RESEARCH ARTICLE

Applied Polymer WILEY
JOURNAL OF *SCIENCE*

Bio-based multilayer paperboard for sustainable packaging application

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Abstract

Bio-based packaging materials are an emerging environment-friendly alternative to conventional plastic food packaging materials, at least for some applications. The innovation of this work was to develop a sustainable cellulosic packaging material based on chitosan/palmitic acid/activated carbon coating with potential applications for single-use food packaging. The study developed a multilayer paperboard (MPB), evaluating the effects of a paperboard surface coating by chitosan (2.0% w/w), palmitic acid (1.8% w/w), and activated carbon (1.2% w/w) applied in three coating layers. The water vapor transmission rate (WVTR) of coated paperboard was reduced compared to uncoated paperboard, associated with the coating suspension filling of the pores of the cellulosic matrix, the palmitic acid hydrophobic characteristic, and the nonpolar nature of activated carbon (acted by repelling the vapor molecules of water). A grease resistance of Kit solution 11 of MPB was observed. The stiffness and elongation capacity increased, indicating the rigidity and flexibility of the MPB. The deposition of palmitic acid and activated carbon influenced the roughness increase. The biodegradability in the soil after 188 days of MPB was 55.01%, and the control (uncoated paperboard) was 69.38%. The coating did not impact the degradation behavior of cellulose.

KEYWORDS

activated carbon, biodegradable, chitosan, coating, packaging, palmitic acid

1 | INTRODUCTION

The environmental challenge in the food packaging sector is to reduce the use of non-renewable and non-biodegradable resources materials.[1] Petroleum-based plastics (synthetic polymers) are materials commonly used in end-consumer products.[2] Around 95% of plastic packaging is discarded after a short first-use cycle.[3] Single-use plastic (SUP) food packaging significantly contributes to the solid waste environmental problem.[4] Notably, after the COVID-19 pandemics,[5] the consumption of packaged foods has increased[6] with the improvement of online food delivery platforms, increasing the plastic waste from SUP.[7] Plastic pollution produces micro and nano plastics, directly impacting human health, marine debris on oceans, and wildlife with unknown adverse effects.[8,9]

Multilayer packaging combines different materials, improving the functional properties, such as barriers and mechanical and thermal resistance.[10] However, the fragmentation and complexity of some multilayer packaging

materials show a low recyclability rate due to technical, economic, social, and legal issues.[4,11]

Sustainable packaging alternatives are increasing in the food packaging industry. Paper is a cellulosic packaging material characterized by thermal resistance, biodegradability, and renewability.[12] Cellulosic paper is considered a high-value and environmentally friendly material.[13] However, cellulosic paper materials have limitations, such as interfacial adhesion, moisture sensitivity,[14] and low barrier properties (gases, aromas).[15] Cellulosic paper properties can be improved by associating it with other materials, such as synthetic polymers (polyethylene, polyethylene terephthalate, etc.), aluminum, waxes, and other materials. Some studies have pointed out the possibility of improving the barrier properties of paper using coatings based on natural polymers.[16–19]

Chitosan is a natural polymer with low toxicity, biodegradability, and antimicrobial activity. It is derived from the deacetylation of chitin. It comprises a stiff, inelastic, and nitrogenous polysaccharide formed by alternating units of $(1 \rightarrow 4)$ N-acetyl glucosamine and glucosamine linked.[20] Chitosan presents hydrophilic nature, so it is interesting to incorporate lipids, such as fatty acids and waxes, to form chitosan-based films and coatings to improve the resistance and moisture barrier properties.[21] Chitosan coating can act on the oxygen and fats barrier and present antimicrobial action.[18,22–24] Kraft paper sheets coated with palmitic acid-chitosan showed reduced water absorption capacity and air and water vapor permeation compared to uncoated paper.[25]

Active packaging may contain antimicrobial, antioxidant agents, aroma emitters, gas and odor adsorbers, etc.[26] The incorporation of gas control agents directly into the polymeric matrix of the packaging material has shown better consumer acceptance than the use of sachets, a commonly used system.[27] Activated carbon is an efficient and versatile adsorber agent for different gases.[28] It is a low-cost adsorber obtained by the thermal decomposition of carbonaceous products, such as coconut straw and pine wood.[29] Activated carbon has a nonpolar surface, and its adsorption capacity is affected by the polarity and chemical bond strength between its surface and the substance to be adsorbed. Activated carbon can adsorb gases such as oxygen, carbon dioxide, and ethylene.[30]

The present work aimed to develop and characterize a sustainable material based on a paperboard coated with a suspension of chitosan, palmitic acid, and activated carbon, applied in three coating layers and forming a multilayer paperboard (MPB). The proposed material searches to present a sustainable alternative that can be used in SUP 'applications, forming a renewable multilayer packaging system in agreement with the current trends in the packaging segment.

2 | MATERIALS AND METHODS

2.1 | Materials

Chitosan with a deacetylation degree of 82% and an average molar mass of 1.47×10^5 g·mol^{-1} (Polymar, Brazil), palmitic acid (Synth), activated carbon powder (Sigma Aldrich, 31,616), and Duplex paperboard with a grammage of 250 g·m^{-2} purchased in local commerce of the city of São Paulo (Brazil).

2.2 | Chitosan suspension with palmitic acid and activated carbon

The suspension of chitosan containing palmitic acid and activated carbon was prepared as described by Yoshida, Oliveira, and Franco.[21] The chitosan powder (2.0%, w/w) was solubilized in an aqueous acid medium, with acetic acid added stoichiometrically, considering the chitosan mass and degree of acetylation, keeping under magnetic agitation for 60 min. Then, 1.8% (w/w) of palmitic acid and 1.2% (w/w) of activated carbon (based on chitosan mass) were added. The dispersion has been strictly homogenized at 20,000 rpm (UltraTurrax homogenizer, T25, IKA, Germany) for 10 min. The concentrations of chitosan, palmitic acid, and activated carbon were determined based on preliminary studies.[31]

2.3 | Multilayer paperboard coating

The coating of the paperboard sheets methodology was carried out as described by Maciel, Franco, and Yoshida.[32] The paperboard sheets were manually coated with the application of 9 mL of chitosan, palmitic acid, and activated carbon suspension under the surface of the paperboard using an extender of 150 μm (Regmed, Brazil) and dried in a forced convection oven (Marconi MA 035/100, Piracicaba, Brazil) at 150°C for 120 s. Applying dispersion and drying was repeated until three coating layers were formed to obtain the MPB.

2.4 | Multilayer paperboard characterization

2.4.1 | Coating homogeneity: Colorimetric method

MPB and uncoated paperboard samples were cut to size 15 cm × 20 cm. The 0.5% erythrosine dye solution in isopropanol was applied to the coated and uncoated multilayer (Control) paperboard area using cotton wool and tweezers,

covering the entire area. The samples were kept upright and dried in an oven (Marconi, MA 035/100, Piracicaba, Brazil) at 50°C for 1 min. The material was visually analyzed on the opposite side of the coating. The assay was performed in triplicate and followed the methodology adapted from Marcy.[33]

2.4.2 | Thickness

The thickness (μm) of MPB and uncoated paperboard (Control) was performed using a manual digital micrometer (1 μm) (Mitutoyo, MDC-25 M, Japan). The measurements were performed at five different points for each sample, using ten specimens.[34]

2.4.3 | Grammage

MPB and Control samples were cut into 12.5 cm × 12.5 cm, and the mass was determined using an analytical balance (Ohaus, ARC 120, Brazil). The test was performed for ten specimens of each sample, and the result was expressed in $g \cdot m^{-2}$.[35]

2.4.4 | Microstructural analysis: Scanning electron microscopy (SEM)

The MPB and Control microstructural analysis was conducted as described by Reis et al.[25] The samples were covered with gold and evaluated in a scanning electron microscope LEO 440i (LEO Electron Microscopy, Oxford, Cambridge, England) at 15 kV, in the direction of the cross-section with a magnification of 200× and the surface direction with a magnification of 1200×.

2.4.5 | Surface analysis: Atomic force microscopy (AFM)

The topography and surface of coated and uncoated paperboard sheets were evaluated in an atomic force microscope (model Flex, Nanosurf, Sweden). The test was performed in tapping mode and model tip Tap190 (Nanosurf, Sweden). The mean roughness (Ra) and mean square roughness (Rq) of the MPB and Control surfaces were expressed in nm.

2.4.6 | Water absorption capacity (abs) – Cobb test

Ten specimens of each sample (12.5 cm × 12.5 cm) were placed in desiccators containing RH equal to $50 \pm 2\%$

and $25 \pm 2°C$ for 72 h. After the pre-conditioning, each sample was weighed in analytical balance (Ohaus, ARC 120, Brazil). The samples were fixed in Cobb equipment (Regmed, Brazil), and 100 mL of distilled water was placed in contact with the coated surface of the samples delimited by the ring of the apparatus for 120 s. The specimens were removed from the equipment after the test time. Excess water was removed by placing the samples between two sheets of absorbent paper and quickly pressing with a cylindrical roller. Then the samples were immediately weighed. The Abs ($g \cdot m^{-2}$) was determined according to Equation (1).[36]

$$Abs = (M_f - M_i)100 \qquad (1)$$

where M_i (g) is the initial mass of the sample, and M_f (g) is the final mass of the sample. The test followed the methodology ASTM D3285-93.

2.4.7 | Water vapor transmission rate (WVTR)

The test was adapted from the methodology ASTM E96/E96M-10.[37] MPB and Control samples were cut into a disc shape. The discs were placed and fixed on the permeation cells containing silica. The cells were stored in desiccators at relative humidity (RH) equal to $50 \pm 2\%$. The samples remained conditioned for 72 h and were periodically weighed. The WVTR (water $g \cdot d^{-1} \cdot m^{-2}$) was determined according to Equation (2).

$$WVTR = \frac{G}{t \cdot A_e} \qquad (2)$$

where G (g) is the mass gain of the system, t (h) is the storage time of the samples, and A_e (m^2) is the area exposed to mass gain.

2.4.8 | Grease resistance

The test followed that proposed by Ham-Pichavant et al.[23] Kit solutions (1–12) were prepared with different castor oil, toluene, and n-heptane concentrations. A drop of each Kit solution was applied to the paperboard surface for 15 s. The excess solution was removed, and the appearance or not of stains on the back of the paperboard was observed. The highest Kit solution value that did not cause staining on the paperboard sheet was adopted as the grease resistance value.

2.4.9 | Mechanical properties: Tensile strength and elongation break

The mechanical properties, tensile strength (σ_r), and elongation at break (ε_r) were determined according to standard ASTM D828-16e1.[38] The MPB and Control samples were cut to 18 cm $\times$ 1.5 cm and fixed in equipment with a 1 kN load cell (Instron, model 5966-E2, EUA). The distance between the claws was kept at 15 cm, and the test speed was 2 cm·min^{-1}. Each sample was analyzed in the direction of machine direction (MD) and cross-machine direction (CD) of cellulosic fibers. The results were expressed in MPa for σ_r and in % for ε_r.

2.4.10 | Taber stiffness

The Taber stiffness test was performed according to the ASTM D5342-97.[39] The MPB and Control samples were cut using a pneumatic guillotine (Regmed, Brazil) in the dimension of 3.81 cm $\times$ 7.0 cm in the MD and CD directions. The samples were conditioned for 48 h at 23 $\pm$ 1°C e 50 $\pm$ 2% of RH. The test used a rigidity meter RI-5000 (Regmed, Brazil). Ten repetitions were performed for each direction of the cellulosic fibers, and their results were expressed in mNm.

2.4.11 | Thermal analysis: Thermogravimetry (TG), differential thermogravimetry (DTG), and differential scanning calorimetry (DSC)

The TG and DTG analyses were performed in a thermogravimetric analyzer TG/DTG (Shimadzu, DTG-60H, Japan). The samples were placed in a hermetically sealed pan in an inert atmosphere of nitrogen (100 mL·min^{-1}) and heated from 25 to 900°C (10°C·min^{-1}). On the other hand, DSC was performed using a differential scanning calorimeter (Shimadzu, DSC-60, Japan). The samples (2.04–2.71 mg) were heated from 25 to 450°C with a heating rate and atmospheric environment as the TG/DTG analyses.

2.4.12 | Biodegradation

The soil biodegradation test of MPB and uncoated paperboard was adapted from Silva et al.[40] The samples were conditioned for 24 h in an RH environment of 50 $\pm$ 2%. Then, the initial mass of the samples was measured in an analytical balance (Ohaus, ARC 120, Brazil). The coated and uncoated paperboards were buried in a plastic container 10 cm from the surface in vegetable-type soil composed of 50% red and 50% brown soil (São Paulo, SP, Brazil). The mass of soil in each container was approximately 790 g. Soil moisture content was monitored and maintained at around RH = 75 $\pm$ 5%. The test was performed in quintuplicate with periodic gravimetric measurements for 188 days. The final biodegradation of the samples was determined according to Equation (3).

$$B = \left(\frac{m_i - m_f}{m_i}\right)100 \qquad (3)$$

where B (%) is the biodegradation of materials in the analyzed period, m_i (g) is the mass of the samples at the start of the test, and m_f (g) is the sample's mass at the end of the test.

2.5 | Statistical analysis

Results were analyzed using Statistica 10.0 software. The comparative difference between the mean values was evaluated using Student's T-Test with $p < 0.05$.

3 | RESULTS AND DISCUSSION

3.1 | Multilayer paperboard characterization

The solid content of the coating applied on MPB was estimated at 21 g·m^{-2} based on the chitosan, palmitic acid, and activated carbon formulation. The MPB presented visual homogeneity; the coating did not delaminate after continuous and rigorous handling, indicating the coating's adherence to the paperboard surface and the chitosan compatibility with the cellulose paperboard sheet.[41]

The homogeneity of the uncoated paperboard (Control, Figure 1a) and the MPB surface (Figure 1b) was observed. A reduced number of dispersed red points on the opposite coating surface of the MPB was observed compared to the Control, indicating that the suspension coating filled the interfibrillar spaces of the cellulose matrix and deposited on the paperboard surface. Similar results were observed on Kraft paper sheets coated with chitosan incorporated with palmitic acid[25] and in reacetylated chitosan-based coatings applied to the paperboard surface.[42]

The MPB properties, average thickness, grammage, Abs (water absorption capacity- Cobb Test), WVTR, and grease resistance are shown in Table 1.

The thickness and grammage of MPB showed a significant increase of 30% and 14% (Table 1), respectively,

FIGURE 1 Homogeneity surface of paperboard sheets: (a) uncoated (Control) and (b) coated with chitosan, palmitic acid, and activated carbon (MPB). [Color figure can be viewed at wileyonlinelibrary.com]
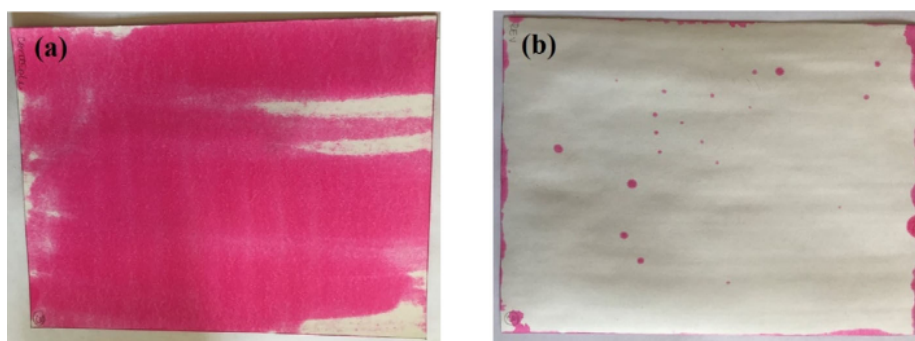
TABLE 1 Average thickness, grammage, water absorption capacity (Abs), water vapor permeability rate (WVTR), and grease resistance of Control (uncoated paper) and multilayer paperboard (MPB).

Property	Control	MPB
Thickness (μm)	337 ± 6^b	439 ± 37^a
Grammage (g·m^{-2})	243 ± 2^b	276 ± 7^a
Abs (g·m^{-2})	38 ± 2^b	74 ± 10^a
WVTR (water g d^{-1}·m^{-2})	168 ± 12^a	160 ± 6^a
Grease resistance (Kit number)	No barrier	11

Note: Different letters on the same line indicate a significant difference ($p < 0.05$) according to Student's T-Test.

compared to Control. The thickness and grammage increase was expected after applying three coating layers, even considering the coating suspension penetration between the pores of the cellulose matrix.

3.2 | Morphological analysis: Scanning electron microscopy (SEM)

The chitosan, palmitic acid, and activated carbon coating penetrated and filled the pores of cellulosic network fibers, forming a film around the cellulosic fibers (Figure 2d). On the surface of the MPB (Figure 2b), it was possible to observe the covering of the paperboard cellulose matrix. The coating suspension was applied in 3 layers, increasing the total solids deposited through the cellulose fiber matrix. The coating adhered to the paperboard surface homogeneous and without delamination, indicating the compatibility between the coating suspension and paperboard. Chitosan coatings filled the paper matrix's pores due to the chitosan film-forming capacity, presenting saturation applied in multiple layers, starting from the third coating layer.[43] The same microstructure was observed in chitosan coatings up to five coating layers,[44] and acetylated cellulose coating in Kraft paper.[45]

3.3 | Surface analysis: Atomic force microscopy (AFM)

MPB showed a significant reduction in Ra (mean roughness) and Rq (mean square roughness) of about 45% compared to Control (Table 2). Figure 3 shows the 2D (two-dimensional) and 3D (three-dimensional) topography of the MPB and Control surface. The Control surface showed greater roughness and non-uniform surface, as seen in Figure 3a, which may be associated with a significant variation in Ra and Rq. Uncoated paper has native cellulose fibers and microfibrils on its surface.[46] The peaks observed in the Control topography represent the cellulose fibers.

The MPB topography was more uniform and smoother (Figure 3b) than the Control. The expressive vertical peaks may be associated with palmitic acid and activated carbon deposited on the paperboard surface. Lipid molecules can influence the formation of the polymer matrix.[47] Palmitic acid in chitosan films forms a more amorphous structure with voids.[21] The roughness of 10 nm for both Ra and Rq was verified for Kraft paper sheets coated with gelatin, palm wax, and lemongrass essential oil.[47] Chitosan coatings applied to the Kraft paper surface presented an Rq of 14.7 nm, a reduction of 83.1% compared to uncoated Kraft paper.[48]

The chitosan, palmitic acid, and activated carbon coating applied in three layers improved the surface of the paperboard, significantly reducing its roughness and non-uniformity. The MPB's roughness was higher compared to those obtained by other authors. It was observed in complementary tests that the high roughness could influence the permeability to air and oxygen.

3.4 | Barrier properties

The water absorption capacity is related to cellulosic material resistance in direct contact with water. Water resistance is an important property required for high-water activity food product packaging, such as fruits and
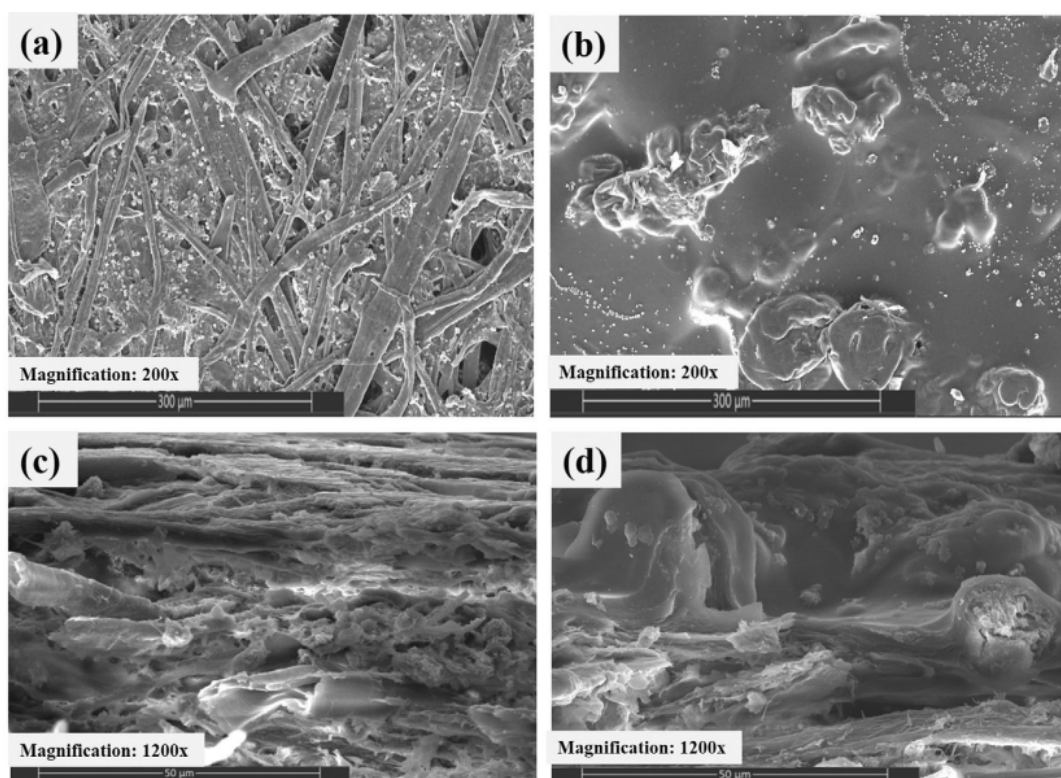
FIGURE 2 Microstructure images of surface paperboard: (a) Control and (b) multilayer paperboard (MPB); and in the cross-sectional area: (c) Control and (d) MPB obtained by scanning electron microscopy (SEM).

TABLE 2 Mean roughness (Ra) and mean square roughness (Rq) values for MPB and Control.

Roughness (nm)		
Paperboard material	**Ra**	**Rq**
Control	42.92 ± 10.75^b	58.06 ± 10.89^b
MPB	23.47 ± 3.97^a	31.95 ± 4.98^a

Note: Different letters in the same column indicate a significant difference ($p < 0.05$) according to Student's T-Test.

vegetables, with an increased respiration rate.[49] The water absorption capacity of MPB presented a higher value than Control (Table 1), which could be related to the hydrophilic nature of chitosan, indicating the interactions between water molecules and the coated material. Applying three coating layers increased the amount of chitosan on the paperboard surface, contributing to higher water absorption capacity values of MPB compared to the Control due to the hydrophilic character of chitosan.[50]

The water vapor permeability control in food packaging is essential to product preservation.[51] The WVTR values of MPB and Control showed no significant statistical difference ($p < 0.05$) (Table 1) using the chitosan, palmitic acid, and activated carbon coating formulation applied in this work. A tendency to reduce the WVTR in MPB could be suggested, associated with the lipid presence (palmitic acid) in the coated formulation and the higher solids content in the number of coating layers applied. The lipid presence in coating formulation could enhance the hydrophobicity and tortuosity, prolonging the transfer distance of water vapor molecules since moisture migrates more rapidly in the hydrophilic matrix than in a hydrophobic phase.[18] The hydrophobic character of palmitic acid and activated carbon have improved the paperboard's barrier to water and water vapor, reducing interactions between the polar groups of water and cellulose.[41,52] The higher solid content contributes by filling the cellulosic pores,[53] reducing the permeation of water vapor molecules.

The grease resistance of food packaging materials will depend on the chemical characteristics of the surface (hydrophobic or hydrophilic), barrier quality, amount of pores present, and substrate and barrier thickness.[54] Kit solutions are made up of nonpolar organic compounds. Kit solutions with higher numbers easily penetrate the cellulosic matrix due to low surface energy.[54,55] The MPB presented a value of fat repellency obtained by Kit 11 (Table 1). The Control did not show grease resistance. The grease resistance of chitosan-based coatings is related to the cationic characteristic of chitosan obtained by the presence of the NH_3^+ groups, which interact electrostatically with anionic groups of oils and fats, repelling and
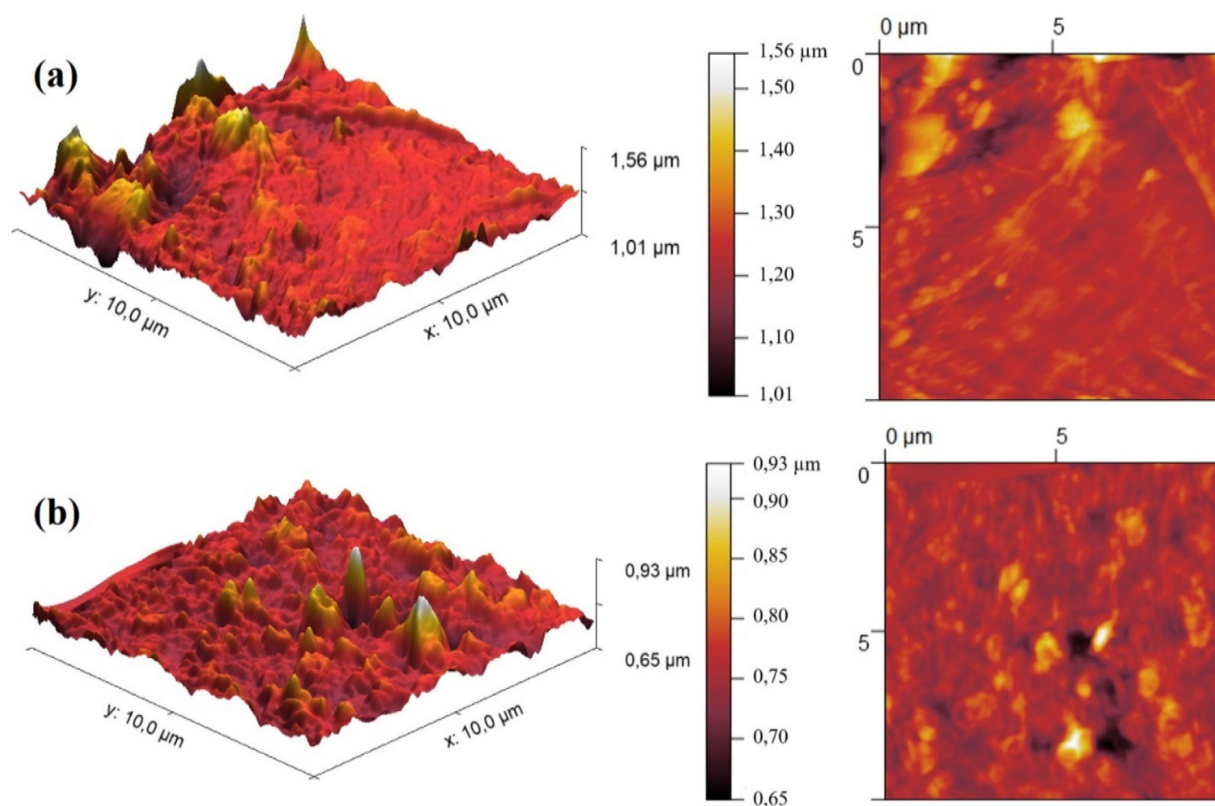
FIGURE 3 2D and 3D surface topography obtained by atomic force microscopy (AFM) for (a) Control and (b) MPB. [Color figure can be viewed at wileyonlinelibrary.com]

reducing the permeation of lipids in the cellulosic matrix.[23] The number of layers applied also increased the grease resistance. Chitosan coatings applied with two layers to the paperboard surface with different drying techniques improved the grease resistance of the material.[56] Chitosan coatings (3% w/w) applied on the Kraft paper surface presented Kit solution equal to 10 and 11.[23]

The test using Kit solutions (according to the Tappi pm-96 (T559) method[57]) evaluates the grease repellency of paper and paperboard treated with fluorochemical compounds. However, several authors have used this methodology with biopolymer coatings on the paper surface to compare with the usual commercial material. The same method was used in chitosan coatings incorporated with lemongrass essential oil for anti-insect action,[41] coating based on poly(lactic) acid (PLA) incorporated with polyethylene glycol (PEG)[58] and coating of chitosan and carboxymethylcellulose blends reinforced with crystalline nanocellulose.[59]

3.5 | Mechanical properties

The paperboard's physical properties are important characteristics for its processing and end-use. Tensile strength and extensibility indicate the potential for cellulosic fibers to break during printing or in another process, in addition to handling and transporting the product.[60,61] Paperboard is considered anisotropic material, as the cellulosic fibers are oriented in two directions in displacement on the papermaking machine, in the machine direction (MD) and the cross-machine direction (CD).[60] The effect of the coating on the mechanical properties of the paperboard was carried out in both directions of the cellulosic fibers. Table 3 presents the tensile strength (σ_r), elongation at break (ε_r), and Taber stiffness in MD and CD directions for Control and multilayer board (MPB) samples.

The flexibility of MPB (ε_r, Table 3) increased significantly in the MD direction of the cellulosic fibers compared to the Control. The increase was 14.28%, indicating a better mechanical performance of MPB, enhancing its application for packaging formation. The increase in ε_r occurs due to the relaxation of the tension of the cellulosic fibers of the paper after being in contact with water during the surface coating process.[62] Paper sheets coated with hydroxypropyl methylcellulose[63] and blends of chitosan and curdlan[60] increased the ε_r of the material. Coatings based on polyvinyl alcohol (PVA) applied as a single layer on the paper's surface increased the elongation by

Property	Direction	Control	MPB
σ_r (MPa)	MD	75.56 ± 2.04^a	75.56 ± 3.70^a
	CD	35.56 ± 0.71^a	35.56 ± 1.14^a
ε_r (%)	MD	1.82 ± 0.07^b	2.08 ± 0.12^a
	CD	4.49 ± 0.01^a	4.57 ± 0.43^a
Taber stiffness (mNm)	MD	4.17 ± 0.57^b	5.20 ± 1.14^a
	CD	7.21 ± 0.80^b	9.66 ± 0.95^a

TABLE 3 Tensile strength (σ_r), elongation at break (ε_r), and Taber stiffness in MD and CD directions for Control and multilayer board (MPB) samples.

Note: Different letters in the same line indicate a significant difference ($p < 0.05$) according to Student's T-Test.

approximately 20% due to the PVA's physical strength and film-forming properties.[64] The sliding between the molecular chains of PVA (a linear polymer) is facilitated when subjected to mechanical stress increasing the elongation at break value.[65]

The σ_r of the MPB did not present a significant difference in any direction (MD or CD) compared to the Control. This effect may be associated with the amount of coating applied to the surface of the paperboard, which did not cause a significant change in tensile strength. The cellulose network seems to have directly controlled the tensile strength. The film-forming dispersion based on chitosan, palmitic acid, and activated carbon penetrated the cellulose fibers, as shown in SEM images. Kjellgren et al.[62] observed the same behavior for σ_r on chitosan-coated greaseproof paper sheets; according to the authors, the non-variation of the σ_r may be associated with the low weight of the applied coating compared to the paperweight. The mechanical properties of coatings/laminates in composite structures would strongly depend on the base substrate.[66] A complementary explanation for the lack of effect of the coating on the tensile strength is the combination of two opposite effects (that may have annulled each other), namely: the tension relaxation between the fibers (as described for the elongation at break) and an increased efficiency of the stress transfer due to the high affinity of the paper fibers with the coating filling the paper pores.[67]

Stiffness is an important property of the paper industry, as it is used as an attribute for quality control.[68,69] A significant increase in the Taber stiffness of the MPB was observed in the MD and CD directions compared to the Control (Table 3), indicating that the MPB became more rigid. Coatings also provided the increase in stiffness based on chitosan (2% w/w) incorporated with anthocyanin (0.25%) as a visual indicator of temperature change (MD = 6.44 ± 0.28 mN e CD = 13.89 ± 0.31 mN).[70] Microfibrillated cellulose-based coatings also increased the stiffness of paper sheets in cellulosic fibers' MD and CD directions.[71] Chitosan acts by introducing positive charges that interact with the negative charges present in the cellulose structure; thus, the strength and flexibility of chitosan films strengthen the interactions of cellulose fibers, positively impacting the mechanical attributes of cellulosic materials.[25,43,70]

3.6 | Thermal analysis: Thermogravimetry (TG), differential thermogravimetry (DTG), and differential scanning calorimetry (DSC)

The thermograms (TG) and the derived curves (DTG) of the MPB and Control are shown in Figure 4. Thermal analyses are important to investigate the stability of polymers,[72] the water distribution within the system, the limiting temperatures of application of the polymer,[73] and to determine the decomposition of the material from the mass loss.[74]

According to TG and DTG (Figure 4), the MPB showed initial mass loss at $85.65°C$ and the Control at $82.53°C$. The initial mass loss is related to the vaporization of the moisture in the samples.[75] The thermal decomposition of MPB started at approximately $224.67°C$ and ended at $358.13°C$. For Control, the thermal decomposition was estimated at $201.37–360.82°C$. Paperboard presents peak thermal decomposition at around $360°C$.[76] The most significant degradation of MPB and Control occurred in the range of $300–400°C$. The main stage of thermal decomposition of cellulose occurs in the range of $240–370°C$, in which glycosidic bonds are broken, and the degree of polymerization is reduced.[77] Chitosan has three stages of thermal decomposition.[73,78,79] The first one (from 40 to $170°C$) is related to the evaporation of residual acetic acid and moisture. The second one (from 170 to $250°C$) is due to the degradation of low molecular weight fractions or evaporation of water structurally bound to chitosan. The third thermal stage (from 250 to $600°C$) is associated with the decomposition of the chitosan structure.[80] It is observed that the MPB followed the uncoated paperboard's thermal degradation behavior.
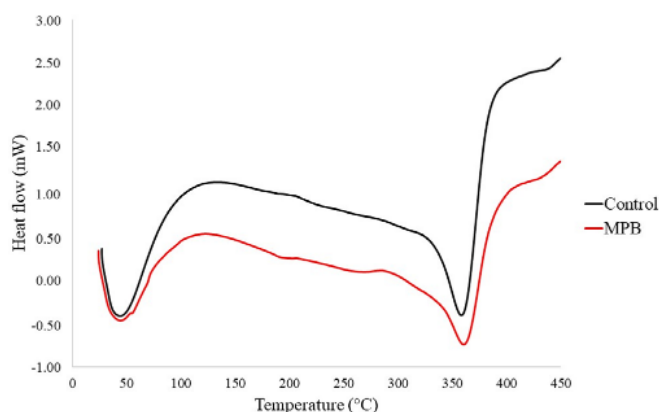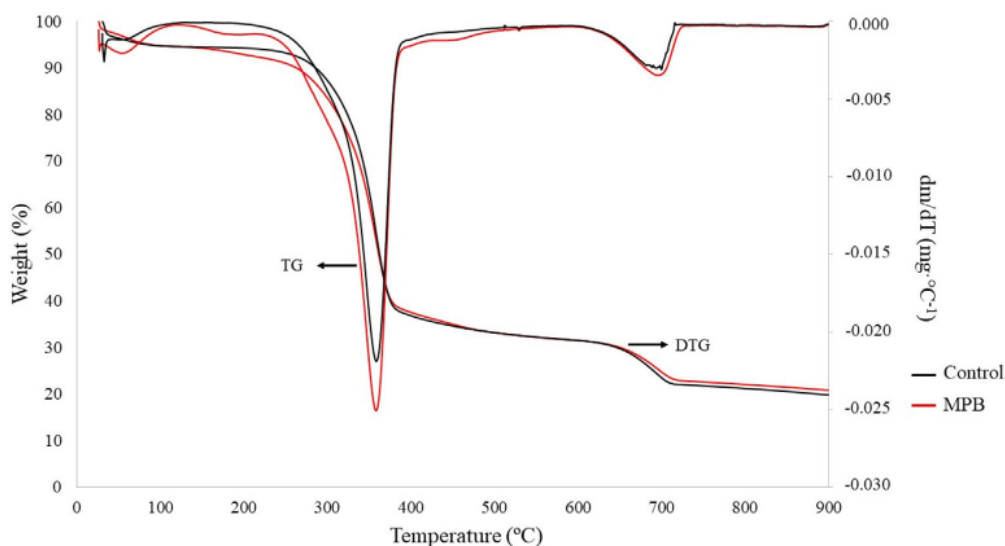
The DSC of MPB and Control showed two endothermic events, as seen in Figure 5. The first endothermic event may be related to the loss of moisture in the samples, causing initial mass loss with a peak at 45.0°C for MPB and 42.5°C for Control. Endothermic peaks between 20 and 100°C may be associated with water in the cellulose and chitosan chains.[42] The second endothermic event was related to the thermal decomposition of the samples, with peaks at around 361 and 359°C for MPB and Control, respectively. Cellulose shows a typical endothermic curve in DSC from 320 to 390°C.[81] Other authors reported the same characteristic curve for cellulose, corresponding to melting its crystalline part.[82–84]

The thermal decomposition of chitosan can be detected in endothermic and exothermic peaks, depending on the balance between the two processes.[85] Chitosan films showed an endothermic peak near 225°C and an exothermic one at approximately 275°C, which may be related to the deacetylation and principal chain decomposition. Palmitic acid has a thermal decomposition peak ranging from 202 to 282°C.[86] Activated carbon has two degradation peaks, the first at approximately 150°C (due to moisture loss) and the second at 150 to 400°C, related to removing volatile compounds.[87] These thermal events were not observed in the MPB samples, indicating that the presence of palmitic acid and activated carbon did not influence the thermal behavior of the resulting material. It was observed that MPB followed a similar pattern of thermal decomposition of cellulose, demonstrating that the coating does not influence the thermal properties of the paperboard.

3.7 | Biodegradation

Biodegradation refers to material degradation and depends on the environmental conditions (temperature, moisture, pH, etc.), the chemical structure (chemical bonding, polymer chain, etc.), and the composition of the microbiota.[88] Figure 6 shows the gravimetric measurements and visual aspects of MPB and Control during 188 days of the biodegradation process in soil. The MPB biodegradation indicated that the chitosan, palmitic acid, and activated carbon coating did not influence the degradation process of the paperboard.

MPB and Control showed mass gain during the first 29 days of testing, which may be associated with soil moisture absorption by the samples. The MPB presented a mass increase of 77.4% and the Control of 72.2%, concerning the initial mass of the samples. The higher mass gain of MPB may be related to the higher solids content of the coating applied to the paperboard surface and the hydrophilic nature of chitosan. There was a mass loss in
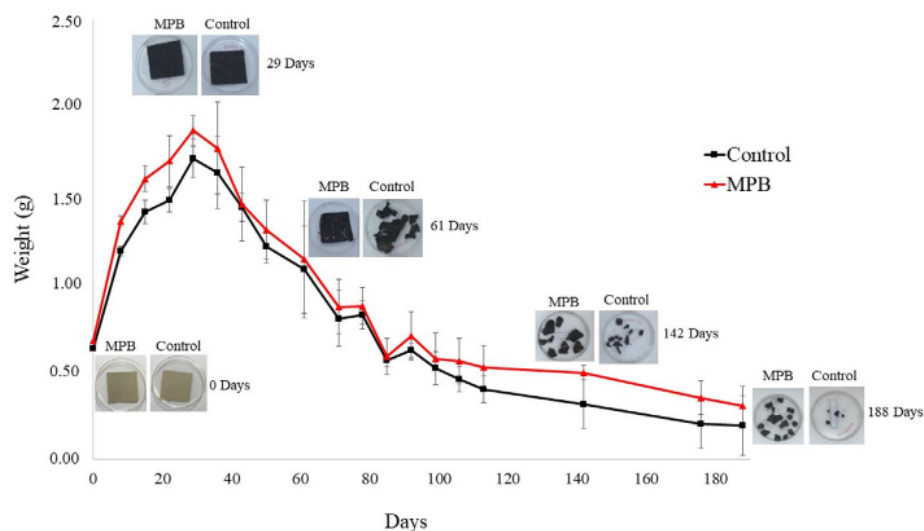
FIGURE 6 Biodegradation process by mass loss as a function of time and visual aspect of Control and multilayer paperboard (MPB). [Color figure can be viewed at wileyonlinelibrary.com]

the samples from the 36th day of the test. On the 92nd day of the test, it was observed that both materials, MPB and Control, showed mass gain attributed to moisture gain due to climatic factors since the samples were exposed to the environment even in a controlled way.

The MPB showed final biodegradation of 55.01 ± 16.24% concerning the initial mass and the Control, 69.38 ± 27.15%, after 188 days of biodegradation in soil. The final biodegradation of the materials showed no significant difference. Thus, it was observed that MPB followed the behavior of cellulose degradation (Control), indicating that the chitosan, palmitic acid, and activated carbon coating did not impact the degradation process of cellulose in soil. The chitosan-based coating maintains the biodegradation paperboard property in the opposite behavior of synthetic polymer coatings, which strongly slows down the degradation rate of cellulose. A similar result was obtained in chitosan and ferrous sulfate paperboard systems developed to indicate hydrogen sulfide (H_2S).[89]

The biodegradation of paper sheets coated with gelatin incorporated with palm wax and lemongrass essential oil was initially verified after 24 days of testing; this effect may have been delayed due to the antimicrobial action of lemongrass essential oil.[47] Silva et al.[40] observed that chitosan films provided complete biodegradation in sandy soil after four months of testing. According to Nazhad et al.,[90] paper sheets coated with low-density polyethylene did not biodegrade in a short period under laboratory conditions and the open field. Sheets of paper covered with polyethylene, applied on both sides of the sheets of paper, showed partial loss of mass during the biodegradation test due to the presence of accessible sites of cellulose for the action of microorganisms. However, the coating layers remained unchanged during the biodegradation tests.[91]

4 | CONCLUSION

The chitosan polymer matrix incorporated palmitic acid and activated carbon in its structure, forming a homogeneous coating matrix on a paperboard surface. Using three coating layers developed, a multilayer paperboard. The suspension coating filled the pores of the cellulosic matrix, enhancing the grease resistance and showing a tendency to reduce WVTR. The coating improved the mechanical properties of the paperboard sheets, increasing their stiffness and elongation at break and promoting a more uniform and smoother surface of the paperboard. The roughness of MPB was higher than other coating systems. The multilayer paperboard followed the behavior of cellulose biodegradation; that is, the chitosan, palmitic acid, and activated carbon coating did not impact the ecological character of the paperboard, reinforcing the ability of renewable raw materials to contribute to the development of packaging with less environmental impact and which contributes to the circularity of the economy.

AUTHOR CONTRIBUTIONS
Jackson Wesley Silva dos Santos: Conceptualization (equal); data curation (equal); formal analysis (equal); investigation (equal); methodology (equal); validation (equal); visualization (equal); writing – original draft (equal); writing – review and editing (equal). **Ana Paula Reis Noletto:** Formal analysis (supporting); methodology (supporting); writing – original draft (supporting); writing – review and editing (supporting). **Henriette Monteiro Cordeiro de Azeredo:** Formal analysis (supporting); methodology (supporting); writing – original draft (supporting); writing – review and editing (supporting). **Rosemary Aparecida de Carvalho:** Formal analysis (supporting); methodology (supporting); resources (supporting); writing – original draft (supporting);

CONFLICT OF INTEREST STATEMENT
The authors declare that there is no conflict of interest.

DATA AVAILABILITY STATEMENT
The data generated during this study are available from the corresponding author upon reasonable request.

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