride (PE-g-MA) and tannin (TA) were used as compatibilizing agents. The PE-g-MA was donated by the company Cristal Master (Joinville, Brazil) and has about 1 to 3% of maleic anhydride content, whereas the tannin was supplied by Tanac (Montenegro, Brazil).

2.2. Processing of the Composites

2.2.1. Extrusion Compounding

After the raw materials were dried, the composite with 5 wt% of BF (according to the parametrization of other works, the addition of bamboo fiber as a reinforcement of up to 5 wt% improves the mechanical properties by up to 13% [26]) and 3 wt% of compatibilizer (according to the parametrization of other works [27]) were produced using a single-screw extruder (Eco Soluções, Viçosa, Brazil) with L/D of 20. The equipment has

four heating/temperature control zones, from the hopper to the die, and the following temperature profile was set: 140 °C (zone 1), 145 °C (zone 2), 150 °C (zone 3), and 190 °C (die). The pure polymer (with no filler) was also processed under the same conditions for comparison purposes. Table 1 shows the mass compositions of the studied composites.

Table 1. Mass compositions of the studied composites.

Sample	Content (wt%)
LDGPE	100
LDGPE/5%BF	95/5
LDGPE/5%BF/3%PE-g-MA	92/5/3
LDGPE/5%BF/3%TA	92/5/3

2.2.2. Injection Molding

After the samples' extrusion compounding, they were granulated and dried. Then, they were submitted to the injection molding process in a mini bench injector, model AXINJET, AX Plásticos Máquinas Técnicas (Diadema, Brazil). The specimens were made to be used in the mechanical tests for tensile strength and Izod impact strength, according to ASTM D-638 [28] and ASTM D-256 [29], respectively.

2.3. Characterization of the Composites

2.3.1. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) analyses were performed to investigate the influence of the reinforcing filler and compatibilizers on the thermal properties (melting temperature (T_m) and crystallization temperature (T_c)) and degree of crystallinity (X_c) of the composites. Equipment from TA Instruments (New Castle, DE, USA), model Q-2000, was used, with nitrogen as a carrier gas, at a constant flow of 50 mL·min^{−1}. The samples were initially heated from 30 to 200 °C at a heating rate of 10 °C·min^{−1}, remaining at this temperature for 3 min to eliminate the thermal history of the samples. After, they were cooled at 10 °C·min^{−1}, from 200 to 30 °C for the determination of T_c and again heated up to 200 °C at a rate of 10 °C·min^{−1}. The degree of crystallinity (X_c) of the samples was determined using Equation (1) [30].

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

where X_c is the degree of crystallinity (%), ΔH_m (J·g^{−1}) is the melting enthalpy of the sample, ΔH_m^0 (J·g^{−1}) represents the theoretical melting enthalpy of a 100% crystalline LDGPE, that is, 293 J·g^{−1}, and W corresponds to the weight fraction of fiber in the formulation [31].

2.3.2. Uniaxial Tensile Test

Tensile tests were performed according to ASTM D-638 [28] in an Instron Universal Testing System, model 5568, with a load cell of 5 kN and strain rate of 10 mm·min^{−1}. At least five specimens were tested per sample.

2.3.3. Izod Impact Strength Test

Izod impact strength tests were performed using Ceast equipment, model RESIL 25 (Instron, São José dos Pinhais, Brazil), according to ASTM D-256. The injection-molded specimens were notched in a Ceast notching machine to a depth of 2.54 ± 0.1 mm. At least eight specimens were tested per sample, at room temperature. In this work, a 5.5 J hammer was used, and none of the specimens suffered total fracture, only partial, which was classified as an NB (non-break).

2.3.4. Scanning Electron Microscopy (SEM)

SEM (Jeol, Tokyo, Japan, model JSM-6610LV) was used to evaluate the matrix-reinforcement adhesion under the use of different coupling agents. Micrographs of the fractured Izod impact strength specimens were obtained. A thin gold layer was deposited onto the material with a metallizer (Bal-Tec, Los Angeles, CA, USA, Mult Coating System MED020).

3. Results

3.1. Characterization of the Composites

3.1.1. Differential Scanning Calorimetry (DSC)

DSC analysis was used to determine possible crystallinity changes to the matrix after the addition of reinforcement and compatibilizers. DSC thermograms of the cooling and second heating are illustrated in Figure 1, using samples obtained after the extrusion process. The values corresponding to the crystallization temperature (T_c), crystallization enthalpy (ΔH_c), melting temperature (T_m), and melting enthalpy (ΔH_m) are given in Table 2.

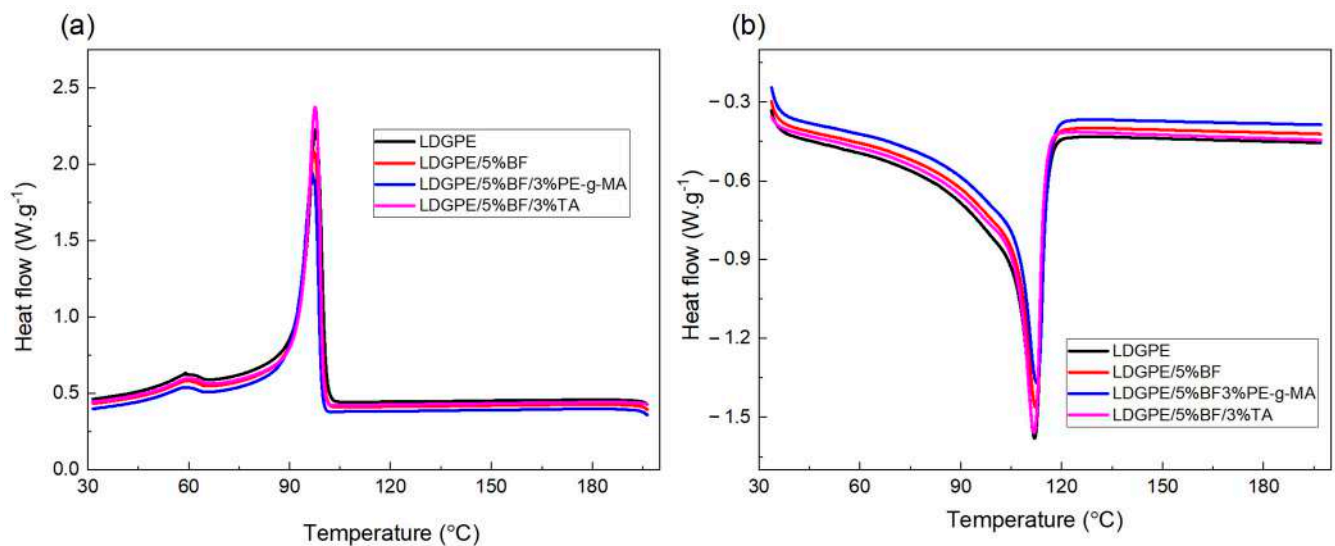


Figure 1. DSC thermograms for the (a) cooling and (b) second heating of the samples studied.

Table 2. Thermal parameters obtained from the DSC analysis.

Samples	T_c (°C)	ΔH_c (J·g ^{−1})	T_m (°C)	ΔH_m (J·g ^{−1})	X_c (%)
LDGPE	97.7	63.4	111.9	69.4	23.7
LDGPE/5%BF	97.3	61.0	112.1	63.6	22.8
LDGPE/5%BF/3%PE-g-MA	96.8	59.3	112.5	63.4	22.7
LDGPE/5%BF/3%TA	97.6	62.9	111.7	62.8	22.5

As shown in Table 2, the addition of bamboo fiber and the compatibilizing agents resulted in small changes in T_m and T_c when compared to LDGPE and a slight increase in T_m of the LDGPE/5%BF and LDGPE/5%BF/PE-g-MA composites when compared to the pure polymer. Furthermore, for T_c , a slight reduction was noted, in which it was considered that the addition of compatibilizers inhibited the growth of LDGPE crystals, which had the effect of forming small and imperfect crystals [21].

It is important to note that the only composite that had a T_m lower than that of pure LDGPE was the one with the addition of TA, following trends already portrayed in the literature. In the work developed by Kim et al. [32], the T_m and T_c of polyvinyl alcohol and hydrothermally treated tannic acid (HTA) composite films decreased as the HTA content increased, related to the increasing disruption in the PVA molecular chains caused

by its hydrogen bonding with the HTA. Similar results were found by Liao et al. [33], who observed a decrease in T_m in PP and cross-linked tannin (TH) composites before UV accelerated weathering, as the TH content became higher.

When referring to ΔH_m , a significant decrease in the enthalpy of the composites was observed when compared to the polymeric matrix alone. In general, LDGPE molecular chains can crystallize on their own through an effect known as self-nucleation or via the introduction of a nucleant, an effect known as heterogeneous nucleation [34]. Additionally, the ΔH_c also showed a decrease for the LDGPE/5%BF composite compared to the polymeric matrix, and when added, the compatibilizing agents induced different behaviors in enthalpy values in relation to the LDGPE/5%BF composite: while the use of PE-g-MA was responsible for decreasing the enthalpy of crystallization, the TA caused an increase in this value.

In addition, the composites exhibited a progressive decrease in X_c when compared with the LDGPE. When comparing the values of crystallinity of the compatibilized and without compatibilizer composites, it can be seen that the incorporation of maleic anhydride and tannin presented decreases in the crystallinity of the materials, attributed to the enhanced adhesion between the LDGPE matrix and the BFs, which disturbs the mobility of polyethylene chains.

3.1.2. Uniaxial Tensile Tests

From the literature, it is known that bamboo fibers present good reinforcement potential for polymeric composites since their unidirectional arrangement provides high stiffness, although their mechanical properties depend on variables such as the type of bamboo and environmental conditions during its growth [35].

Regarding the elastic modulus (Figure 2a), it can be observed that the composites presented a differentiated behavior when compared to pure LDGPE; it was proven that the bamboo fiber provided a considerable increase in the modulus (~40%). However, similar results were found for the compatibilized composites (LDGPE/5%BF/3%PE-g-MA and LDGPE/5%BF/3%TA) when compared to the uncompatibilized sample (LDGPE/5%BF). This behavior may be an indication that the presence of compatibilizing agents did not improve the interfacial adhesion and/or dispersion state of the bamboo fiber through the LDGPE matrix [36].

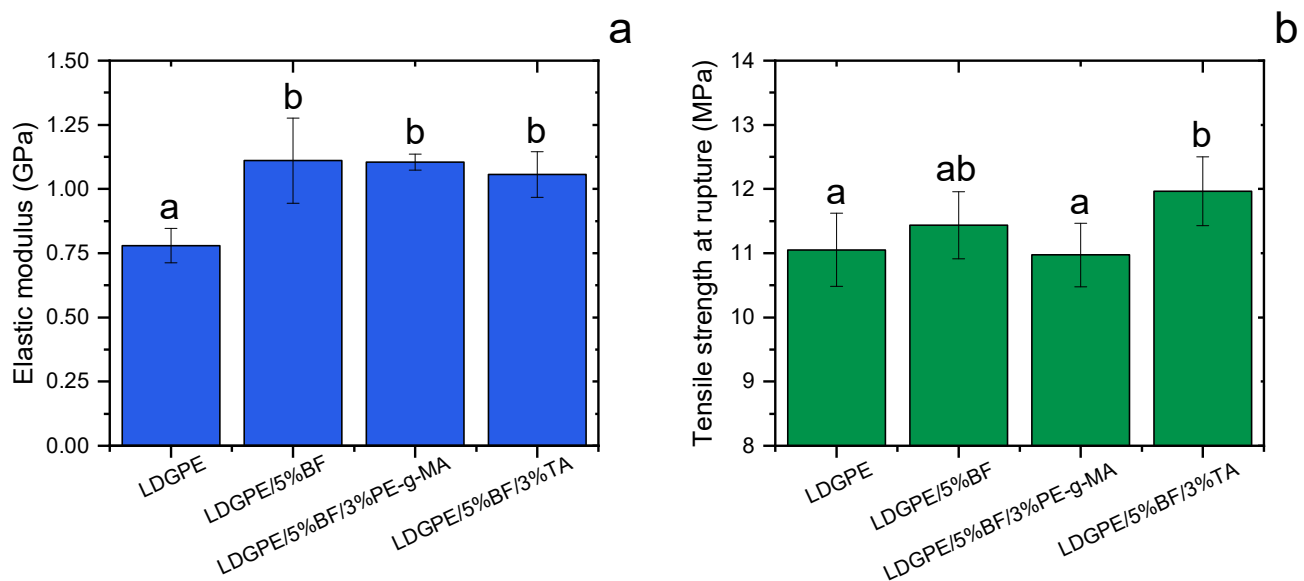


Figure 2. Elastic modulus (a) and tensile strength at rupture (b) of the LDGPE composites. Values followed by at least one letter in common indicate non-significant distinctions at a 95% confidence ($p < 0.05$) level according to Fisher's LSD test.

For thermoplastic composites, the elastic modulus is generally improved by incorporating a reinforcement because the filler restricts the mobility of the polymer chains and also has a higher stiffness compared to the matrix, contributing to an increase in the stiffness of the composite [22]. It is also believed that the ability of a composite interface to transfer elastic deformation depends on the interfacial stiffness and static adhesion strength [37]. A similar trend was demonstrated in the work of Daramola et al. [38], where an increase in the elastic modulus of high-density polyethylene (HDPE)/bamboo fiber composites was noted when compared to the polymer matrix.

The LDGPE/5%BF and LDGPE/5%BF/3%TA composites showed a slight improvement in tensile strength (Figure 2b). However, for the LDGPE/5%BF/3%PE-g-MA composite, no increase was observed. Meanwhile, as previously discussed, the elastic modulus increased for all composites reinforced with BF, which was related to higher stiffness by other authors [39]. The increase in tensile strength at breaking suggests a small additional degree of interfacial compatibility between the filler and matrix [40], with similar results being found in the work conducted by Salmah et al. [41]. Generally, compatibilized composites with higher crystallinities compared to non-compatibilized composites may result in the improvement of their mechanical properties [42]. In this work, although the crystallinity of the composites was not increased, the tensile strength of the LDGPE/5%BF and LDGPE/5%BF/3%TA composites proved to be the highest found among all the compositions tested (both in the same statistical homogeneous group), elucidating a possible ability of TA to prevent tearing or the breakdown of BF and possibly improving the transfer of mechanical stress between the polymeric matrix and the reinforcing agents.

The addition of tannin could potentially increase the plasticity of the LDGPE/5%BF/3%PE-g-MA composite, suggesting that the tannin could be uniformly dispersed in the polymeric matrix and possibly form stable hydrogen-bonding interactions with the bamboo fiber [43], while its non-polar parts (such as aromatic rings) could interact with the LDGPE [44]. In these scenarios, it is important to highlight that the dispersion of compatibilizers, especially TA, was not investigated in the present research. Furthermore, some studies suggest the ability of compatibilizers to cleave the polymer chain length, causing a decrease in the mechanical performance of the matrix itself [45,46]. Considering this, the low gains obtained in the tensile strength values of compatibilized composites may be due to a weakened matrix.

Based on the values found in Figure 3, it was observed that the composites exhibited a progressive decrease in the strain at break when compared to the LDGPE, having as a consequence the weak matrix-reinforcement interaction [47], which was unexpected since the strain in the rupture of the reinforced composite and the PE-g-MA- and TA-containing composites was statistically the same. In contrast, the LDGPE/5%BF/3% PE-g-MA and LDGPE/5%BF/3%TA composites showed a slight improvement over LDGPE/5%BF due to the use of compatibilizing agents, which are responsible for providing better interfacial adhesion.

3.1.3. Izod-Type Impact Strength Test

The impact strength test is used to measure a material's toughness, i.e., its ability to absorb energy during impact. The value generated through this analysis is an important measure in the selection of materials for engineering applications. The results of this test can be seen in Figure 4 and Table 3.

The composites showed higher impact energy than the LDGPE. The sample LDGPE/5%BF showed a mean increase of 18% compared to the polymer matrix. The introduction of bamboo fibers promoted an improvement in the impact strength of the composites compared to the matrix; i.e., the energy required to break the samples was higher, proving that the fibers act as reinforcement in the composites [48]. In this work, the composites presented the "fiber bridging" mechanism, in which not all components were fractured during the impact. This happens because part of the load applied to the matrix is transferred to the fibers, which deform, increasing the impact strength of the composite [48]. Similar

observations were made by Candido et al. [49], where the authors prepared polyester composites reinforced with sugarcane bagasse.

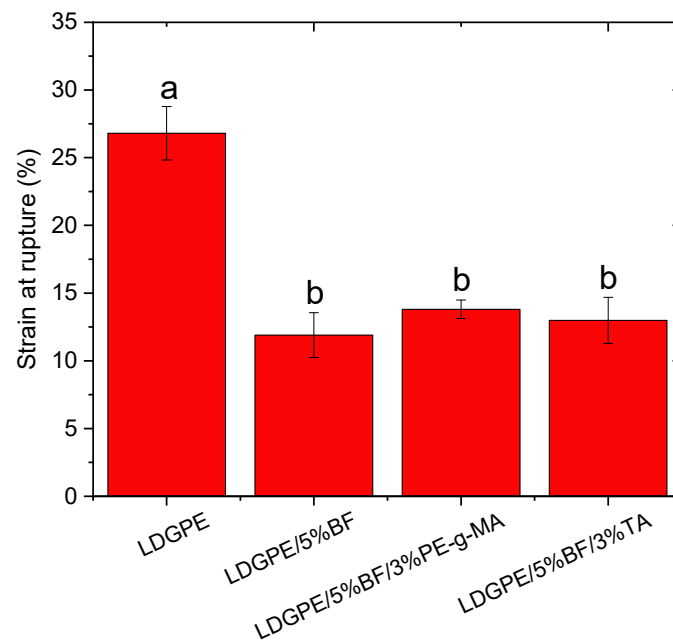


Figure 3. Values of the strain at rupture of tensile strength tests. Values followed by at least one letter in common indicate non-significant distinctions at a 95% confidence level ($p < 0.05$).

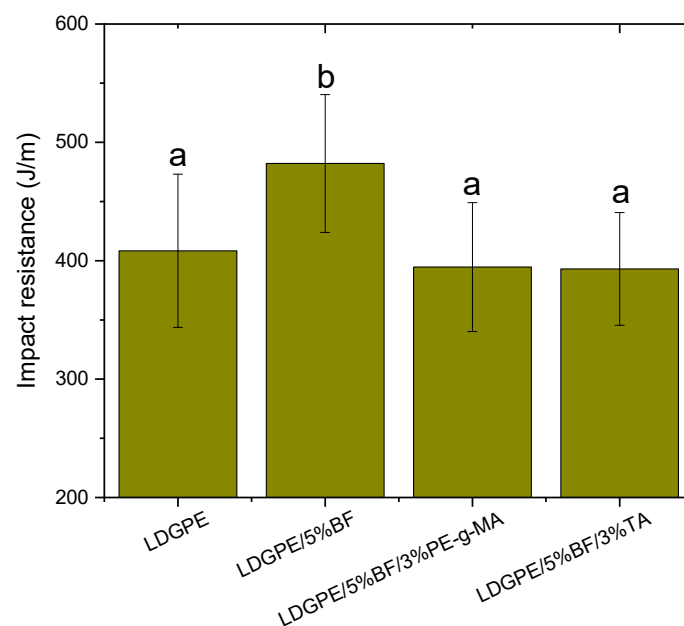


Figure 4. Izod-type impact strength. Values followed by at least one letter in common point to non-significant distinctions at a 95% confidence condition ($p < 0.05$).

Table 3. Impact strength test values.

Samples	Impact Resistance (J/m)
LDGPE	408.4 ± 64.7
LDGPE/5%BF	482.1 ± 58.2
LDGPE/5%BF/3% PE-g-MA	394.7 ± 54.4
LDGPE/5%BF/3%TA	393.1 ± 47.6

However, when the compatibilizing agents were added, no significant improvements were observed. This could be explained due to the increased compatibility of the composite after the addition of the PE-g-MA and TA, causing the increased brittleness of the material, which contributes to the composite fracture mode changed from “fiber extraction” to “fiber breakage” [50], in addition to fiber agglomeration [38].

The decrease in impact strength or reduced variation in strength upon the addition of compatibilizer may also be due to the induction of micro-spaces between the fiber and the LDGPE, which generate numerous micro-cracks when impact occurs, enabling crack propagation [13]. It has been noted that PE-g-MA acted as an “anticompatibilizer” in polypropylene composites and that it may have contributed to the pull-out of the reinforcement, as the compatibilizer used was incompatible with the matrix [51]. In the work developed by Yang et al. [21], it was found that, as reinforcement was added, the mechanical properties of the polypropylene/cellulose fiber composites suffered a decrease. This could be explained because the filler used could not be homogeneously dispersed with the tannin. Previous records in the literature report that the molecular weight of the grafted polymer chain, as well as the spacing of the MA units resulting from the grafting, could induce the aforementioned behavior [52–54].

3.1.4. Scanning Electron Microscopy (SEM)

The morphology of composites is closely related to their properties and particularly to their mechanical strength. As such, changes in the structure of composites can explain the trends that are obtained from their mechanical parameters. Figure 5 shows the SEM micrographs obtained from the fracture surface of the samples after performing the Izod impact strength tests.

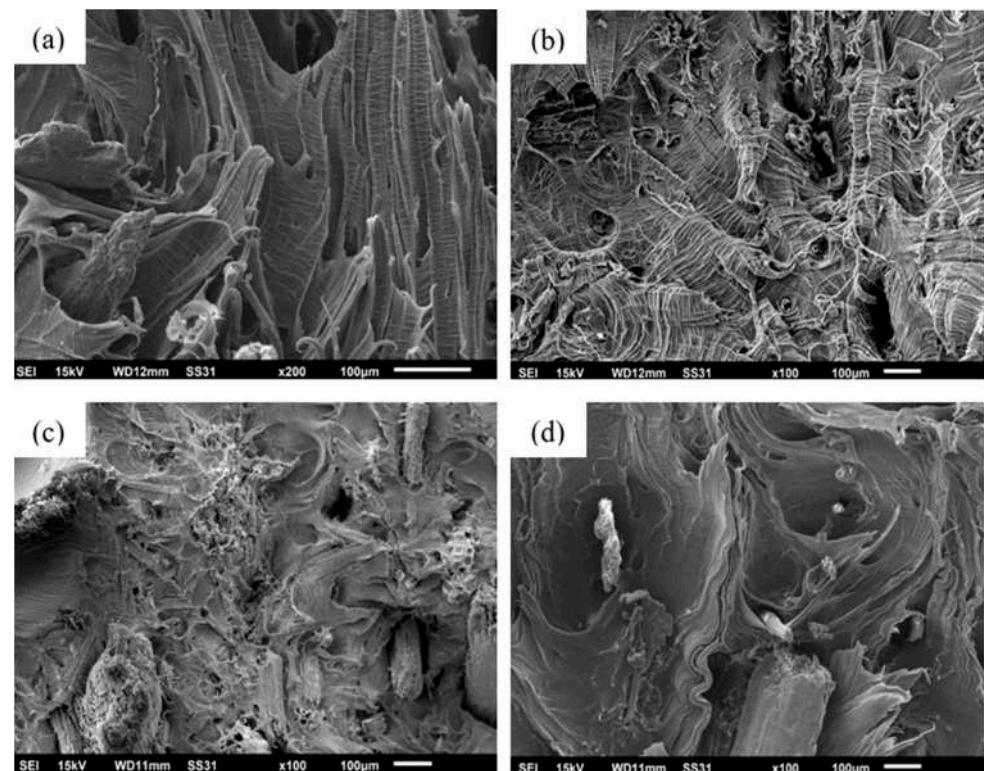


Figure 5. SEM micrographs obtained from the fracture surface of the samples: (a) LDGPE; (b) LDGPE/5%BF; (c) LDGPE/5%BF/3%PE-g-MA; (d) LDGPE/5%BF/3%TA.

As shown in Figure 5a, the fracture surface of LDGPE is comparatively smooth with crack propagation marks [55]. The unstable propagation of cracks is not a consequence of the lack of reinforcement; rather, the lack of reinforcement to control crack growth results

in the type of cracks observed. Cracks propagate unstably under external loading, and the main consequence is a lack of reinforcement to control their growth. Although the crack progresses rapidly through the material, there may be a stretching mechanism. This is because this property is directly related to the stress supported and the deformation before rupture [56].

The addition of bamboo fiber in the matrix promotes a significant increase in impact strength, with values of 482.14 J/m. This improvement is fundamentally associated with the ability of the fibers to transfer loads longitudinally, and it can be justified by fracture toughness theory. When the LDGPE/5%BF composite is subjected to impact conditions, several micro-cracks are generated. Consequently, the fibers along these micro-cracks unfold, thus finishing their growth. It was also observed that the presence of short fibers significantly improved the properties related to impact strength [30].

As shown in Figure 5a, the LDGPE has a loose and flaky structure with the presence of microvoids, showing ductile failure at multiple points, which may be related to the fact that its surface is not fully impermeable to moisture and its mechanical integrity is limited in the absence of reinforcement [38].

For the LDGPE/5%BF composite in Figure 5b, several fibers can be described as clustered together, which contributes to a gradual increase in the number of holes and voids, suggesting a ductile fracture. The fibers appear to have separated from the polymer matrix during deformation, which is a clear indication of poor interfacial adhesion [42]. However, the fibers of this material break apart when the composites are broken. This phenomenon occurs due to the good mechanical properties of bamboo fiber, for which more energy is required to break the composites, which results in a higher impact strength [57].

In the work of Daramola et al. [38], it was observed that HDPE composites reinforced with concentrations above 4%-by-weight bamboo fiber exhibited fiber displacement and pullout. The congestion observed for the composites reinforced with 10% by weight means that more load is absorbed via the fibers. The poor adhesion observed for this composite also provides a free path for moisture ingress. The results of Daramola et al. [38] corroborate our findings and reinforce the importance of fiber concentration as a determining factor in failure due to displacement and fiber pullout in HDPE composites. Roumeli et al. [42] found that all HDPE composites reinforced with hemp fibers separated from the polymer matrix during deformation, with a clear indication of lower interfacial adhesion, in addition to voids between the fibers and HDPE.

The failure characteristics shown on the fracture surface of the composites in Figure 5c,d comprise microcracks in the matrix, fiber breakage, and detachment. The micrographs show that the fibers, although pulled out of the matrix (pull-out phenomenon), did not break along with the fracture surface [55]. The pull-out occurrence happened less intensely for the LDGPE/5%BF/3% PE-g-MA composite, in which part of the fibrils of the reinforcement was coated with a polymer. However, for the LDGPE/5%BF/3%TA composite, this phenomenon was more pronounced. This may be closely associated with the structure of this composite consisting of individual microfibrils, which are characterized by forming an irregular fiber surface, and a slight increase in the fiber/matrix interaction area [58]. There was also poor adhesion between fibers and a decrease in impact strength for compatibilized composites and only a slight increase in strength for the LDGPE/5%BF composite [55]. In the study by Anggono et al. [59], it was observed that sugarcane bagasse-reinforced polypropylene composite compatibilized with maleic anhydride showed the displacement and separation of one fiber of the polypropylene, while the fracture of some fibers also occurred.

The LDGPE/5%BF and LDGPE/5%BF/3%TA composites present similar failure characteristics, such as microcracks in the matrix, breakage, and the detachment of fibers (Figure 5c,d). However, in-depth analysis reveals differences in the intensity and distribution of these failure mechanisms between materials. In the LDGPE/5%BF composite, fiber detachment is the dominant mechanism, observed in the separation of fibers from the

matrix without their fracture [55]. This characteristic can be attributed to good compatibility between the matrix and the fibers, providing an efficient stress transfer [58].

In contrast, the LDGPE/5%BF/3%TA composite presents a more intense pullout of fibers, evidenced by the partial removal of the fibers from the matrix, accompanying fracture in some cases [55]. This difference is due to the structure of the fibers in this composite, formed via individual microfibrils that generate an irregular surface and increase the area of interaction with the matrix. Furthermore, poor adhesion between the fibers and the matrix, evidenced by a decrease in impact resistance [60], contributes to more pronounced fiber pullout.

Similar studies using polypropylene composites compatibilized with maleic anhydride also demonstrated the displacement and separation of fibers, with the fracture of some of them [59]. Liao et al. [37], in their research, used tannin and lignin as compatibilizers in polypropylene composites and, through results obtained via SEM, observed the poor adhesion of the reinforcement/matrix. In addition, cross-linked tannin particles of irregular shapes were found, confirming the formation of thermosetting tannin particles. Agüero et al. [61], on the other hand, reported that the presence of a significant gap in PLA–flax fiber composites was related to low toughness, and this gap did not allow a good load transfer from the matrix to the fiber. Another factor that may have contributed to the decrease in the related properties is the shear action in single-screw extruders being relatively weaker than in twin-screw extruders, causing less fiber pull-out from the main bundles [62].

4. Conclusions

Natural plant-based fibers have a great advantage over traditional synthetic fibers due to their lightweight, non-abrasive, non-toxic, and biodegradable nature. The composites prepared with 3% PE-g-MA or TA did not act as nucleation agents since the crystallinity of the composites did not increase. Mechanical analysis revealed a progressive decrease in the strain at rupture, with the LDGPE/5%BF composite exhibiting the highest impact energy. In tensile strength tests, the LDGPE/5%BF composite showed an improved elastic modulus compared to LDGPE alone, while the LDGPE/5%BF/3%TA composite demonstrated the best tensile strength among all tested compositions. This suggests the potential of TA as a compatibilizing agent in composites. Although the crystallinity of the composites was not enhanced, the LDGPE/5%BF/3%TA composite exhibited the highest tensile strength, indicating TA's possible role in preventing tearing or the breakdown of BF and enhancing the transfer of mechanical stress between the polymeric matrix and the reinforcing agents. Future work can make valuable contributions to this topic through the development and study of composites blended exclusively with TA, helping uncover the impacts of this natural agent in LDGPE matrices.

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RESEARCH ARTICLE OPEN ACCESS

Improved Thermal and Structural Performance of LDPE Reinforced With Bamboo Cellulose Nanocrystals via PE-g-MA Compatibilization

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ABSTRACT

This study investigates low-density green polyethylene (LDPE) nanocomposites reinforced with bamboo-derived cellulose nanocrystals (CNCs) and compatibilized with polyethylene-graft-maleic anhydride (PE-g-MA). Four materials were prepared by melt extrusion and injection molding (neat LDPE; LDPE with 1.0 and 1.5 wt% CNCs; and LDPE with 1.0 wt% CNC + 1.0 wt% PE-g-MA) and evaluated by thermal, mechanical, and structural analyses. Fourier-transform infrared spectroscopy (FTIR) indicated interactions between maleic- anhydride groups and CNC hydroxyls, supporting improved interfacial compatibility. X-ray diffraction (XRD) showed increased crystallinity in CNC-containing samples, consistent with a nucleating effect. Thermogravimetric analysis/derivative thermogravimetry revealed single-step LDPE decomposition with an upward shift of the degradation-rate peak upon CNC addition; residues remained below 2% at these low loadings. Under uniaxial tension, stiffness increased significantly at 1.5 wt% CNC and in the compatibilized composite, while tensile strength improved only with PE-g-MA; elongation decreased with CNCs irrespective of compatibilizer, remaining highest for neat LDPE. After accelerated aging (UV + humidity), modulus and strength exhibited modest declines across all materials, comparatively larger in the compatibilized system, suggesting time-dependent changes at the CNC-matrix interface. Overall, bamboo-CNC/PE-g-MA provides a sustainable route to tailor thermal performance and load-bearing response of LDPE for applications that prioritize stiffness and thermal resistance over ductility.

1 | Introduction

Bio-based polyethylenes have emerged as promising alternatives to conventional fossil-based polymers, combining well-established processing characteristics with improved

environmental performance. In particular, low-density green polyethylene (LDPE), produced from renewable sources such as sugarcane ethanol, has attracted increasing attention in both academic and industrial contexts due to its potential to reduce greenhouse gas emissions throughout the product lifecycle [1].

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This growing interest is driven not only by environmental concerns, but also by the need to deliver a high-performance, multi-functional product at low cost [2].

Within this broader sustainability landscape, bamboo-derived reinforcements have shown promise across different polymer matrices, improving mechanical or functional performance in applications ranging from flexible/impact-sensing laminates to energy, harvesting devices, underscoring the relevance of bamboo-based fillers for bio-based composites [3–6].

Incorporating cellulose nanocrystals (CNCs), including those derived from bamboo, into LDPE is a promising strategy to enhance the mechanical stiffness of bio-based polymers. For instance, LDPE/CNC composites prepared via solid-state shear pulverization (SSSP) exhibited significant increases in Young's modulus compared to neat LDPE, an effect attributed to the excellent CNC dispersion and the strong matrix–filler interfacial interactions [7, 8].

Nevertheless, the properties of CNC-based composites are strongly influenced by the method used to produce the nanocrystals. In studies with linear low-density polyethylene (LLDPE), Anžlovar et al. demonstrated that acetylated CNCs achieved improved dispersion within the matrix, but at the expense of reduced polymer crystallinity, which limited the mechanical reinforcement achieved [9].

A likely explanation for these limitations lies in the intrinsic incompatibility between CNCs and hydrophobic polyolefins such as LLDPE and LDPE. The hydrophilic nature of CNC surfaces, rich in hydroxyl groups, tends to promote filler aggregation and weak interfacial adhesion, both of which can compromise the mechanical and thermal performance of the resulting composites [10].

To overcome these interfacial limitations, the incorporation of compatibilizing agents such as polyethylene grafted with maleic anhydride (PE-g-MA) plays a crucial role. PE-g-MA introduces polar functional groups that promote chemical interactions between the hydroxyl-rich surface of CNCs and the non-polar matrix of LDPE, thereby enhancing interfacial adhesion and facilitating more efficient stress transfer across phases [11, 12].

However, despite the widespread assumption of performance improvements, the actual impact of PE-g-MA incorporation on the mechanical and thermal properties of LDPE/CNC composites remains dependent on several factors, including filler content, processing conditions, and interfacial morphology [13].

Against this backdrop, the present study investigates the development of LDPE nanocomposites reinforced with CNCs derived from bamboo fibers, using PE-g-MA as a compatibilizer. The CNCs were produced via sulfuric acid hydrolysis and incorporated into the polymer matrix through melt extrusion, a process compatible with scalable industrial practices. The work investigates how incorporating CNCs at 1.0 and 1.5 wt%, and a third formulation, 1 wt% CNCs plus 1 wt% PE-g-MA, affects the thermal, structural, and mechanical properties of the resulting nanocomposites.

A comprehensive suite of characterization techniques was employed, including X-ray diffraction (XRD), Fourier-transform

infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), uniaxial tensile testing, and accelerated aging experiments. The findings are used to evaluate the effectiveness of PE-g-MA in mitigating CNC agglomeration, enhancing interfacial adhesion, and promoting efficient stress transfer within the composite structure. These improvements are particularly relevant for applications demanding high stiffness, thermal resistance, and dimensional stability, such as sensor housings, electronic modules and connectors in wind or solar energy systems, where ductility is not a primary design constraint [14, 15].

2 | Experimental

2.1 | Materials

LDPE (*I'm green*, SLD4004, Braskem S/A, Triunfo, RS, Brazil), produced from sugarcane ethanol, served as matrix (melt flow index: 0.2 g min^{−1} at 190°C/2.16 kg; density: 0.923 g cm^{−3}). PE-g-MA (Cristal Master, Joinville, SC, Brazil) was used as compatibilizer (1–3 wt% MA content) at 1 wt% relative to total polymer mass. Bamboo culms (*Bambusa vulgaris*), used as the *cellulose source for CNC production*, were collected in Morro Redondo, RS, Brazil, dried at 50°C, milled (MA30, Marconi), and sieved to < 32 mesh (ASTM E11). Reagents (NaOH, NaClO, H₂SO₄) were analytical grade. Prior to processing, LDPE and PE-g-MA were dried at 50°C for 24 h.

2.2 | Sample Preparation

2.2.1 | Cellulose Extraction and CNC Production

Cellulose was obtained from milled bamboo via alkaline treatment (10% w/v NaOH, 80°C, 1 h), followed by washing to neutral pH and bleaching in 20% (w/v) NaClO at room temperature. CNCs were produced by sulfuric-acid hydrolysis (35% v/v H₂SO₄, 45°C, 1 h, 1:20 w/v), then quenched, centrifuged, dialyzed to neutral pH (MWCO 3500 g/mol), and freeze-dried. Full step-by-step protocols are provided in the [Supporting Information](#).

2.2.2 | Processing of LDPE/CNC Nanocomposites via Extrusion

The nanocomposites were processed using a single-screw extruder (Eco Soluções, Viçosa, Brazil) with a length-to-diameter (L/D) ratio of 20. The barrel temperature profile was set to 140°C (zone 1), 145°C (zone 2), and 150°C (zone 3), with a die temperature of 190°C. All formulations, including the neat LDPE reference, were compounded at a constant screw speed of 70 rpm to ensure a comparable shear history across batches. Neat LDPE was processed under the same conditions for comparison. Four formulations were prepared (Table 1).

2.2.3 | Injection Molding of Test Specimens

After extrusion, the samples were pelletized and dried at 50°C for 24 h. They were then molded using a benchtop injection

TABLE 1 | Formulations of LDPE/CNCs nanocomposites and compatibilized system.

Sample	Description	LDPE (wt%)	CNCs (wt%)	PE-g-MA (wt%)
LDPE	Neat LDPE	100.0	0.0	0.0
LDPE/1% CNCs	LDPE reinforced with 1% (w/w) CNCs	99.0	1.0	0.0
LDPE/1.5% CNCs	LDPE reinforced with 1.5% (w/w) CNCs	98.5	1.5	0.0
LDPE/1% CNCs/1% PE-g-MA	LDPE with 1% (w/w) CNCs and 1% (w/w) PE-g-MA	98.0	1.0	1.0

Note: Compositions expressed in weight percent (w/w) relative to the total formulation.

molding machine (AXINJET, AX Plásticos, Diadema, Brazil). Dog-bone-shaped specimens, each weighing approximately 5 g, were fabricated for mechanical tensile testing in accordance with ASTM D638. Injection molding was carried out at 190°C, with the mold temperature set at 80°C. The injection pressure was applied manually through a mechanical lever system, allowing precise control of the molten polymer flow into the mold cavity.

2.3 | Characterization of the Composites

2.3.1 | Thermogravimetric Analysis (TGA)

TGA was conducted to assess the thermal stability of the samples. The measurements were carried out using a high-precision thermobalance (TG 209 F1 Iris, Netzsch, Selb, Bavaria, Germany). The heating rate was set at 20°C/min, from room temperature up to 700°C. Nitrogen was used as the purge gas at a constant flow rate of 50 mL/min.

2.3.2 | Differential Scanning Calorimetry (DSC)

DSC analysis was employed to assess the effect of different CNC concentrations on the melting temperature (T_m), crystallization temperature (T_c), and degree of crystallinity of the composites. Analyses were performed using a DSC apparatus (Q2000, TA Instruments, New Castle, DE, USA), under nitrogen atmosphere with a constant flow rate of 50 mL/min. The samples were initially heated from room temperature to 200°C at a rate of 10°C/min and held at that temperature for 3 min. Subsequently, they were cooled to 30°C at 10°C/min to determine the T_c , followed by a second heating cycle up to 200°C, also at 10°C/min. DSC analyses were conducted on samples obtained after extrusion processing. The second heating cycle was used for data

interpretation, as it is not influenced by the thermal history of the material. The degree of crystallinity (X_c) was calculated according to Equation (1), based on the approach proposed by Tarani [16].

$$X_c = \frac{\Delta H_m}{\Delta H_0(1 - \phi)} \times 100\% \quad (1)$$

where ΔH_m is the experimental melting enthalpy, ΔH_0 is the melting enthalpy of 100% crystalline LDPE (293 J/g), and ϕ is the mass fraction of the reinforcing agent.

2.3.3 | Tensile Strength Test

Tensile strength tests were performed in accordance with ASTM D638 using a universal testing machine (5569, Instron, Norwood, MA, USA). A 5 kN load cell was employed, with a grip separation of 115 mm and a crosshead speed of 10 mm/min. The width and thickness of the specimens were measured with a digital caliper (Mitutoyo, Kawasaki, Kanagawa, Japan) with a precision of ± 0.001 mm. Five specimens were tested for each composition.

2.3.4 | Scanning Electron Microscopy (SEM)

The fracture surface morphology of the composites was investigated by a SEM microscope (JSM-6610LV, Jeol, Tokyo, Japan) equipped with energy-dispersive X-ray spectroscopy. Specimens were obtained from fractured surfaces of injection-molded bars previously subjected to Izod impact loading, following the ASTM D256 standard, solely for the purpose of generating representative fracture surfaces. Prior to imaging, the samples were sputter-coated with a thin gold layer using a metal coater (MED020, Bal-Tec, Los Angeles, CA, USA). SEM micrographs were acquired to evaluate CNC dispersion and interfacial characteristics.

2.3.5 | Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were acquired using an infrared spectrometer (VERTEX 70, Bruker, Ettlingen, Germany). The measurements were performed in the range of 500–4000 cm^{-1} , directly on the surface of the nanocomposites without additional sample preparation.

2.3.6 | X-Ray Diffraction (XRD)

The crystalline structure of the nanocomposites was examined using an X-ray diffractometer (XRD 7000, Shimadzu, Kyoto, Japan), equipped with a copper tube and operated at 40 kV. Measurements were carried out over a 2θ range of 10°–80°, with a scan rate of 3°/min and a wavelength of 1.5418 Å. The crystallinity index (CI) was calculated using Equation (2), as described by [17].

$$CI = \frac{A_{\text{crystal}}}{A_{\text{crystal}} + A_{\text{amorph}}} \times 100\% \quad (2)$$

where A_c and A_a are the areas of the crystalline and amorphous regions, respectively, obtained integrating the area under the XRD curves using OriginLab software [18].

2.3.7 | Accelerated Aging Test

Accelerated aging tests were conducted using a weathering chamber (UVV-STD-SPRAY-4400/2013, BASS Equipamentos, Barueri, SP, Brazil) in accordance with ASTM G154. The exposure consisted of two daily cycles: 3 h 45 min of condensation (dew), 15 min of water spray, and 8 h of UV lamp irradiation. Samples were removed at intervals of 30, 60, 90, and 120 days, and subsequently subjected to tensile strength tests using the same conditions described in Section 2.3.3.

3 | Results and Discussion

3.1 | Thermogravimetric Analysis (TGA) and Derivative Thermogravimetry (DTG)

TGA and DTG analyses were performed to screen the thermal stability and degradation pathway (single vs. multi-step) of the LDPE/CNC nanocomposites and to examine the effects of CNC content and PE-g-MA.

Figure 1 shows the TGA (Figure 1a) and DTG (Figure 1b) curves obtained for LDPE, LDPE/1% CNCs, LDPE/1.5% CNCs, and LDPE/1% CNCs/1% PE-g-MA as a function of temperature.

The main stage of thermal decomposition begins at approximately 350°C, and extends up to around 515°C, as evidenced by the marked mass loss in the TGA curves (Figure 1a) and the appearance of a single well-defined peak in the DTG curves for all samples (Figure 1b). This pattern is characteristic of polyethylene thermal degradation, whose linear, saturated, and low-polarity structure favors a single-phase decomposition [19]. The

peak temperature observed in Figure 1b indicates the point of maximum degradation rate and serves as a reliable parameter for comparing the relative thermal stability among the systems. This peak occurs at 465°C for pure LDPE, while the addition of 1% and 1.5% CNCs shifts this temperature to 475°C in both formulations. This phenomenon can be attributed to the high crystallinity of CNCs, which act as physical barriers to heat transfer and the diffusion of degradation products, while also restricting the mobility of polymer chains, thereby delaying the thermal decomposition of the matrix. Similar results were reported by [20] for microfibrillated cellulose filaments (CFs) and acid-hydrolyzed cellulose nanocrystals (CNC-H).

The incorporation of the compatibilizer PE-g-MA does not materially change the thermal stability relative to the CNC-only formulations: the DTG peak of LDPE/1% CNC/1% PE-g-MA remains at ~474°C and the onset/endset temperatures are similar. However, the compatibilized system shows a slightly higher final residue. This is consistent with literature reports that neat CNC yields ~20 wt% [21]; at the low CNC loadings used here (1–1.5, wt%), the increment in residue is small and approximately proportional to the CNC content, so no large residual mass is expected in the nanocomposites.

3.2 | Differential Scanning Calorimetry (DSC)

Following the thermal analysis discussed in the previous section, DSC was performed to evaluate the thermal transitions and crystallization behavior of pure LDPE and its nanocomposites containing different concentrations of CNCs and PE-g-MA. The resulting curves are shown in Figure 2, while the values for melting temperature (T_m), crystallization temperature (T_c), and degree of crystallinity (X_c) are presented in Table 2.

Figure 2a,b present the DSC curves for neat LDPE and the nanocomposites during the cooling and second-heating runs.

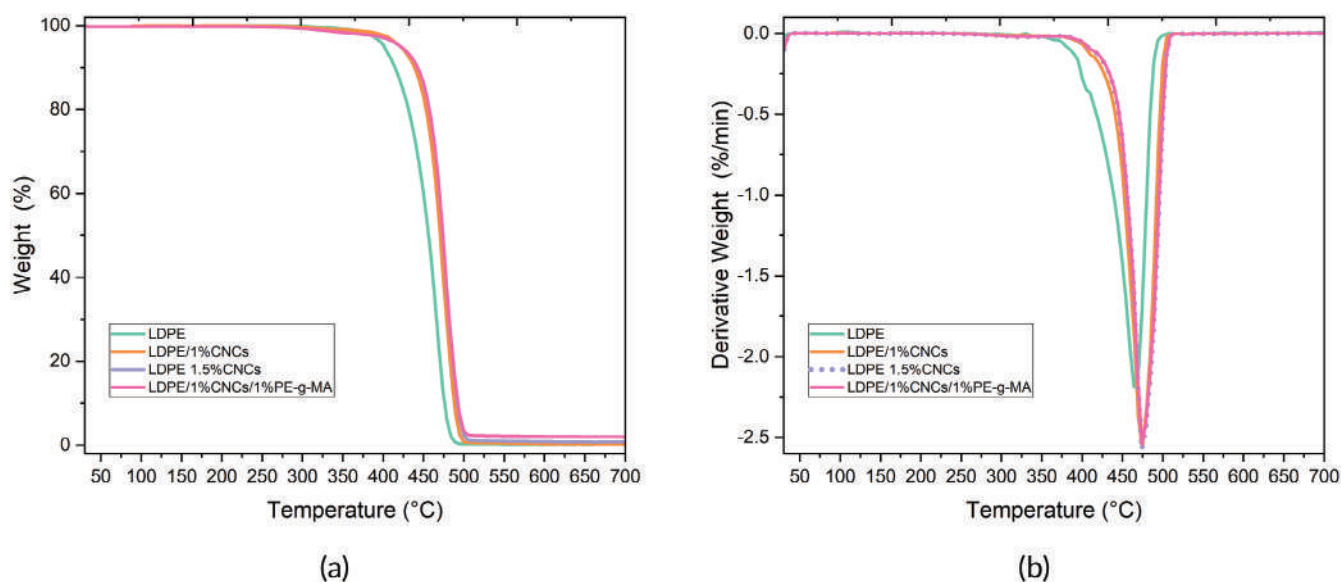


FIGURE 1 | (a) TGA and (b) DTG curves of LDPE and its nanocomposites with different concentrations of CNCs and compatibilizer. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.58181)]

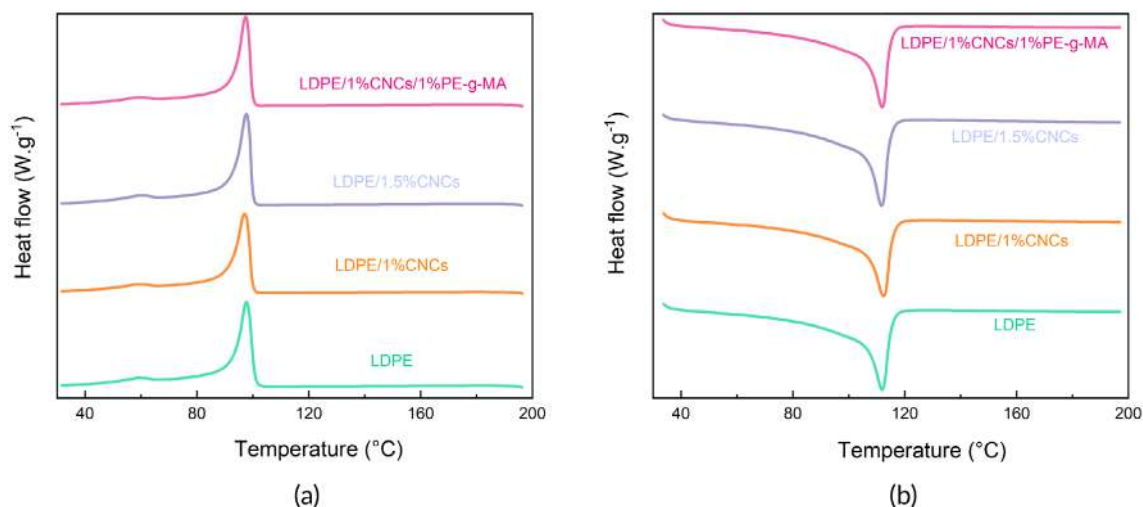


FIGURE 2 | Differential Scanning Calorimetry curves of LDPE and nanocomposites: (a) during the cooling cycle and (b) during the second heating cycle. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

TABLE 2 | DSC results for crystallization temperature (T_c), melting temperature (T_m), and degree of crystallinity (X_c).

Sample	T_m (°C)	T_c (°C)	X_c (%)
LDPE	111.9	97.7	23.7
LDPE/1% CNCs	112.5	97.1	23.4
LDPE/1.5% CNCs	111.8	97.7	26.1
LDPE/1% CNCs/1% PE-g-MA	111.9	97.5	23.5

uncertainty, these results indicate that the additives do not measurably affect the main thermal transitions or the nucleation/crystal-growth kinetics of the LDPE matrix.

Therefore, although the DSC data provide useful thermal transition insights, additional analytical techniques, such as XRD, are necessary to confirm or clarify the potential structural changes induced by CNCs and the compatibilizer. These complementary evaluations will be addressed in Section 3.3.

3.3 | Crystalline Structure Characterization by XRD

Figure 3 presents the XRD patterns of the samples. They exhibit characteristic diffraction peaks of LDPE at $2\theta \approx 21.6^\circ$ and $2\theta \approx 23.9^\circ$, corresponding to the (110) and (200) crystallographic planes of the orthorhombic structure of polyethylene [22]. These peaks indicate the semicrystalline nature of LDPE, which is maintained in all composites.

In addition to the characteristic LDPE reflections, a weak diffraction peak was consistently observed at $2\theta \approx 35.9^\circ$ across all samples. This feature is not commonly associated with LDPE or CNCs. A plausible explanation is the incorporation of trace amounts of metallic residues from milling and extrusion processes, which may introduce iron-based contaminants. Notably, magnetite (Fe_3O_4) exhibits a prominent (311) reflection at approximately $2\theta = 35.4^\circ$, closely aligning with the detected signal. Given its high crystallinity and thermal resistance, magnetite can remain stable throughout processing and may be responsible for the persistent presence of this peak in the XRD patterns [23].

The incorporation of CNCs leads to a modest increase in the intensity of the LDPE reflections and a slight reduction of the amorphous halo in all cellulose-containing formulations (LDPE/1% CNCs, LDPE/1.5% CNCs, and LDPE/1% CNCs/1% PE-g-MA). Although no additional cellulose-I peak is resolved, but an increase in area and a subtle asymmetry appear within $2\theta = 22^\circ - 23^\circ$, where the cellulose-I (200) reflection ($\sim 22.6^\circ$)

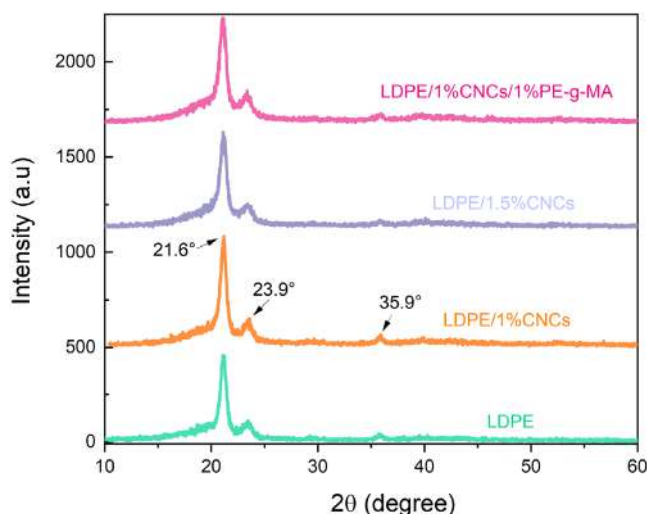


FIGURE 3 | XRD patterns of LDPE and its nanocomposites with 1% and 1.5% CNCs, with and without 1% PE-g-MA. The peaks near 21.6° and 23.9° 2θ indicate typical crystalline planes of LDPE. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

All samples show the expected crystallization and melting events of semicrystalline LDPE, and the addition of CNCs, either alone or with PE-g-MA, does not visibly shift the peak positions. Consistently, Table 2 reports nearly constant melting temperatures ($T_m \approx 112^\circ\text{C}$) and crystallization temperatures ($T_c \approx 97^\circ\text{C}$) for all formulations. Within experimental

TABLE 3 | Crystallinity index of the studied samples.

Sample	Crystallinity index (%)
LDPE	50.11
LDPE/1% CNCs	83.03
LDPE/1.5% CNCs	80.01
LDPE/1% CNCs/1% PE-g-MA	86.76

overlaps the LDPE (110)/(200) peaks ($\sim 21.6^\circ / \sim 23.9^\circ$). This overlap, together with the reduced amorphous background, accounts for the higher XRD crystallinity indices observed for all CNC-containing samples, particularly the compatibilized one.

The presence of sharper and more defined peaks in the compatibilized system (LDPE/1.5% CNCs/1% PE-g-MA) supports the hypothesis that PE-g-MA contributes to better nanofiller distribution, leading to a more ordered crystalline structure. This enhanced crystallinity, in turn, is consistent with the thermal stability trends observed in TGA and the morphological improvements noted in SEM analyses.

In addition to the qualitative analysis of the diffraction peaks, the crystallinity index (CI) of the samples was estimated based on the area ratio between crystalline and amorphous regions, as described in Section 2.3.6. The results are presented in Table 3. Notably, all nanocomposites exhibited a higher CI compared to neat LDPE, indicating that the presence of CNCs promoted a more ordered molecular arrangement within the polymer matrix. The highest CI was observed for the sample LDPE/1% CNCs/1% PE-g-MA, reaching 86.76%, which suggests that the compatibilizer may have further enhanced crystallization, possibly due to improved dispersion and stronger interfacial interactions between the polymer and CNCs.

It is important to remark that in contrast to the DSC values, the XRD CI for the same four samples is numerically higher because it quantifies a different property and aggregates additional crystalline contributions. This is because, DSC quantifies the mass fraction of thermally melting LDPE crystals, computed from ΔH_m and ΔH_0 (Equation 1), whereas the XRD CI (Equation 2) is an intensity/area-based metric that includes all crystalline phases in the composite.

Therefore, beyond the LDPE reflections (110 and 200 at $\sim 21.6^\circ$ and $\sim 23.9^\circ$), XRD also integrates cellulose-I peak from CNCs ($\sim 22.6^\circ$), which increase the total crystalline area and raise the CI.

3.4 | Uniaxial Tensile Strength Test

The results of uniaxial tensile tests, including *elastic modulus* (as a measure of stiffness), *tensile strength* (as an indicator of material strength), and *elongation at break* (as a parameter of ductility), are summarized in Table 4. These properties provide insight into the mechanical performance of the LDPE matrix and its nanocomposites reinforced with CNCs and PE-g-MA.

TABLE 4 | Results of uniaxial tensile testing: Elastic modulus, tensile strength, and elongation at break for each sample.

ID	Composition	Elastic modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
G1	LDPE	309.2 $\pm 25.0^a$	11.05 $\pm 0.57^a$	67.01 $\pm 4.94^a$
G2	LDPE/1% CNCs	337.6 $\pm 21.6^a$	11.17 $\pm 0.49^a$	47.52 $\pm 7.09^b$
G3	LDPE/1.5% CNCs	361.0 $\pm 12.8^b$	10.76 $\pm 0.53^a$	51.45 $\pm 2.22^b$
G4	LDPE/1% CNCs/1% PE-g-MA	354.0 $\pm 22.2^b$	13.15 $\pm 0.66^b$	54.50 $\pm 1.72^b$

Note: Different superscript letters within a column indicate significant differences (one-way ANOVA + Tukey, $\alpha = 0.05$). Grouping by column—Modulus: {G1, G2}^a, {G3, G4}^b; Strength: {G1, G2, G3}^a, {G4}^b; Elongation: {G1}^a, {G2, G3, G4}^b.

Relative to neat LDPE (309.2 ± 25.0 MPa), adding 1% CNC yielded a modest increase in tensile modulus to 337.6 ± 21.6 MPa (+ 9.2%), which was not statistically different from LDPE ($p > 0.05$). Raising the CNC content to 1.5% increased the modulus to 361.0 ± 12.8 MPa (+ 16.8%), and the compatibilized composite with 1% CNC and 1% PE-g-MA reached 354.0 ± 22.2 MPa (+ 14.5%). Both LDPE/1.5% CNC and LDPE/1% CNC/1% PE-g-MA were significantly stiffer than LDPE ($p < 0.05$) and did not differ from each other ($p > 0.05$), indicating that statistically reliable stiffness gains arise either at the higher CNC loading or with compatibilization.

Tensile strength formed two statistical groups according to one-way ANOVA/Tukey ($\alpha = 0.05$), namely: {LDPE LDPE/1% CNCs, LDPE/1.5% CNCs}^a and {LDPE/1% CNCs, LDPE/1.5% CNCs}^a and {LDPE/1% CNCs/1% PE-g-MA}^b. The compatibilized composite was significantly stronger than the other three, which did not differ from each other. In absolute terms, corresponds to an increase of $\sim 19\%$ versus LDPE for the compatibilized system. This pattern indicates that low CNC loadings do not translate into higher ultimate strength unless dispersion and interfacial adhesion are enhanced by compatibilization, in line with prior observations for polymer/CNC systems [24, 25].

Finally, the elongation at break data reveal important insights into the ductile behavior of the materials. The pure LDPE exhibited the highest ductility (67.01%), as expected for a non-reinforced polymer with high chain mobility. Upon the addition of CNCs, a marked decrease in elongation was observed, dropping to 47.52% for the 1.0% CNC formulation and to 51.45% for the 1.5% CNC sample. This reduction reflects the typical stiffening effect of nanofillers, which limit polymer chain movement and hinder plastic deformation. Interestingly, the formulation with 1% CNC and 1% PE-g-MA exhibited slightly improved ductility (54.5%) compared to the CNC-only samples, suggesting that the compatibilizer may partially mitigate the embrittlement effect by enhancing interfacial adhesion and promoting a more homogeneous stress distribution. Nonetheless, all reinforced formulations showed lower ductility

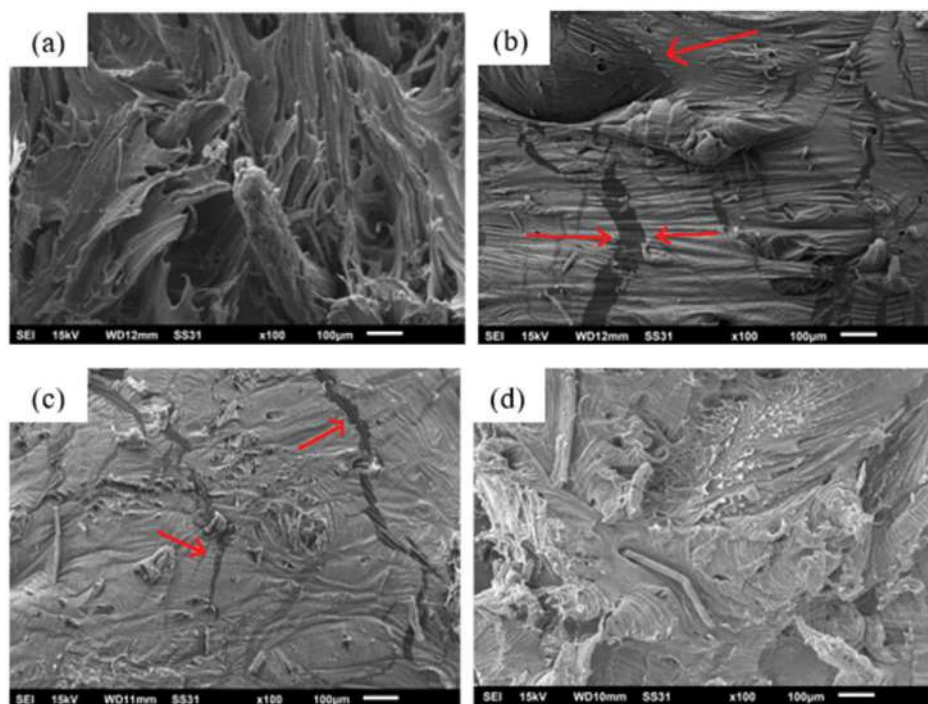


FIGURE 4 | SEM micrographs of the fracture surfaces of (a) LDPE, (b) LDPE/1% CNCs, (c) LDPE/1.5% CNCs, and (d) LDPE/1% CNCs/1% PE-g-MA. All images were obtained from specimens fractured under Izod impact to evaluate the dispersion of CNCs and interfacial adhesion within the polymer matrix. Red arrows highlight typical fracture features and regions of filler–matrix interaction. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.58181)]

than neat LDPE, highlighting the inherent trade-off between stiffness and flexibility in nanocomposite design.

3.5 | Fracture Surface Morphology by SEM

Figure 4 presents SEM micrographs of the fracture surfaces of the samples subjected to Izod impact testing, highlighting morphological aspects associated with fracture behavior under dynamic loading conditions. This approach is essential to avoid misinterpretations that might arise from the analysis of fracture surfaces obtained from tensile tests, which involve different mechanical solicitation.

In the micrograph of the neat LDPE sample (Figure 4a), a highly deformed surface is observed, without a clearly defined fracture plane. This behavior is consistent with the high ductility reported in the mechanical tests, reflecting a typically ductile fracture dominated by extensive plastic deformation and high polymer chain mobility.

With the incorporation of 1% CNCs (LDPE/1% CNCs, Figure 4b), the fracture surface becomes less rough, with more evident shear markings and a more oriented structure. This change suggests an increase in stiffness and a reduction in plastic deformation capacity, consistent with the reduced elongation at break previously observed. The presence of CNCs restricts chain mobility and promotes more brittle fracture mechanisms. Such crack-path tortuosity and local microvoiding/deflection are commonly reported for nanofiller-reinforced polyolefins and are linked to filler–matrix interactions [26, 27].

The LDPE/1.5% CNCs sample (Figure 4c) shows an even more organized fracture morphology, with clearer lamellar features and flatter regions, indicating greater structural rigidity. The increase in elastic modulus observed for this sample supports this morphology. Moreover, the improved CNC dispersion may have contributed to less localized fracture and more homogeneous stress dissipation, as suggested by the slight recovery in elongation at break compared to LDPE/1% CNCs [28, 29].

Finally, the compatibilized formulation (LDPE/1% CNCs/1% PE-g-MA, Figure 4d) exhibits a more cohesive fracture surface, with oriented and continuous fracture propagation lines. This morphological pattern aligns with the structural and mechanical results, which indicate a slight recovery in ductility and maintained stiffness. The addition of PE-g-MA likely improved interfacial adhesion and promoted more uniform CNC dispersion, leading to a more controlled and less abrupt fracture. Despite the reduced tensile strength observed, this behavior suggests enhanced impact performance, emphasizing the beneficial effect of compatibilization on fracture dynamics. Overall, no micron-scale agglomerates are evident in our SEM; we note, however, that nanoscale clustering cannot be resolved by SEM and would require higher-resolution or complementary techniques.

3.6 | FTIR Analysis of LDPE-Based Nanocomposites

Figure 5 displays the FTIR spectra of all samples, revealing characteristic absorption bands associated with polyethylene [30].

The most prominent peaks include those at approximately 2915 and 2848 cm^{-1} , corresponding to the asymmetric and symmetric stretching vibrations of CH_2 groups, respectively. Additionally, the bands near 1465 and 720 cm^{-1} are assigned to CH_2 bending and rocking modes, respectively, confirming the presence of the polymer backbone.

Incorporation of CNCs (LDPE/1% CNCs and LDPE/1.5% CNCs) did not introduce new distinct absorption peaks, which is expected due to the low concentration of filler and the dominance of the LDPE matrix in the spectra. Nevertheless, slight intensity variations can be observed in the region around 1050–1100 cm^{-1} , which may be associated with C–O stretching from the cellulose backbone. These subtle changes are more noticeable in the LDPE/1.5% CNCs sample, suggesting a slightly higher contribution of the CNC phase.

The characteristic absorption band near 1730 cm^{-1} , typically attributed to the C=O stretching vibration of maleic anhydride groups present in PE-g-MA, as highlighted by [31], is not clearly discernible in the FTIR spectrum of the LDPE/1.5% CNCs/1% PE-g-MA formulation (Figure 5). This absence can be attributed to the relatively low concentration of PE-g-MA used in the formulation, combined with possible overlap from adjacent polyethylene bands, which hinders the clear identification of this signal.

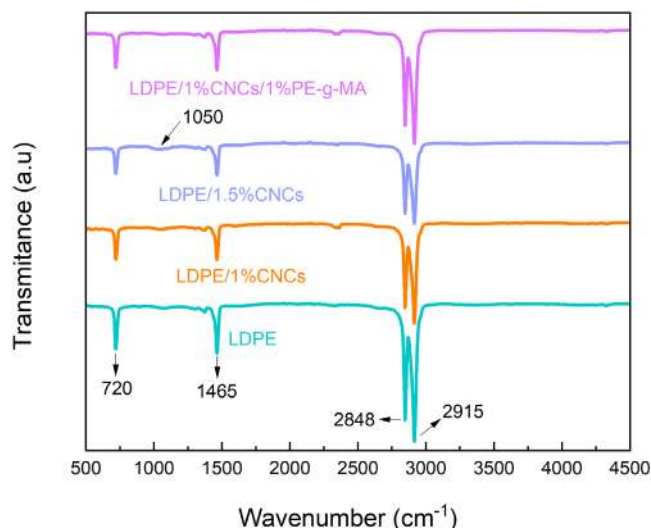


FIGURE 5 | FTIR spectra of neat LDPE and nanocomposites: LDPE/1% CNCs, LDPE/1.5% CNCs, and LDPE/1% CNCs/1% PE-g-MA. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

3.7 | Accelerated Aging Test

Table 5 presents the elastic modulus values of the nanocomposite samples after exposure to an accelerated aging protocol for up to 120 days. Measurements were conducted at five time points (0, 30, 60, 90, and 120 days), allowing evaluation of mechanical degradation or stabilization behavior over time.

Overall, the pure LDPE sample exhibited a gradual increase in elastic modulus over time, likely due to post-crystallization effects or physical aging that increased chain ordering. Interestingly, LDPE/1% CNCs also maintained a similar trend until 90 days, followed by a slight drop at 120 days, suggesting moderate structural rearrangement.

For the nanocomposites containing 1.5% CNCs, the modulus values decreased steadily throughout the aging period. This reduction may be associated with the onset of microstructural damage or CNC-matrix interfacial degradation under prolonged exposure. The compatibilized sample with 1% CNCs and 1% PE-g-MA initially showed promising performance at 60 days, but exhibited the sharpest decline by 120 days, indicating that while PE-g-MA improves short-term interactions, long-term exposure might induce hydrolysis or degradation of the interfacial bonds.

Interestingly, the LDPE/1.5% CNCs/1% PE-g-MA sample displayed the highest modulus at 60 days, but also a progressive decrease after this point. These behaviors highlight the delicate balance between CNC concentration, interfacial stability, and aging resistance. These results emphasize that while CNCs and PE-g-MA contribute positively to initial stiffness and crystallinity, long-term durability depends on the stability of interfacial interactions under environmental stressors.

4 | Conclusions

This study demonstrated that the incorporation of CNCs, extracted from bamboo culms, into LDPE matrices can significantly enhance the structural and functional performance of the resulting nanocomposites. The CNCs acted as effective nucleating agents, promoting increased crystallinity as confirmed by XRD and DSC analyses, especially in the presence of the compatibilizer PE-g-MA.

FTIR analysis revealed characteristic polyethylene bands and provided indirect evidence of interactions between PE-g-MA and CNCs. Although the typical absorption band near 1730 cm^{-1} associated with the maleic anhydride groups was not sharply

TABLE 5 | Elastic modulus (MPa) of the samples subjected to accelerated aging for 0, 30, 60, 90, and 120 days.

Sample	0 days	30 days	60 days	90 days	120 days
LDPE	309.2 ± 25.0	293 ± 2	295.2 ± 25.6	325 ± 1	347 ± 2
LDPE/1% CNCs	337.6 ± 21.6	323 ± 1	301.6 ± 35.6	345 ± 2	300 ± 4
LDPE/1.5% CNCs	361 ± 12.7	323 ± 4	309.6 ± 24.3	314 ± 3	297 ± 2
LDPE/1% CNCs/1% PE-g-MA	354 ± 22.1	317 ± 2	345.6 ± 22.6	322 ± 3	266 ± 4

resolved—likely due to overlapping and low concentration—mechanical and morphological data support the hypothesis of improved interfacial adhesion.

Thermogravimetric analysis showed a slight improvement in thermal stability for CNC-reinforced systems, with the most thermally stable formulation being LDPE/1% CNCs/1% PE-g-MA. SEM further confirmed the enhanced dispersion and interfacial compatibility in compatibilized nanocomposites, reinforcing the synergistic role of PE-g-MA.

Mechanical testing under uniaxial tension showed that CNC addition increased stiffness; the gain was statistically significant for the 1.5wt% CNC formulation and for the compatibilized composite, whereas LDPE and LDPE/1wt% CNC did not differ. Tensile strength formed two statistical groups, {LDPE, LDPE/1%CNC, LDPE/1.5%CNC}^a and {LDPE/1%CNC/1%PE-g-MA}^b, with the compatibilized system presenting the highest values. Following accelerated aging (UV + humidity), both modulus and strength exhibited modest declines across all materials, with a comparatively larger decay in the compatibilized composite, suggesting time-dependent changes at the CNC–matrix interface (e.g., degradation of grafted moieties) and microstructural rearrangements.

Overall, the results indicate that combining bamboo-derived CNCs with PE-g-MA is a sustainable and effective route to improve the thermal performance and load-bearing response of LDPE composites. The resulting materials are particularly suitable for components that prioritize high stiffness, tensile strength, and thermal resistance, but not necessarily ductility, such as electronic housings, motor covers, and connectors used in wind and solar energy systems, provided dispersion and interfacial adhesion are adequately controlled.

Looking ahead, three points warrant attention: impact performance, moisture effects during aging, and nanoscale dispersion. Fracture-surface SEM at 1–1.5wt% CNC showed no micron-scale agglomerates, but nanoscale clustering cannot be ruled out meriting a deeper investigation. Future work should also quantify water uptake, assess humidity effects on viscoelastic response, and probe dispersion with higher-resolution methods. To mitigate the stiffness–ductility trade-off without altering the LDPE/CNC + PE-g-MA architecture, we suggest exploring low-level addition of a bio-based EVA soft phase.

Author Contributions

Mariane Weirich Bosenbecker: conceptualization (equal), data curation (equal), formal analysis (lead), investigation (equal), software (equal), validation (equal), visualization (equal), writing – original draft (equal), writing – review and editing (equal). **Eduarda Vieira Silva:** data curation (supporting), formal analysis (supporting), project administration (supporting), software (supporting), validation (supporting). **Patricia Oliveira Schmitt:** data curation (supporting), validation (supporting), writing – original draft (supporting). **Tiago Thomaz Migliati Zanon:** investigation (equal), software (equal), validation (equal). **Débora da Silva Rodrigues:** investigation (supporting), methodology (supporting), validation (supporting). **Everton Granemann Souza:** data curation (supporting), investigation (supporting), methodology (equal), software (equal), validation (equal), writing – original draft (equal), writing – review and editing (equal). **Chiara das Dores**

do Nascimento: data curation (equal), formal analysis (equal), methodology (equal), validation (equal), writing – original draft (equal), writing – review and editing (equal). **Juliano Marini:** conceptualization (equal), data curation (equal), supervision (lead), writing – review and editing (equal). **Amanda Dantas de Oliveira:** conceptualization (lead), funding acquisition (lead), project administration (lead), supervision (lead).

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Data will be made available on request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. **Data S1:** Supporting Information.

Mechanical characterization of HDPE reinforced with cellulose from rice husk biomass

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Abstract

High-density polyethylene (HDPE) reinforced with cellulose from rice husk (RH) were prepared and studied. The RH biomass was submitted to acid extraction and bleaching process and then analyzed for its cellulose extraction efficiency by X-ray diffraction (XRD) and Fourier transformation infrared spectroscopy (FTIR). After that, the RH cellulose (RHC) was incorporated to the HDPE matrix by melt blending with different filler contents (5, 10 and 15 wt%), and then characterized in terms of mechanical properties and morphology. The RHC incorporation in the HDPE matrix resulted in an increase in elastic modulus regardless the filler content added; also, the impact resistance was maintained for RHC contents up to 10%. The morphological analysis of the composites showed that the cellulose was well dispersed in the matrix, which contributed to the improvement of the final rigidity of these materials, indicating the feasibility of incorporating this residue in the production of HDPE composites.

Keywords: *cellulose, biomass, polymeric composites, rice husk.*

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1. Introduction

Polymeric composites reinforced with vegetable fibers have been the target of great academic and industrial interest for replacing, generally with cost advantages and lightness, materials made of conventional polymeric composites. These composites are less aggressive and toxic, since they are reinforced with raw materials of plant origin, such as oils, starch and cellulose. Besides coming from renewable sources, meeting the requirements of biodegradability and preservation of the environment throughout its cycle of life^[1], they can be an alternative for the reduction of inappropriate waste disposal when the utilized fibers are from agroindustrial waste^[2].

Rice is the most popular food in the world, its importance can be noted by its numbers of consumption and production. The consumption of rice as food for 2017 was estimated at 53.7 kg/person. To meet this demand, rice production forecasts, for the same year, were estimated at 759.6 million tonnes according to the Food and Agriculture Organization (FAO)^[3]. In this context, the Brazilian production of rice is in the order of 12 million tons/year and the state of Rio Grande do Sul represents 60% of this production^[4]. For each ton of rice produced, it is estimated that 0.23 ton of RH are formed during the rice refining process, being the most voluminous by-product^[5]. In this way, RH is an agroindustrial large quantity residue in Rio Grande do Sul.

The average chemical composition of RH is defined in 35% cellulose, 25% hemicellulose, 20% lignin and 20% of others^[6]. It is important to note that these contents may vary significantly according to type of paddy, crop year, climatic and geographical conditions and sample preparation for analysis.

These peels have low commercial value because the contained silica (SiO₂) and the fibers do not have nutritional value, therefore they are not used in human or animal feeding. The destination found for the RH, in the last years, has been the discharge into crops and river bottoms, resulting in serious environmental impacts. In other cases, RH has been used as a source of energy for parboiling, but it is also a problem as it contributes to air pollution.

Polymeric composites using cellulose as reinforcing agent have several advantages, generally these natural reinforcements are lighter, more economically attractive and provide greater resistance when compared with inorganic reinforcing agents^[7]. But interestingly, there are no reports on the use of cellulose obtained from RH in HDPE matrix.

Therefore, the objective of this work was to evaluate the use of cellulose extracted from RH in the obtention of composites with HDPE by melt blending, offering an alternative reuse for this agroindustrial residue. The work

also aimed to promote an improvement in the mechanical properties of HDPE.

2. Materials and Methods

High density polyethylene - HDPE (GM9450F) obtained from Braskem S/A was used as polymeric matrix. The rice hulks were obtained from a cereal supply located in Pelotas/RS – Brazil. All reagents used in this work had analytical grade.

2.1 Cellulose obtaining from RH

Figure 1 presents a flowchart of the methodology used for the RHC obtention.

Firstly, the rice hulks were milled in a knife mill (Marconi – Model MA 340). After that, the milled biomass was submitted to the first step treatment which consists in an acid treatment to remove the hemicellulose and lignin present in the RH. The milled RH was added in a solution of water, acetic acid and nitric acid at a ratio of 6:5:1 v/v, respectively, under mechanical stirring and reflux at 80°C for 4h. The resulting material was washed and filtered with distilled water until reached the neutral pH.

The bleaching process was done by the immersion of the resulting material from the first step in a solution of sodium hypochlorite for 24h. After the steady time, the material was filtered using distilled water until was neutralized. The non-passing material was the RHC, which was dried at 60°C for 24h.

2.2 Cellulose characterization

2.2.1 X-ray diffraction (XRD)

The XRD analyzes were performed using a diffractometer (D8 Advance Bruker) with wavelength of $\lambda = 1,541 \text{ \AA}$, operating at 40 KV and 40 mA. The scans were performed in the range of 2θ between 10 and 50°, at a rate of 1/min.

2.2.2 Fourier transformation infrared spectroscopy (FTIR)

The analyses were done using a Spectrum 1000 spectrophotometer from Perkin Elmer, in the range between 400 and 4000 cm^{-1} . Each spectrum corresponds to the average of 10 scans at a resolution of 4 cm^{-1} .

2.2.3 Scanning electron microscopy (SEM) analysis

The microscopy analyses of the RH in natura, the RH after the first treatment and the RH cellulose were performed by SEM using a Shimadzu, modelo SSX-550 Superscan equipment.

2.3 HDPE/Cellulose composites preparation

2.3.1 Melting blending process

To produce the composites, a single screw extruder (CIOLA, model MEP-18) with L/D = 22 was used. The temperature profile used was 180/190 °C in the two heating zones and 190 °C for the matrix. The composites were obtained with 5, 10 and 15 wt% by mass of cellulose. The pure polymer also was obtained using the same processing conditions in order to have their results compared to those obtained to the composite materials.

2.3.2 Composites molding

The materials obtained from the extrusion process were pelletized and then molded by compression at 200°C in a hydraulic press (Marconi, MA098/A) using the following cycle: pre-heating (for 2 min) / pressing (3 ton for 2 min) / relief / pressing (5 tons for 2 min) / forced cooling in water at room temperature. This process results in plates with 10 cm of length, 10 cm of width and 3.2 mm of thickness. The specimens for tensile and impact mechanical tests were stamped from the plates obtained.

Figure 2 shows a schematic of all the steps involved in processing of the composites.

2.3.3 Composites evaluation

2.3.3.1 Mechanical characterization

The mechanical properties were determined by tensile and Izod impact tests. The dimensions of the samples were defined according to the American Society for Testing Materials (ASTM) standards.

Tensile strength test

The tensile tests were performed according to ASTM D-638 on a universal testing machine (INSTRON E3000) with a load cell of 5000 N, distance between claws of 115 mm and deformation rate of 5 $\text{mm} \cdot \text{min}^{-1}$. The widths and thicknesses of the specimens were measured using a caliper gauge (Mitutoyo, $\pm 0.001 \text{ mm}$).

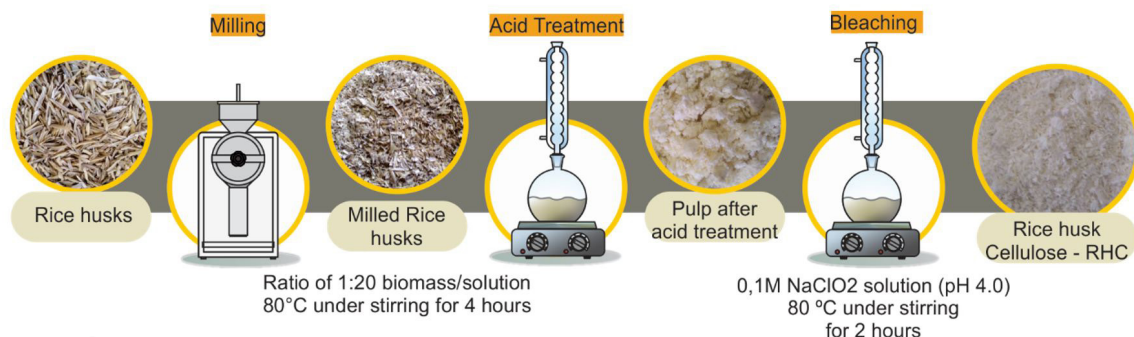


Figure 1. Flowchart of the RHC obtention process.

Izod impact test

For the Izod impact tests (RESIL 25, from Ceast) the specimens were notched with a depth of 2.54 ± 0.1 mm, with minimum notch speed in accordance with ASTM D256. The tests were performed at room temperature.

2.3.3.2 SEM analysis

The fracture surfaces of the impacted specimens were observed by SEM, using a Jeol JSM- 6610LV equipment. A thin layer of gold was deposited on the material with metallizer.

3. Results and Discussions

3.1 Cellulose characterization

The in natura RH color is brown and after the first chemical treatment a brown-orange coloration was observed. After the bleaching, the material appears completely white (see Figure 1). These color changes are directly associated with the removal of non-cellulosic materials^[8]. Thus, the white color observed in the final product was an indication of a high purity of the cellulosic material. However, further analysis is required, such as chemical composition, morphology, crystallinity and functional groups for its characterization^[9].

3.1.1 X-ray diffraction (XRD)

X-ray diffraction was used to investigate the crystalline structure of RH before and after the chemical treatments used. In addition, microcrystalline cellulose (MCC) of commercial origin was analyzed for comparison. The diffractograms are represented in Figure 3.

It is reported in the literature, that cellulose have crystalline structure, due to Van der Waals' bonds, while hemicellulose and lignin have an amorphous characteristic^[10]. As expected, natural rice husk has low crystallinity. There is an increase in the crystallinity of the samples according to the chemical treatments used, which may be related to the partial elimination of hemicellulose and lignin, indicating the efficiency of the procedure used to obtain the cellulose from rice husk. The peaks at approximately 16° , 22° and 34° are characteristic of type I cellulose^[9], corresponding to the (101), (002) and (004) planes, respectively.

3.1.2 Fourier transformation infrared spectroscopy (FTIR)

Figure 4 shows the spectra of the in natura rice husk, after acid extraction, RHC and MCC.

It is possible to observe in all spectra the presence of two major regions of absorbance^[11]. The first region at high wavenumbers ($2700\text{--}3500\text{ cm}^{-1}$) can be attributed to different vibrations in polysaccharides and the second

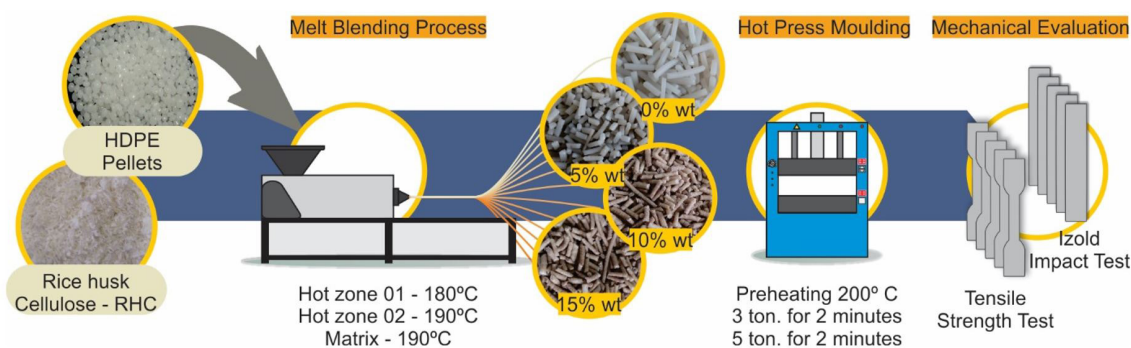


Figure 2. Flowchart of the composites processing.

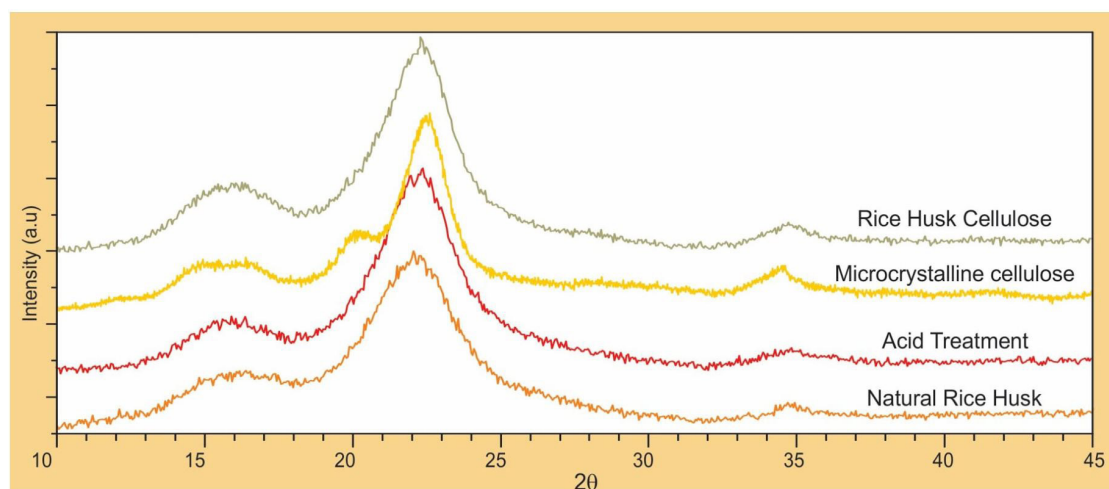


Figure 3. X-ray diffractograms of RH, RH after acid treatment, RHC and MCC.

region at lower wavenumbers (800 to 1800 cm^{-1}) is typical assigned to cellulose^[12].

The peak in the region between 3500 – 3000 cm^{-1} confirms the presence of hydroxyl groups (O-H). For the RHC, the increase in the area of this band indicates the presence of a greater number of OH groups^[13] and, consequently, an increase in RHC hydrophilicity.

The peak in 2921 cm^{-1} is observed in all spectra and it is due to the presence of C-H stretching vibration in polysaccharides, evidencing the presence of cellulose and hemicellulose^[12,14].

The bands in the range of 1700 – 1730 cm^{-1} are attributed to the vibration of acetyl and uronic groups of hemicellulose, or even to the ester linkage of carboxyl and p-coumaric acids in lignin^[15]. In this region a peak reduction was observed, according to the chemical treatment sequences, thus confirming the partial removal of hemicellulose and lignin^[11]. A small band was observed in the range of 1629 – 1621 cm^{-1} , which can be attributed to the water absorbed in cellulose^[12]. In general, the FTIR spectra have confirmed that RHC have a more open structure related to their greater wettability as the hemicellulose is dissolved or removed^[13]. The band at 1170 cm^{-1} corresponds to the asymmetric stretching of the C-O-C bond of cellulose, hemicellulose and lignin^[16].

The bands observed at approximately 1030 cm^{-1} and at 800 cm^{-1} in the spectra correspond to the stretching bonds of C=O in guaiacyl rings^[17] and CH deformations in cellulose^[15], the latter one presents an increase in intensity as the treatment is performed, indicating an increase in cellulose content.

3.1.3 SEM analysis

Through the SEM images it was possible to investigate the changes in the structure of the RH, as well as the cellulose, as shown in Figure 5.

The RH, Figure 5A, presented a more compact structure, with an irregular outer surface of hemicellulose, lignin, inorganic components and lumps or protuberances^[18], when compared to the RHC, Figure 5B and C, in which the bleached fibers had a fibrous and rough structure, with a mean diameter of $5\text{ }\mu\text{m}$ ^[8]; also some particulates are observed, which can be related to residual material from the synthesis or even remained impurities. It was also observed the presence of some pores in the rough surface of the fibers, indicating that there may be an increase in the effective surface area for contact with the polymeric matrix, which contributes to the improvement of the mechanical properties.

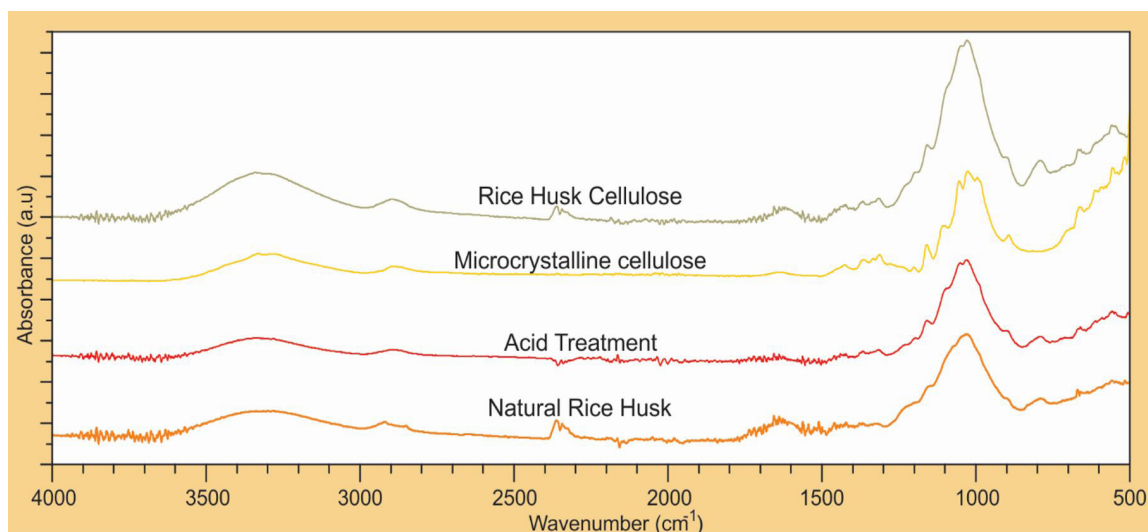


Figure 4. FTIR spectra of HR biomass, HR after the acid extraction, RHC and MCC.

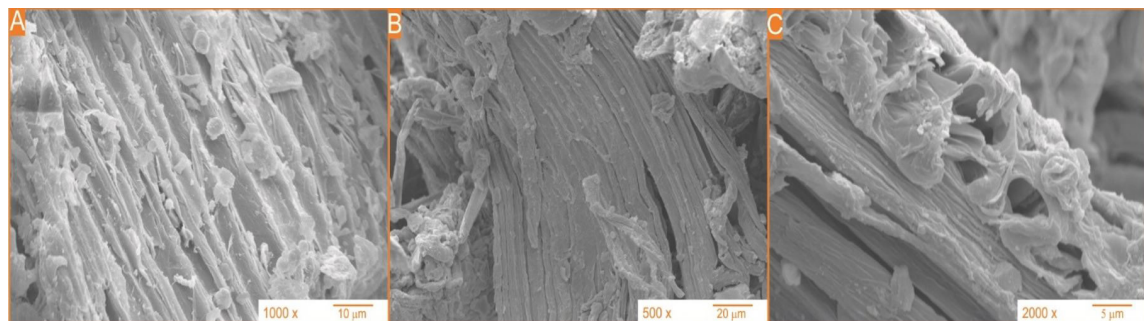


Figure 5. SEM micrographs of: (A) RH; (B) and (C) RHC.

3.2 Composites characterization

3.2.1 Mechanical characterization

Figure 6 presents the graphs for the mechanical characterization.

Tensile strength test

In Figure 6A it is possible to observe that the modulus of elasticity of the composites presented different behaviors in relation to the HDPE. The HDPE composites have higher elastic modulus than pure HDPE. On the other hand, when analyzing the results obtained for composite materials prepared with different filler contents, it is verified that the values of elastic modulus presented by these materials have no significant difference. It is known that when a composite is reinforced with cellulose, the tensile modulus of the polymer compound can improve considerably. However, this property change will also depend on the strength and effectiveness of the interfacial adhesion between cellulose and matrix [19], which can be improved with prior treatment and also of the amount of filler used. Low contents of cellulose can form regions of high mechanical stress, by a not so homogeneously dispersed mixture, resulting in a decrease in elastic modulus. Higher contents of cellulose, in its turn, can result in a better distribution of stresses, and thus greater modulus [20].

This small increase in the values of elastic modulus indicates a low interaction between the polymer and the matrix, and this can be explained by its lack of chemical affinity, since the HDPE is apolar and the cellulose is known for its polarity, as can be confirmed by FTIR.

Izod impact test

In Figure 6B it is observed that HDPE presented an average impact resistance of 178.65 J/m, higher than the composites with 5, 10 and 15 wt% of cellulose, with values of 172.99 J/m, 162.54 J/m and 126.36 J/m, respectively. Its already established in literature that HDPE has a high Izod impact strength, which is decreased when reinforced with vegetable fibers [21].

Considering the standard deviations, it can be affirmed that the addition of up to 10 wt% of RHC does not promote significant reductions in the impact resistance when compared to pure HDPE. The HDPE/15 wt% RHC presented a greater decrease impact resistance, breaking more easily, and also making it a material with greater rigidity lower tenacity. This can be explained since the introduction of reinforcements can promote stress concentration, generating the presence of micro-interfacial voids, which make the microcracks to propagate easily in the composite, and then reducing impact resistance [22]. Also, RH is fragile and therefore, have a low capacity to absorb energy during the propagation of the fracture. Similar results of decrease in impact strength with increasing cellulose content was observed in literature [19], who reported an increase in its brittleness due to large amounts of cellulose in a HDPE matrix. This decrease in impact strength of the polymer matrix can also be reverted by the use of impact modifiers, which improve the matrix / reinforcement interface.

3.2.2 SEM analysis

Its well established that interfacial adhesion matrix/filler and dispersion of the filler in the polymer matrix are determining factors in mechanical properties of any composite material [23]. In this way, the mechanical results can be confirmed to the observed in SEM analysis. Figure 7 presents SEM micrographs obtained from the fracture surface of the samples after the Izod impact tests were performed.

The micrographs revealed a heterogeneous distribution of the RHC in HDPE matrix, with RHC presenting different morphologies, such as rods-like structures, particulates and also agglomerates. These different morphologies can be justified by the fragmentation of RHC during the composites extrusion and the agglomeration due the greater affinity of cellulose with itself than with the matrix.

Considering the amount of RHC used represents most of the composite volume, we can affirm that it was possible to achieve a good adhesion between the phases, with the RHC distributed in the polymer, contributing to the increase of the elastic modulus when comparing to the HDPE. However, it is possible to observe regions of detachment of the RHC

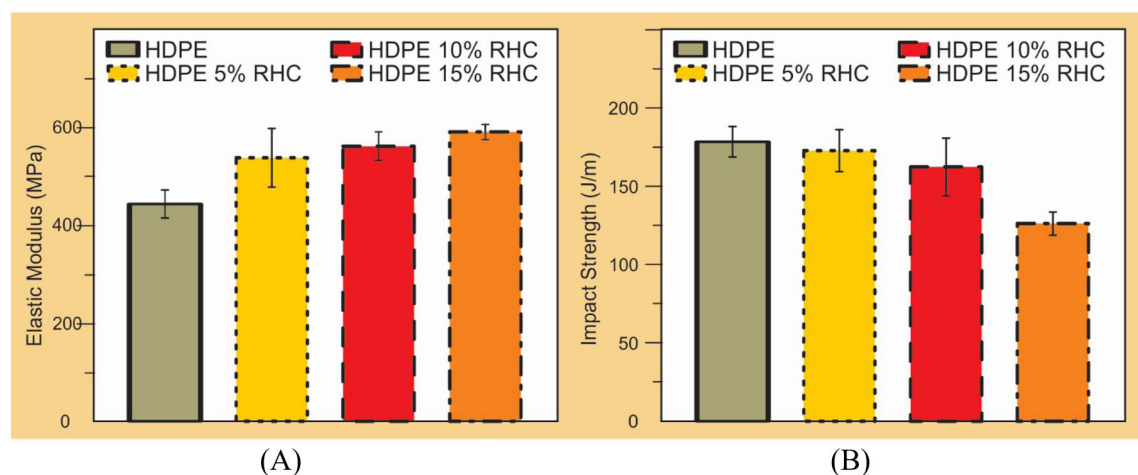


Figure 6. (A) Elastic modulus and (B) Impact strength for pure HDPE, HDPE 5wt% RHC, HDPE 10wt% RHC and HDPE 15wt% RHC composites.

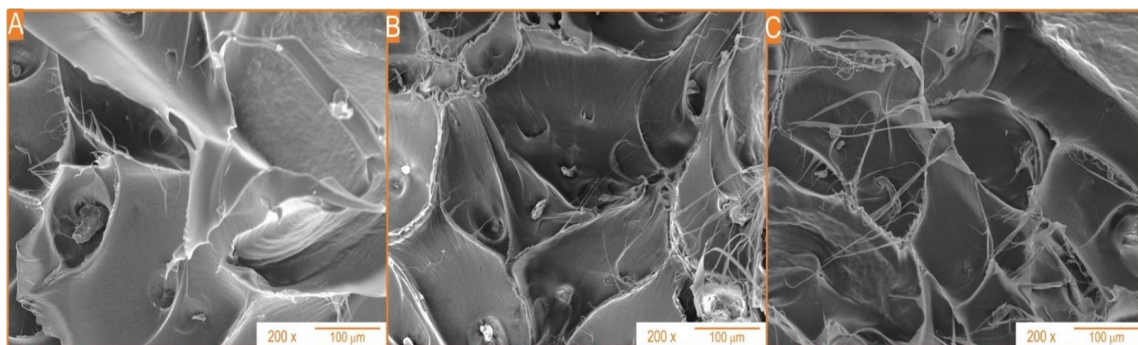


Figure 7. SEM micrographs of (A) HDPE 5wt% RHC, (B) HDPE 10wt% RHC and (C) HDPE 15wt% RHC.

from the matrix, forming voids. The more RHC was used, the more detachments could be perceived, due to the higher amount of RHC. In the same way, more voids are formed. The appearance of defects as voids with the increase in the amount of RHC used, justifies the results obtained by the impact resistance tests.

All observed fracture surfaces are rough, indicating that the addition of RHC did not change the fracture behavior of the polymeric matrix, which remained plastic.

4. Conclusions

Considering that the results of FTIR, XRD and SEM are in agreement with the literature, we can say that the treatment used was efficient for obtaining cellulose from RH biomass.

The addition of RHC in the HDPE polymer matrix had good effect on the elastic modulus of the composites, as we can confirm by the improvement in the rigidity of the composites when compared to the pure matrix, but without significant changes for higher contents of RHC. The impact strength have decreased as the RHC content increase in the polymeric matrix. Micrographs obtained by MEV from the fractured surface obtained by impact test of the composites, revealed some adherence between RHC-matrix. In this context, the results obtained for the HDPE composites with the addition of RHC present a superiority over the pure matrix and thus create the possibility of its use in composites and an alternative to use this residue.

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Article

Polyvinyl Alcohol Films Reinforced with Nanocellulose from Rice Husk

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Abstract: Progress in the field of biodegradable materials has been significantly accelerated in recent years, driven by the search for sustainable substitutes for fossil-derived resources. This study investigates the formulation of biodegradable films composed of polyvinyl alcohol (PVA) and nanocellulose extracted from rice husk. The rice husk underwent alkaline treatment and bleaching for cellulose extraction, followed by sulfuric acid hydrolysis to obtain nanocellulose. The cellulose and nanocellulose were characterized through Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), and Thermogravimetric Analysis (TGA). Films of pure PVA and those reinforced with 1 wt. % of nanocellulose were prepared using the solvent casting method. The evaluations showed that the modulus of elasticity and tensile strength of the PVA/nanocellulose films were increased by 295.45% and 29.6%, respectively, compared to the pure PVA film. The PVA/nanocellulose film exhibited the lowest solubility and water vapor permeability. Optical Microscopy confirmed a flawless surface for the nanocellulose-reinforced film, while the cellulose- and rice husk-reinforced films displayed irregularities. In the biodegradability assessment, the nanocellulose-reinforced film was the only one that withstood the experimental conditions. The results highlight the effectiveness of nanocellulose in enhancing PVA properties, making these films promising for sustainable packaging applications.

Keywords: agroindustrial waste; sustainable materials; composites; biodegradable; packaging



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1. Introduction

Recently, there has been a surge in research focused on biodegradable materials for packaging applications to reduce the impact on the environment caused by the exacerbated growth of petroleum-based synthetic polymers. Thus, biodegradable materials emerge as an alternative for the development of packaging and can replace synthetic polymers,

either as reinforcements or in blends. In this context, the use of raw materials from natural sources is gaining prominence due to their non-toxic nature, renewability, and abundance. This is exemplified by materials like cellulose, starch, chitosan, chitin, and others [1].

Recent studies have shown that reinforcing PVA with materials such as starch, chitosan, and bacterial cellulose can enhance mechanical and barrier properties [2–4]. Our study highlights the unique advantages of using rice husk-derived nanocellulose compared to these materials.

In this sense, the use of cellulose for the manufacture of biodegradable materials is related to the fact that this material is a natural polymer with a semi-crystalline structure and is present in an abundant form in the environment, and besides endowing the final product with a low cost, can increase the strength of the material. Its extraction can be performed by different methods, such as those using agricultural waste, wood, and bacteria. However, cellulose presents some limitations when incorporated into a polymeric matrix, such as affinity with some materials, and disadvantages regarding barrier properties, thus impairing the final material [5].

Therefore, nanocellulose serves as an alternative reinforcement for the development of biodegradable packaging. Generally, when added to a polymer matrix, it leads to an increase in the mechanical properties of the material compared to the pure polymer; this increase in the mechanical characteristics of the material is due to its large surface area, facilitating effective dispersion within the matrix. Furthermore, when used as reinforcement, nanocellulose enhances the material's barrier properties through its capacity to form hydrogen bonds, thus inhibiting the penetration of water molecules. Therefore, its use in the packaging industry is very promising in relation to adding important characteristics to the final material, besides providing a low cost and reducing the environmental impacts caused by synthetic polymers [6].

The production of agroindustrial byproducts encompasses a diverse spectrum, and relates to varied sectors engaged in the processing of agricultural derivatives. Nevertheless, the indiscriminate disposal of such residues has been instigating a succession of environmental predicaments, leading to the contamination of terrestrial and aquatic ecosystems through leaching phenomena [7]. Rice husk, a byproduct of agricultural activities, is notably rich in cellulose, constituting up to 38% of its composition. In terms of global production, rice contributes around 741 million tons, subsequently resulting in substantial quantities of rice husks due to the intricacies of the processing methodology [8].

Rio Grande do Sul is the largest rice producer in Brazil, accounting for approximately 70% of the country's rice production. Consequently, significant amounts of rice husks are generated as a byproduct of rice processing. However, the slow natural degradation of rice husks can lead to environmental issues, such as air and water pollution, if not properly managed. Therefore, valorizing this abundant agricultural waste by converting it into nanocellulose for polymer reinforcement presents an environmentally sustainable solution [9,10].

Thus, the use of biomass-based materials, such as rice husks, not only supports sustainable development, but also reduces carbon footprints, aligning with global sustainability goals [7,11].

Polyvinyl alcohol (PVA) is known for being a biodegradable polymer and non-toxic, and for its ability to form films, besides being biocompatible with natural fibers and presenting good optical transparency. The combination of PVA with natural fibers yields a material with excellent mechanical properties and a decrease in the cost of the final product when compared to the pure polymer, besides improving the barrier properties of the material. These characteristics impart the PVA with great potential for application as a matrix in biodegradable films [12].

Therefore, because of the above considerations, the present study aimed to use rice husk to obtain cellulose via alkaline treatment and bleaching, followed by isolating the nanocellulose through the process of acid hydrolysis. The intention was to add the reinforcement into a matrix of polyvinyl alcohol to develop biodegradable films via the solvent casting method, aiming at applying this material in packaging with improved properties and lower negative impacts, such as those generated by synthetic polymers.

This study stands out by demonstrating the potential of nanocellulose derived from rice husks to significantly improve the properties of PVA films, offering a sustainable and efficient alternative for biodegradable packaging. By focusing on rice husks generated in Rio Grande do Sul, the largest rice-producing region in Brazil, this research addresses a significant waste management challenge faced by the country's agricultural sector. The study promotes the sustainable use of agro-industrial residues, contributing not only to Brazil's efforts to develop eco-friendly materials, but also aligning with global commitments to sustainability, waste reduction, and the advancement of circular economies.

2. Materials and Methods

2.1. Materials

2.1.1. Rice Husk (RH)

The rice husk (RH) used in this study was donated by Cerealista Polisul, located in the city of Pelotas/RS. The husk was used as a fine powder and has been characterized during the development of this research.

2.1.2. Polyvinyl Alcohol (PVA)

The polymer utilized in this study was procured from Vetec, possessing a molar mass of 86.09 g/mol and an 87.84% hydrolysis index.

2.2. Extraction of Cellulose from Rice Husk

For CNC extraction, commercial brands of sodium hypochlorite (NaClO, Girando Sol), sodium hydroxide (NaOH), and sulfuric acid (H₂SO₄), acquired from Dinâmica Química Contemporânea LTDA in Brazil, were utilized. All solvents and reagents were applied without any further purification.

The procedure to the extraction of cellulose from rice husk was conducted following the methodology outlined by Bosenbecker et al. [13], with some adaptations. The extraction of cellulose from rice husk was performed in three steps: a pre-treatment of the husk in natural form, followed by the alkaline treatment, and finally, the bleaching. The husks were washed in running water and dried in an oven for 24 h at 50 °C to remove the humidity. After complete drying, the material was ground in a Marconi MA 340 knife mill and sieved with a 32 mesh sieve to maintain particle size uniformity.

After the process involving alkaline treatment, bleaching was performed, where the fiber was added in a solution of 2.5% *w/v* (fiber to sodium hypochlorite) of sodium hypochlorite for 24 h in order to remove remaining components of lignin, thus obtaining the white color characteristic of cellulose. The resulting material was filtered and washed with distilled water until it reached neutral pH, then dried in an oven at 60 °C for 24 h [14]. Figure 1 illustrates the resulting material after the treatments involved.

Subsequently, the rice husk in natural form was submitted to alkaline treatment with a sodium hydroxide solution with a concentration of 10% *w/v* (10% NaOH in relation to the weight of the biomass), aiming to remove components of lignin and hemicellulose in the fiber. This concentration was determined through previous studies by the research group [14]. The fibers were in contact with this solution for 1 h at 80 °C under magnetic stirring. Following this, the fibers were separated through filtration and washed repeatedly

with distilled water until the filtration residue reached a neutral pH level. After pH adjustment, the fibers were dried in an oven at 50 °C for 24 h [15–17].

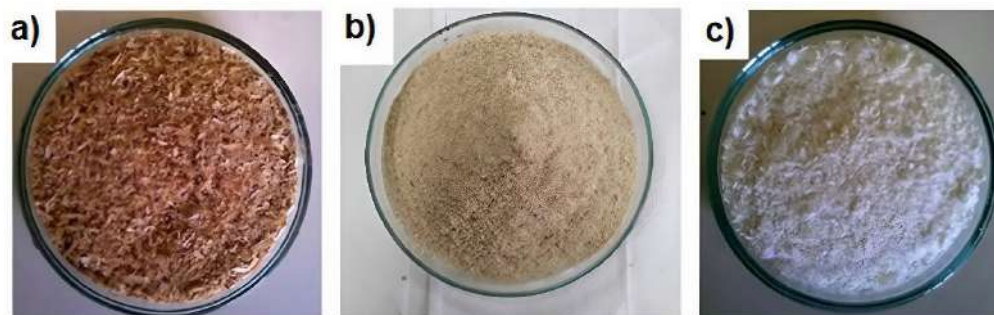


Figure 1. Images of: (a) rice husk in natura, (b) rice husk after pre-treatment, (c) pulp after alkaline treatment and bleaching.

2.3. Obtaining the Nanocellulose

The procedure to isolate nanocellulose (NC) from cellulose was conducted following the methodology outlined by Rashid and Dutta [5], with some adaptations. The process involved the acid hydrolysis of cellulose using 65% sulfuric acid at a ratio of 1:20 *w/v* (cellulose to sulfuric acid) for a duration of 90 min at 45 °C under ultrasound. The reaction was terminated by the addition of distilled water and centrifugation was performed in an Excelsa Centrifuge, model 206 BL, at 2260 × RCF *g* or 12,000 rpm for 10 min to remove excess acid.

This centrifugation process was repeated five times until the supernatant was completely separated from the precipitate. Subsequently, the suspension was dialyzed using a 26 (Spectra/Por 6, MWCO = 3500 g/mol) dialysis membrane until it reached a neutral pH. Following dialysis, the suspension was freeze-dried in a freeze-dryer model MSSL-404 for 48 h under a pressure of 60 mm Hg and a temperature of −42 °C to obtain the nanocellulose in powdered form for material characterization.

2.4. Film Preparation

The solvent casting technique was used to prepare the PVA films with the respective rice husk, cellulose and nanocellulose reinforcements. The films were prepared with a fixed concentration of 1 wt. % by mass for each formulation; a control film of pure PVA was also prepared. The methodology adopted was from Kord et al. [18] with some modifications.

2.5. Characterization

2.5.1. Characterization of Rice Husk, Cellulose and Nanocellulose

Initially, a solution was concocted by combining 5 g of PVA and 1 g of glycerol in 95 mL of distilled water, subjected to a temperature of 70 °C for 60 min, under magnetic stirring to ensure the dissolution of PVA. Following this, the rice husk, cellulose, and nanocellulose reinforcements were integrated into the solution, maintaining constant stirring and a temperature of 45 °C to facilitate the uniform dispersion of the reinforcements within the matrix. The resultant solution, encompassing the reinforcements along with the control solution of unadulterated PVA, were each placed in 20 mL quantities onto glass plates (100 mm diameter) and subjected to a drying process within an oven for 24 h at a temperature of 40 °C to imitate water evaporation. Following the drying phase, the films were demolded and preserved for subsequent analyses [19].

$$IC = \frac{I(002) - I(am)}{I(002)} \times 100 \quad (1)$$

where I_{am} is the intensity referring to the region of $2\theta = 16^\circ$; I_{002} is the maximum intensity of the diffraction peak, attributed to the crystalline material, in the region of $2\theta = 22^\circ$.

2.5.2. Film Characterization

Thickness, Weight and Density

To ascertain the thickness of the films, an external micrometer, spanning a range of 0 to 25 mm and boasting a reading precision of 0.01, manufactured by Eda Professional, was deployed. Measurements were executed at five disparate points for each film composition.

The thickness of the films was measured using a micrometer with a precision of 0.01 mm, at five different points for each sample. The pure PVA film showed an average thickness of 0.158 mm, with a standard deviation of ± 0.050 mm, indicating moderate variation in thickness uniformity. The PVA film reinforced with rice husk exhibited an average thickness of 0.180 mm, with a standard deviation of ± 0.029 mm, reflecting greater regularity. For the film reinforced with cellulose, the average thickness was 0.156 mm, with a standard deviation of ± 0.040 mm. Finally, the PVA film with nanocellulose presented an average thickness of 0.222 mm, with a standard deviation of ± 0.049 mm.

For the quantification of the film's weight, Equation (2) was employed [20]:

$$G = \frac{m}{A} \quad (2)$$

where the weight is represented by G (g/cm^2), the mass by m (g) and the area by A with a unit (cm^2). The films were cut with the same area of 16 cm^2 and weighed on an analytical balance [21]. The densities of the films were ascertained from the weight and dimensions of the films using Equation (3) [22]:

$$D = \frac{m}{A \times T} \quad (3)$$

where m is the mass (g), A is the area (cm^2), and T is the thickness of the films in (cm).

Transparency

The visual integrity and flexibility of the films were evaluated utilizing a camera with a resolution of 12 megapixels. A uniform distance of 10 cm was maintained for capturing transparency photographs across all film specimens [23].

Solubility

The solubility of the films was determined in adherence to the methodology delineated in Luchese et al. [24]. Three specimens, each dimensioned at $4 \text{ cm} \times 4 \text{ cm}$, were configured for each formulation. Initially, these specimens were oven-dried at 60°C for a duration of 24 h to establish their inaugural weight. Subsequently, the films were submerged in a beaker containing 50 mL of distilled water at ambient temperature and agitated for a period of 24 h. Following this immersion, the films were extracted from the water and subjected to a drying process in an oven set at 45°C for an additional 24 h to ascertain the final weight. The solubility was then computed employing Equation (4):

$$\text{Variation in mass (\%)} = \frac{(M_i - M_f)}{(M_i)} \cdot 100 \quad (4)$$

where M_i is the initial weight of the film and M_f is the final weight of the film after immersion in water.

Water Vapor Permeability Rate (WVPR)

The properties of water vapor permeability were scrutinized to evaluate the implications of the reinforcements for the barrier attributes of the material, conducted in accordance with the ASTM E 96/E standard [25]. Utilizing containers with circular apertures, each having an area of 0.0007 m², the films were positioned atop glass and situated within a desiccator containing silica at ambient temperature. The cumulative weight loss of the system was documented at 24 h intervals over a span of five days (represented as “G” in the subsequent equation). This series of measurements was executed in duplicate for each formulation, and the Water Vapor Permeability Rate (WVPR) was derived by applying Equation (5) [24],

$$TPVA = \frac{G}{tA} \quad (5)$$

where G corresponds to the weight variation, t is the duration of the test every 24 h, and A is the test film area (0.0007) in m². Thus, the final unit of WVPR is g/m² in 24 h [26].

Optical Microscopy (OM)

The morphological characteristics and the distribution of the reinforcements within the PVA matrix were assessed through optical microscopy analysis. Imagery was captured utilizing a trinocular stereomicroscope, model 06-KTESD5000, of the Laborama brand, employing a 4× zoom magnification.

Thermogravimetry (TGA)

In order to investigate whether there was interference in the thermal stability of the films with reinforcement compared to the PVA film (Pure), the thermogravimetric analysis (TGA) was performed. The conditions of the equipment were the same as are described in Section 2.5.1.

Differential Scanning Calorimetry (DSC)

The melting temperature of the films was investigated through DSC analysis, employing the TA Instruments model Q2000, under a nitrogen atmosphere maintaining a constant flow of 50 mL/min. The films were subjected to a temperature elevation from ambient to 200 °C at a progression rate of 10 °C/min, and were sustained at this temperature for a duration of three min. Subsequently, the samples were reverted to a temperature of 30 °C at a cooling rate of 10 °C/min.

Evaluation of Biodegradation in Soil

For the preparation of soil, a concoction was formulated using 1.4 kg of beach sand, 1.4 kg of horse manure dried for a duration of 48 h, and 1.4 kg of equal parts of fertile soil. This mixture was subsequently blended with the aid of a shovel and moisturized to maintain soil hydration. Prior to the insertion of the films, the soil mixture was allowed a maturation period of three months within a container, aligning with the stipulations of ASTM G 160-03 [27]. The biodegradation rates of the films were then ascertained by examining the mass loss, computed via Equation (6) [28]:

$$\text{Mass Loss (\%)} = \frac{(M_i - M_f)}{(M_i)} \cdot 100 \quad (6)$$

where M_i is the initial mass and M_f corresponds to the final mass.

For the analysis, soil, already matured, was allocated in plastic containers, following which the films were trimmed to dimensions of 5 × 5 cm. The films, sorted according to each composition type, were designated to individual containers, subsequently placed in an oven

set at 30 °C, and thereafter extracted at predetermined intervals of 15, 30, 45, and 60 days. Following each interval, the films were cleansed and subjected to weighing procedures.

Tensile Test

The mechanical characterization for tensile properties was conducted utilizing a Dynamic-Mechanical Analyzer (DMA), model Q800TM, version 20.6.4, facilitated by TA Universal Analysis 2000 software version 4.5A Build 4.5.0.5. The analysis was executed at 25 °C, employing an 18 N load cell and administering a pre-load of 0.5 N, at a testing velocity of 3 N/min. Accordingly, the films were precision-cut to dimensions of 5 mm in width and 30 mm in length.

3. Results and Discussion

3.1. Characterization of Rice Husk, Cellulose and Nanocellulose

3.1.1. Fourier Transform Infrared Spectroscopy (FTIR)

The Fourier Transform Infrared Spectroscopy (FTIR) technique was employed to discern alterations in the chemical structure of the pristine rice husk, cellulose, and nanocellulose subsequent to the applied treatments.

Figure 2 delineates the FTIR outcomes for the examined samples. A notably intense region between 3321 cm^{-1} and 3376 cm^{-1} is observable across all samples, the spectra of which are attributed to the axial elongation of hydroxyl groups (O-H), originating from intramolecular hydrogen bonds typical of Type I cellulose [29]. The spectrum identified in the 2907 cm^{-1} region is ascribed to symmetric bond elongation (C-H) vibrations. The regions at 898 cm^{-1} and 1035 cm^{-1} signify cellulose β -glycosidic bonds, corresponding to stretching vibrations (C-O-C). Herein, a pronounced increase in intensity is perceivable for cellulose and nanocellulose samples, indicative of enhanced crystalline stability in the material structures post-treatments [8].

The band positioned at 1719 cm^{-1} is correlated with the stretching vibrations of carbonyl groups (C=O), inherent to hemicellulose. The 1438 cm^{-1} band is indicative of the structural configuration of lignin's aromatic rings, represented by stretches (C=C). Consequently, cellulose and nanocellulose exhibit a diminution in the intensities of these peaks upon treatment, suggesting a reduction in the hemicellulose and lignin constituents within the treated samples [30].

In the nanocellulose specimen, an amplified intensity in the regions of 1250 cm^{-1} and 818 cm^{-1} is notable, linked to the stretching vibrations of (C-O-S) and (S=O). This transformation denotes the incorporation of acid sulfate groups onto the fiber surface, substantiating the efficacy of the sulfuric acid hydrolysis treatment [31].

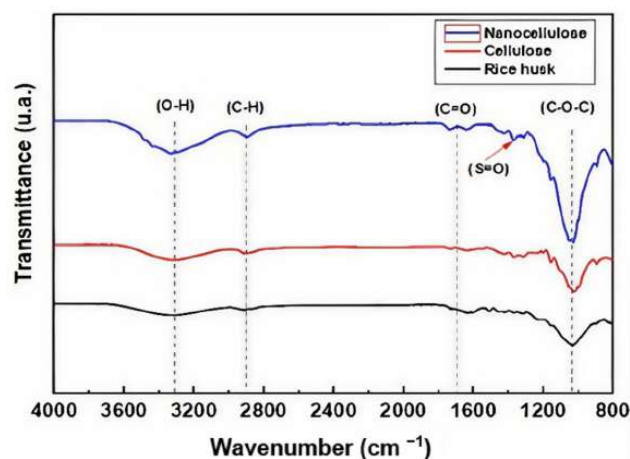


Figure 2. FTIR spectra for rice husk, cellulose and nanocellulose.

3.1.2. X-Ray Diffraction (XRD)

X-ray diffraction (XRD) analyses were performed using a Shimadzu XRD-6000 diffractometer (at the Barueri, SP/Brazil). The scanning parameters included a scanning rate of $0.5^\circ/\text{min}$ over a 2θ range of 10° to 90° , with a wavelength (λ) of $1.541 \text{ \AA}$. The equipment was operated at 40 kV and 40 mA.

The X-ray diffractograms facilitated the exploration and verification of the chemical structures of the rice husk, cellulose, and nanocellulose samples, as illustrated in Figure 3.

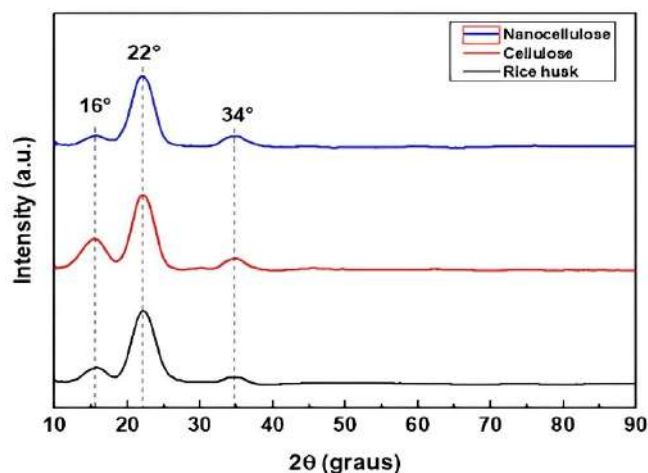


Figure 3. XRD of rice husk, cellulose and nanocellulose.

The depicted curves reveal the occurrence of three distinctive peaks for each sample, each with varying intensities, correlating to the type I crystalline structure of native cellulose.

The diffraction signals showcase intensities at 2θ of 16° , pertaining to the 110 plane, 22° , attributed to the 002 plane, and 34° , corresponding to the 004 plane [8]. In analyzing the diffractograms, it is observable that all samples exhibit a semi-crystalline structure, with peaks at 16° representing the amorphous region and those at 22° denoting the crystalline region, typical of such materials [32].

Furthermore, a diminished peak intensity is discernible in the 16° region for the nanocellulose sample, a decrease attributable to the extraction of amorphous constituents like lignin and hemicellulose inherent in the rice husk structure. Nonetheless, the enhancement in crystallinity and the reduction in amorphous components are conjectured to augment film attributes upon their integration into the polymer matrix [33].

The diffractograms made it possible to calculate the crystallinity index for the studied samples, and the results are presented in Table 1.

Table 1. Crystallinity index values.

Samples	Crystallinity Index (%)
Rice husk	46%
Cellulose	62%
Nanocellulose	74%

It is discernible that there was an elevation in the crystallinity index of the cellulose and nanocellulose samples subsequent to the treatments, attaining values of 62% for cellulose and 74% for nanocellulose. This increment indicates the successive diminution of the amorphous components inherent in the fiber structure, thereby validating the efficacy of the procedures applied to the fiber.

As articulated by Rashid and Dutta [8], the enhancement in the crystallinity index of processed materials, in contrast to their unprocessed counterparts, is attributed to the

reordering of crystals into configurations of superior orientation, as well as due to the elimination of amorphous substances such as lignin and hemicellulose.

3.1.3. Thermogravimetry (TGA)

The thermal resilience of rice husk (RH), cellulose (CE), and nanocellulose (NC) was scrutinized utilizing mass loss curves in correlation with temperature (TGA) and the derivative of mass alteration (DTG), as depicted in Figure 4.

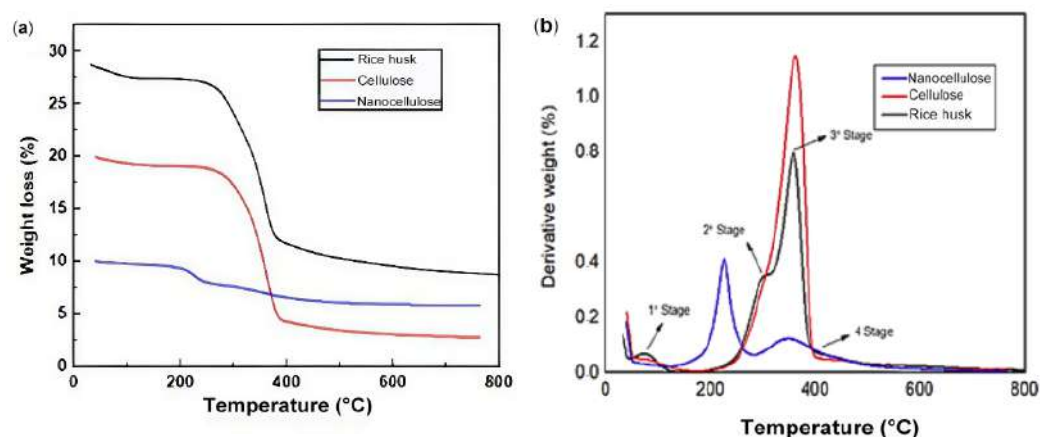


Figure 4. Thermogravimetry analysis—(a) TGA and (b) DTG curves of rice husk, cellulose and nanocellulose samples.

The initial stage, ranging between 25 °C and 123 °C, signifies an early mass reduction due to the evaporation of water and other volatile extractives. The second stage, manifest solely in the rice husk sample, transpires between approximately 232 °C and 300 °C, arising from the decomposition of hemicellulose. The absence of this stage in the cellulose and nanocellulose samples substantiates a reduction in amorphous material following the implemented treatments [34].

Evolving into the third stage, occurring in the range of 300–355 °C, the behavior is synonymous with the degradation of cellulose, marked by dehydration and the decomposition of its glycosidic units. The ensuing fourth stage, occurring between 400 °C and 600 °C, is indicative of the degradation of lignin and silica, resulting in the breakdown of residual carbon compounds [32].

While meticulously examining the TGA and DTG curves, a nuanced reduction in the thermal stability of nanocellulose becomes evident, occurring around 220 °C and corresponding to the third stage, indicative of a comparative analysis with rice husk and cellulose samples. This subtle decline is interpreted as the consequence of the incorporation of sulfate groups from sulfuric acid onto the surface of nanocellulose, facilitating the degradation of the material at relatively lower temperatures [35,36].

3.2. Films Characterization

3.2.1. Thickness, Weight and Density

With the data accumulated for thickness, weight and density, as outlined in Table 2, it was possible to explore the potential changes in film properties due to the incorporation of reinforcements.

Thickness stands as a crucial attribute requiring meticulous evaluation, as it governs the dispersion control of the reinforcement within the matrix.

Table 2. Obtained thickness, weight and density values for the films.

Samples	Thickness (mm)	Grammage (g/cm^{-2})	Density (g/cm^{-3})
PVA	0.16 ± 0.02	0.020 ± 0.003	1.25 ± 0.15
PVA/RH	0.22 ± 0.04	0.031 ± 0.002	1.41 ± 0.05
PVA/CE	0.20 ± 0.03	0.028 ± 0.001	1.40 ± 0.03
PVA/NC	0.18 ± 0.03	0.023 ± 0.002	1.27 ± 0.06

Subsequently, thickness variability bears significant implications in relation to diverse film characteristics, including mechanical, permeability, and optical properties. An assessment of Table 2 reveals a progressive increase in thickness values with the incorporation of reinforcement within the matrix. The film exhibiting the greatest thickness was the PVA fortified with rice husk, and the one with minimal thickness was pure PVA; this increment is rationalized by the granule dimensions of the rice husk and its subordinate dispersion in the PVA matrix. In contrast, the PVA film fortified with nanocellulose did not manifest a substantial thickness elevation compared to pure PVA film, attributed to its proficient dispersion within the matrix, ensuring optimal homogeneity between matrix and reinforcement [37].

Table 2 additionally enumerates the weight specifications of the films; this attribute is intricately linked to the mass of the material, and hence, can significantly impact the mechanical characteristics of the films. It is noteworthy that the PVA film fortified with rice husk manifested the highest weight values in comparison to its counterparts, a phenomenon resulting from the integration of untreated rice husk in natura form, inducing larger particles and challenging distribution within the matrix, consequently contributing to this weight augmentation [38].

Density, being interconnected with the weight and thickness of the films, plays a pivotal role in shaping the barrier and mechanical attributes of the material. An examination of the density data presented in Table 2 indicates that the PVA film with nanocellulose does not exhibit a considerable deviation in density values compared to the pure PVA film. This finding is ascribed to the interaction dynamics between PVA and nanocellulose, culminating in a structure that is more compact and less dense. Conversely, films reinforced with rice husk and cellulose illustrated a significant increase relative to the pure PVA film, attributed to the inferior dispersion capability of these materials within the matrix [39].

3.2.2. Transparency

The addition of polyvinyl alcohol gives the material important properties for packaging applications, such as excellent transparency and flexibility [23].

Figure 5 illuminates the aesthetic qualities of the films, wherein both pure PVA and PVA/nanocellulose films are discerned to exhibit sleek and uniform surfaces with negligible roughness. The excellent performance of the nanocellulose-reinforced film is due to the effective dispersion of nanocellulose within the PVA matrix, which is facilitated by the interaction and particle size.

**Figure 5.** Evaluation Transparency.

This synergy fosters robust adhesion between the nanocellulose and the matrix, rendering transparency attributes analogous to those observed in pure PVA films. Lee et al. [23] have similarly reported no alterations in the transparent properties of PVA upon the integration of nanocellulose.

Conversely, films fortified with rice husk and cellulose presented a cloudiness over the symbols coupled with a textured surface, resulting in films characterized by diminished visibility. These observations highlight the challenges in dispersing these materials within the PVA matrix, causing agglomerates that may reduce the films' mechanical properties [22].

3.2.3. Solubility

Polyvinyl alcohol, despite its advantages, faces limitations in humid environments, restricting its application mainly to areas with controlled temperatures.

Therefore, probing into the films' performance in aqueous settings becomes pivotal. The elucidations pertaining to the solubility of the films are depicted in Figure 6.

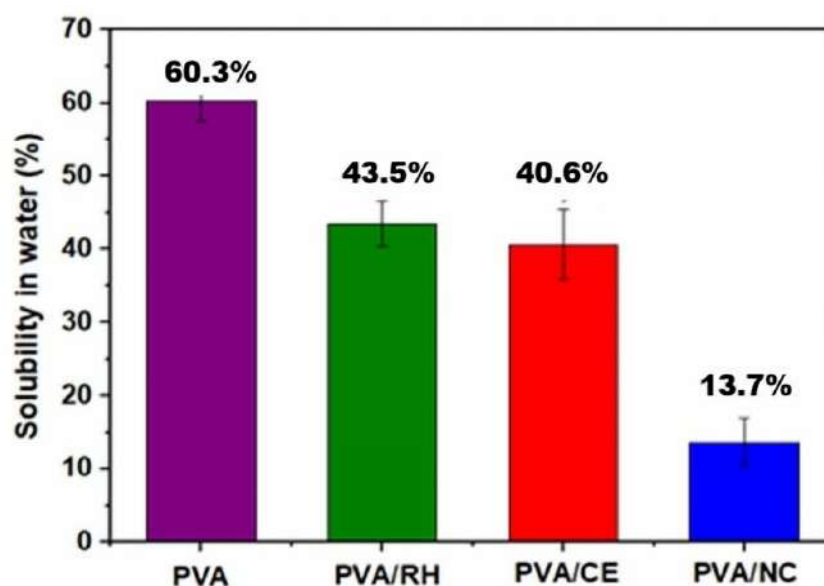


Figure 6. Percentage of solubility of PVA, PVA/RH, PVA/CE and PVA/NC films.

It is discernible that the pristine PVA film exhibited the most pronounced aqueous solubility, around 60.3%. This tendency is ascribed to its inherent hydrophilic nature and its propensity for high solubility in water, facilitated by the presence of hydroxyl groupings within its structure.

This promotes molecular penetration into the matrix, corroborating its susceptibility to hydrolytic degradation [40]. Conversely, it is observed that the incorporation of reinforcements decreases the solubility of PVA to 43.5% for the film fortified with rice husk and 40.6% for the cellulose-reinforced film, rendering these films more resistant to water relative to the pure PVA film due to the water-insoluble nature of these materials [41].

Regarding the nanocellulose-reinforced PVA film, a diminution in solubility is noted, with a recorded value of 13.7%. This phenomenon is linked to the diminution of accessible hydroxyl groupings within the PVA structure post-nanocellulose incorporation, resulting in the formation of a physical barrier within the film's structure, constraining chain mobility, and thereby conferring enhanced retention against the infiltration of water molecules. Such improved performance is pivotal for extending the shelf life of food products within packaging exposed to unregulated humidity conditions [22].

Patel and Joshi [38] documented analogous reductions in water solubility for PVA films augmented with nanocellulose derived from banana agricultural residue. They

recognized that films containing 1 wt. % of reinforcement exhibited a solubility reduction of approximately 2.04% in contrast to the pristine PVA film—a trend consistent with films comprising 2 wt. % and 5 wt. % of nanocellulose. This is rationalized by the crystalline nature of nanocellulose and the intermolecular forces established between the matrix and the reinforcement.

Noshirvani et al. [42] developed films incorporating PVA, starch, and cellulose nanocrystals, noting a decrease in film solubility coinciding with the incorporation of cellulose nanocrystals. This was substantiated by the formation of hydrogen bonds amongst the hydroxyl groups inherent in PVA, starch, and cellulose nanocrystals, facilitating a three-dimensional network that stabilized chain movement, thereby reducing water absorption for the fortified films.

3.2.4. Water Vapor Permeability Rate (WVPR)

The evaluation of Water Vapor Permeability Rate (WVPR) is crucial for materials destined for packaging applications. This assessment is instrumental in determining the extent of water transferred by the film, which is pivotal since ideal films should effectively shield products from external agents, translating to lower WVPR values.

Table 3 illustrates the variations in mass loss and transmission rates as water molecules traverse through the films over a 120 h period. It is observed that the introduction of reinforcements to the PVA matrix causes a decrement in both mass loss and WVPR values. This implies that the films incorporating reinforcements exhibit greater resistance to water molecule penetration compared to the pristine PVA film.

Table 3. Calculated values of mass loss and water vapor permeability rate of the films.

Samples	Weight Loss (g/120 h)	WVP (g/m ² ·120 h)
PVA	0.28 ± 0.12	410 ± 60
PVA/RH	0.27 ± 0.10	392 ± 40
PVA/CE	0.25 ± 0.09	357 ± 50
PVA/NC	0.23 ± 0.14	339 ± 33

In the context of nanocellulose-augmented samples, the mass loss registered was 0.237 g, indicative of the lowest water vapor transmission rate relative to the other variants. This outcome implies a harmonious interaction between nanocellulose and PVA, stemming from their mutual affinity attributed to the presence of hydroxyl groups. This affinity facilitates the formation of a hydrogen barrier obstructing water molecule passage, resulting in an enhancement of around 17% in the film's barrier properties compared to the unaltered PVA film [43]. It can be inferred, thus, that the integration of reinforcements into the matrix correlates with a diminished water vapor transmission rate.

Therefore, as a reinforcement is introduced into the PVA matrix, the water vapor transmission rate decreases.

In a study conducted by Srivastava et al. [44], PVA films were fabricated and reinforced with varying concentrations of nanocellulose—0.1, 0.5, 1.3, and 5%. The findings reveal a decline in the permeability of the films as nanocellulose was integrated, enhancing the barrier properties by approximately 29.7% when compared to the pure PVA films. Analogously, Espinosa et al. [45] incorporated nanocellulose extracted from wheat straw, both with and without lignin, into a PVA matrix in their research. It was observed that the introduction of nanocellulose led to a reduction in permeability values, creating a physical barrier that obstructs moisture passage, irrespective of the type of nanocellulose utilized.

3.2.5. Optical Microscopy (OM)

In previous studies conducted by the same research group, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses were performed to investigate the morphology and dispersion of nanocellulose in similar polymer matrices. These studies, described in [14], demonstrated that the nanocelluloses exhibited a uniform needle-like morphology, with nanometric dimensions and reduced aggregation compared to the initial fibers. Furthermore, the removal of amorphous components, such as lignin and hemicellulose, contributed to the production of well-defined cellulose nanocrystals (CNCs) with higher crystallinity and potential to enhance the properties of polymer nanocomposites due to their large surface area and exposed hydroxyl groups, which favor matrix–reinforcement interaction.

In addition, the production and characterization of nanocellulose in the present study were inspired by the methodology described by Zhang et al. [5], who successfully extracted nanofibrillated cellulose (NFC) from *Enteromorpha prolifera* with a diameter of 20–40 nm, a length of several microns, and a crystallinity index of 57.2%. These characteristics enabled its effective integration with polyvinyl alcohol (PVA) matrices, improving mechanical and barrier properties. Based on these findings, we assumed the successful production of nanocellulose in our work and proceeded with similar characterization techniques to confirm its properties. This comparison underscores the alignment of our results with those of Zhang et al. while exploring potential advancements in the application of nanocellulose as a reinforcing agent.

In the present study, optical microscopy was employed as a complementary approach to observe the morphology and dispersion of the reinforcements in the PVA matrix, aiming to correlate these results with the functional properties of the developed films.

The images secured through the stereomicroscope with 4× magnification are illustrated in Figure 7.

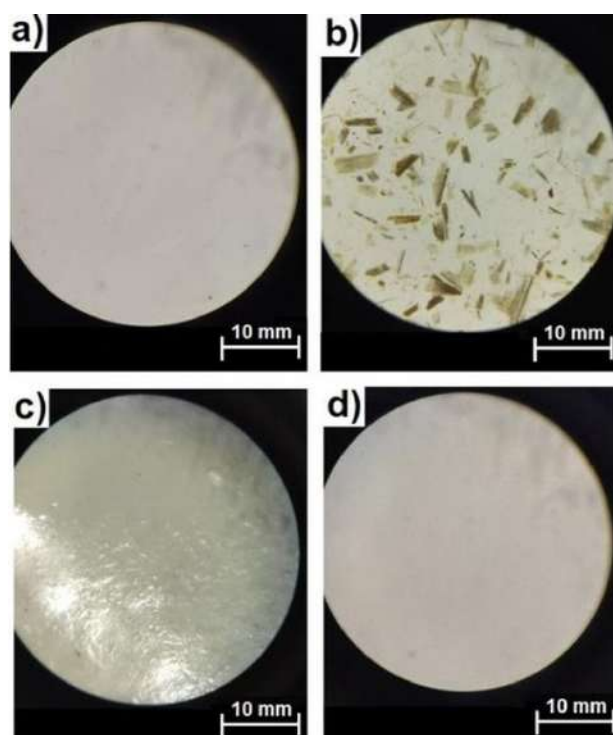


Figure 7. Microscopy images of: (a) PVA, (b) PVA reinforced with rice husk, (c) PVA reinforced with cellulose, (d) PVA reinforced with nanocellulose.

Figure 7a delineates that the pure PVA film features a smooth and uniform surface, thereby exhibiting an absence of defects such as bubbles or fissures.

Contrarily, the PVA film fortified with rice husk, as depicted in Figure 7b, distinctly displays fibers of uneven configurations throughout its structure, accompanied by clusters and void spaces, a representation of suboptimal dispersion.

Figure 7c illustrates the texture of the PVA films bolstered with cellulose, revealing a coarse surface interspersed with bubbles and displaying uneven distribution. These imperfections can potentially compromise the mechanical properties of the films. On the other hand, the PVA films integrated with nanocellulose, as seen in Figure 7d, reflect properties strikingly similar to those of the pure PVA film. They showcase a smooth, immaculate surface, a feature ascribed to the smaller scale of nanocellulose relative to cellulose and rice husk reinforcements, facilitating enhanced synchronization between the reinforcement and the matrix [45].

Wang et al. [46] also explored PVA films strengthened with cellulose nanofibers derived from rice straw in their research. They too discerned enhanced dispersion and uniformity in the films compared to those fortified with cellulose microfibrils. Moreover, the integration of cellulose nanofibers not only augmented the mechanical properties, but also elevated the transparency of the films.

3.2.6. Thermogravimetry (TGA)

The execution of TGA analyses was pivotal to exploring how the infusion of reinforcements could potentially alter the thermal stability of the films. The curves depicting mass loss relative to temperature (TGA) and the derivative of mass variation (DTG) for the films are illustrated in Figure 8.

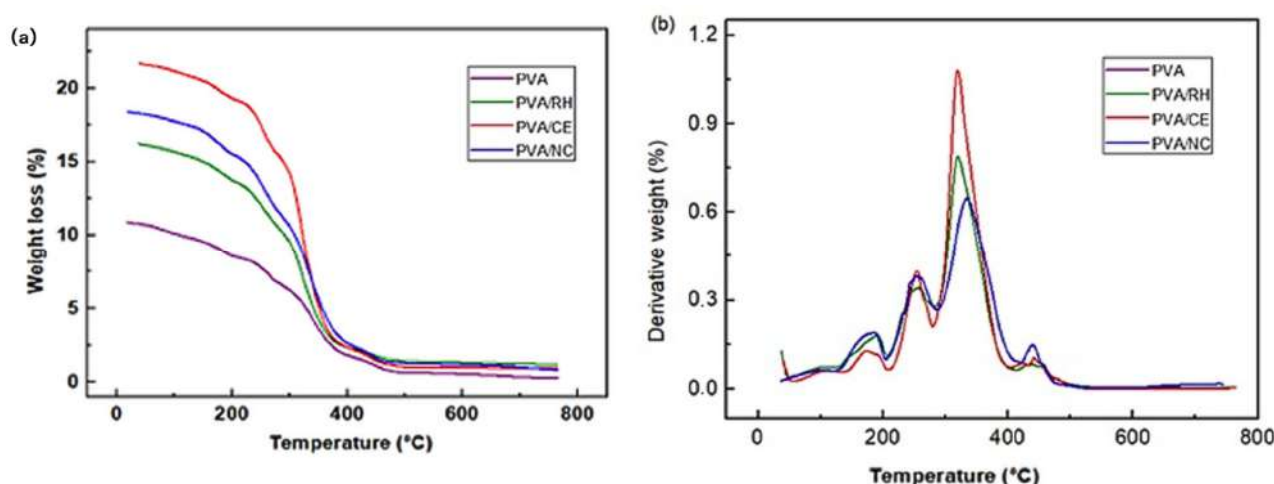


Figure 8. Thermogravimetry analysis—(a) TGA and (b) DTG curves of the films.

Surveying the TGA and DTG curves reveals that every film underwent three principal phases of mass reduction. The initial phase, ranging between 50 °C and 130 °C, is ascribed to the decomposition of substances on the films' surface and the evaporation of entrained moisture [47]. Following this, a second phase emerges between approximately 287 °C and 370 °C, linked to the decomposition of oxygen-bearing functional groups in the PVA structure and the liberation of volatile compounds contained within the films. A close inspection of the DTG curves displayed in Figure 8b discloses a marginal enhancement in the thermal resilience of both PVA and nanocellulose-augmented PVA films compared to their rice husk- and cellulose-reinforced counterparts.

Such outcomes intimate that integrating this type of reinforcement with the polymer matrix could manifest thermal characteristics analogous to those of uncontaminated PVA without markedly impacting its thermal robustness [48].

Conclusively, the last phase, unfolding between 425 °C and 487 °C, pertains to the decomposition of carbonaceous compounds and the breakdown of functional entities inhabiting the principal chain of polyvinyl alcohol [49].

3.2.7. Differential Scanning Calorimetry (DSC)

DSC analysis was utilized to scrutinize the thermal attributes of the films, yielding insights into melting temperature (T_m), crystallization temperature (T_c), enthalpy alteration (ΔH), and the crystallinity degree (X_c). The heating and cooling thermograms are depicted in Figure 9.

The parameters derived from the DSC assessments are cataloged in Table 4.

Table 4. Data obtained from the DSC curves.

Samples	T_m (°C)	T_c (°C)	ΔH (J/g)	X_c (%)
PVA	163	126.14	13.92	8.73
PVA/RH	164	122.34	12.94	8.11
PVA/CE	170	134.15	11.58	7.26
PVA/NC	165	129.14	11.39	7.14

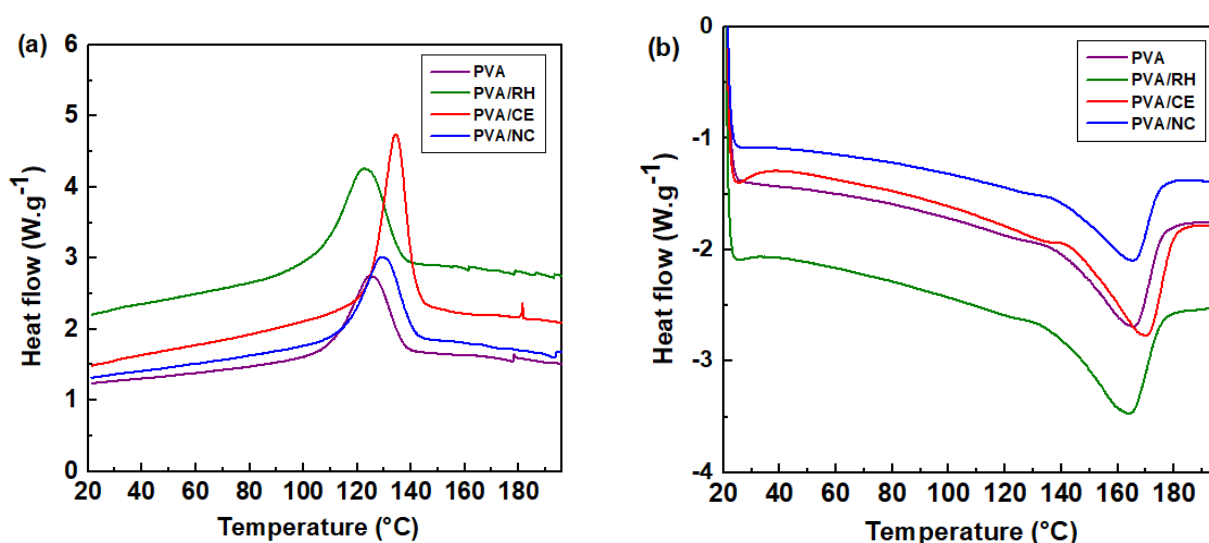


Figure 9. DSC curves—(a) cooling for the films and (b) heating for the films.

The films predominantly demonstrated analogous onset melting temperatures, around 140 °C, with negligible alterations. This occurrence is linked to the disruption of intermolecular bonds in the films' hydroxyl groups. Pertaining to the melting temperature, a modest augmentation is discernible in the values for the films with filler integration, notably for the cellulose-reinforced film, in comparison to the pristine PVA film. This observation could be correlated with the interaction proficiency between PVA and the reinforcements, thereby illustrating the enhancement of the films' thermal stability [42,50].

Following the integration of the reinforcements, a surge in T_c was manifested, especially in the cellulose-inclusive film, displaying approximately 134.15 °C in contrast to the pure PVA's 126.14 °C. This modification in T_c could be related to the impact of the reinforcements on the matrix, serving as nucleation facilitators, hence fostering an elevation in crystallization temperature [51,52].

Moreover, the X_c values, deduced by interpreting the DSC curves via the applicable equation, witnessed a gradual decline. This can potentially be ascribed to the reinforcements instigating the formation of new hydrogen bonds with PVA molecules, disrupting the regular arrangement of the molecular chains, and subsequently impeding PVA's crystallization [53].

3.2.8. Evaluation of Biodegradation in Soil

The appraisal of the material's biodegradability in soil is critical when contemplating its deployment for packaging solutions. Soil biodegradation is influenced by various factors like humidity, the activity of microorganisms, and the presence of fungi and bacteria within the soil [54]. In this research, the biodegradability of the films was assessed based on mass loss at intervals of 0, 15, 30, 45, and 60 days of burial in soil, with the outcomes displayed in Table 5.

Table 5. Average in grams of film weights over time.

Samples	Day 0	Day 15	Day 30	Day 45	Day 60
PVA	0.432	0	0	0	0
PVA/RH	0.494	0	0	0	0
PVA/CE	0.452	0	0	0	0
PVA/NC	0.444	0.267	0.065	0.037	0

The only film displaying resilience to the biodegradation examination was the one reinforced with nanocellulose. Despite the hydrophilic nature of both PVA and nanocellulose, the incorporation of nanocellulose escalated the film's resistance to biodegradation. Nevertheless, despite its slowed degradation rate, the nanocellulose-infused film experienced a 100% mass loss before the completion of 60 days, illustrating a commendable outcome relative to conventional packaging materials.

This performance echoes previous solubility findings, where nanocellulose-reinforced films exhibited reduced solubility levels, signifying that the integration of nanocellulose enhances the polymer's resilience in humid conditions.

These results can be credited to the ability of the PVA matrix and nanocellulose to establish hydrogen bonds, creating a compact and dense three-dimensional configuration, and generating a convoluted route within the material. This intricate structure impedes microbial activities and minimizes water molecule penetration into the material, thereby constraining available space within the structure and reducing interface gaps between PVA and nanocellulose [5,55].

The data compiled in Table 5 facilitate the calculation of the percentage of mass loss subsequent to each period of sample retrieval, although this was solely applicable to the film fortified with nanocellulose. In the initial 15 days, a substantial weight reduction of 39.8% was recorded. In the following days (30 and 45), the degradation increased to 85.3% and 91.6%, respectively, due to water molecules and microorganisms penetrating the film structure, reducing its strength. Consequently, after 45 days, the moisture in the soil led to the complete dissolution of the nanocellulose film [56].

Moreover, alterations in the visual characteristics of the nanocellulose-reinforced PVA film over the 0-, 15-, 30-, and 45-day intervals were discernible, as illustrated in Figure 10. The images conspicuously depict a sustained reduction in film mass, concluding the 60-day period with no remnants of film residues observable.



Figure 10. Evaluation of the visual appearance of the PVA/NC film after the biodegradation test.

Ong et al. [57] explored the soil biodegradability of PVA matrix films bolstered with 3, 5, and 10 wt. % by mass of various reinforcements. The reinforcements included microcrystalline cellulose, cellulose nanocrystals extracted from palm fiber, and commercial nanocrystals. They observed that the films exhibited a rapid rate of degradation; all the films underwent complete degradation after just 7 days of being buried in the soil.

The difference observed in degradation time between this study (more than 45 days) and the aforementioned study (7 days) can be attributed to several factors, such as the nature of the reinforcement, the process of obtaining nanocellulose and the experimental biodegradation conditions. While the previous study used commercial cellulose nanocrystals and higher concentrations, in this work, the nanocellulose was obtained from rice husk, an abundant agro-industrial residue, which can influence the structure and interaction of the reinforcement with the PVA matrix. The greater stability observed is due to the formation of a dense three-dimensional network between PVA and nanocellulose through hydrogen bonds, which limits water penetration and microbial activity [58,59].

This result reinforces the novelty of the present study, as it demonstrates that the use of nanocellulose extracted from agro-industrial waste can not only improve the mechanical and barrier properties of the film, but can also prolong its resistance under degradation conditions, making it more suitable for applications in packaging with greater durability, without compromising its final biodegradability.

3.2.9. Tensile Strength Test

Determining the mechanical properties of materials is critical, especially when understanding the interaction between reinforcement and matrix to ensure superior mechanical performance and uphold the product's integrity. Figure 11a illustrates the results for Young's modulus, while Figure 11b displays the values for tensile strength of the samples under consideration.

Examining Figure 11a, a progressive escalation in the elastic modulus is evident upon the integration of reinforcements into the PVA matrix. The elastic modulus relates to the material's rigidity; thus, a higher modulus denotes increased stiffness [60]. This observation implies that films fortified with nanocellulose showcased the best elastic modulus, marking a noteworthy enhancement in comparison to the unmodified PVA film. This augmented mechanical resilience is attributed to the potent interaction and hydrogen bonding between PVA and nanocellulose, fostering optimal affinity and the homogeneous dispersion of nanocellulose within the PVA matrix [45]. This enhancement in modulus and overall mechanical strength demonstrates the successful synergism between the matrix and the reinforcement, crucial for applications requiring elevated mechanical stability.

When it comes to the tensile strength of the films, Figure 11b reveals that the pure PVA film acquired a value of 2.5 MPa, whereas the films reinforced with rice husk and cellulose registered lower values. More specifically, the rice husk-reinforced film (PVA/RH) exhibited a value of 1.7 MPa and the cellulose-reinforced film (PVA/CE) yielded 1.45 MPa. This suggests a non-uniform dispersion of the reinforcement within the matrix, resulting in uneven tension transfer across the material. Conversely, the nanocellulose-incorporated

film demonstrated an enhancement, reaching 3.24 MPa. This improvement is correlated to the robust interaction between the hydroxyl groups in nanocellulose and PVA, engendering hydrogen bonds, and thus establishing strong interfacial adhesion and a better tension distribution throughout the material [50,61].

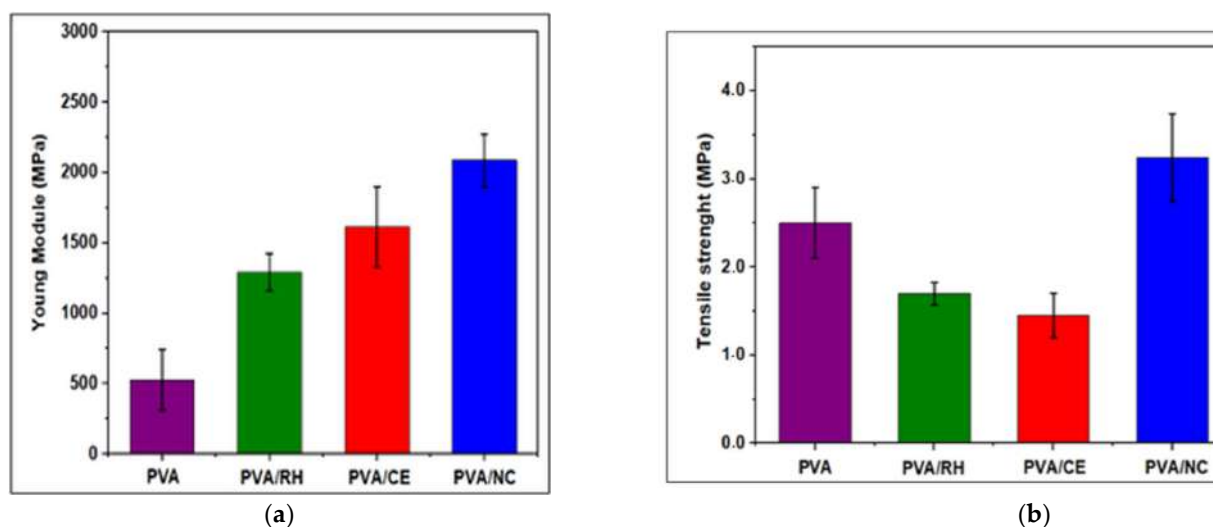


Figure 11. Graph of the average values of the Young's Modulus (a) and tensile strength (b) of the films.

Similar findings were noted by Ong et al. [49] when assessing the mechanical performance of PVA films reinforced with cellulose nanocrystals. These nanocrystals, extracted from palm oil fiber, were used in proportions of 3, 5, and 10 wt. % by mass. They reported augmented tensile strength and elasticity modulus, particularly in films containing 5 wt. % cellulose nanocrystals, relative to the pure PVA film.

The mechanical and barrier properties obtained align with recent findings on PVA/nanocellulose composites, where the addition of nanocellulose improved tensile strength and reduced WVTR [62].

In summary, rice husk waste is a significant byproduct of rice production in Rio Grande do Sul, presenting both challenges and opportunities for sustainable management and utilization.

Furthermore, Srivastava et al. [44] elucidated that incorporating 3 wt. % by mass of nanocellulose into the PVA matrix led to a 14.3% increment in the films' tensile strength relative to pure PVA. This enhancement is principally attributed to the presence of hydroxyl bonds within the material's structure, fostering a strongly intertwined three-dimensional network. This network ensures superior interfacial adhesion between the reinforcement and the matrix, thereby elevating the tensile strength of the films. This structural synergy and increased interaction between matrix and reinforcement underscore the potential use of nanocellulose in enhancing the mechanical properties of polymer composites.

4. Conclusions

This study established that the employed methodologies for cellulose extraction and nanocellulose acquisition were efficacious, as substantiated by the FTIR and XRD analyses. These analyses reveal alterations in the chemical structures of the fibers and a diminishment in amorphous constituents after the applied treatments. The TGA analysis pertaining to the fibers' thermal properties disclosed a decrement in the thermal stability of the nanocellulose sample. Evaluations of the films' thickness, grammage, and density revealed augmented values for those integrated with reinforcements in the PVA matrix.

The PVA/nanocellulose film demonstrated the lowest solubility, showcasing enhanced water resilience in comparison to its counterparts. Concurrently, there was a notable reduction in the water vapor permeability rate for films integrated with reinforcements, primarily those strengthened with nanocellulose. The examination of optical microscopy images highlighted suboptimal dispersion, evident voids, and agglomerations in films fortified with cellulose and rice husk. This outcome is attributed to particle size disparities, leading to the non-uniform dispersion of reinforcements within the matrix. Conversely, films bolstered with nanocellulose displayed optimal dispersion and characteristics analogous to pure PVA films.

For thermal properties, the TGA results showed slight instability in the cellulose-reinforced film, while DSC analysis revealed minimal differences between reinforced and pure PVA films.

The obtained results illuminate the advantageous impact of nanocellulose incorporation within the PVA matrix. Nanocellulose not only elevated the water and biodegradation resistance, but also preserved the inherent flexibility and transparency, of the films, all while enhancing their mechanical properties. Such enhancements make nanocellulose-fortified materials a practical and beneficial alternative for applications like quick-use packaging, including films for dry food trays and seedling planting bags, consolidating them as promising solutions in the realm of sustainable packaging. This aligns with the growing emphasis on environmentally friendly alternatives, reflecting an integration of innovation and sustainability in material science.

This study has significant advantages over similar research. One of the main pros is the sustainable use of agro-industrial waste, such as rice husks, which promotes the reuse of discarded materials, reducing environmental impacts and costs. In addition, the films developed showed notable improvements in mechanical and functional properties, such as greater tensile strength and modulus of elasticity, and a reduction in solubility and water vapor permeability. Another positive point is the greater stability of the films in biodegradation tests, with prolonged degradation for more than 45 days, which makes them more suitable for practical applications in packaging.

On the other hand, there are some cons to consider. Processing nanocellulose involves intensive chemical steps, such as acid hydrolysis, which can be economically costly and generate additional waste. In addition, difficulties have been observed in the uniform dispersion of larger-scale reinforcements, such as cellulose and rice husk, which have a negative impact on the optical and mechanical properties of the films. Finally, the scalability of the process on a large scale is still a challenge, requiring further studies to make industrial production of the developed materials feasible.

In addition, by using agro-industrial waste, such as rice husks from Rio Grande do Sul, Brazil's largest rice producer, this research helps to solve the significant waste management challenges faced by the Brazilian agricultural sector. The recovery of this waste not only reduces environmental pollution and the costs associated with improper disposal, but also aligns with global sustainability commitments and the principles of the circular economy.

These points highlight the advances and limitations of the study, highlighting its innovative potential, but also pointing out the areas that require optimization for future commercial applications.

Author Contributions: G.M.C.: methodology, writing, data analysis, conceptualization, investigation, verification, roles/writing—original draft. M.W.B.: roles/writing—original draft, data analysis. A.A.R.: methodology. C.A.G.B.: methodology, writing—review and editing. T.C.F.: methodology. N.D.F.: review and editing. N.V.V.d.N. roles/review and editing. A.F.G.: methodology, data analysis. A.L.M.: supervision, methodology, data analysis, writing—review and editing. A.D.d.O.: supervision, methodology, data analysis, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Sistema Pesquisa - Pesquisador: Mariane Weirich Bosenbecker

Retornar

Dados Gerais:

Projeto N°:

44152

Título:

MANUFATURA AVANÇADA UTILIZANDO MATERIAIS COMPOSITOS, POLIMEROS NANOCARREGADOS E BIOPOLIMEROS PARA VASOS DE PRESSÃO

Área de conhecimento:

Materiais Conjugados Não-Metálicos

Início:

09/05/2023

Previsão de conclusão:

09/05/2028

Situação:

Projeto em Andamento

Origem:

Escola de Engenharia
Programa de Pós-Graduação em Engenharia de Minas, Metalúrgica e de Materiais

Projeto Isolado com linha temática:

Manufatura avançada, controle e automação

Local de Realização:

Instituto de Química

Não apresenta relação com Patrimônio Genético ou Conhecimento Tradicional Associado.

Objetivo:

Desenvolver um projeto tecnológico e de engenharia dedicado à manufatura avançada, focando em materiais compósitos para vasos de pressão, combinando competências e infraestrutura de instituições do RS para geração de inovação

Palavras Chave:

COMPÓSITOS
MANUFATURA AVANÇADA
VASOS DE PRESSÃO

Equipe UFRGS:

Nome: SANDRO CAMPOS AMICO
Coordenador - Início: 09/05/2023 Previsão de término: 09/05/2028
Nome: CESAR LIBERATO PETZHOLD
Pesquisador - Início: 09/05/2023 Previsão de término: 09/05/2028
Nome: Cristiane da Silva Fonseca
Ensino: mestrado - Início: 09/05/2023 Previsão de término: 09/05/2028
Nome: Henrique Ramirez Mença
Ensino: mestrado - Início: 09/05/2023 Previsão de término: 09/05/2028
Nome: MAURÍCIO CARPE DIEM FERREIRA XAVIER
Pesquisador - Início: 09/05/2023 Previsão de término: 09/05/2028
Nome: OTÁVIO BIANCHI
Pesquisador - Início: 09/05/2023 Previsão de término: 09/05/2028
Nome: Tainá Klein
Ensino: mestrado - Início: 09/05/2023 Previsão de término: 09/05/2028
Nome: PÉRICLES LOPES SANTANA
Pós-doutorado - Início: 31/05/2024 Previsão de término: 30/04/2026
Nome: Patricia Alves da Silva
Pós-doutorado - Início: 04/11/2024 Previsão de término: 30/04/2026

Nome: MARIANE WEIRICH BOSENBECKER
Pós-doutorado - Início: 09/01/2025 **Previsão de término:** 31/07/2025

Equipe Externa:

Nome: Daiane Romanzini
Instituição: Instituto Federal de Educação, Ciência e Tecnologia do Rio Grande do Sul - Câmpus Porto Alegre
Pesquisador desde 09/05/2023

Nome: Daniel Tavares
Instituição: Universidade Federal de Pelotas
Pesquisador desde 09/05/2023

Nome: Lucas Leal Agne
Instituição: Universidade Federal de Santa Maria
Pesquisador desde 09/05/2023

Nome: Cristiane Miotto Becker
Instituição: Serviço Nacional de Aprendizagem Industrial
Pesquisador desde 09/05/2023

Nome: Camila Figueiró
Instituição: Serviço Nacional de Aprendizagem Industrial
Pesquisador desde 09/05/2023

Nome: Estêvão Santos Laureano da Cunha
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Nome: Maikson Luiz Passaia Tonatto
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Pesquisador desde 09/05/2023

Nome: Rafael de Avila Delucis
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Nome: Frederico Eggers
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Pesquisador desde 09/05/2023

Nome: Mara Zeni Andrade
Instituição: Instituto Federal de Educação, Ciência e Tecnologia do Rio Grande do Sul - Câmpus Porto Alegre
Pesquisador desde 09/05/2023

Avaliações:

Comissão de Pesquisa de Engenharia - Aprovado em 22/05/2023 [Clique aqui para visualizar o parecer](#)

Situação do projeto em relação à ODS:

Não informado

Apoio Externo:

Instituição: UFPEL - Universidade Federal de Pelotas
Instituição: UFSM - Universidade Federal de Santa Maria
Instituição: SENAI - Serviço Nacional de Aprendizagem Industrial
Instituição: IFRS - Instituto Federal de Educação, Ciência e Tecnologia do Rio Grande do Sul - Câmpus Porto Alegre
Instituição: IPF - Leibniz-Institut für Polymerforschung Dresden e. V.

Anexos:

[Projeto Completo](#)

Data de Envio: 09/05/2023

[Documento de Aprovação](#)

Data de Envio: 09/05/2023

Referências WEB:

<https://www.linkedin.com/company/macopv/>

Bolsas:

Projeto associado à bolsa PROBIC FAPERGS-UFRGS **No Período:** 01/09/2023 a 31/08/2024
Bolsista: Laura Ayune de Andrade Gonçalves **no período de** 01/09/2023 a 31/08/2024
Projeto associado à bolsa BIC UFRGS **No Período:** 01/09/2024 a 31/08/2025
Bolsista: Amanda Terme Machado Pioner **no período de** 01/09/2024 a 31/08/2025
Projeto associado à bolsa PIBIC CNPq-UFRGS **No Período:** 01/09/2024 a 31/08/2025
Bolsista: FELIPE ROCHA STIMAMIGLIO **no período de** 01/09/2024 a 31/08/2025
Projeto associado à bolsa Programa de Bolsas de Iniciação Científica Meninas na Ciência **No Período:** 01/09/2024 a 31/08/2025
Bolsista: Hellena Braga Domingues **no período de** 01/09/2024 a 31/01/2025
Bolsista: Emanuelli Moraes Martins **no período de** 01/02/2025 a 31/08/2025
Projeto associado à bolsa Programa de Bolsas de Iniciação Científica Meninas na Ciência **No Período:** 01/09/2024 a 31/08/2025
Bolsista: AGNES TSO SOARES **no período de** 01/09/2024 a 31/01/2025
Bolsista: LETÍCIA MORAES BALLARDIN **no período de** 01/02/2025 a 31/08/2025
Projeto associado à bolsa PROBIC FAPERGS-UFRGS **No Período:** 01/10/2024 a 31/08/2025
Bolsista: DANTE AMBRÓSIO DE SOUZA BENVENUTTI **no período de** 01/10/2024 a 31/08/2025

Solicitação de Bolsa:

Projeto associado à solicitação de bolsa na situação aprovada quanto ao mérito **no processo** BICFEM2025
Projeto associado à solicitação de bolsa na situação aprovada quanto ao mérito **no processo** IC2025
Projeto associado à solicitação de bolsa na situação aprovada quanto ao mérito **no processo** IC2025
Projeto associado à solicitação de bolsa na situação aprovada quanto ao mérito **no processo** IC2025
Projeto associado à solicitação de bolsa na situação aprovada quanto ao mérito **no processo** BICFEM2025
Projeto associado à solicitação de bolsa na situação aprovada quanto ao mérito **no processo** ITAF2025

Processos - Colaborador Convidado:

Projeto associado ao processo de colaborador do tipo Pós-Doutorado **de** PÉRICLES LOPES SANTANA **no período** 31/05/2024 a 30/04/2026
Projeto associado ao processo de colaborador do tipo Pós-Doutorado **de** Patricia Alves da Silva **no período** 04/11/2024 a 30/04/2026
Projeto associado ao processo de colaborador do tipo Pós-Doutorado **de** MARIANE WEIRICH BOSENBECKER **no período** 09/01/2025 a 31/07/2025



DESENVOLVIMENTO DE FILMES DE NANOCOMPÓSITOS DE POLIETILENO DE ALTA DENSIDADE (PEAD)

1. Identificação

Título do **DESENVOLVIMENTO DE FILMES DE NANOCOMPÓSITOS DE POLIETILENO DE ALTA DENSIDADE (PEAD)/NANOCRISTAIS DE CELULOSE PARA APLICAÇÃO EM EMBALAGENS**

Data **26/04/2017**

Unidade: **CDTEC - Centro de Desenvolvimento Tecnológico**

Grupo de Pesquisa: **LabCom**

Período de Realização: **04/04/2017** até **04/04/2019**

Carga Horária Semanal: **15** Código COCEPE: **7878**

2. Dados Gerais

Grande Área **3.00.00.00-9 - Engenharias**

Área CNPQ: **3.03.00.00-2 - Engenharia de Materiais e Metalúrgica**

Resumo: **A aplicação de materiais poliméricos na produção de embalagens aumentou enormemente nos últimos anos e estes materiais se tornaram elementos inevitáveis no processo de obtenção de embalagens, tais como, embalagens de alimentos. Isso levou a problemas ambientais graves uma vez que estes materiais não são biodegradáveis. Assim, na era do descarte, a degradabilidade dos polímeros utilizados como embalagens representa um aspecto de fundamental importância. O desenvolvimento de embalagens ecológicas, de alto desempenho e com boas propriedades de barreira pode ser alcançado pelo desenvolvimento de novos polímeros com boas propriedades de biodegradação ou ainda melhorando a biodegradabilidade dos polímeros existentes. Este último requisito é o eixo central das motivações para o presente projeto. A solução aqui proposta consiste em incorporar nanocristais de celulose (NCC) em uma matriz de polietileno de alta densidade (PEAD) através da técnica de extrusão com o objetivo de acelerar a biodegradação deste polímero e ao mesmo tempo desenvolver uma embalagem com boas propriedades de barreira a gases. Os nanocristais de celulose serão extraídos da casca de arroz, um resíduo agrícola que traz sérios transtornos ao meio ambiente quando descartado sem os controles adequados. Serão preparados filmes de nanocompósitos de PEAD e nanocristais de celulose, utilizando o polietileno de alta densidade enxertado com anidrido maleico (PEAD-g-MA) como agente compatibilizante. A influência da concentração de NCC sobre as propriedades térmicas, mecânicas e de barreira do PEAD, bem como sobre a sua taxa de biodegradação, será investigada.**

Envolve experimentação com modelos de animais sob **Não**

Objetivos: **O presente projeto traz como objetivo geral o desenvolvimento de filmes de nanocompósitos poliméricos utilizando como matriz polimérica o polietileno de alta densidade (PEAD) e nanocristais de celulose (NCC) obtidos a partir da casca de arroz como agente de reforço, para aplicação no setor de embalagens. . Objetivos específicos • Obtenção dos nanocristais de celulose a partir da casca de arroz; • Caracterização dos nanocristais de celulose obtidos; • Incorporar os nanocristais de celulose em filmes de PEAD utilizando o processo de extrusão; • Avaliar o efeito da adição do agente compatibilizante PEAD-g-MA e do teor de carga nas propriedades mecânicas, térmicas, de barreira e na morfologia dos nanocompósitos obtidos; • Avaliar a biodegradabilidade dos nanocompósitos.**

3. Equipe

Coordenador

SIAPÉ	Nome	Email
2263875	AMANDA DANTAS DE OLIVEIRA	amandaoliveira82@gmail.com



DESENVOLVIMENTO DE FILMES DE NANOCOMPÓSITOS DE POLIETILENO DE ALTA DENSIDADE (PEAD)

Professores

SIAPE - Nome	Unidade	C.H. Sem.	C.H. Total
1444919 - NEFTALI LENIN VILLARREAL CARRENO	CDTEC - Centro de Desenvolvimento Tecnológico	5	525

Alunos

Matrícula - Nome	Curso	C.H. Sem.	C.H. Total
15200151 - GABRIEL MONTEIRO CHOLANT	Engenharia de Materiais	15	2355
16201441 - MARIANE WEIRICH BOSENBECKER	Ciência e Engenharia de Materiais	30	3150
14104098 - SHEILA REGINA COSTA CROCHE	Engenharia de Materiais	15	2355
17101773 - OSCAR GIORDANI PANIZ	Ciência e Engenharia de Materiais	10	1050
17101766 - JONAS EICHELBERGER GRANADA	Ciência e Engenharia de Materiais	20	2100
03695074957 - José Henrique Alano	Não UFPel	5	525

4. Fonte financiadora

Nenhuma fonte encontrada

O Coordenador deste projeto declara, formalmente, que:

- I. Tem pleno conhecimento dos trâmites a serem seguidos para cadastro junto ao Departamento de Pesquisa da Pró-reitoria de Pesquisa e Pós-graduação (PRPPG) e o registro no COCEPE;
- II. Se responsabiliza pelo encaminhamento do projeto em seu Departamento e no Conselho Superior da unidade para sua aprovação;
- III. Assume inteira responsabilidade pela veracidade das informações contidas na presente solicitação e pelos danos pessoais, materiais e ambientais, decorrentes da execução do projeto e aplicação de seus

.....
AMANDA DANTAS DE OLIVEIRA - Coordenador
29 Maio 2017

.....
Chefe do Departamento

.....
Presidente do Conselho Departamental



ATESTADO DE PARTICIPAÇÃO

Atestamos, para os devidos fins, que **MARIANE WEIRICH BOSENBECKER** exerceu até o presente momento as funções listadas abaixo no Projeto “**Desenvolvimento de Materiais Compósitos Sustentáveis**” promovido pelo(a) Centro de Desenvolvimento Tecnológico, da Universidade Federal de Pelotas, num total de **2340** horas.

Função	Início	Término	Horas	Ênfase
Participante - Ação: Desenvolvimento de Materiais Compósitos Sustentáveis	09/08/2021	05/08/2024	2340	Pesquisa



Cadastro de Projeto de Pesquisa

1. Identificação

PRORROGAÇÃO

Título do Projeto: **DESENVOLVIMENTO DE FILMES DE NANOCOMPÓSITOS DE POLIETILENO DE ALTA DENSIDADE (PEAD)/NANOCRISTAIS DE CELULOSE PARA APLICAÇÃO EM EMBALAGENS**

Data Cadastro: **18/07/2018**

Unidade: **CDTEC - Centro de Desenvolvimento Tecnológico**

Grupo de Pesquisa: **LabCom**

Período de Realização: **05/04/2019** até **20/12/2020**

Carga Horária Semanal: **8** Código COCEPE: **9368**

2. Dados Gerais

Grande Área CNPQ: **3.00.00.00-9 - Engenharias**

Área CNPQ: **3.03.00.00-2 - Engenharia de Materiais e Metalúrgica**

Envolve experimentação com modelos de animais sob registro CEEA: **Não**

Principais Resultados: **No momento os alunos envolvidos no trabalho estão obtendo celulose a partir da casca de arroz, e a partir desta celulose será obtida a nanocelulose. A celulose obtida já foi caracterizada por FTIR, difração de raios-X e microscopia eletrônica de varredura, esta mesma celulose já foi também incorporada em uma matriz de polietileno de alta densidade (PEAD) e foram obtidos materiais compósitos com três diferentes teores de celulose (5, 10 e 15%). Foram avaliadas as propriedades mecânicas e térmicas destes compósitos. Os próximos passos seriam a obtenção e a caracterização da nanocelulose e também a obtenção dos filmes e dos nanocompósitos de PEAD/nanocelulose**

Justificativa: **O motivo do pedido de prorrogação se dá em virtude do tempo e da dificuldade que estamos encontrando em se obter a nanocelulose. Várias metodologias já foram adotadas, mas com pouco sucesso. Além disso, a quantidade de nanocelulose obtidas após o processo é bem pequena e precisamos de uma grande quantidade deste material para se conseguir processar os nanocompósitos e os filmes poliméricos**

Cronograma: **2018/02 - Caracterizar morfologicamente os compósitos com 5, 10 e 15% de celulose. Paralelamente obter mais celulose; 2019/01 - Obter nanocelulose a partir da celulose e caracterizar a nanocelulose obtida; 2019/02 - Obtenção dos nanocompósitos PEAD/nanocelulose. Ao mesmo tempo produzir mais celulose e nanocelulose; 2020/01 - Obter os filmes; 2020/02 - Caracterizar os filmes.**

3. Equipe

Coordenador

SIAPE	Nome	Email
2263875	AMANDA DANTAS DE OLIVEIRA	amandaoliveira82@gmail.com

Professores

SIAPE - Nome	Unidade	C.H. Sem.	C.H. Total
1444919 - NEFTALI LENIN VILLARREAL CARRENO	CDTEC - Centro de Desenvolvimento Tecnológico	5	525

Alunos

Matrícula - Nome	Curso	C.H. Sem.	C.H. Total
17101773 - OSCAR GIORDANI PANIZ	Ciência e Engenharia de Materiais	10	1050
16201441 - MARIANE WEIRICH BOSENBECKER	Ciência e Engenharia de Materiais	30	3150
17101766 - JONAS EICHELBERGER GRANADA	Ciência e Engenharia de Materiais	20	2100
16100315 - PAULO ROBERTO DOS REIS DA ROSA	Engenharia de Materiais	10	690
15200151 - GABRIEL MONTEIRO CHOLANT	Engenharia de Materiais	15	540



Cadastro de Projeto de Pesquisa

Bolsistas

Matrícula - Nome	Curso	Bolsa Tipo	C.H. Total
15200151 - GABRIEL MONTEIRO CHOLANT	Engenharia de Materiais	PVIP/UFPel	468
15200151 - GABRIEL MONTEIRO CHOLANT	Engenharia de Materiais	PROBIC/FAP ERGS	168
17102402 - MARIANA RIBAS DE SÁ	Engenharia de Materiais	PBIP- AF/UFPel	1060
17102507 - VITOR FERNANDES DA SILVA	Engenharia de Materiais	PIBIC/CNPq	1060
16100315 - PAULO ROBERTO DOS REIS DA ROSA	Engenharia de Materiais	PROBIC/FAP ERGS	468

4. Fonte financiadora

Nenhuma fonte encontrada

O Coordenador deste projeto declara, formalmente, que:

- Tem pleno conhecimento dos trâmites a serem seguidos para cadastro junto ao Departamento de Pesquisa da Pró-reitoria de Pesquisa e Pós-graduação (PRPPG) e o registro no COCEPE;
- Se responsabiliza pelo encaminhamento do projeto em seu Departamento e no Conselho Superior da unidade para sua aprovação;
- Assume inteira responsabilidade pela veracidade das informações contidas na presente solicitação e pelos danos pessoais, materiais e ambientais, decorrentes da execução do projeto e aplicação de seus resultados.

.....
AMANDA DANTAS DE OLIVEIRA - Coordenador

25 Junho 2025

.....
Chefe do Departamento

.....
Presidente do Conselho Departamental



ATESTADO DE PARTICIPAÇÃO

Atestamos, para os devidos fins, que **MARIANE WEIRICH BOSENBECKER** exerceu até o presente momento as funções listadas abaixo no Projeto “**Obtenção e caracterização de filmes de nanocompósitos biodegradáveis a base de amido**” promovido pelo(a) Centro de Desenvolvimento Tecnológico, da Universidade Federal de Pelotas, num total de **342** horas.

Função	Início	Término	Horas	Ênfase
Colaborador - Ação: Obtenção e caracterização de filmes de nanocompósitos biodegradáveis a base de amido	01/09/2020	23/12/2021	342	Pesquisa



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PROPRIEDADES TÉRMICAS DE COMPÓSITOS DE POLIETILENO DE ALTA DENSIDADE REFORÇADOS COM CELULOSE

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Palavras-chave: celulose, polietileno de alta densidade, casca de arroz, compósitos

Resumo

Este trabalho buscou desenvolver compósitos utilizando como matriz polimérica o polietileno de alta densidade e como reforço foi utilizada a celulose obtida a partir da casca de arroz. Os compósitos obtidos foram preparados nas proporções de 5, 10 e 15% em massa de celulose, utilizando-se para isto uma extrusora de rosca simples. A celulose obtida foi caracterizada por difração de raios X. Os materiais compósitos foram caracterizados através das técnicas de análise termogravimétrica e calorimetria exploratória diferencial. Por meio dos resultados de difração de raios X foi possível comprovar um aumento do índice de cristalinidade da celulose após sucessivos tratamentos químicos, assim como ligeiro aumento na estabilidade térmica com a adição de carga. No entanto, os dados obtidos por calorimetria exploratória diferencial mostraram que aparentemente a celulose não apresenta influência significativa nas temperaturas de transição do polímero.

THERMAL PROPERTIES OF HIGH-DENSITY POLYETHYLENE COMPOSITES REINFORCED WITH CELLULOSE

Keywords: cellulose, high density polyethylene, rice husk. composites

Abstract

This study sought to develop composites using polymeric matrix the high-density polyethylene and cellulose was used as reinforcement obtained from rice husk. The composites were prepared in the proportions of 5, 10 and 15% by mass of cellulose, using for this a single screw extruder. The cellulose pulp obtained was characterized by x-ray diffraction. Composite materials were characterized by thermogravimetric analysis and differential scanning calorimetry. Through the results of x-ray diffraction it was possible to demonstrate an increase in the index of crystallinity of cellulose after successive chemical treatments, as well as a slight increase in thermal stability with the addition of load. However, the data obtained by differential scanning calorimetry did not show a significant improvement in their results.

INTRODUÇÃO

A crescente demanda por materiais de fontes renováveis com propriedades diferenciadas tem possibilitado a inserção de produtos e resíduos da agricultura (agroindustriais) em diferentes áreas de pesquisa. O aproveitamento de resíduos da atividade agrícola na produção de compósitos e nanocompósitos poliméricos, pode reduzir os custos do produto final, além de promover um destino adequado a estes resíduos, agregando-lhes valor (SIQUEIRA et al., 2010).

Neste sentido, estudos têm demonstrado interesse na incorporação de fibras vegetais em matrizes poliméricas, proporcionando melhoria de suas propriedades e por substituírem, geralmente com vantagens econômicas e de densidade, os convencionais reforços inorgânicos como as fibras de vidro (PÖLLÄNEN, 2013).

A casca de arroz (CA) é um resíduo agroindustrial produzido em grandes quantidades no Rio Grande do Sul (IBGE, 2018). Estas cascas possuem baixo valor comercial, pois a sílica e as fibras contidas não possuem valor nutritivo e por isso não são usadas na alimentação humana ou animal, resultando em sérios impactos ambientais. Mais recentemente este material tem sido empregado também como reforço em materiais compósitos poliméricos. A CA caracteriza-se também por ser considerada como a fonte mais abundante de celulose a partir de resíduos agroindustriais do mundo (ROSA et al., 2012; JOHAR; AHMAD; DUFRESNE, 2012).

Além disso, não há trabalhos publicados na literatura sobre a utilização da celulose obtida a partir da CA em matriz de polietileno de alta densidade (PEAD) principalmente em pesquisas realizadas no Brasil) (BATTEGAZZORE et al., 2014). Neste contexto, o objetivo deste trabalho foi caracterizar a celulose e avaliar o efeito da utilização de diferentes concentrações de carga nas propriedades térmicas de materiais compósitos com matriz de PEAD.

MATERIAL E MÉTODOS

Materiais

O polímero utilizado neste trabalho foi o polietileno de alta densidade (PEAD), conhecido comercialmente

como PEAD IG58, fornecido pela Petroquímica Braskem S/A. A casca de arroz utilizada foi doada pela empresa Cerealista Polisul, localizada na cidade de Pelotas-RS, Brasil.

Obtenção da Celulose a partir da Casca de Arroz

A obtenção das fibras de celulose a partir da casca de arroz envolveu duas etapas: tratamento alcalino e branqueamento. O tratamento alcalino foi realizado com o objetivo de remover a hemicelulose e a lignina da casca.

Para isto, 35 gramas de casca na forma de um pó fino, doada pela empresa Cerealista Polisul, foi colocada em uma solução de 700 ml de água destilada, 290 ml de ácido acético (CH_3COOH) e 60 ml de ácido nítrico (HNO_3), esta solução foi deixada em banho-maria durante 4 horas. No término da reação, a solução foi filtrada e o material sólido obtido foi lavado várias vezes até atingir um pH neutro.

Após tratamento alcalino, o processo de branqueamento foi realizado com adição da casca tratada em solução de 700 ml de hipoclorito de sódio (NaClO) comercial durante 24 horas. O material resultante foi filtrado e também lavado com água destilada. Em seguida, foi seco em estufa de secagem da marca Quimis a 60°C , por 24 horas.

Preparação dos Compósitos PEAD/Celulose

Os compósitos foram obtidos pelo método de mistura no estado fundido, com o auxílio de uma extrusora de rosca simples com temperaturas de 180° , 180° e 190°C , nas zonas 1, 2 e 3, respectivamente.

Difração de Raios X (DRX)

A técnica de DRX permite identificar a estrutura cristalina do material, bem como o seu grau de cristalinidade.

As análises de DRX foram realizadas utilizando-se um difratômetro D8 Advance Bruker, com comprimento de onda ($\lambda = 1,541 \text{ \AA}$), operando a 40 KV e 40 mA. A varredura foi realizada na faixa de 2θ entre 10° e 50° , a uma taxa de $1^\circ/\text{min}$.

Com os difratogramas obtidos foi possível determinar o índice de cristalinidade da celulose de acordo com a Eq. 1, segundo a metodologia proposta por Segal et al. (1959):

$$I_c = \frac{I(002) - I(\text{am})}{I(002)} * 100\%$$

Eq. (1)

onde: I_{002} é o valor de intensidade máximo de difração do pico próximo a $2\theta = 22^\circ$, relacionado a parte cristalina do material, enquanto I_{am} é a intensidade do halo de difração do pico de que representa o material amorfo em $2\theta \sim 18^\circ$ (SEGAL et al., 1959).

Análise Termogravimétrica (TGA)

A análise termogravimétrica tem como objetivo avaliar a estabilidade térmica do material estudado. Para esta análise foi utilizado um equipamento da TA Instruments, modelo TGA Q50, a uma taxa de $20^\circ\text{C}/\text{min}$, a partir da temperatura ambiente até 700°C , sob atmosfera de nitrogênio.

Calorimetria Exploratória Diferencial (DSC) do Compósito

A calorimetria exploratória diferencial (DSC) foi realizada para avaliar o efeito da celulose nas temperaturas de fusão (T_m), de cristalização (T_c), e no grau de cristalinidade do polímero. Foi utilizado um equipamento da TA Instruments, modelo Q-1000, com nitrogênio como gás de arraste, em fluxo constante de 50 ml/min (ASTM E1269 - 11).

As amostras foram inicialmente aquecidas da temperatura ambiente até 200°C a uma taxa de aquecimento de $10^\circ\text{C}/\text{min}$, permanecendo nesta temperatura por 3 minutos. Logo após foram resfriadas até 30°C a uma taxa de $10^\circ\text{C}/\text{min}$ para a determinação da temperatura de cristalização (T_c) e novamente foram aquecidas até 200°C a uma taxa

de $10^\circ\text{C}/\text{min}$. Para a realização das análises foram utilizados os termogramas do segundo aquecimento por não possuírem influência da história térmica das amostras.

Através da Eq. 2 foi determinado o grau de cristalinidade (X_c) dos materiais estudados (CANEVAROLO, 2006):

$$X_c = \frac{\Delta H_m}{\Delta H_0(1-\phi)} * 100\%$$

Eq. (2)

RESULTADOS E DISCUSSÃO

O Difração de Raios X (DRX)

A difratometria de raios X foi utilizada para investigar a estrutura cristalina da casca de arroz antes e após os tratamentos químicos. A celulose é de natureza cristalina devido a interações de ligações de hidrogênio e forças de Van der Waals entre moléculas adjacentes contrárias à hemicelulose e à lignina, que possuem uma estrutura amorfa (PRADO; SPINACÉA, 2015).

Os difratogramas de raios X das amostras obtidas estão apresentados na Figura 1, no qual podemos observar a presença de três picos característicos de celulose tipo I, em aproximadamente 16° , 22° e 34° correspondentes aos planos (101), (002), (040), respectivamente (HALAL et al., 2015).

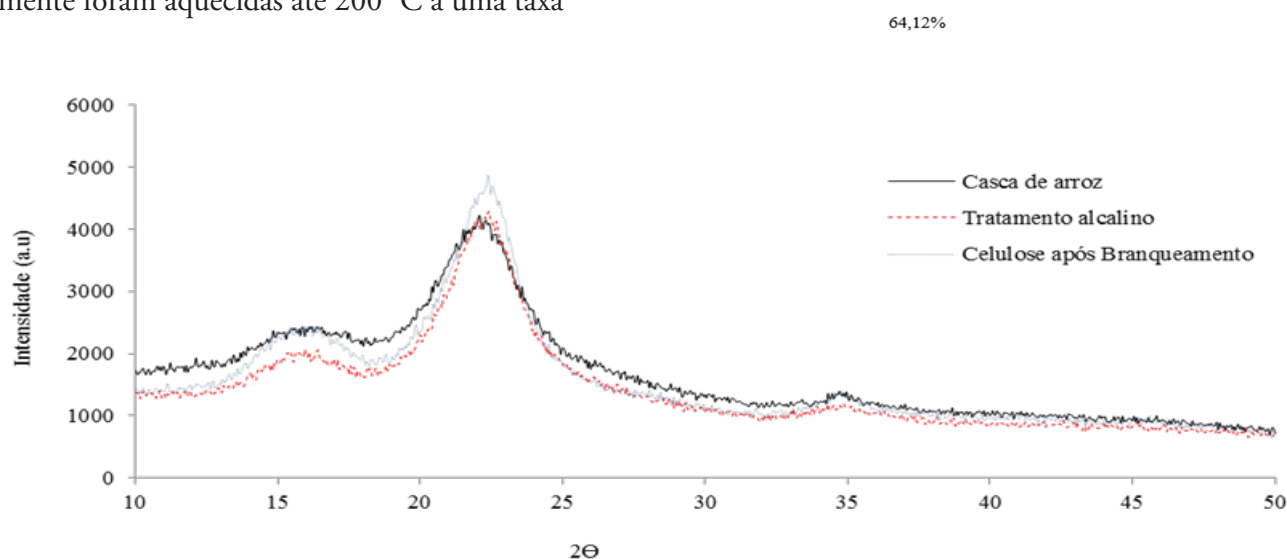


Figura 1. Difratograma de raios-x das amostras obtidas

Na Tabela 1, estão apresentados os resultados para cristalinidade obtidos a partir do método de Segal et al (1959). Pode-se notar o aumento da cristalinidade para a celulose obtida após branqueamento em relação à casca

de arroz, a qual apresentou um Ic de 64,12%, este resultado é devido à remoção de materiais não celulósicos (BETTAIEBA et al., 2015).

Tabela 1. Índice cristalinidade (% Ic) calculado através do método de Segal

Amostras	Casca de Arroz	Tratamento Alcalino	Branqueamento
% Cr	47,80	58,65	64,12

Análise Termogravimétrica (TGA)

Os termogramas de TGA da celulose e dos compósitos com 5, 10 e 15% de celulose são relatados

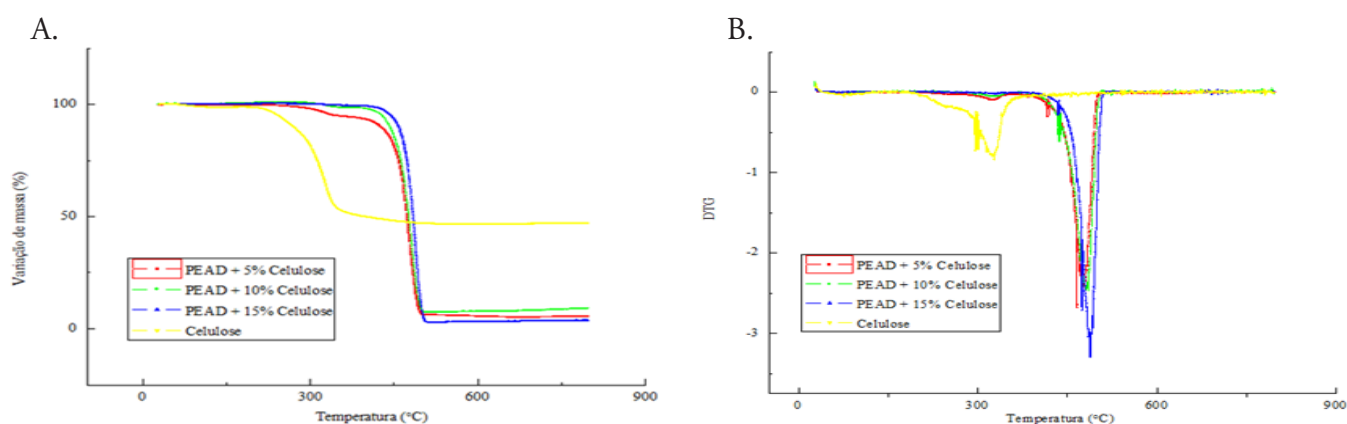


Figura 2. A. Curvas de TGA e B. Curvas de DTG da celulose e dos compósitos estudados.

O primeiro processo refere-se à uma perda de massa inicial em torno de 100°C, ficando em aproximadamente em 2% para a celulose, que foi devido à desidratação do material, que, mesmo tendo sido seco antes das análises, apresenta caráter hidrofílico, dificultando a total eliminação de água. A segunda perda de massa ocorreu entre 200 e 400°C e foi atribuído à degradação da hemicelulose, pectina, lignina e celulose (ROSA et al., 2010).

Analisando os resultados obtidos para os materiais compósitos podemos notar que há um pequeno aumento da estabilidade térmica do compósito com o aumento do teor de carga (ROSA, et al 2010).

O resultado deste trabalho está de acordo como reportado por Johar e Ahamad (2012), onde o compósito praticamente não perdeu peso em 400°C; contudo, a partir de 450 °C, a perda de peso foi rápida e acentuada, resultando em resíduos mínimos.

A Figura 2B mostra a curva da primeira derivada da perda de massa (DTG), onde é observado um primeiro pico em aproximadamente 327 °C para a celulose,

na Figura 2A enquanto na Figura 2B a derivada das curvas de perda de massa (DTG) é apresentada.

Segundo a literatura, a decomposição térmica das fibras naturais ocorre em diferentes temperaturas. A decomposição da hemicelulose inicia-se por volta de 220°C e continua até os 300°C, a celulose tem sua degradação iniciada perto dos 310°C até os 400°C, enquanto a lignina apresenta temperaturas de degradação entre 200°C até 700°C (ABRAHAM et al., 2011).

Através da análise da curva de TGA para a celulose é possível observar dois processos de decomposição.

referente à máxima taxa de decomposição da celulose. Um segundo pico é evidenciado em aproximadamente 487 °C e que equivale à máxima taxa de decomposição do PEAD, onde observa-se uma sobreposição dos picos, indicando que a adição de celulose na matriz polimérica contribui para a obtenção de compósitos sem gerar perdas na estabilidade térmica (BORSOI et al., 2011).

Calorimetria Exploratória Diferencial (DSC)

Na Figura 3A e B encontram-se os termogramas de DSC do resfriamento e do segundo aquecimento, respectivamente, que foram utilizados para caracterizar o PEAD e os compósitos com 5, 10 e 15% em massa de celulose. Os valores correspondentes a temperatura de fusão cristalina (T_m), entalpia de fusão (ΔH_m), temperatura de cristalização (T_c), entalpia de cristalização (ΔH_c), estão demonstrados na Tabela 2.

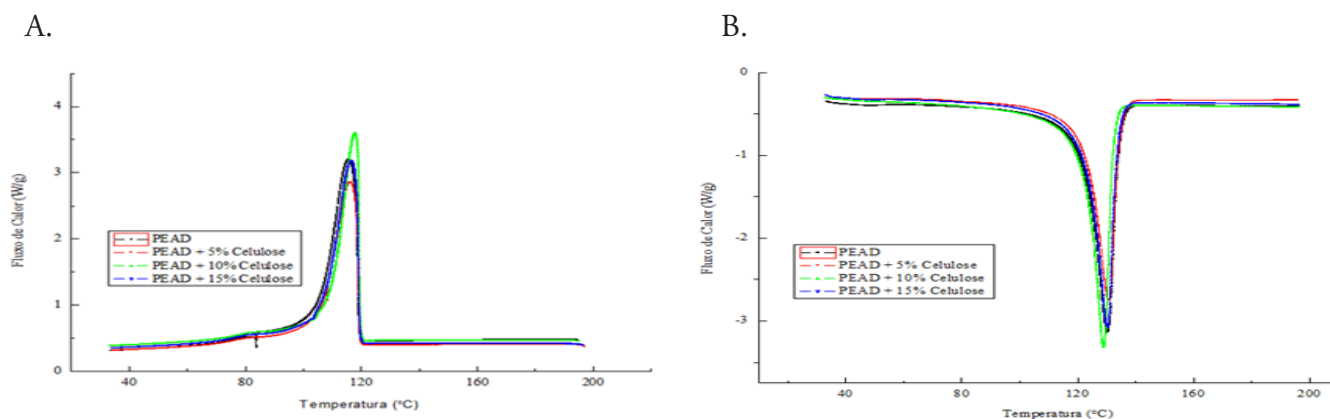


Figura 3. A - B. Termogramas de DSC dos materiais estudados referente ao resfriamento e segundo aquecimento, respectivamente.

Tabela 2. Valores obtidos por DSC da temperatura de cristalização (T_c), temperatura de fusão (T_f), entalpia de cristalização (ΔH_c), entalpia de fusão (ΔH_f) e grau de cristalinidade ($\%X_c$).

Amostra	T_c (°C)	T_m (°C)	ΔH_c (J/g)	ΔH_m (J/g)	X_c (%)
PEAD	115,52	132,54	164,50	182,20	62,18
PEAD + 5% Celulose	116,82	132,61	99,04	134,20	45,80
PEAD + 10% Celulose	117,90	131,06	140,20	158,40	54,06
PEAD + 15% Celulose	116,63	132,01	138,60	160,60	54,81

Analisando a Tabela 2 é possível observar que os valores de temperaturas de fusão e de cristalização dos materiais compósitos foram similares aos valores obtidos para o PEAD puro. (BORAN et al., 2016). Resultados semelhantes foram obtidos por Fernandes (2015), que estudou materiais compósitos com matriz de epóxi reforçada com cinza de casca de arroz. O autor observou que as curvas de DSC dos compósitos e da matriz são muito similares, indicando que a presença de diferentes concentrações de cinza não alterou significativamente o comportamento térmico do polímero (FERNANDES, 2015).

Analisando as entalpias de fusão e cristalização, percebe-se um aumento dos valores de entalpia com o aumento do teor de celulose, porém com uma pequena redução para o compósito de 15% de celulose e quando comparado com o PEAD puro, observa-se uma diminuição bastante pronunciada em relação aos compósitos estudados.

Os valores de grau de cristalinidade para os compósitos foram calculados usando a cristalinidade

do PEAD virgem (ΔH 100%) como parâmetro, 293 KJ/mol. O grau de cristalinidade encontrado neste trabalho (62,18%) está de acordo com o relatado na literatura, onde a faixa do grau de cristalinidade para o PEAD está na faixa de 62 e 82% (BECERRA, 2015).

Todos os compósitos apresentaram um grau de cristalinidade menor que o PEAD, que pode ser um indício de que as cargas utilizadas não atuaram como agentes nucleantes, que aumentariam a cristalinidade do compósito conforme relatado na literatura (GOMES; VISCONDE; PACHECO, 2013).

CONCLUSÃO

O método utilizado para a obtenção da celulose a partir da casca de arroz foi eficiente, revelando um aumento da cristalinidade após tratamentos químicos. Verificou-se um ligeiro aumento na estabilidade térmica com a adição de carga a matriz polimérica, no entanto, não foi observado uma mudança significativa nas temperaturas de fusão e de cristalização para as amostras estudadas. Vale ressaltar que o reaproveitamento deste resíduo contribui para a diminuição do impacto ambiental e reutilização deste material.

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Article

Sustainable Films Derived from *Eucalyptus* spp. Bark: Improving Properties Through Chemical and Physical Pretreatments

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Abstract: This study investigates the sustainable use of *Eucalyptus* spp. bark through different chemical (hydrothermal, acid, alkaline, and bleaching) and physical (milling) pretreatments in the production of sustainable films. Valorization of agro-industrial residues and the demand for sustainable materials pose challenges for environmentally responsible solutions. *Eucalyptus* spp. bark, rich in cellulose, hemicellulose, and lignin, is a promising source for creating sustainable materials like films. In this study, the use of chemical and physical treatments aims to optimize biomass extraction and improve the chemical, thermal, mechanical, and optical properties of the films. The films showed an excellent light barrier capacity, with a transmittance below 1%. Crystallinity indices varied with the pretreatment: 8.15% for hydrothermal, 7.01% for alkaline, 7.63% for acid, and 10.80% for bleaching. The highest crystallinity value was obtained through bleaching, by removing amorphous components like lignin and hemicellulose. The alkaline pretreatment yielded stronger films (maximum stress of 8.8 MPa, Young's modulus of 331.3 MPa) owing to the retained lignin and the hemicellulose reinforcing the material. This study contributes to the field of sustainable development by converting residues into valuable materials and by advancing the circular economy. The films' specific properties make them suitable for applications like sustainable packaging, addressing environmental and industrial challenges.

Keywords: sustainable materials; chemical pretreatments; physical treatment; films; crystallinity



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1. Introduction

The genus *Eucalyptus*, belonging to the Myrtaceae family, is native to Australia, New Guinea, and Indonesia, and has been widely introduced in various parts of the world owing to its adaptability to different environmental conditions [1]. This forest genus, known for its robustness and accelerated growth capacity, has played a crucial role in the commercial forestry sector, being a predominant genus in the formation of forests for the pulp and paper industry [2]. Owing to their adaptability, *Eucalyptus* spp. have become some of the most extensively cultivated species globally. In Brazil, they serve as the primary raw

material for planted forests dedicated to cellulose production, highlighting their significant economic importance in the industrial sector [3].

The extensive cultivation of *Eucalyptus* spp. has brought significant economic benefits, such as the provision of timber for construction [4], pulp for paper [5], and medicinally active products [6]. However, the introduction of this genus outside of its native range has also brought substantial ecological challenges, including competition with native species and reduced biodiversity [7]. These negative impacts are a direct consequence of the expansion of eucalyptus plantations, which often suppress local ecosystems and affect native flora and fauna [8].

In the industrial context, a significant part of eucalyptus biomass is harvested during felling, which generates residual sawdust composed of pieces of bark, leaves, and sawn trunks [9,10]. *Eucalyptus* spp. bark, which can correspond to 10–18% of the total volume of processed wood, is a notable example of this type of residue frequently discarded or used for energy generation [11,12].

Eucalyptus spp. bark is an abundant source of valuable constituents, including cellulose (60–65%), hemicellulose (15–30%), and lignin (16–35%) [10,13,14]. This composition makes it a promising raw material to produce new materials, such as biodegradable polymeric films. Recent studies have explored the use of barks from several plant species as raw material to produce sustainable films for different purposes, such as food, packaging, pharmaceuticals, biocomposites, and drug carriers [15]. Notable examples include the use of willow bark [16] and western red cedar bark [17], both of which have demonstrated promising mechanical characteristics such as high strength and flexibility.

These plant-based materials are distinguished by their remarkable properties, such as high strength, flexibility, and their ability to degrade in the environment without leaving toxic residues, making them a sustainable alternative to traditional polymers [14,18]. In this context, the use of *Eucalyptus* spp. bark is especially relevant, considering that Brazil is one of the world's largest producers of this tree, with cultivations occupying 5.1 million hectares [19], corresponding to almost 61.5% of the areas designated for forestry [20].

To transform eucalyptus bark into films, it is necessary to make significant modifications to the structure of the biomass, a process which is complex due to the presence of lignin and other components that hinder the accessibility and processing of the cellulose [21]. Therefore, chemical pretreatments are essential in this process, as they facilitate the separation and purification of the main components of the biomass [22]. Methods such as acid and alkaline hydrolysis play a crucial role, as acid hydrolysis degrades the hemicellulose and part of the lignin, while alkaline hydrolysis removes the lignin more efficiently [23–25]. These treatments, along with other chemical and physical processes, such as bleaching, aim to improve film-forming properties such as mechanical strength, transparency, and crystallinity. The hydrothermal pretreatment, which uses only water and heat, stands out as a more sustainable option, as it eliminates the need for chemical agents in film formation [26]. Among the advantages of these processes is their efficiency in cellulose purification and film property improvement, making them interesting for various industrial applications [15]. Furthermore, these methods offer greater flexibility, enabling adaptation of the material's characteristics according to the specific needs of each application. However, challenges include environmental impacts associated with the use of strong acids and chlorinated agents, which generate potentially harmful residues, requiring proper treatment to minimize contamination. Another challenge is the high energy and time consumption, especially in relation to thermal and chemical processes, which can increase operational costs. Finally, it is crucial to balance the technical efficiency of pretreatments with the need to mitigate environmental impacts, reinforcing the importance of balancing technical efficiency and environmental impact in the development of sustainable materials.

Although each pretreatment technique has different yields, advantages, and limitations, this study aims to explore the potential of *Eucalyptus* spp. bark for film production, applying chemical and physical pretreatments to optimize the extraction of lignocellulosic biomass constituents and improve the properties of the films. The uniqueness of this research lies in the combination of chemical and physical techniques without the addition of additives, such as crosslinkers, plasticizers, or stabilizers, for film formation, expanding its relevance in the literature.

This study significantly contributes to the valorization of agro-industrial waste, such as *Eucalyptus* spp. bark, through the implementation of sustainable practices aligned with the principles of the circular economy. The transformation of this material into biodegradable films through chemical and physical pretreatments demonstrates an innovative and efficient approach that combines advanced technologies with environmental responsibility.

Therefore, this study directly contributes to the Sustainable Development Goals (SDGs), especially SDG 12 (responsible consumption and production), by promoting circular economy practices and waste reduction, using *Eucalyptus* spp. bark to produce renewable materials. Moreover, by applying technologies that enhance the lignocellulosic structure, the work supports SDG 9 (industry, innovation, and infrastructure), developing biodegradable alternatives to replace conventional polymers. The study also supports SDG 13 (climate action) by reducing human dependence on non-renewable materials and mitigating environmental impacts, such as carbon emissions and plastic pollution [27]. Thus, this work demonstrates how scientific and technological advancements can align technical efficiency with global sustainability goals, contributing to a more responsible and ecological future.

2. Materials and Methods

2.1. Material

The raw material used was woody biomass, more specifically tree bark of the genus *Eucalyptus* spp., provided by the company CMPC (Companhia Manufacturera de Papeles y Cartones, Pelotas, Brazil), located in the port of the city of Pelotas-RS, Brazil. The reagents used in this study were: sulfuric acid (H_2SO_4 , technical grade 98%, Labsynth, Diadema, Brazil), sodium hydroxide (NaOH , technical grade 98%, Dinâmica Química Contemporânea LTDA, Indaiatuba, Brazil), and sodium hypochlorite (NaClO , technical grade 6%, Dinâmica, Indaiatuba, Brazil).

2.2. Material Preparation

The *Eucalyptus* spp. bark was previously conditioned in an oven with air circulation at 60 °C for 24 h and was then manually separated and ground in a knife mill (MARCONI, MA 340, Piracicaba, Brazil). Subsequently, the raw material was sieved to obtain standardized particles with a granulometry of 60 mesh [28].

2.3. Chemical Pretreatments

The raw material was subjected to different chemical pretreatments, with the aim of separating the constituents such as cellulose, hemicellulose, lignin, and others (Figure 1). The acid pretreatment was based on the methodology of Acosta et al. (2022) [29]. A total of 30 g of raw material was added to a glass bottle with a lid containing 2% H_2SO_4 , ratio of 1:10 (w/v). The system was autoclaved at 121 °C and 0.101 Pa for 1 h. After autoclaving, the solution was vacuum filtered and washed with hot water until it reached a neutral pH, followed by drying in an oven at 50 °C for 24 h. An alkaline pretreatment with 7% NaOH was performed under identical conditions but for a duration of 30 min based on the methodology described by Alvira et al. (2010) [30].

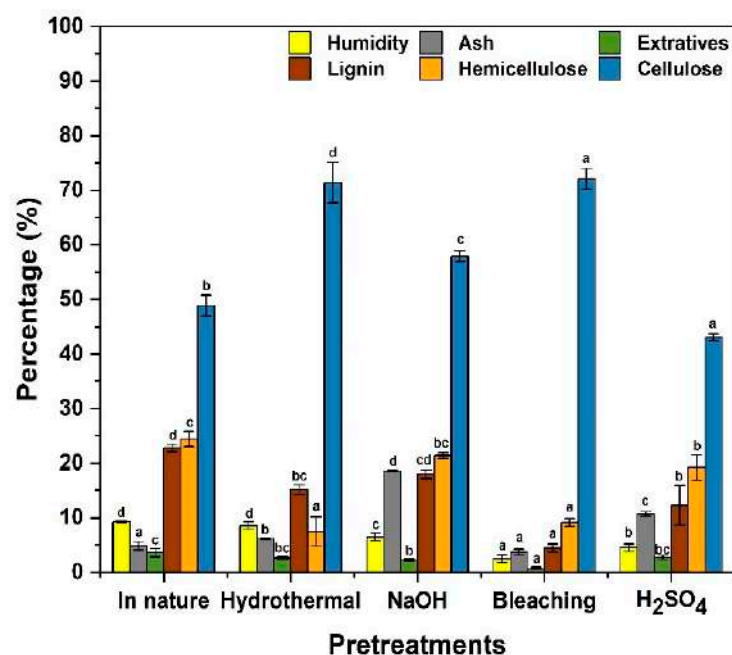


Figure 1. Mean values and standard deviations of the chemical constituents of the different analyzed samples of *Eucalyptus* spp. bark. The same letters above the values indicate non-significant statistical differences according to Fisher's LSD test at a significance level of 5%.

The hydrothermal pretreatment was based on Aridi et al. (2021) [31]. A total of 30 g of raw material was mixed with distilled water at a ratio of 1:10 (*w/v*) in a sealed glass jar. The mixture was then autoclaved at 121 °C and 0.101 Pa for 30 min. Then, the sample was mechanically mixed at a speed of 3600 rpm, performing the process three times for 10 min, with the function of flexibilization and defibrillation of the particles. Subsequently, it was vacuum filtered and washed with hot water until it reached a neutral pH, followed by drying in an oven at 50 °C for 24 h.

The bleaching pretreatment occurred in two stages. The first stage involved delignification as described in the alkaline pretreatment but using 120 g of raw material. The second stage was based on the methodology described by Asadieraghi et al. (2014) [32]. For this, a 2% NaClO solution was added to the sample, in a proportion of 1:10 (*w/v*), for 20 h at room temperature. Then, it was vacuum filtered and washed with hot water until it reached a neutral pH before being placed in an oven at 50 °C for 24 h.

2.4. Physical Treatment

A total of 20 g of samples from each chemical pretreatment was processed in a supermass colloid mill (Masuko Sangyo, Kawaguchi-city, Japan) at 1500 rpm, in multiple passes, with the addition of distilled water until a homogeneous gel was obtained. The final concentration was adjusted to 2% by weight of each pretreatment, according to the methodology described by Acosta et al. (2022) [29].

2.5. Film Production

The films were obtained following a methodology based on Acosta et al. (2022) [29]. A total of 3.5 mL of gel, previously obtained in the physical treatment, was used and diluted in 4 mL of distilled water. The resulting solution was submitted to a filtration system (kitassato, Büchner filter, and nylon filter membrane with a diameter of 47 mm and a porosity of 0.22 µm) connected to a vacuum pump. The films formed on the nylon membrane were stored in a desiccator until the water completely evaporated and the films were formed.

2.6. Characterization Techniques

2.6.1. Chemical Analysis

A chemical analysis was performed according to TAPPI T 222 om-11 standards [33] using powdered samples of lignocellulosic biomass after chemical pretreatments. The following determinations were made: ethanol–toluene extractive content, Klason lignin content, cellulose content, holocellulose (remaining mass up to 100%), moisture content, and ash content to quantify inorganic materials. The results, presented as the mean $\pm$ SD, were analyzed with ANOVA and Fisher's LSD tests to identify significant differences, using a significance level of 5% to compare the means between treatments and the control.

2.6.2. Morphological Analysis

Morphological analyses were performed using a scanning electron microscope (SEM, model JEOL JSM-6610LV, Tokyo, Japan), operating with a beam current of 1 pA and a voltage of 15 kV. Images were obtained at magnifications of 500 $\times$ and 1000 $\times$, allowing detailed observation of the particle surface and providing information on the morphology and structure of the samples at the microscopic level. For preparation, the films were fixed to aluminum sample holders with carbon adhesive tape, according to a methodology based on the study by Ribeiro et al. (2023) [34].

2.6.3. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The films were analyzed using a Fourier transform attenuated total reflection infrared (FTIR) spectrometer (Shimadzu Prestige-21, Kyoto, Japan). The analyses were performed with 90 transmittance scans in the range of 600 cm^{-1} to 4000 cm^{-1} , with a spectral resolution of 4 cm^{-1} , in accordance with the guidelines of ASTM E1252-13 [35] for infrared spectroscopy. For each test, the equipment lamp was aligned, and the background spectra were collected. This approach allowed us to identify the main functional groups present in the samples.

2.6.4. Thermal Analysis

The thermal stability of the samples was evaluated by thermogravimetric analysis (TGA) using a Shimadzu DTG-60 thermal analyzer (Kyoto, Japan), following the ASTM E1131-08 [36] standard for determining the thermal properties of solid materials. The samples were heated from 28 $^{\circ}\text{C}$ to 800 $^{\circ}\text{C}$, with a heating rate of 10 $^{\circ}\text{C}/\text{min}$, under an inert nitrogen (N_2) atmosphere at a flow rate of 50 mL/min. The mass loss and mass loss as a function of temperature (dw/dt) were determined, allowing for the accurate characterization of the thermal concentration and thermal stability of the films.

2.6.5. Wettability Analysis

The contact angle measurement is a standard method for evaluating the wettability and surface properties of materials. The films were placed on a glass slide and positioned in an optical tensometer (Theta Lite; TL100, Stockholm, Sweden) controlled by the OneAttension software. A microsyringe was used to deposit a drop of distilled water on the surface of the films, and the image of the drop was recorded using the goniometer camera immediately after contact. The analysis software was used to measure the contact angle between the water drop and the surface of the films for 60 s.

2.6.6. Tensile Strength Analysis

The films produced were mechanically analyzed in a universal texturometer LY-TX-700 (Lamy Rheology, Champagne-au-Mont-d'Or, France) with a 10 N force sensor. The tensile test was performed following the parameters described by ASTM D882-18 [37], adjusted to a speed of 12 mm/min. The data obtained for maximum stress and modulus of elasticity

were subjected to normality and variance analyses, with subsequent Fisher least significant difference (LSD) analysis to detect significant differences between the values found. All analyses were conducted at a significance level of 5%.

2.6.7. Transmittance Analysis

To characterize the optical properties of the obtained films, transmittance spectroscopy analyses were performed in the UV–Vis region. The transmittance spectra were recorded using an UV-Vis spectrophotometer (Shimadzu, model UV-2600, Kyoto, Japan), in the wavelength range of 400 nm to 800 nm, allowing for the evaluation of the interactions between the films and electromagnetic radiation in this spectral region.

2.6.8. Colorimetric Analysis

To determine the colorimetric parameters, the CIELab system (L^* a^* b^*) was used using the following coordinates: luminosity (L^*), green–red axis (a^*), and blue–yellow axis (b^*). A CR-400 colorimeter (Konica Minolta, Tokyo, Japan), with an observation angle of 10° calibrated with the porcelain calibrator and configured using a D65 light, was used to determine the coloration of the films. This analysis was performed in triplicates.

The colorimetric parameters were analyzed: (i) L^* , the closer to 100, the lighter the color and the closer to 0, the darker the color, (ii) a^* , green–red coordinate, negative markings indicate green colors, positive markings indicate red colors, and (iii) b^* , blue–yellow coordinate, negative markings indicate blue colors, positive markings indicate yellow colors. For the analysis of color changes (ΔE), Equation (1) was used:

$$\Delta E = \sqrt{(\Delta L^2 + \Delta a^2 + \Delta b^2)} \quad (1)$$

where ΔE is the variation of all colors, ΔL is the variation of lightness, Δa is the variation of the red–green coordinate, and Δb is the variation of the blue–yellow coordinate. The results, presented as the mean $\pm$ SD, were analyzed through ANOVA and Fisher's LSD tests to identify significant differences, using a significance level of 5% to compare the means between treatments.

3. Results and Discussion

3.1. Chemical Analysis

Figure 1 presents the results of the mean values and standard deviations of the chemical characterization of the moisture, ash, extractive, lignin, hemicellulose, and cellulose content of the samples studied after each pretreatment, in addition to the in natura material from the bark of *Eucalyptus* spp.

The contents of the in natura form were found to consist of 49% cellulose, 24% hemicellulose, 23% lignin, 3% extractives, 4% ash, and 9% moisture. These results are consistent with the values found in lignocellulosic materials, such as eucalyptus residues, which have structures rich in plant fibers. The studies by Fernandes et al. (2022) and Souza et al. (2021) [10,13] reveal similar compositions, with approximately 50–60% cellulose, 20–30% hemicellulose, 20–30% lignin, 2–5% extractives, and 4–7% ash. These components are responsible for the rigidity and resistance of the biomass, which can be used in several applications.

The hydrothermal pretreatment resulted in 71% cellulose, 7% hemicellulose, and 15% lignin. The extractive and moisture contents were 2% and 8%, respectively, while the ash content was 6%. As observed by Mosier et al. (2005) [38], hydrolysis causes the partial depolymerization of hemicellulose and lignin, facilitating the release of cellulose. These findings were corroborated by Alvira et al. (2010) [30], who emphasize that hydrolysis can be performed on the entire biomass, allowing for a greater recovery of cellulose.

Furthermore, the hydrothermal pretreatment does not require specific reagents, using only water to neutralize the hemicellulose present. Thus, it promotes the formation of non-toxic acetyl groups and reduces the presence of inhibitory substances, characterizing itself as an ecological and sustainable process [39,40].

The results found for the NaOH pretreatment reveal a cellulose content of 57%, a hemicellulose content of 21%, and a lignin content of 18%. This confirms the effects of the alkaline treatment, which breaks the bonds between the lignin and the hemicellulose, in addition to removing phenolic compounds. According to Sun and Cheng (2002) [41], the use of NaOH is effective at degrading the lignocellulosic matrix, facilitating the total or partial removal of lignin and hemicellulose. Studies also state that NaOH can increase the cellulose content in the lignocellulosic biomass by up to 60%, aligning with the results of this study [42].

It was observed that the extractive and moisture contents were relatively low, 2% and 6%, respectively; however, the ash, which presented a value of 18%, increased as a result of the addition of salts during the treatment. Alkaline solutions, such as NaOH, are widely used in the extraction of cellulose for composites, as they promote the structural desquamation of the fibers, especially by removing hemicellulose and lignin. This process favors defibrillation, exposing the hydroxyl groups on the surface of the fibers and forming active sites for interaction with the polymer matrix. As a result, adhesion is improved, since a larger surface area of the fibers allows interactions, such as hydrogen and covalent bonds, improving the mechanical properties of the composite.

After the pretreatment by bleaching, the cellulose content was 72%, the hemicellulose content was 9%, the lignin content was 4%, the extractive content was 0.7%, the moisture content was 2%, and the ash content was 3%. According to the study by Aridi et al. (2021) [31], NaClO is one of the most effective oxidizing agents at removing lignin and hemicellulose, increasing the cellulose content. This process removes unwanted compounds, such as lignin and other components present in the pulp, which can impart color and affect the quality of paper production [43].

In the H₂SO₄ pretreatment, there was a small increase in the cellulose content, which was 43%, while the hemicellulose content was degraded to 19% and the lignin content was reduced to 12%. Both moisture content, at 4%, and extractive content, at 3%, remained low, while the ash content increased to 10%. According to Kumar et al. (2009) [44], acid hydrolysis with H₂SO₄ preferentially degrades hemicellulose, generating soluble components that are removed during washing, but it can also partially degrade cellulose, as observed in this study. Taherzadeh and Karimi (2007) [45] also highlight that H₂SO₄ is widely used for hemicellulose degradation, although cellulose loss is a disadvantage in acidic conditions. The cellulose obtained from this process undergoes acid hydrolysis mainly in the amorphous regions, preserving the crystalline regions which can be beneficial for specific applications, including reinforcement in composites and packaging [46].

By comparing the pretreatments, it can be concluded that NaClO showed the best results with respect to increasing cellulose content, followed by hydrothermal and alkaline treatments with NaOH, while the treatment with H₂SO₄ was the least effective. These findings agree with several studies that demonstrate the significant influence of pretreatments on the chemical composition of the lignocellulosic biomass. Variations in ash, extractive, and moisture contents reflect the conditions of each process and their impact on the final structure of the biomass, being essential for selecting the most appropriate treatment for specific applications.

3.2. Morphological Analysis

The SEM images, presented in Figure 2, show changes in the structure of the fibers in the film matrix, allowing a detailed evaluation of the changes that occurred.

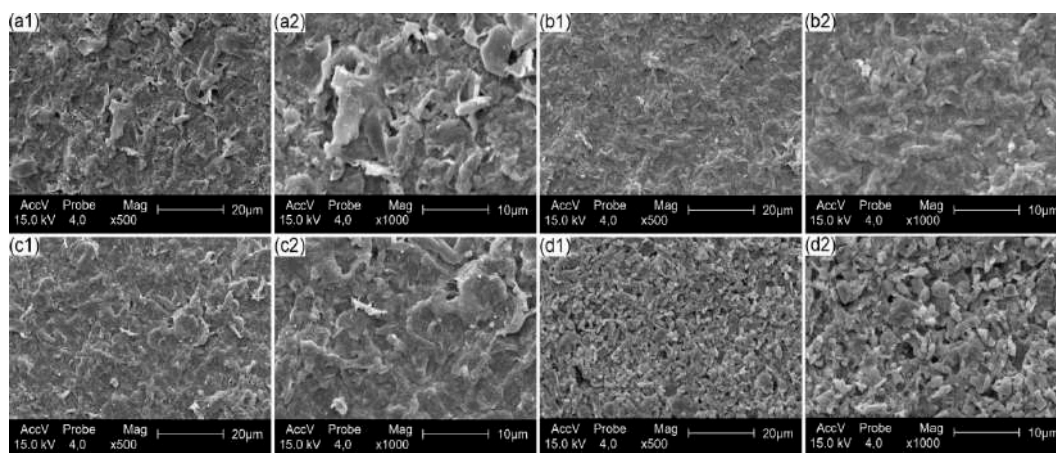


Figure 2. Micrographs at (a1,b1,c1,d1) 500× and (a2,b2,c2,d2) 1000× of the biomass films pretreated as follows: (a1,a2) hydrothermal, (b1,b2) NaOH, (c1,c2) bleaching, and (d1,d2) H₂SO₄.

In the biomass, lignin acts as a ‘binding agent’ between the cellulose and hemicellulose chains, conferring rigidity and resistance to the biomass. The hemicellulose, on the other hand, is intrinsically more of a ‘filling agent’. The presence or absence of these materials influence the morphological properties of the films.

The films obtained from the hydrothermally pretreated biomass in Figure 2(a1,a2) presented an irregular surface. In contrast, the films from the biomass pretreated with NaOH in Figure 2(b1,b2) revealed a more uniform and compact surface. These results differ from the studies by Babu et al. (2022), Khathirselvan et al. (2019), and Jiang et al. (2019) [47–49]. The studies by Babu et al. (2022) and Khathirselvam et al. (2019) [47,48] indicate that an alkaline pretreatment generates more irregular surfaces in the fibers and is potentially applicable to the reinforcement of polymeric matrices. Jiang et al. (2019) [49], when analyzing films with different lignin contents, found that the film with the highest lignin content presented a denser and more compact surface.

As reported in Section 3.1., alkaline pretreatments are effective at destructuring the lignocellulosic matrix, facilitating the removal of lignin and hemicellulose. Although NaOH does not completely remove lignin and hemicellulose [50], the residual amount of these compounds present between the voids of the fibers, in addition to the roughness of the cellulose fibers caused by this pretreatment followed by a physical treatment, suggests a greater exposure of the hydroxyl groups (–OH) in its structure, which favors cohesion between adjacent cellulose fibers, resulting in a more compact film and a smoother surface appearance, in contrast to the micrograph obtained following the hydrothermal treatment. From Figure 2(c1,c2), it can be seen that the bleaching process resulted in more fragmented fibers compared to the alkaline pretreatment. This pretreatment removed most of the biomass constituents, leaving the cellulose more evident.

Alternatively, films derived from biomass pretreated with H₂SO₄ (Figure 2(d1,d2)) presented micrographs with smaller particle sizes, with a more irregular surface distribution and the presence of pores on the surface of the films, resembling the results of Ban et al. (2022) [51] from biomass pretreated with sulfuric acid for biochar production. Wang et al. (2020) [52] explain that the cellulose resulting from acid hydrolysis makes the amorphous regions of these fibers more susceptible to chemical reactions with strong acids, due to the natural disorganization of the molecules in this region. This facilitates the accessibility of

acids and, consequently, the hydrolysis of the cellulose chains present in these regions, in contrast to the crystalline regions which are insoluble in these products.

Additionally, acid hydrolysis also modifies the structure of these crystals. H_2SO_4 reacts with the hydroxyl groups on the surface of these cellulose crystals through an esterification process, allowing the grafting of anionic sulfate ester groups [52]. Lin and Dufresne (2014) [53] report that these sulfate groups are randomly distributed on the surface of cellulose nanoparticles, and these negatively charged sulfate ester groups induce the formation of a negative electrostatic layer and promote their dispersion in solvents, resulting in electrostatic repulsion between individual nanoparticles.

By combining these reports, from a morphological point of view, it can be concluded that H_2SO_4 selectively hydrolyzes the less crystalline parts of the cellulose fibers, leaving the crystalline regions intact, the latter being represented by particles. In this way, these particles are modified by the insertion of sulfate groups obtained after the pretreatment and thus acquire electrostatic repulsion, a phenomenon which suggests the formation of pores on the surface of the films.

In summary, the controlled presence of lignin and hemicellulose, the exposure of the hydroxyl groups of the cellulose fibers, and the interaction between these constituents can influence the morphology of the films obtained through different pretreatments of eucalyptus bark biomass, possibly affecting the physical, chemical, and colorimetric properties. These topics are discussed in more detail later.

3.3. FTIR Analysis

Figure 3 presents the normalized FTIR spectra of the films. The analysis allowed for the identification of the changes in the functional bonds and chemical groups present, providing interesting information about the structural transformations resulting from the different biomass pretreatments applied.

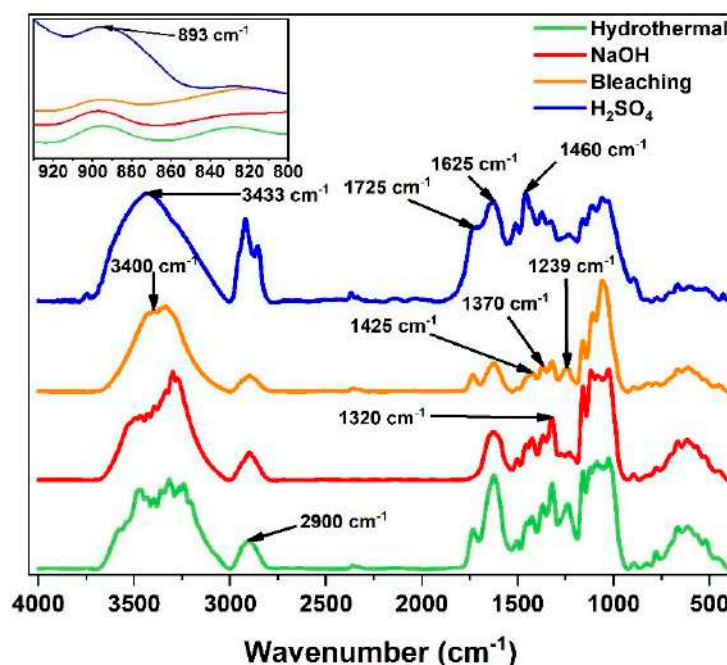


Figure 3. FTIR spectra of the films from the pretreated biomass.

The characteristic bands of OH ($3500\text{--}3000\text{ cm}^{-1}$), C=O ($1870\text{--}1540\text{ cm}^{-1}$), C-H (2900 cm^{-1}), C=C ($1700\text{--}1400\text{ cm}^{-1}$), C-O-C ($1500\text{--}1000\text{ cm}^{-1}$), and C-H ($900\text{--}500\text{ cm}^{-1}$) are associated with lignin, cellulose, and hemicellulose [54–56], explained in more detail in Table 1.

Table 1. FTIR spectral range of cellulose, hemicellulose, and lignin.

Spectral Range (cm ^{−1})	Vibration	Functional Group	Chemical Compound	Reference
3500–3000	O–H stretching	Hydroxyls	Cellulose, hemicellulose, lignin	[54,55,57–59]
1870–1540	C=O stretching	Carbonyls	Hemicellulose	[55,57,59]
2900	C–H stretching	Aliphatic C–H	Cellulose, hemicellulose, lignin	[54,55,57–59]
1700–1400	C=C stretching	Aromatic ring (C=C)	Lignin	[55,57,59]
1500–1000	C–O–C stretching	C–O–C (glucose/ester)	Cellulose, hemicellulose, lignin	[54,55,57–59]
900–500	C–H stretching	C–H in aromatic rings	Lignin	[54,55,59]

The alkaline pretreatment, compared to the hydrothermal pretreatment, for example, resulted in a more intense band in the region of 3600–3000 cm^{−1}, a phenomenon which aligns with the study by Qi et al. (2023) [60] on the surface properties for white oak and poplar wood, reflecting the greater exposure of the hydroxyl groups which may be due to the removal of lignin and hemicellulose, as reported in Section 3.2. Furthermore, the decrease in the bands at 1730 cm^{−1}, 1625 cm^{−1}, and 1239 cm^{−1} suggests a significant removal of lignin and hemicellulose, contributing to the structural alteration of plant fibers [48] which is consistent with the findings of Ajouguim et al. (2019) [61] for the plant *Stipatenacisima* L. Additionally, Poulouse et al. (2022) [50] report that alkaline pretreatments partially remove lignin, waxes, hemicellulose, and pectin that surround cellulose in cell walls.

The chromophore groups present in the lignin structure, such as quinones, for example, which can be conjugated with C=C bonds and C=O functional groups, play an essential role in light absorption, directly influencing the optical properties and color of the films, since they are responsible for darker tones [62,63]. Pretreatment with NaOH, combined with a physical treatment, in addition to modifying the cellulose structure, was able to reduce the intensity of aromatic bands such as C=C and C=O, a phenomenon which may have caused the rupture of the bonds, leading to the partial discoloration of the lignin which can cause an increase in the luminosity (L*) of the films, as discussed in Sections 3.7 and 3.8 of this study.

In the film obtained from the biomass bleaching pretreatment, the characteristic band at 1625 cm^{−1} also showed a reduction in its intensity compared to that of the films obtained from the hydrothermal and alkaline pretreatments. Sayakulu and Soloi (2022) [64] found similar characteristics when analyzing the effect of different concentrations of NaOH (4–13%) on the cellulose yield through the pretreatment of empty oil palm bunches followed by the bleaching process with 1.7% sodium chlorite (NaClO) solutions. They observed that the frequency of the aromatic C=C group of the lignin (~1600–1590 cm^{−1}) was reduced after the alkaline treatment and completely absent after bleaching.

The acid pretreatment showed more intense bands, mainly around 3500 cm^{−1}, 2900 cm^{−1}, 1625 cm^{−1}, and 1460 cm^{−1}. Poulouse et al. (2022) [50] report that acid hydrolysis, in addition to removing lignin and hemicellulose, can introduce sulfate groups on the surface of cellulosic materials, as well as producing simpler sugars and/or altering the cellulose structure, phenomena which may justify the broadening of the bands.

The crystallinity of the films was evaluated based on the calculation of the ratio of the areas of the cellulose crystalline bands (around 1370 cm^{−1}, 1425 cm^{−1}, and 2900 cm^{−1}) to the total area of the spectrum, as shown in Equation (2) [65]. These areas were estimated from the integration of the FTIR spectra using the Origin software (version 2018, 95E).

$$CI(\%) = \frac{\text{Crystalline region spectrum area}}{\text{Total region spectrum area}} \times 100 \quad (2)$$

Therefore, the total spectrum crystallinity index (CI) assumed values of 8.15%, 7.01%, 7.63%, and 10.80% for the hydrothermal, alkaline, acid, and bleached pretreatments, respectively. The bleaching pretreatment promoted the highest crystallinity index owing to the

removal of fewer crystalline constituents, such as lignin and hemicellulose. The chemical and physical pretreatments had a direct impact on the crystallinity index and, consequently, on the optical properties of the films. More crystalline structures tend to have a greater density and molecular packing, phenomena which can result in greater light absorption and, thus, lower transmittance.

3.4. Thermogravimetric Analysis

Based on the data in Figure 4a for the film formed from the hydrothermally pretreated biomass, multiple stages of decomposition can be analyzed. The first stage, which presented a mass loss of 6.11%, occurred at relatively low temperatures in the range of 104.85 °C to 129.63 °C and was associated with the evaporation of residual water or the release of light volatile compounds. This observation is consistent with previous studies reporting the volatilization of light compounds and the removal of moisture in thermally treated lignocellulosic materials [66].

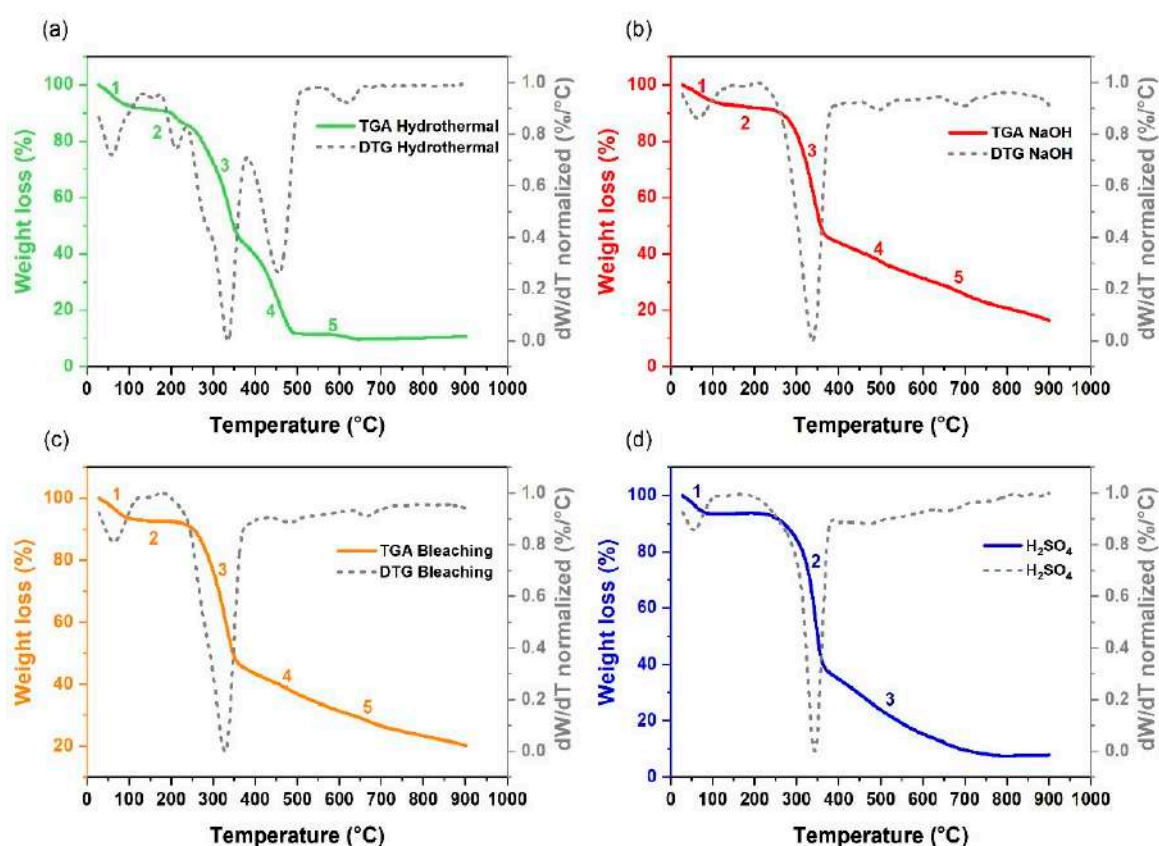


Figure 4. TGA analysis for films obtained from biomass subjected to different pretreatments: (a) hydrothermal, (b) NaOH, (c) NaClO, and (d) H₂SO₄.

The second stage, characterized by a mass loss of 5.47% between 198.15 °C and 219.04 °C, was related to the initial decomposition of light organic components, such as hemicelluloses. The presence of two subsequent stages, i.e., third and fourth, with significant mass losses of 41.14% (302.38 °C to 351.64 °C) and 31.11% (429.56 °C to 477.02 °C), respectively, was attributed to the thermal decomposition of cellulose and more resistant components, such as lignin. This behavior has been widely documented in studies on the thermal decomposition of biomaterials [67]. The Tonset and Tpeak for the main decomposition stages can be found in Table 2.

Table 2. Tonset and Tpeak values obtained for the main stage of thermal decomposition of the films analyzed by TGA.

Films Obtained by Pretreatment	Main Stage		
	Tonset (°C)	Tpeak (°C)	Mass Loss (%)
Hydrothermal	302.38	351.64	41.14
NaOH	300.53	361.24	50.11
NaClO	281.70	350.48	50.44
H ₂ SO ₄	311.65	357.42	64.54

The last, i.e., fifth, stage, which occurred between 593.89 °C and 635.46 °C, presented a small mass loss of 1.68%, possibly associated with the decomposition of carbonaceous residues or the oxidation of inorganic materials present in the film. These results suggest that the film derived from the lignocellulosic material subjected to the hydrothermal process has a moderate thermal stability up to 219.04 °C, which may be adequate for some applications, but may limit the use in high-temperature environments, as indicated by other authors when evaluating similar materials [68].

Figure 4b shows the TGA for the film resulting from biomass pretreated with NaOH. This chemical treatment, known to remove hemicelluloses and other impurities, resulted in a matrix rich in cellulose and lignin. Two main significant stages were observed. The first, occurring between 300.53 °C and 361.24 °C and characterized by a mass loss of 50.11%, indicates the degradation of a relatively pure matrix of cellulose and hemicellulose, possibly due to the simplification of the biomass structure by the treatment. The literature supports this observation, showing that the alkaline treatment promotes the removal of hemicelluloses and the exposure of cellulose, resulting in a thermal decomposition range of around 300 °C [41].

The second stage, occurring between 697.40 °C and 702.34 °C and characterized by a mass loss of 14.96%, corresponds to the decomposition of lignin or carbonaceous residues modified by NaOH, making them more resistant and requiring temperatures above 700 °C for decomposition. This behavior was observed by other researchers, who highlight the role of NaOH in modifying the lignocellulosic structure, conferring greater thermal resistance to carbonaceous residues [68]. The film obtained from biomass pretreated with NaOH, therefore, demonstrates greater initial thermal stability, concentrating the decomposition within a higher temperature range which may be desirable in applications that require a polymeric matrix with a lower impurity content.

Figure 4c shows the TGA for the film formed from the bark pretreated with NaClO, also revealing two significant stages: the first stage, with a mass loss of 50.44% between 281.70 °C and 350.48 °C, and the second stage, with a mass loss of 8.20% between 705.20 °C and 710.85 °C. The magnitude of the loss in the first stage indicates that this is the main phase of degradation of the material and decomposition of the main components, such as cellulose and lignin. The pretreatment by bleaching (oxidizing agent) may have weakened the structure of both cellulose and lignin, facilitating the breakdown of these macromolecules and resulting in a large mass loss. NaClO can introduce oxygenated groups into the structure, making it more susceptible to thermal decomposition [57,69].

The second stage probably reflects the decomposition of carbonaceous residues or resistant components that were not completely degraded in the first stage. Compared to the hydrothermal and NaOH treatments, the NaClO treatment resulted in a significant loss of mass at lower temperatures, suggesting a lower thermal stability of the material, as reported in studies using similar treatments [70].

Finally, Figure 4d shows the TGA for the film obtained from the biomass pretreated with H₂SO₄. This pretreatment also revealed two main stages of decomposition. The first, with a significant mass loss in the temperature range of 311.65 °C to 357.42 °C, corresponds

to the main decomposition of the polymeric components, such as cellulose and lignin. The high mass loss of 64.54% suggests that most of the structural components of the film are degraded during this stage, in accordance with studies indicating that H_2SO_4 promotes acid hydrolysis, fragmenting the polymer chains [32].

The second main stage of decomposition, with a mass loss of 13.11% between 665.43 °C and 671.15 °C, suggests the presence of carbonaceous residues or components more resistant to decomposition.

It was observed that the films obtained from the biomass subjected to the alkaline and acid pretreatments presented a high amount of carbonaceous residue in relation to the other pretreatments. The literature indicates that strong acids or bases tend to form more complex carbonaceous residues, a phenomenon which may explain the observed thermal resistance [71,72]. These results suggest that the treatment with H_2SO_4 weakened the film structure, facilitating its thermal degradation in comparison to other pretreatments.

The thermogravimetric analysis (TGA) results provide critical insights into the practical applicability of the films in real-world scenarios, particularly in the context of packaging solutions for environments with extreme temperatures. NaOH-treated films, which exhibit an improved thermal stability, are particularly suitable for applications requiring resistance to elevated temperatures. These include packaging for processed foods, ready-to-eat meals, or products subjected to reheating or thermal processes during transportation and storage [73,74].

In contrast, the films treated by bleaching, which demonstrate a lower thermal stability, may be more appropriate for packaging solutions intended for cold storage environments, where thermal demands are lower. Additionally, these films often exhibit good optical clarity, making them ideal for applications where product visibility is crucial, such as in the display of fresh produce or refrigerated goods [75].

The selection of the pretreatment process, and, consequently, the type of film, should not only consider thermal properties, but also account for the specific requirements of the final application, such as mechanical strength and optical clarity. The results presented herein highlight the potential of NaOH-treated films for applications in hot environments, while bleached films offer sustainable solutions for conditions involving reduced temperatures. By tailoring the pretreatment methods to the intended use, these biopolymer-based films can address a range of practical needs, aligning with sustainability goals and expanding the applicability of bio-based materials in diverse packaging industries.

3.5. Wettability Analysis

Figure 5 presents the results of the surface wettability analysis of the films studied over 60 s, allowing for the evaluation of their hydrophilic ($\theta < 90^\circ$) or hydrophobic ($\theta > 90^\circ$) behavior. These contact angle values, used to determine the degree of wettability, are in agreement with the parameters established by [76,77].

The results obtained show significant differences with respect to the hydrophobic and hydrophilic behavior of the different films. The film resulting from the biomass subjected to the hydrothermal pretreatment initially presented a contact angle of $\theta \sim 96^\circ$, indicating a hydrophobic behavior. However, over time, this value decreased, until it reached $\theta \sim 48^\circ$ at 60 s, reflecting an increase in hydrophilicity. This behavior can be attributed to the presence of functional groups exposed on the surface of the film. The hydrothermal pretreatment exposes a greater number of hydroxyl groups, intensifying the interaction with water. These results are in agreement with the observations by Wang and Howard (2017) [78], who reported that thermal pretreatments modify the surface structure of the films, resulting in significant variations in wettability.

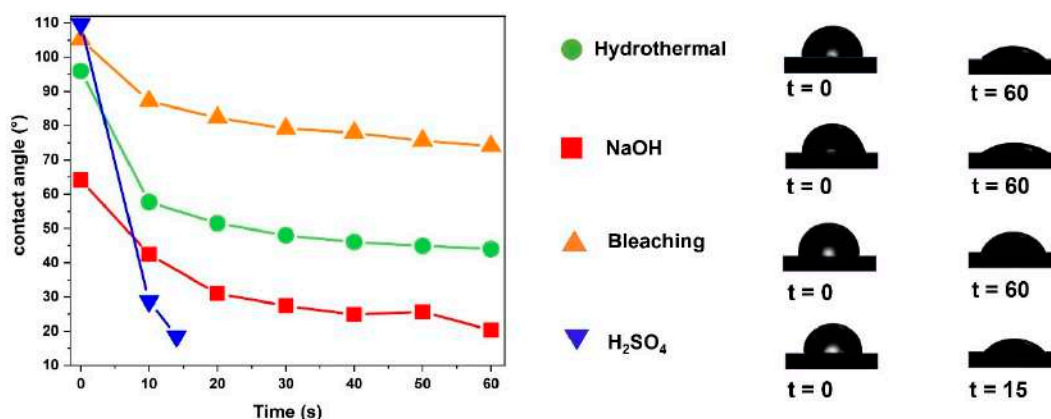


Figure 5. Wettability analysis of films from the pretreated biomass.

For the film originated from the biomass pretreated with NaOH, the initial contact angle was $\theta \sim 64^\circ$, indicating a greater hydrophilicity compared to the film derived from the hydrothermal pretreatment. Water absorption occurred more slowly, resulting in an angle of $\theta \sim 21^\circ$ at 60 s. The action of NaOH promoted the partial removal of surface constituents, exposing a greater number of hydroxyl groups which, in turn, increased the hydrophilicity of the films. These results corroborate those reported by Li et al. (2017) [79].

The films obtained from the biomass that was processed by bleaching exhibited an initial contact angle of approximately $\theta \sim 105^\circ$, presenting a slower water absorption compared to the other films analyzed. After 60 s, the final contact angle was $\theta \sim 85^\circ$, which indicates a smaller variation in wettability and a greater stability of the film surfaces.

According to Rbihi et al. (2020) [80], monolayer ($\theta \sim 52.9^\circ$) and bilayer ($\theta \sim 45.6^\circ$) cellulose films demonstrate a greater tendency toward wettability, while cellulose/TiO₂ films exhibit reduced contact angles ($\theta \sim 10^\circ$ in 5 min). On the other hand, the bleached films showed more pronounced hydrophobic properties, attributed to the efficient removal of lignin and hemicellulose. This removal resulted in greater compaction of the cellulose fibers, conferring greater resistance against water penetration. These characteristics make the bleached films promising for applications requiring stability and low water absorption.

The chemical bleaching process removes non-cellulose components and impurities from the surface of the fibers, resulting in greater exposure of the cellulose fibers. This removal increases the contact area between the fibers, favoring more robust physical and chemical interactions between them. With the cellular structure more exposed, the fibers intertwine more effectively, increasing the density and integrity of the fibrous network. As a result, the surface of the films becomes more resistant to water absorption, since the greater compaction of the fibers reduces moisture permeability, making it difficult for water molecules to penetrate.

The films generated from the biomass pretreated with H₂SO₄ initially exhibited a contact angle of approximately $\theta \sim 110^\circ$, which suggests a more pronounced hydrophobic behavior compared to the other films analyzed. This high contact angle value indicates a low affinity with water in the initial interaction phase. However, over time, a rapid water uptake was observed, with the contact angle decreasing drastically to $\theta \sim 15^\circ$ in just 15 s, evidencing a transition to a highly hydrophilic behavior. This phenomenon can be explained by the hydrolysis promoted by the acid treatment which results in the partial degradation of the surface components of the material and the exposure of hydroxyl groups. As described by Wu et al. (2020) [81], acid hydrolysis breaks the bonds between macromolecules, exposing polar groups such as hydroxyls which significantly increase the interaction of the material with the water molecules.

3.6. Tensile Strength Analysis

Figure 6 shows the data resulting from the tensile strength tests performed on the films. It is important to highlight that the film obtained from the biomass pretreated with H_2SO_4 could not be analyzed, since the acid hydrolysis process caused structural damage to the cellulose chains, resulting in a fragile and brittle film which made it difficult to perform the analysis. According to Huang and Fu (2013) [82], H_2SO_4 , when catalyzing hydrolysis, attacks the glycosidic bonds of the cellulose, converting the cellulose polymers into smaller molecules, such as oligosaccharides and monosaccharides. Thus, this process reduces the length and integrity of the cellulose chains, weakening the overall structure of the material.

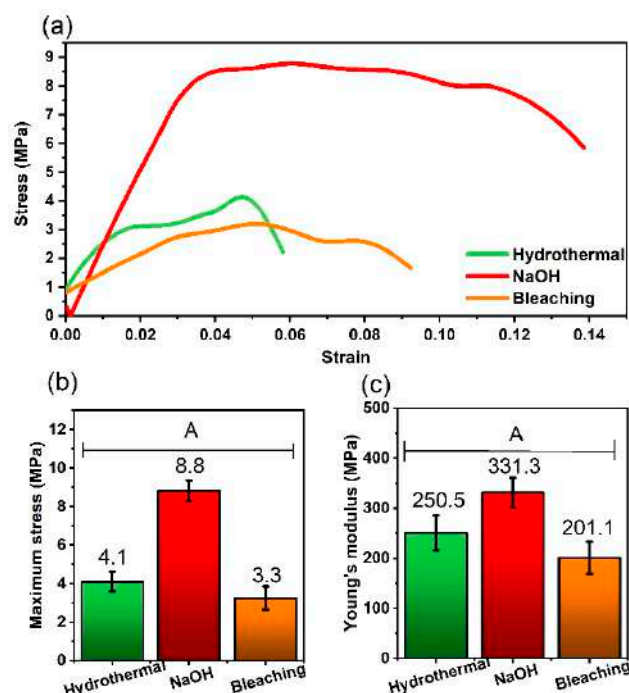


Figure 6. Mechanical properties in terms of (a) stress–strain curves, (b) maximum stress, and (c) Young’s modulus of the films produced from differently pretreated biomass. The same letters above the bar charts indicate non-significant statistical differences according to a Fisher’s LSD test at a significance level of 5%.

As illustrated in Figure 6b, the maximum stresses of the films subjected to the different pretreatments varied as follows: the films resulting from the hydrothermally pretreated biomass presented a maximum stress of 4.1 MPa, with NaOH, they reached 8.8 MPa, while the bleaching resulted in a maximum stress of 3.3 MPa. Although the differences between the treatments were not statistically significant, it can be observed that the film of the bark pretreated with NaOH stood out both in terms of the Young’s modulus (331.3 MPa) (Figure 6c) and in terms of the maximum stress (8.8 MPa), surpassing the films obtained from the other pretreatments.

The removal of lignin and hemicellulose during chemical pretreatments plays a crucial role in improving the mechanical properties of films. Lignin, being a highly branched three-dimensional polymer, contributes to the rigidity and compressive strength of biomass. Its partial or total removal increases the ability of cellulose fibers to interact with each other, creating a more compact and cohesive matrix. Similarly, hemicellulose, which acts as an amorphous polymer around the fibers, limits the formation of interfacial bonds. Its removal allows for a closer positioning of the cellulose fibers, contributing to increased mechanical strength.

The superior performance of the film formed from the biomass pretreated with NaOH can be attributed to its action in the partial depolymerization process of lignin which promotes the breaking of long polymer chains into smaller segments. This phenomenon facilitates the integration of lignin into the cellulose matrix, improving its homogeneous dispersion within the polymer structure. The presence of lignin with shorter and better distributed chains results in a reduction in film porosity, as reported in Section 3.2. Less porous films tend to exhibit better mechanical properties, as they present greater mechanical strength. In addition, the physical treatment performed after the pretreatment with NaOH contributed to an additional reduction in particle size which further contributed to the dispersion and reduction of film porosity. This combination of treatments, both chemical and physical, resulted in the formation of a more cohesive and mechanically stable structure, explaining the increase in tensile strength and the superior performance in terms of Young's modulus (Figure 6c).

Another relevant factor is related to the interaction between the polymer chains of the cellulose. The depolymerization promoted by NaOH exposes free hydroxyl groups (OH) in the cellulose chains, allowing the formation of stronger hydrogen bonds between the chains and contributing to a greater internal cohesion of the material. These additional bonds result in a mechanically resistant matrix.

The results obtained for the films pretreated with NaOH are consistent with the study by Sun and Cheng (2002) [41], who reported a mechanical strength in the range of 8–10 MPa for lignocellulosic films treated with alkaline solutions. This similarity reflects the positive impact of lignin removal and exposure of active functional groups on improving structural cohesion. In contrast, the hydrothermally treated films presented lower values, in line with the results of Mosier et al. (2005) [38], who report reduced strength due to the presence of residual hemicellulose.

In comparative terms, the mechanical properties of the films obtained in this study are as good as those of other biodegradable films reported in the literature. For example, Xia et al. (2021) [24] report a tensile strength of 7 MPa for modified cellulose films, values slightly lower than those obtained with the alkaline pretreatment described here. Furthermore, the observed maximum strength exceeds that of films based on starches or chitosans, which generally present values between 3 MPa and 6 MPa, as reported by Chen et al. (2019) [18].

The differences in mechanical properties can be attributed to the interaction between the type of pretreatment and the resulting structural characteristics. The alkaline pretreatment not only efficiently removes lignin and hemicellulose, but also facilitates a homogeneous distribution of the fibers and the formation of robust intermolecular bonds. In contrast, the pretreatment by bleaching, although effective at removing lignin, results in more fragmented fibers and less exposure of hydroxyl groups, compromising the mechanical performance.

These observations highlight the importance of aligning pretreatments with the specific demands of the end applications, whether they are focused on mechanical strength, flexibility, or biodegradability.

NaOH-treated films, owing to their greater mechanical strength, are particularly suitable for applications where a robust and durable material is required. Examples include packaging for the transport of heavy or sharp products, such as metal tools and utensils, and industrial applications where materials are subjected to significant mechanical stresses. In addition, their high strength makes them ideal for use in protective films that require durability under adverse conditions, such as in logistics processes or prolonged storage.

3.7. Transmittance Analysis

The transmittance of a film is a crucial parameter for evaluating its optical properties, especially with respect to applications such as biodegradable packaging, where transparency can directly influence the functionality and aesthetics of the final product [83]. Films with high transmittance are desirable for applications that require visibility of the contents, while films with low transmittance can be useful as protective light barriers [84].

In this study, the transmittance of the films was evaluated, as illustrated in Figure 7, and the values are presented in Table 3. The transmittance analysis was performed at two specific wavelengths, i.e., 400 nm (at the UV–visible edge) and 633 nm (in the visible range), to evaluate the impact of the pretreatments on the optical properties of the films. It is important to highlight that the analysis of the film obtained from the acid-pretreated biomass could not be performed. This is due to the fact that the film proved to be fragile and brittle, as previously reported.

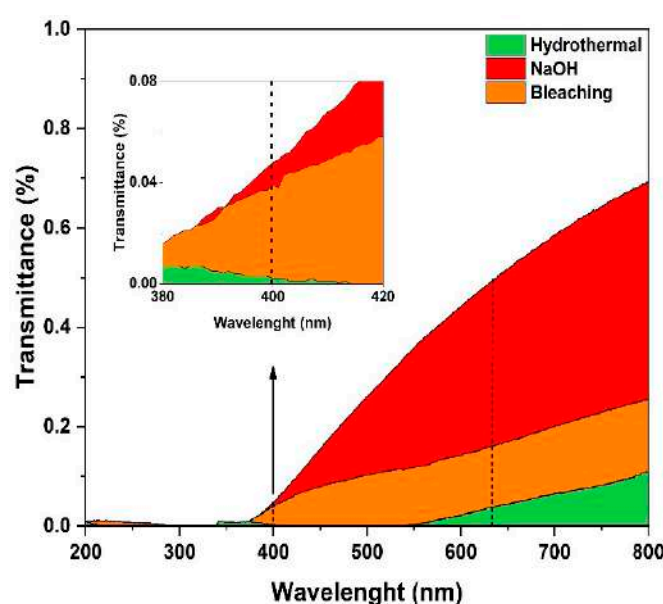


Figure 7. UV–Vis spectra of the films from the pretreated biomass.

Table 3. Transmittance values of the films from the pretreated biomass.

Films Obtained by Pretreatment	T (%) at 400 nm	T (%) at 633 nm
Hydrothermal	0.002	0.038
NaOH	0.048	0.492
Bleaching	0.039	0.160

The films resulting from the pretreated biomass presented significant variations in transmittance values (%T), reflecting the different compositions and structures resulting from these pretreatments.

In general, the films had a high light barrier capacity, exhibiting a relatively low transmittance range of less than 1%. With respect to applications requiring a light barrier, such as light-sensitive food packaging or visual control materials, these films are the most promising owing to their low transmittance values.

The film obtained from the hydrothermally pretreated biomass showed extremely low values of optical transmittance in the wavelength ranges of 400 nm (0.002%) and 633 nm (0.038%). This sharp reduction in transmittance can be attributed to changes in both the morphology and crystallinity of the material. The morphological analysis by SEM in Section 3.2 revealed an irregular and rough surface, which intensifies the scattering and

absorption of light, directly contributing to the decrease in transmittance. Rough surfaces generate multiple points of reflection and refraction of light, reducing the transparency of the film. Another factor to be considered is the crystallinity of the film. Film resulting from hydrothermally pretreated biomass showed a higher crystallinity index (CI%) than the films pretreated with NaOH and bleach, as reported in Section 3.3. Crystallinity affects the optical properties of the material by influencing the degree of ordering of the polymer chains [85]. In contrast, the film obtained from the biomass pretreated with NaOH, which presented a higher transmittance of 0.048% at 400 nm and 0.492% at 633 nm, had a smoother surface and a lower degree of crystallinity, explaining the better optical performance observed.

The film obtained from the biomass pretreated by bleaching presented a transmittance of 0.039% at 400 nm and a transmittance of 0.160% at 633 nm, indicating an optical behavior intermediate between that of the films subjected to hydrothermal and NaOH pretreatments. This behavior may be related to the partial degradation of the cellulose during bleaching, a process that enhances the oxidation of cellulose hydroxyls, altering its crystallinity and increasing light absorption, thus contributing to the greater opacity of the film.

The scattering properties and light absorption of the films developed in this study can be compared with those of materials commonly used as light barriers in packaging, such as synthetic polymers (e.g., opaque polyethylene terephthalate) and metallized polymers. While synthetic polymers do not have additives to reduce transmittance, films derived from hydrothermally treated biomass exhibited effective light barrier abilities with a transmittance of only 0.002% at 400 nm, owing to their high crystallinity index and irregular surface which intensify light absorption and scattering. Likewise, films treated with NaOH, despite presenting lower crystallinity, also demonstrated good efficiency as light barriers, comparable to opaque polymers owing to their structural uniformity and ability to scatter light. Unlike metallized materials, which have high environmental impacts, biomass-based films stand out for their sustainable origin and biodegradability, providing a sustainable alternative with a competitive performance in the context of applications that require light protection.

Thermogravimetric analysis results provide critical insights into the practical applicability of films in real-world scenarios, particularly packaging solutions for extreme temperature environments. NaOH-treated films, which exhibit improved thermal stability, are particularly suitable for applications requiring resistance to elevated temperatures. This includes packaging for processed foods, ready-to-eat meals, or products subjected to reheating or thermal processes during transportation and storage. The improved thermal stability of these films can be attributed to the efficient removal of amorphous components, such as hemicellulose, and to the exposure of the hydroxyl groups which increase the structural cohesion of the material [56,61]. In contrast, bleach-treated films, which demonstrate a lower thermal stability, may be more appropriate for packaging solutions intended for cold storage environments, where thermal demands are lower. Furthermore, these films generally exhibit a superior optical clarity, making them ideal for applications where product visibility is crucial, such as in the display of fresh or refrigerated products [77,78]. The selection of the pretreatment process, and, consequently, the type of film, should not only consider thermal properties, but also the specific requirements of the end application, such as mechanical strength and optical clarity. The results presented here highlight the potential of NaOH-treated films for applications in hot environments, while bleached films offer sustainable solutions for conditions involving reduced temperatures. By tailoring the pretreatment methods to the intended use, these biopolymer-based films can address a variety of practical needs, aligning with sustainability goals and expanding the applicability of bio-based materials across a range of packaging industries.

3.8. Colorimetric Analysis

The chromaticity results are associated with the removal of biomass constituents which occurs because of the different chemical pretreatments applied. This removal directly impacts the optical properties of the films, reflecting significant changes in their color, as shown in Figure 8 for the chromatic parameters L^* , a^* , and b^* .

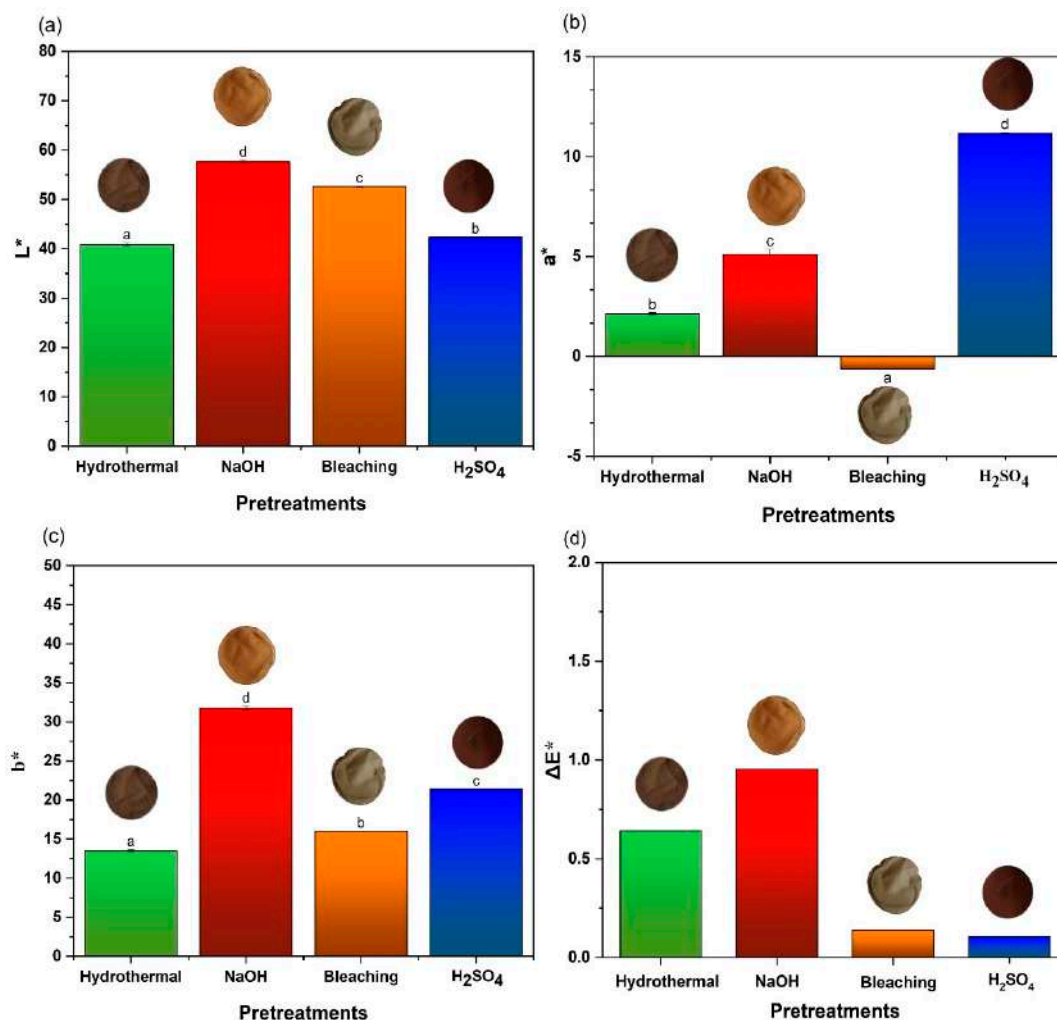


Figure 8. Colorimetry: (a) luminosity (L^*), (b) green–red coordinate (a^*), (c) blue–yellow coordinate (b^*), (d) variation of all colors (ΔE^*). The same letters above the bar charts indicate statistically insignificant differences according to a Fisher’s LSD test at a 5% significance level.

In general, luminosity (L^*) varied significantly across the different pretreatments. The films from the biomass pretreated hydrothermally and with H_2SO_4 presented lower L^* values of 40.89 and 42.34, respectively, indicating a darker coloration. In contrast, the films produced from the biomass subjected to alkaline and bleaching pretreatments exhibited higher luminosity values of 57.65 and 52.57, respectively. The abundance of lignin is a crucial factor for the decrease in the luminosity of the films, since lignin contributes to the darker coloration, usually brown [86].

In the case of the film formed from the hydrothermally pretreated biomass, which presented a significant lignin content of 15%, as reported in Section 3.1, this resulted in low luminosity and a darker appearance. The film resulting from the bark subjected to the alkaline pretreatment, such a bark containing an even higher lignin content of 18%, exhibited a lighter coloration. This discrepancy in luminosity can be attributed to the effect of the alkaline pretreatment, which is capable of removing or modifying the chromophore

compounds present in the lignin which are responsible for light absorption and the dark coloration. NaOH causes the breaking of the chemical bonds in chromophore groups, such as C=O and C=C, resulting in partial discoloration of the lignin and, consequently, in films with higher luminosity.

Thus, although both biomass pretreatments resulted in films containing high amounts of lignin, the difference in the chemical processing explains the significant variation in the color of the resulting films.

The chromaticity of the a^* coordinate (green–red) resulted in films exhibiting reddish tones, except for the film obtained from the biomass subjected to the bleaching pretreatment. This can be explained by the fact that, in such a treatment, lignin is practically eliminated, with the cellulose remaining predominant. In the b^* coordinate (blue–yellow), all films presented a yellowish tone.

4. Conclusions

The study demonstrates that *Eucalyptus* spp. bark, subjected to different chemical and physical pretreatments, is a promising source to produce biodegradable films with varied chemical, thermal, mechanical, and optical properties. The alkaline pretreatment resulted in films with a greater mechanical strength and thermal stability, while the bleaching pretreatment promoted increased crystallinity and lower hydrophilicity. Conversely, the hydrothermal pretreatment influenced the reduction in optical transmittance and the modification of the surface morphology, generating films with a greater light barrier capacity. Each biomass pretreatment conferred specific characteristics to the films, making them interesting for different applications, such as biodegradable packaging and materials with improved optical properties. To improve performance and sustainability, further optimization of the pretreatment conditions—such as adjusting temperature, time, and reagent concentrations—could enhance film properties, including mechanical strength and thermal stability. Additionally, the incorporation of natural fibers or nanoparticles could increase the functionality of the films, providing further advantages in terms of resistance and performance. The development of multilayer films or active coatings could extend their use, not only as food packaging but also for agricultural purposes, such as biodegradable seed coatings or soil moisture control. Thus, this work contributes to the development of sustainable solutions by valorizing agro-industrial waste and promoting the use of biopolymers to replace conventional polymers, in line with the principles of the circular economy. These solutions could significantly reduce plastic waste in the food packaging and agricultural sectors, demonstrating a path toward a more sustainable future.

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