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Valorization of a by-product of the yerba mate industry by assembling with cassava starch adhesive for packaging material production

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Abstract

Yerba mate industrial processing produces tons of powder as a by-product, this yerba mate powder (YMP) is an excellent source of biomass to develop biodegradable materials. Cassava starch modified with 1,2,3,4-butane tetracarboxylic acid (BA) in the presence of sodium propionate as a catalyst is an eco-friendly option to obtain bioadhesives. This work aimed to develop sustainable laminates from starch-based adhesives and yerba mate powder and to study their physico-chemical, structural, and mechanical properties. Blends of bioadhesive and YMP were prepared (1:1, adhesive:YMP). Monolayer materials were obtained by thermo-compression and later assembled with adhesive to obtain bilayer laminates. Bioadhesive was able to bind the yerba mate by-product fibers, as evidenced by SEM microstructure analysis, the interactions of adhesive:substrate were elucidated by ATR-FTIR and supported by chemometrics analysis. The incorporation of the catalyst decreased the rugosity of materials and their mechanical performance was improved by the action of both acid concentration and catalyst presence, requiring higher energy for puncture.

Thus, it was feasible to obtain mono and bilayer laminates as an eco-compatible alternative for the design of sustainable tray-like materials based on the industrial by-product of yerba mate.

Keywords: biobased adhesives, cassava starch, yerba mate by-product, sustainable trays, mechanical and microstructural properties

1. Introduction

Most consumers notice plastic containers in a negative form due to the considerably high number of residues that are produced in daily life. However, they ignore the positive impact of these types of receptacles on sustainability through the protection of the products in containers [1]. Although the transport and storage of consumer goods and foodstuffs is inconceivable without packaging, a large amount of waste is generated by the disposal of non-biodegradable material packaging. Corralo Spada et al. [2] have reported that among petroleum polymer-based packaging, the use of expanded polystyrene stands out due to its low production cost, low density, high resistance to humidity, and dimensional stability. However, its improper disposal and difficulty in recycling, together with its non-biodegradability, can cause serious environmental problems. Knowing that there is no way to prevent the population from using this material, the present study aimed to produce an eco-friendly tray based on biopolymers. Bioplastic packaging materials based on renewable biomass could be used as a sustainable alternative to petrochemical-originated plastic ones. In this sense, Hamed et al. [3] have reported that the polymers extracted from biowastes offer great opportunities to decrease the devastating overuse of plastic-based packaging.

Yerba mate (*Ilex paraguariensis*) is a tree originally from South America, that grows in a limited area within Argentina, Brazil, and Paraguay, being Argentina the largest producer and consumer [4]. Throughout the elaboration process of yerba mate, a series of products

(sticks, leaves, powders) are obtained. During milling, the sticks and the leaves are crushed together, generating small-sized particles (powders) that must be eliminated from the elaborated yerba mate, generating a disposal problem in most mills [5].

In this context, the use of the above-mentioned "yerba mate powder (YMP)" as a lignocellulosic source is an unexplored proposal to design tailor-made biopolymer composites.

In the same way, the development of eco-friendly adhesives obtained from renewable biomass, as a promising substitute for synthetic adhesives, has attracted considerable attention to obtaining sustainable trays [6]. Bioadhesives based on cassava starch have remarkable properties, including high paste viscosity, high paste clarity, and high freeze-thaw stability which are advantageous for industrial applications [7]. Despite its great advantages, cassava starch's low hydrophobicity and insufficient binding strength have limited its applicability [8]. Therefore, the chemical modification of this biopolymer has found applications in the packaging and bioplastic sectors [9]. In this sense, 1,2,3,4-butane tetracarboxylic acid has been explored as a green and sustainable formaldehyde-free crosslinker agent of starch, has the advantages of safety and non-toxicity, and has four carboxyl groups in its structure, which can provide more reaction sites for esterification [7, 10, 11].

Currently, many authors have reported the design of starch-based composite materials added with different types of fibers obtained from diverse agroindustrial residues [12-16]. However, the combination of bio-based materials with green adhesives to obtain bilayer or multilayer structures has not yet been explored. In this regard, the layer-by-layer assembly generates a stratified structure with improved properties due to confinement and/or interfacial effects, whose interactions depend on the characteristics of the involved polymers [6].

To the best of our knowledge, there is no report about materials based on yerba mate by-products and cassava starch-based adhesives. In the literature, yerba mate domestic residues have been used in the production of composite films [17, 18]. Whereas yerba mate industrial waste has only been recycled for agronomic applications [5, 19].

This work aimed to develop sustainable materials from yerba mate powder by-product using cassava starch modified with a polycarboxylic acid as bioadhesives and to study their structural, physico-chemical, and mechanical properties. As an innovative and sustainable proposal, sodium propionate was used as a non-phosphorus catalyst as a strategy to promote and enhance the adhesive-substrate interaction network due to cross-linking reactions between the starch and lignocellulosic compounds of YMP.

2. Materials and Methods

2.1. Yerba mate powder characterization

Yerba mate powder was provided by the Instituto Nacional de la Yerba Mate (INYM, Argentina) and was collected from industries of Misiones, Argentina. YMP is 89.4% organic matter and 60% of its particle size is below 250 μm [19].

Soluble solids were determined by an adaptation of AOAC and ISO methods to determine this property at ambient temperature. In brief, 2 g of powder was mixed with 200 mL of water. Then, the suspension was centrifuged at 1800 rpm for 10 min (Rolco, CM2036 Duron, Argentina), the upper layer was removed, and the precipitate was dried in a convection oven at 100 °C to constant weight. The results were expressed as percentages on a dry basis.

Total, soluble, and insoluble dietary fiber contents of YMP were analyzed according to the enzymatic-gravimetric method [20]. A modification of the method described by Soest & Wine [21] and Robertson and Van Soest [22] was applied in an ANKOM200/220 Fiber Analyzer (ANKOM Technology, Macedon, NY, USA) according to Dello Staffolo et al. [23]. This method measures Acid Detergent Fiber (ADF), Neutral Detergent Fiber

(NDF), and lignin. Then, cellulose and hemicellulose contents were obtained by calculations. Assays were performed by duplicate.

2.2. Obtaining and rheological characterization of the bio-based adhesives

Cassava starch (*Manihot esculenta*) was supplied by the Cooperativa Agrícola Mixta de Montecarlo (Misiones, Argentina). Starch-adhesive suspensions 5% w/w were gelatinized at 90 °C for 20 min in a thermostatic bath. Then, analytical grade 1,2,3,4 butane-tetracarboxylic acid, BA, (Sigma Aldrich, USA) was added to the gelatinized suspensions in concentrations ranging between 20 and 40% (polycarboxylic acid weight /100g starch). Native cassava starch was included as a filler at room temperature (5g/100g gelatinized starch suspension) [7,15]. The incorporation of the sodium propionate catalyst (C) was also studied at 50% with respect to the BA (g /100g BA).

Rheological analysis was performed by using a Rheo-Stress 600 ThermoHaake (Haake, Germany) rheometer equipped with a PP35 sensor following the protocol described in Monroy et al. [7]. To investigate time-dependent rheological behavior of adhesive formulations rotational assays were performed. The Ostwald de Waele model was used to fit the rheological behavior of adhesives and the corresponding thixotropic or anti-thixotropic values were estimated. The apparent viscosity of non-Newtonian samples was calculated at 500 s^{-1} . Measurements were performed at least in duplicate.

2.3. Design of sustainable materials

To obtain the sustainable materials, 5g of YMP was mixed with the adhesive formulations in equal proportions as previously standardized [15]. The mixture (10g) was placed on Teflon sheets and the materials were obtained by thermo-compression in a hydraulic press

applying a pressure of 300 kg cm^{-2} at $140 \text{ }^\circ\text{C}$ for 5 min. The influence of different adhesive formulations was studied by evaluating the quality characteristics and final properties of the obtained materials. Formulations of bi- or trilayer laminates were also prepared by bonding the monolayers with the bioadhesive between them thermo-compressing at 300 kg cm^{-2} for 5 min. The composition and nomenclature of the obtained samples are listed in Table 1.

Table 1. Composition and nomenclature of mono and bilayers

Adhesive (% BA)	Catalyst (NaP)	Nomenclature for monolayer	Nomenclature for bilayer
20	No	M BA20	B BA20
20	Yes	M BA20+C	B BA20+C
40	No	M BA40	B BA40
40	Yes	M BA40+C	B BA40+C

2.4.Sustainable materials characterization

2.4.1. Physicochemical properties

The moisture content of the materials was determined by measuring their loss of weight, upon drying in an oven at $105 \pm 1 \text{ }^\circ\text{C}$ until reaching constant weight (dry sample weight). Samples were analyzed at least in triplicate and results were expressed as g water/100 g material.

Thickness measurement of the materials was performed with a digital meter microprocessor CM-8222 for non-conductive and non-ferrous substrates (SOLTEC, Argentina) according to Monroy et al. [15]. The density of the material (g cm^{-3}) was determined gravimetrically by using a precision balance with an accuracy of 0.1 mg on specimens of $2 \text{ cm} \times 2 \text{ cm}$, with known thickness. These measurements were performed in quintuple.

The roughness of the samples was determined by using a PCE-RT 1200 roughness tester (Schwyz, Switzerland) by measuring the average roughness (Ra) and the mean peak-to-

valley height (Rz). The roughness tester's calibration was checked using a standard reference plate with Ra and Rz values of 1.72 μm and 4.92 μm , respectively. Fifteen measurements were taken randomly from both surfaces of each sample in triplicate.

2.4.2. Water affinity

The surface wettability of the materials was studied by the contact angle determination, performed in a Goniometer (model 190, Ramé-Hart, Instrument Co., USA) following the procedure used in earlier research [7]. For every sample, at least eight determinations were made using two independent batches.

On the other hand, to determine the water absorption capacity (WAC) of sustainable materials, samples of 2 \times 2 cm were placed in a container with 100% relative humidity (RH), previously conditioned at a controlled temperature of 20 $^{\circ}\text{C}$. Weight gain was recorded as a function of time. The water absorption capacity of the samples during immersion (WAC_i) was determined by weighing 2 cm \times 2 cm samples and soaking them in distilled water for 1 min and 30 min. After removing excess water, the samples were reweighed. The amount of water adsorbed was calculated as the difference in weight and expressed as the mass of water absorbed per mass of the initial sample [12]. The assay was performed in triplicate.

2.4.3. Color

The surface color of the laminates was evaluated using a Chroma Meter CR 400 (Konica Minolta Sensing, Japan) calibrated with a white standard plate (Y=93.2, x=0.3133, y=0.3192). The chromaticity parameters (a*, b*) and luminosity (L) were recorded.

At least 12 assessments were conducted for every sample (two independent samples), using randomly selected positions. Color differences (ΔE) were calculated according to Lopez et al. [24] with respect to the standard plate parameters.

2.4.4. Mechanical properties

A TAXT2i texturometer was used to conduct puncture testing (Stable Micro Systems Ltd., Godalming, Surrey, UK). A cylindrical probe of 2 mm diameter was employed at a constant rate of 1 mm s⁻¹. Every informed value is equivalent to a minimum of ten determinations made at random locations, for three independent samples. Curves of force (N) as a function of deformation (mm) were recorded automatically by the Texture Expert Exceed software. The area under the curve was calculated to determine the energy required to fracture the material. Also, maximum force and deformation at rupture were evaluated and the stress (MPa) values were informed.

2.4.5. Microstructure studies

Cross-sections produced by cryofracture under liquid nitrogen and the surface of the sustainable laminates were examined by SEM using a low vacuum FEI model Quanta 200 scanning electron microscope (The Netherlands). Samples were mounted on metal stubs with a double-sided adhesive tape and were examined at an acceleration voltage of 10 kV. Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR) in conjunction with Principal Component Analysis (PCA) was performed to evaluate the interactions between the different bioadhesive formulations and the YMP by-products. ATR-FTIR spectra were performed on a Nicolet iS10 Thermo Scientific (Madison, USA) fixed with a pressure-arm accessory (Smart iTX accessory), following the procedure described by Monroy et al. [7, 15]. Omnic 8 software (ThermoScientific) was used to analyze the data recorded within the range of 400-4000 cm⁻¹ by accumulating 32 scans with a resolution of 4 cm⁻¹. Unscrambler® software (version 8, CAMO, Norway) was used to perform PCA on the ATR-FTIR spectral data. Samples of YMP, bioadhesive formulations, and monolayer and bilayer materials were analyzed. For PCA analysis, at least fifteen determinations were performed in three different samples at random locations.

Chemometric analysis was performed in the spectral region between 1200 and 700 cm^{-1} to evaluate the spectral differences between the composite materials (PCA).

2.4.6. Statistical analysis

Analysis of variance (ANOVA) and comparison of means with the Fisher's least significant difference (LSD) test were conducted, at a significance level $p=0.05$. For this purpose, InfoStat Software (Version 2009) (InfoStat Group, Agricultural Sciences College, National University of Cordoba, Argentina) was used.

3. Results and Discussions

3.1. Adhesive formulations characterization

Cassava starch-based adhesives exhibited a rheological behavior characteristic of a pseudoplastic fluid. The addition of BA significantly ($p<0.05$) decreased the apparent viscosity of gelatinized starch suspensions, although all formulations preserved the pseudoplastic character (Table 2). These results are explained considering that BA promotes the hydrolysis of starch polymeric chains [7], as supported by ATR-FTIR studies (Figure S1). Similarly, the thixotropy values indicate the structure recovery after shear removal. According to Zhang et al. [25], the formation of a new structure might be in response to the hysteresis phenomenon in the viscosity recovery.

Table 2. Viscoelastic behavior of native and chemically modified cassava starch suspensions: parameters of the mathematical model.

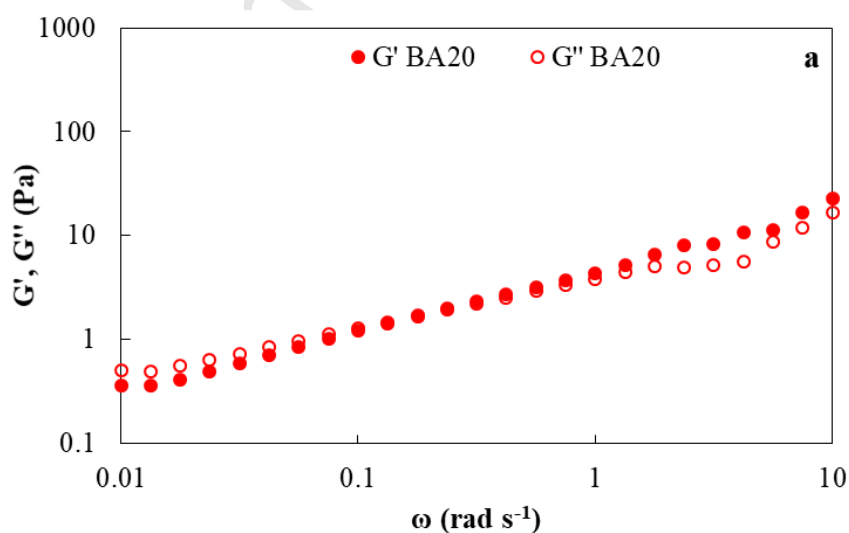
Samples	Storage moduli G' (Pa)		Loss moduli G'' (Pa)		Thixotropy (Pa s^{-1})	$\eta_{\text{app}} 500\text{s}^{-1}$ (mPa s)
	$G' = a\omega^b$		$G'' = c\omega^d$			
	Parameter a (Pa s^b)	Parameter b	Parameter c (Pa s^d)	Parameter d		

BA0	4.6±0.1	0.6±0.05	4.1±0.01	0.8±0.002	21840 ± 1272 ^a	718 ± 11 ^a
BA20	4.9±0.4	0.5±0.03	3.9±0.1	0.4±0.01	15665 ± 64 ^b	647 ± 11 ^b
BA40	4.3±0.03	0.4±0.03	3.2±0.5	0.4±0.02	13055 ± 248 ^c	543 ± 16 ^c

Reported values correspond to the mean ± standard deviation.

The hydrolysis of the starch chains is promoted in the presence of BA and consequently, this would affect their realignment and rearrangement during the gelation and retrogradation process at short times, which is reflected in the thixotropy values obtained (Table 2).

The bioadhesive formulations containing BA exhibited a concentrated solution behavior at the initial time (Figure 1a). Regardless of the BA concentration, the elastic modulus (G') values increased throughout the tested frequency range compared to those corresponding to the gelatinized suspension of native cassava starch (Figure 1b). This increase could be explained by the entanglement of shorter amylose chains, which form more hydrogen bonding during cooling before gelation takes place [15].



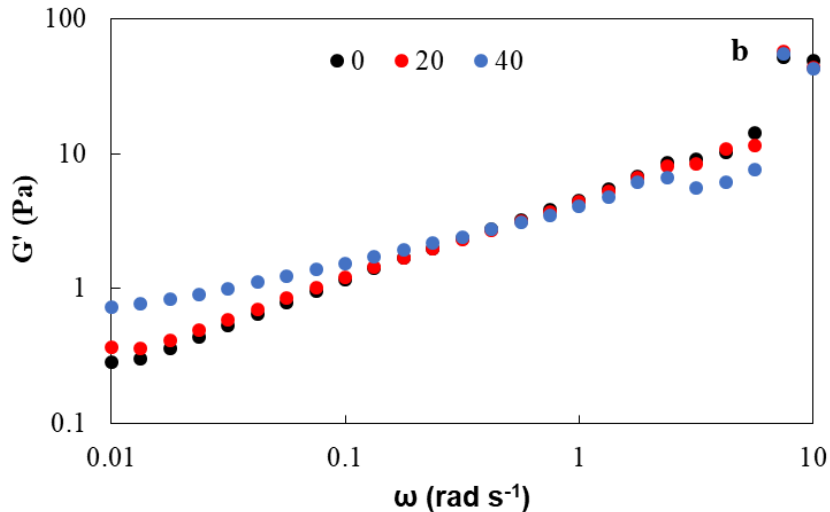


Figure 1. a) Evolution of the elastic (G') and viscous (G'') modulus of adhesive formulations based on cassava starch modified with BA; b) Effect of acid concentration on the evolution of the elastic modulus (G') of adhesive formulations based on cassava starch modified with BA. Nomenclature BA = 1,2,3,4 butane-tetracarboxylic acid, the next number (20, 40) indicates the concentration of acid % (g acid/100 g starch).

3.2. Analysis and interrelationship of material properties based on yerba mate by-product

3.2.1 Morphological and structural analysis

Having standardized the thermo-compression conditions for processing starch-based adhesives [7, 15], materials were obtained by thermoforming mixtures of bioadhesive and yerba mate powder (Figure 2). The bioadhesive made it possible to integrate the powder particles and obtain monolayer materials but also to assemble them and obtain the laminates (bi and trilayers) (Figure 2).

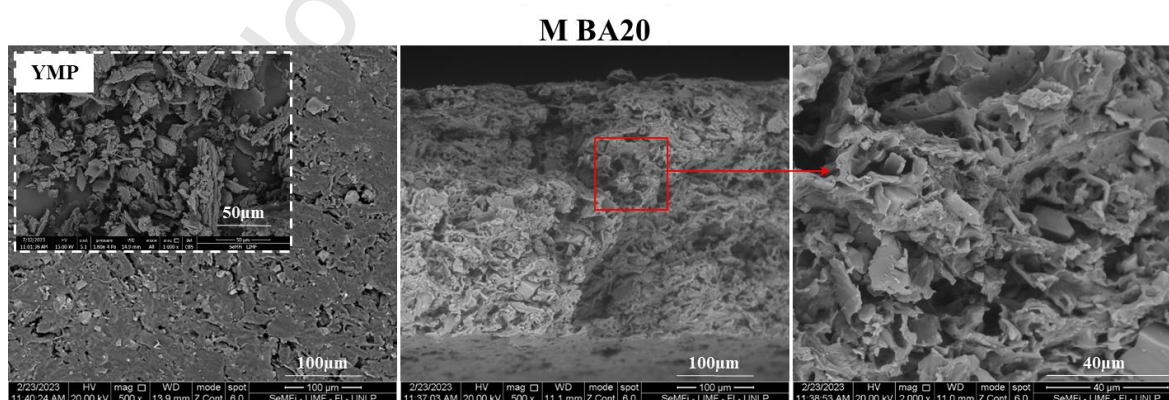


Figure 2. Sustainable materials obtained with bioadhesive formulations and yerba mate powder by thermo-compression. Monolayer (M), bilayer (B), and trilayer (T) systems using BA20 adhesive. Nomenclature BA = 1,2,3,4 butane-tetracarboxylic acid, the next

number (20) indicates the concentration of acid incorporated into the adhesive % (g acid/100 g starch).

Complementary studies were carried out by SEM (Figure 3). Micrograph insert shows that YMP has an irregular shape and that the morphology of the YMP particles was determinant in the arrangement or microarchitecture of the materials obtained.

As shown in Figure 3, all surface images and cross sections showed that the bioadhesive was able to bind the yerba mate by-product fibers. The material formation process allowed for the integration of the system components. Micrographs of the monolayers showed that the surfaces were porous with the presence of microvoids in their structure. Therefore, the properties of the materials will largely depend on the BA concentration and the resulting porosity of the microvoids, in which the catalyst plays a relevant role. The acid concentration in the adhesive formulation affected the microarchitecture of the samples, with a more compact matrix being observed at low BA content. This fact could be related to the fluidity of the adhesive since the polymer chains were hydrolyzed to a lesser extent than those with a higher acid content. In the same way, the presence of a catalyst provoked noticeable modifications.



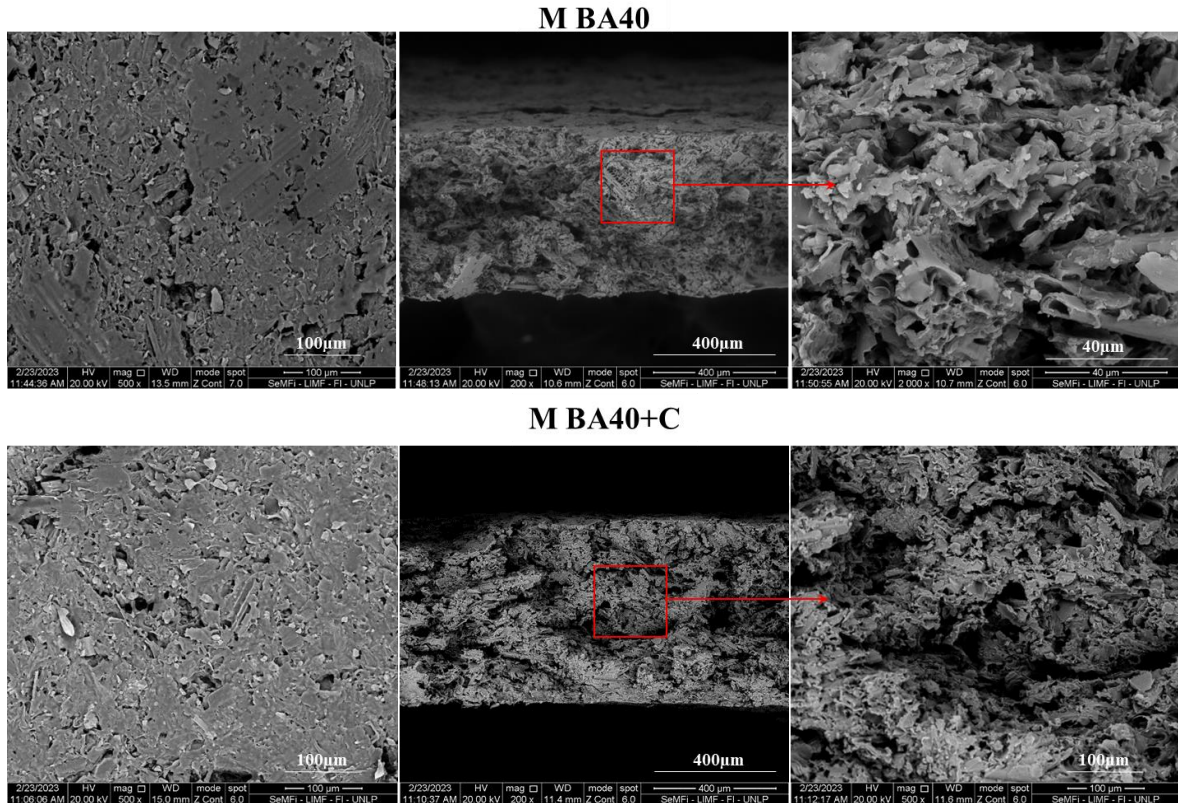


Figure 3. SEM micrographs of the surface and cross-section of YMP-based materials. Nomenclature is referred to in Table 1. The magnification is indicated in the micrographs.

Figure 4 shows the interface of the bilayer systems (B BA40+C), where the adhesive penetrated the monolayers and efficiently bonded the materials, demonstrating the compatibility between the laminate components. These micrographs confirm that YMP particles impregnated with the adhesive being subjected twice to the thermo-compression process favored a more compact structure, denser than monolayer samples ($p=0.0465$, Table 3). A second thermo-compression treatment induced a greater interaction between the components of the YMP particles and the modified starch. This is due to the cross-linking resulting from the molecular reaction between the reactive hydroxyl groups on the starch and the YMP phenolic compounds, leading to higher network linkages. Consequently, an improvement in the material strength is expected.

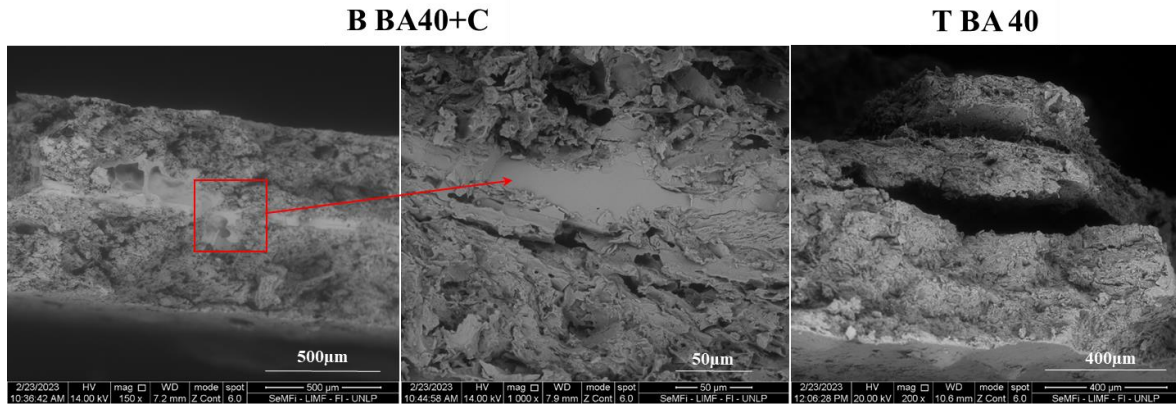


Figure 4. SEM micrographs of the cross-section of YMP-based materials (B BA40+C and T BA40). Nomenclature BA = 1,2,3,4 butane-tetracarboxylic acid, the next number (40) indicates the concentration of acid incorporated into the adhesive % (g acid/100 g starch), B=bilayer, T=trilayer, C= indicates catalyst presence. The magnification used is indicated in the micrographs.

The trilayer systems, having an excess of adhesive, showed cracks and bubbles, probably caused by water evaporation during the second compression step (Figure 4). Therefore, this material was not further investigated as these characteristics are not desirable, negatively affecting the mechanical properties.

Besides SEM morphological studies, roughness measurements suggest the surface quality of the material, the parameters associated with the roughness of the laminates are presented in Figure 5. The values of arithmetic mean roughness (Ra) and mean roughness (Rz) obtained are within the range of those reported for composite laminates based on by-products of medium-density fiberboard (MDF) (Ra = 0.48–8.10 µm and Rz = 3.97–50.12 µm), [7, 15, 26]. For BA20 and BA40 composites, a significant decrease ($p=0.001$) was observed in the roughness parameters of the material with the addition of the catalyst. This result could be associated with the better orientation of the YMP by-product particles and the interactions promoted by the catalyst during the thermo-compression process.

According to Nemli et al. [27], more compact and dense structures correlated with lower surface roughness parameters in particleboard-type materials. Additionally, Dewi et al. [28] reported a decrease in surface roughness with the use of ammonium dihydrogen phosphate as a catalyst agent in bio-based adhesives formulated with maltodextrin.

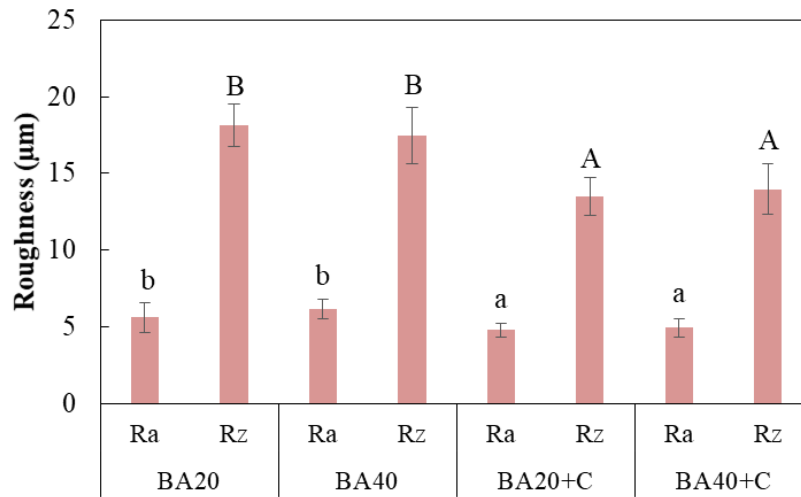


Figure 5. Roughness parameters (μm) of monolayer materials obtained with and without catalyst. Different lowercase letters indicate significant differences between Ra and Rz parameters ($p < 0.05$). Different capital letters indicate significant differences between Rz parameters ($p < 0.05$).

3.2.2. Physicochemical properties

The moisture content of monolayers and bilayers were $5.40 \pm 0.02\%$ and $4.50 \pm 0.08\%$, respectively. Whereas, Table 3 shows thickness, density, and color differences in YMP-bioadhesive materials. Concerning thickness, all monolayer systems exhibited values around $550 \mu\text{m}$ ($p > 0.05$), whereas, for bilayer ones, both the BA concentration ($p = 0.0040$) and catalyst ($p = 0.0019$) presence produced a significant effect on this parameter.

Density values were between 0.75 and 0.92 g/cm^3 for monolayer systems and within the range of 0.93 - 1.11 g/cm^3 for bilayer materials. These results were higher than those reported for expanded polystyrene, close to 0.04 g/cm^3 [13], and higher than those informed by other authors for trays based on cassava starch blended with agroindustrial residues [14, 29].

Regarding color parameters, YMP showed values of $L = 74.3 \pm 0.3$, $a^* = -0.69 \pm 0.04$ denoting greenish color, and $b^* = 17.2 \pm 0.4$ indicating a contribution of yellow tones, these values are consistent with those informed by Schmalko and Alzamora [30], for yerba mate. The negative values in the chromaticity a^* parameters indicate that the green color was predominant. However, the parameter a^* increased in comparison with the raw YMP,

which indicates that after the heat treatment by thermo-compression process, the green color was reduced, with values in the range of 3.6 - 5.5. In addition, the hot-pressing treatment also increased the chromaticity parameter b^* , related to the yellow color, obtaining values in the range of 20-22.9 and decreased the luminosity which was around 40.9-50.5, suggesting that the temperatures used to obtain the material caused a greater degradation of chlorophyll and, consequently, modified the color difference.

In the monolayer materials, the color difference (ΔE) significantly increased ($p < 0.0001$) with the presence of the catalyst (Table 3). The effect was magnified for the higher concentration of BA in the adhesive formulation. Whereas, for bilayer materials, the ΔE parameter was around 53 except for B BA20+C samples which exhibited lower values (Table 3).

Table 3. Thickness, density, and color difference in YMP-bioadhesive laminates

	Thickness (μm)	Density (g/cm^3)	ΔE
M BA20	507 \pm 51 ^a	0.92 \pm 0.0 ^a	49.87 \pm 1.46 ^a
M BA40	523 \pm 39 ^a	0.75 \pm 0.0 ^a	49.66 \pm 0.55 ^a
M BA20+C	585 \pm 86 ^a	0.768 \pm 0.0 ^a	50.65 \pm 1.26 ^b
M BA40+C	558 \pm 24 ^a	0.814 \pm 0.04 ^a	52.19 \pm 0.09 ^c
B BA20	1018 \pm 28 ^B	1.11 \pm 0.002 ^B	52.85 \pm 0.41 ^B

B BA40	1010±41 ^B	0.93±0.09 ^B	53.40±0.58 ^B
B BA20+C	987±49 ^A	1.02±0.21 ^B	50.12±0.99 ^A
B BA40+C	904±48 ^A	1.03±0.13 ^B	52.61±1.32 ^B

For thickness and ΔE , different letters indicate significant differences ($p < 0.05$) between mean values for each system type (lowercase letters for monolayer materials and capital for bilayer ones). For density, different letters indicate differences between the type of material (mono or bilayer system) ($p < 0.05$).

3.2.3 Water-related properties

Considering the material microstructure, the porosity favored the wettability of the samples, which, coupled with the hydrophilic character of the system components, resulted in contact angle values between 52 to 58° ($p > 0.05$). These low values indicated a matrix with structural integrity but whose surface hydrophilicity was attributed to the exposure of OH groups capable of interacting with water.

In addition, the pores observed at the surface and evidenced by SEM (Figure 4) could act as microchannels that facilitate the diffusion and/or penetration of water into the matrix. Ulker [26] has demonstrated a strong dependence on the wettability or capacity to absorb water molecules of the material with the roughness of the surface of the trays.

As previously described, the obtained materials were hydrophilic, a property probably explained by the water affinity of YMP components, since the soluble extract of yerba mate powder at room temperature was 30%. In this sense, yerba mate soluble extract is rich in saponins, phenolic compounds (mainly di- or mono-caffeoylquinic acids), feruloylquinic acids, hydroxycinnamic acids, carbohydrates, and xanthines [31-33]. Moreover, the lignin content of YMP determined in the present work was 5.5%, hemicellulose 8.9% and cellulose 21.4%, these results would also explain the high water affinity since hydroxyl groups from cellulose interact with water [34].

Figure 6a shows that WAC was around 4% after 6 h of the assay with a significant effect of acid concentration ($p = 0.0153$), samples with higher BA content absorbed a higher

amount of water, regardless of the studied system (mono or bilayer). Meanwhile, WAC at 24 h of exposure at high relative humidity conditions was around 10%, without significant differences between samples ($p > 0.05$, Figure 6a). These relatively low WAC values are important when projecting a final use of these materials as trays for refrigerated storage packaging with elevated ambient humidity. Similar WAC was found in previous work panels bonded with modified cassava starch-based adhesives [7] and by Salgado et al. [12] who found values around 10.5% at 90% HR conditioning of biodegradable trays foams based on cassava starch, sunflower proteins, and cellulose fibers.

WAC_i was reduced in bilayer systems compared to monolayer ones regardless of the assayed time (Figure 6b, $p = 0.0001$ for 1 min and $p = 0.0208$ for 30 min). This WAC_i decrease was inversely related to the density values of the materials. In this sense, Ferreira et al. [29], also found this relationship between density and WAC when studying trays made of brewer's spent grain and potato starch. Similarly, Marques et al. [35] working on composite materials with rice husk and expanded cork by-products explained that materials with lower densities have more air gaps, allowing water to penetrate the samples more easily. Moreover, in a short time, the presence of a catalyst had a significant effect leading to a higher water absorption during immersion in monolayer systems. Somewhat, at 30 minutes of immersion, the effect of acid concentration was remarkable ($p < 0.0186$), with the samples with the highest BA concentration having a higher degree of crosslinking, and generally absorbing less amount of water.

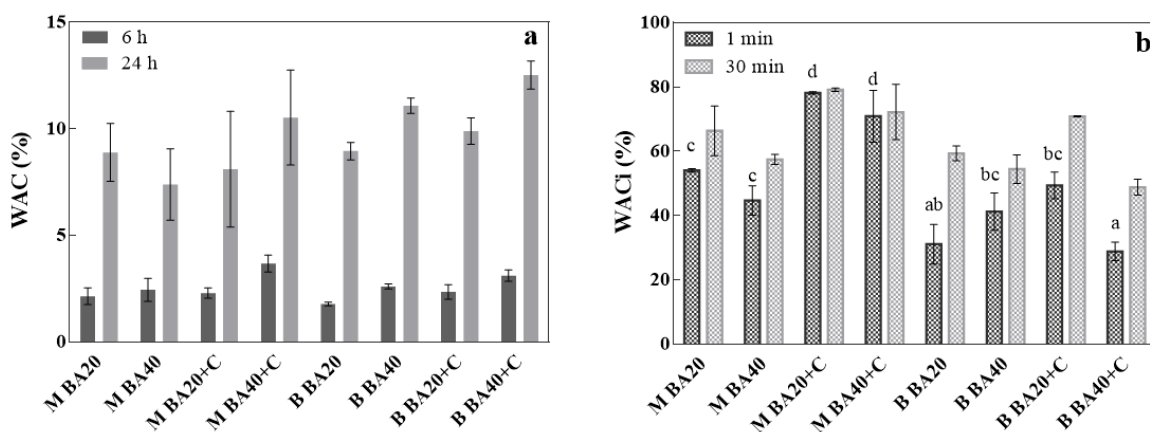


Figure 6. Effect of different materials on **a)** Water absorption capacity (WAC) (6 and 24 h); and **b)** Water absorption capacity during immersion (WAC_i) (1 and 30 min), different letters indicate significant differences for samples tested at 1 min (triple interaction effect) ($p < 0.05$).

Furthermore, WAC_i percentages are close to that found for other biodegradable materials, Cruz-Tirado et al. [36], determined between 55 and 99% WAC for biodegradable trays based on different starch species, Salgado et al. [12] found values between 30 and 50% in cassava starch trays.

3.2.4 Mechanical properties

Testing packages to emulate its manipulation during transport, market, and even from market to houses results in an important request. In this regard, it's crucial to use tests to simulate all handling situations, as the materials must be resistant enough [37]. In this respect, the mechanical profiles show a maximum related to the initial damage in the laminate, corresponding to the starting point of the crack that will develop into a fracture. This test shows how the specimens break, allowing characterizing the failure mode of each specimen. As expected, the mechanical profiles (Figure 7a) showed increased puncture resistance in bilayer systems. This is a positive result, considering the importance of obtaining packaging materials with good impact resistance properties that help to preserve food until it is consumed. The structural similarity between the components of YMP and the starch resulted in a strong network between the polymer matrix chains and the fibers used to fabricate a tray-like material. A similar explanation was proposed by Ferreira et al. [14] when studying the design of biodegradable trays using a blend of cassava starch with agroindustrial residues such as sugarcane and malt or orange bagasse or cornhusk.

Processing by thermo-compression led to compaction of the formulations, since it induced a reduction of the pore space between the YPM particles, favoring the contact with the adhesive, an accentuated behavior in bilayer systems that was confirmed by SEM studies (Figure 4). According to Ferreira et al. [14], the material compaction process promotes a

decrease in the porous space between particles, with the rearrangement of the matrix in the materials, being this process dependent on external pressure. Thus, the rearrangement and orientation of the YPM particles gave rise to a cohesive mass in the matrix of the tray-like material due to the hot-pressing treatment. Likewise, cross-linking reactions between the starch components partially hydrolyzed by BA [7], and the yerba mate by-product components were promoted. This effect was enhanced in the presence of the catalyst and was facilitated by the increased availability of reaction sites. In addition, the internal bond is significantly influenced by density, as a stronger internal bond increases the density of the composite and therefore its strength [14]. This could suggest a relationship between the strength and density of the laminates, being the bilayer materials the ones that presented the highest strength values and turned out to be materials with higher density in comparison to monolayer ones (Table 3).

On the other hand, the combined action of the acid at a concentration of 40% and the catalyst led to better mechanical behavior, obtaining materials that require higher energy needed for puncture, with a significant effect ($p < 0.0001$) for bilayer materials (Figure 7d).

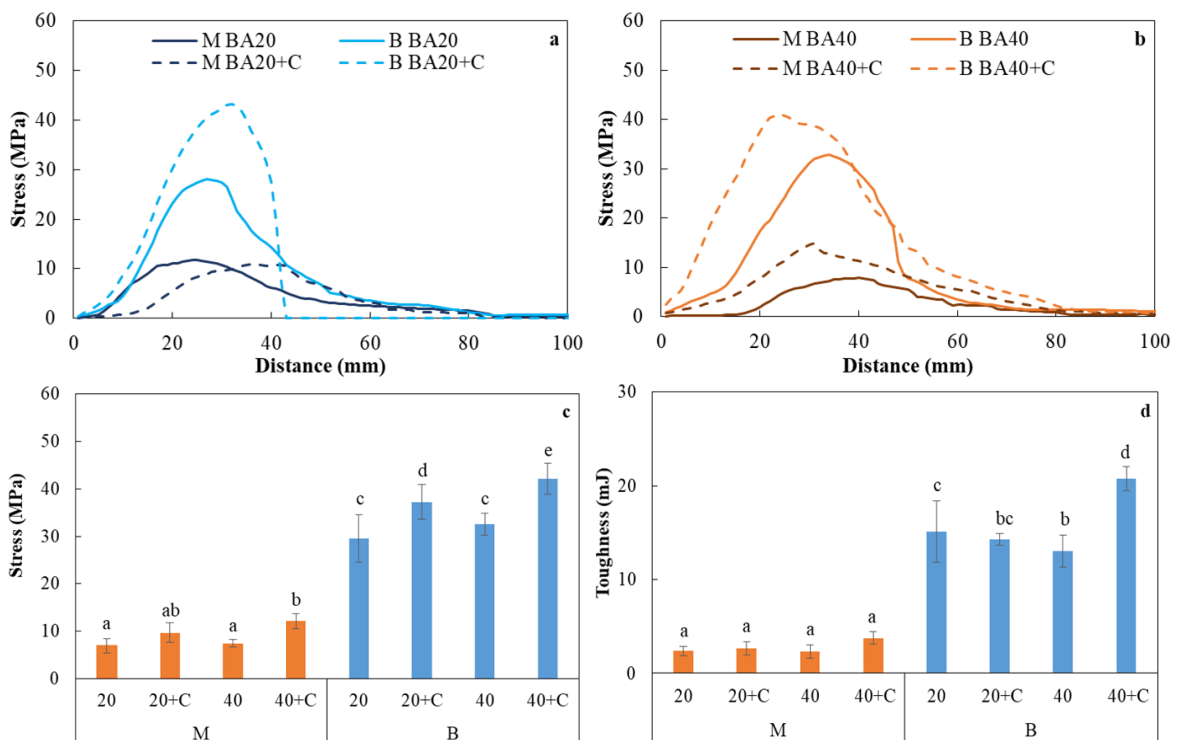


Figure 7. a-b) Mechanical profiles of the puncture test for the different materials obtained from the different adhesive formulations, **c)** effect of the bioadhesive formulation (concentration and presence of catalyst) and number of layers (monolayer M, bilayer B) on the mechanical properties of composite materials and **d)** energy to reach their fracture. The nomenclature corresponds to Table 1.

As expected, the stress values increased significantly ($p < 0.0001$) with the formation of bilayers corresponding to resistant materials (Figure 7c). Mechanical profiles of bilayer laminates with 20% BA showed an increase of 219% in puncture resistance compared to monolayer materials. There was a close relationship between the stress values of bilayers and the density (Table 3). Similar behavior was observed by Salgado et al. [12].

3.3. Study of adhesive-substrate interactions through ATR-FTIR analysis

Figure 1S shows further information from infrared spectroscopy analysis to understand the crosslinking mechanism of the adhesive compounds with the thermo-compression treatment. The ATR-FTIR spectrum of BA presented a sharp peak at 1689 cm^{-1} assigned to the carboxyl carbonyl stretching (Figure 1Sa). In this sense, cassava starch-based adhesives formulated with BA with and without catalyst exhibited a peak at 1711 cm^{-1} (Figure 1Sb). According to Monroy et al. [7] this shift could be indicative of the interaction between the starch chains. On the other hand, the heat treatment of the adhesives in the presence of propionate as catalyst confirmed the cross-linking reactions of starch mediated by BA, which proceeds through esterification via the formation of a cyclic anhydride intermediate aided by the catalyst [38,39,40]. Because of thermo-compression treatment, starch esterified with carboxylic acids typically showed an ester carbonyl peak at around 1725 cm^{-1} , more accentuated in the presence of the catalyst (Figure 1Sb). According to Patil et al. [41], the catalyst dehydrates by weakening the hydrogen bond in BA to form cyclic anhydrides, thus providing higher crosslinking efficiency. This suggests that the catalyst is capable of producing carboxylate esters, detected at 1584 cm^{-1} for the thermally treated samples.

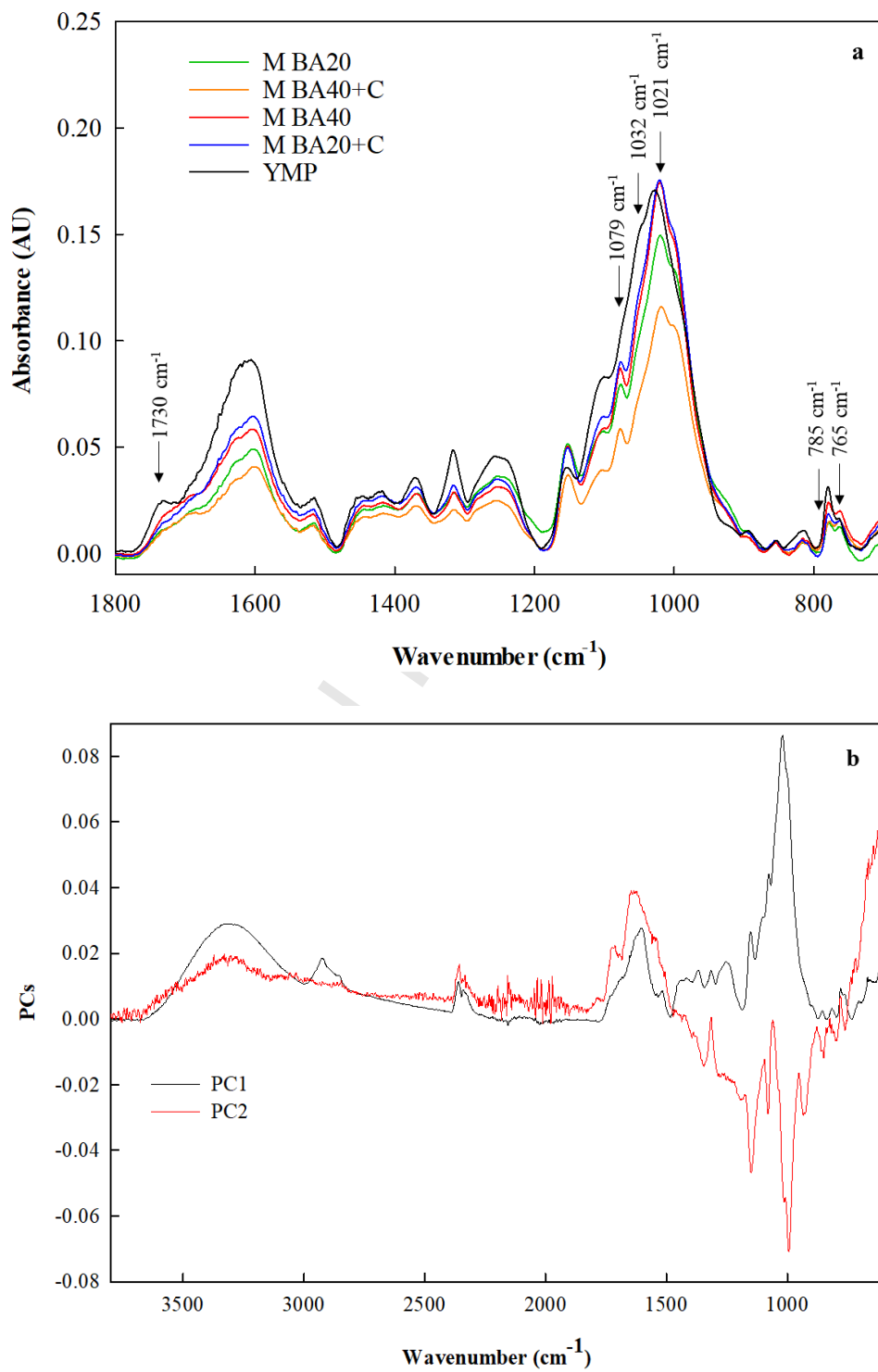
Figure 8a shows ATR-FTIR spectra in the 1800-700 cm^{-1} zone of raw YMP and the monolayer materials. As a result of adhesive-substrate interactions, a new absorption peak at 1730 cm^{-1} was observed, corresponding to the stretching vibration of C=O in the ester linkage [11, 15, 41]. With increasing BA concentration and in the presence of the catalyst, the definition of the peak of C=O in the ester bond is slightly noticeable. The spectra show that the carboxyl groups in BA were esterified and cross-linked with the hydroxyl groups of starch and the polymers from yerba mate by-product (cellulose, hemicellulose, lignin). A similar analysis was performed by Liu et al. [11] working on xylan/polyvinyl alcohol composite film crosslinked with 1,2,3,4-butane tetracarboxylic acid.

As can be seen in Figure 8a, vibrations and glycosidic linkages typical of polysaccharide structures were detected. The bands in the fingerprint region ascribed to the stretching of the C–O–C glycosidic bond vibrations and side group C-O-H link bonds at 1079 cm^{-1} , and skeletal vibrations involving the C–O stretching at 1021 cm^{-1} , were observed. In materials formulated with bioadhesives containing 40% BA, with or without catalyst, the absorption at 1079 cm^{-1} was more pronounced, as a result of cross-linking.

The YMP spectrum shows an absorption peak at 785 cm^{-1} and a shoulder at 765 cm^{-1} , indicating the presence of pyranoses in α -configuration in the polysaccharide. Regardless of the BA concentration and the presence or absence of catalyst, the signal at 765 cm^{-1} was intensified in the monolayer materials compared to the YMP spectrum, which could be attributed to the presence of cassava starch. Furthermore, the band around 1032 cm^{-1} in the YMP spectrum, which is related to the presence of polyphenols [42] appeared at 1021 cm^{-1} , this shift could be attributed to the interactions established with the bioadhesive.

Whereas, studying the reactions between adhesive and the substrate (YMP) in materials requires a deeper exploration. In this regard, the analysis of principal components of the spectra, and the examination of their loadings vs. wavenumber provided detailed information to understand the complexity of the samples (Figure 8b). The loadings analysis

was presumably related to the interactions between carboxylic groups of the adhesive and phenolic and lignocellulosic compounds from YMP.



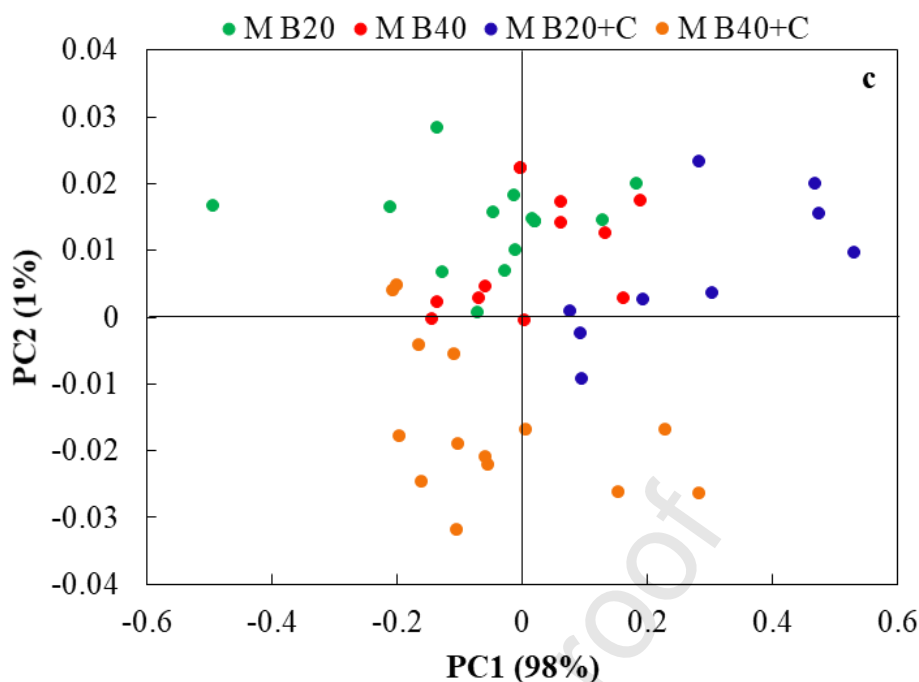


Figure 8. a) ATR-FTIR spectra of YMP by-product and monolayer materials obtained with and without catalyst and different BA concentrations (20-40%) in the 1800-700 cm^{-1} wavenumber range; b) first two principal component loadings PC1 and PC2 vs. wavenumber; c) principal component analysis of the ATR-FTIR spectra in the range between 1200-700 cm^{-1} .

The PCA chemometric analysis of the fingerprint region allowed the explanation of the total variance through two components (Figure 8c), PC1 (98%) and PC2 (1%), thus indicating the accuracy of discerning the ATR-FTIR spectra of monolayer materials. In this way, the high variance explained by PC1 could be attributed to natural differences of the sample constituents in the spectra, as deduced from the loadings plot (Figure 8b), Miranda et al. [43] proposed a similar explanation. Both components showed a strong positive correlation with the wavenumbers assigned to ester linkages formation (around 1700 cm^{-1}). Whereas the loading of PC1 had a strong positive correlation at regions of 1200-700 cm^{-1} , while the loading of PC2 had a strong negative correlation in the same region.

Analysis of Figure 8c shows overlapped clusters of samples without catalyst situated in the positive quadrant of PC2 centred along PC1 and the separation of samples with sodium propionate along PC1 in opposite quadrants of PC2. Thus, PC2 even when it explained

only 1% of the total variance of the spectra, was important for the differentiation of the spectra. This affirmation was based on the negative loadings at 1342, 1148, 1076, 988, 927, and 844 cm^{-1} , signals involved in cross-linking reactions between starch and lignocellulosic compounds activated by catalyst and heat in the presence of BA [44,45].

4. Conclusions

It was feasible to obtain mono and bilayer laminates from bioadhesive formulations based on chemically modified cassava starch, as an eco-compatible alternative for the design of sustainable tray-like materials based on the industrial by-product of yerba mate.

The formulated bio-based adhesives allowed the integration and aggregation of the YMP particles, as evidenced by SEM micrographs, promoting the formation of monolayer materials by thermo-compression. The study and characterization of the monolayer systems allowed the understanding of the relationship between the composition and its properties. The addition of the catalyst improved the adhesive-substrate interactions, acting as a promoter of cross-linking reactions that affected the microstructure of the material and its mechanical performance. Moreover, the strategy of developing bioadhesive bilayer materials led to improvements in WAC_i and mechanical performance, properties that determine the material's application. Chemometric tools confirmed that the addition of the catalyst determined the cross-linking action of BA, as was observed in surface microstructure, roughness, WAC_i, and mechanical properties. Thus, the formulated bioadhesives represented eco-compatible alternatives for the design of sustainable tray-type materials based on the use of industrial yerba mate waste. These materials can be used to pack a wide variety of foods as a sustainable alternative to replace packaging formulated with petrochemical derivatives.

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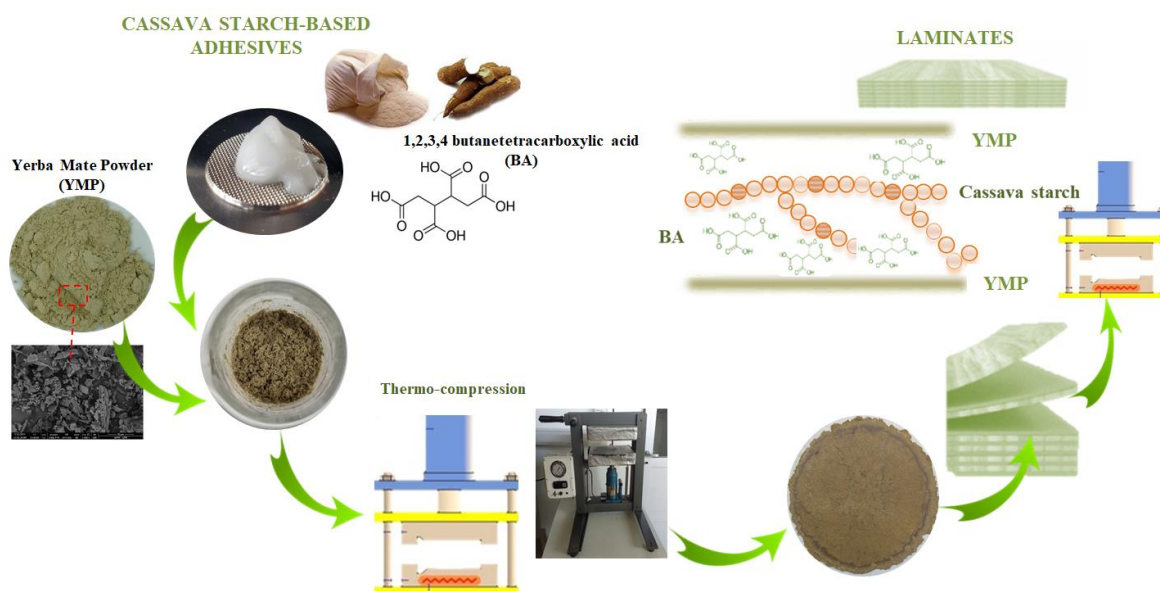
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Declaration of interests

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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Graphical abstract



Highlights

Yerba mate by-product can be used as raw material to produce thermo-compressed trays

Cassava starch-based adhesives allowed the sustainable tray development

The combined action of the acid and the catalyst led to better mechanical behavior

The chemometric analysis confirmed the crosslinking between components