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ORIGINAL ARTICLES

Production and characterization of pLA/PBAT-based films incorporated with natural and maleinized vegetable oils

Raquel do Nascimento Silva[1], Maria Eloisa Sousa Santos[2], Tatianny Soares Alves[1,2], Lucas Rafael Carneiro da Silva[3], Ruth Marlene Campomanes Santana[3], Laura Hecker de Carvalho[4], Amanda Dantas de Oliveira[5] and Renata Barbosa[1,2]*

[1]Programa de Pós-graduação em Ciência e Engenharia dos Materiais, Universidade Federal do Piauí – UFPI, Teresina, PI, Brasil

[2]Graduação em Engenharia de Materiais, Universidade Federal do Piauí – UFPI, Teresina, PI, Brasil

[3]Programa de Pós-graduação em Engenharia de Minas, Metalúrgica e de Materiais, Universidade Federal do Rio Grande do Sul – UFRGS, Porto Alegre, RS, Brasil

[4]Programa de Pós-graduação em Ciência e Engenharia de Materiais, Universidade Federal de Campina Grande – UFCG, Campina Grande, PB, Brasil

[5]Programa de Pós-graduação em Ciência e Engenharia de Materiais, Universidade Federal de Pelotas – UFPel, Pelotas, RS, Brasil

rrenatabarbosa@yahoo.com

Abstract

This manuscript explored film production for food packaging using Ecovio® and natural additives (Babassu, Castor, and Cotton Vegetable Oil), emphasizing the oil's maleinization to optimize compatibility with the polymer. The thermogravimetric analysis revealed variations in the maximum thermal decomposition temperature of maleinized vegetable oils (Thermal event II; natural oil to maleinized oil): from 402 to 338 °C (Babassu), 441 to 446 °C (Castor), and 413 to 430 °C (Cotton). The films were produced by casting, resulting in average thicknesses varying between 0.047 and 0.065 mm, and presented low surface defects. Optical micrographs showed that films with maleinized vegetable oil were more homogeneous due to maleic anhydride. Infrared spectroscopy showed that unsaturated fatty acid bonds affected the matrix and oil interaction. The presence of oils impacted the thermal stability, moisture content, and mechanical properties. This research promotes the use of renewable resources, contributing to the development of sustainable packaging.

Keywords: *casting, Ecovio®, maleinization, packaging, vegetable oil.*

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1. Introduction

The demand for polymer materials, commonly known as plastics, has increased considerably in the industrial sector and society due to their commercial availability, low density, and processability in different shapes and sizes. The favorable characteristics of plastics have led to substantial research into their potential applications in a wide range of areas. Without a doubt, plastics have become ubiquitous and indispensable in our daily lives, as they are used in various industries, such as packaging, construction, electronics, and medical devices[1,2]. Although plastics derived from non-renewable sources, such as petroleum, offer many advantages, the increase in their global production and consumption, especially of single-use plastics, has resulted in a high generation of plastic waste and rampant pollution of the environment. A promising approach to minimizing the harmful effects of non-biodegradable plastics on the environment is their replacement with biodegradable polymers, mainly in the food packaging industry[3-5].

Ecovio® is an ecological alternative to conventional petroleum-derived plastics (e.g., Polyethylene and Polystyrene) among the biodegradable polymers available. It was developed from a polymer blend of Poly(Butylene Adipate-*co*-Terephthalate) (PBAT) and Poly(Lactic Acid) (PLA), sold by BASF. PBAT provides flexibility while PLA provides rigidity, resulting in a polymer suitable for various applications, such as packaging film production[6,7], which sparked interest in this research. Using vegetable oils as natural additives incorporated into polymers can provide several advantages compared to petrochemical-based additives. For example, it can reduce production costs and act as a plasticizer, providing greater flexibility to the polymer film. Final properties can be adjusted by varying the type and content of oil incorporated into the

polymer matrix. Because vegetable oils are produced from sustainable and renewable resources, the resulting films can have a reduced environmental impact, making them a more environmentally friendly option[8,9].

Wide availability and relatively low cost make vegetable oils an industrially attractive material for the plastics industry[10]. Among the different types of vegetable oils, babassu, castor, and cotton oils are attractive for various applications, including as additives in biodegradable polymers to optimize properties, as already mentioned, and can even act as a compatibilizing agent[11]. These oils are abundant in Brazilian territory, being triglycerides rich in fatty acid, linoleic acid, ricinoleic acid, and lauric acid. The properties of vegetable oils depend mainly on the chemical structure of fatty acids. In other words, this involves the number and position of double bonds and the chain length. Due to their unsaturated chains, fatty acids can insert themselves between polymer chains, improving mobility. On the other hand, ester groups can interact effectively with the functional sites of the polymer, resulting in greater compatibility with the matrix[12,13]. The chemical modification of vegetable oils can be done through maleinization, aiming to increase reactivity and improve their compatibility with the polymer. This process involves the reaction of maleic anhydride with the double bonds of unsaturated fatty acids[14,15].

Given the above, the novelty of this research lies in combining a biodegradable polymer with vegetable oil from babassu, castor, and cotton in its natural and maleinized form for producing polymer films intended for future application in food packaging. These films, made from renewable and abundant resources, can potentially reduce the environmental footprint of food packaging. The maleinization process chemically modifies the vegetable oils and facilitates their integration into the polymer matrix. This adaptability opens up many potential applications and functionalities for biodegradable polymers, sparking curiosity and further exploration. Producing these films using the casting method allows the production of relatively homogeneous films, promoting a sustainable and ecological approach. This approach promotes sustainability and reduces dependence on petrochemical resources, instilling confidence in the ecological soundness of the process.

2. Materials and Methods

2.1 Materials

The polymer matrix used was Ecovio® (PBAT/PLA), grade F2224, supplied by BASF (Germany), with a mass density of 1.24-1.26 g/cm^3 (ISO 1183), Melt Volume Rate (MVR) of 3.0-6.5 mL/10 min at 190 °C/5 kg (ISO 1133), and Melting Temperature (T_m) of 110-155 °C. The vegetable oils included babassu (COPPALJ, Maranhão, Brazil), castor (Mercado Central, Piauí, Brazil), and cotton oil (ICOFORT, Ceará, Brazil). Maleic anhydride (99% purity) from Sigma-Aldrich (USA) was used for maleinization, and chloroform from Synth (Brazil) was used as the solvent for film production.

2.2 Vegetable oil maleinization process

The vegetable oil maleinization process involved heating each oil (100 g) with maleic anhydride (27 g) in a 500 mL volumetric flask at 100 °C with magnetic stirring for 4 h. After the reaction, the maleinized oils were cooled to room temperature. This methodology was adapted from Eren et al.[16] and Alarcon et al.[17]. The oils were labeled as follows: BN and BM (babassu), CAN and CAM (castor), and CON and COM (cotton) for the natural and maleinized forms, respectively.

2.3 Film production using the casting method

Ecovio® was dried in an oven at 80 °C for 2 h (Solab, Brazil) before creating a film-forming solution. This involved diluting it in 50 mL of chloroform and stirring it magnetically for 90 min. After resting for 24 h, an additional 20 mL of chloroform was added, and the solution was heated and stirred again at 80 °C for 90 min. The solution was transferred to a beaker, topped up to 100 mL with solvent, and poured onto glass plates to evaporate at room temperature for 24 h (control film). These films were removed and stored in desiccators for analysis[18]. The same procedure was used to create films with natural and maleinized vegetable oils (Table 1), added after the polymer-based solution (neat Ecovio®) had rested for 24 h.

2.4 Characterizations

The thermal stability of vegetable oils and films produced was analyzed using Shimadzu TGA-50 equipment. The analysis was conducted in a platinum crucible under a nitrogen atmosphere (N_2) with a 50 ml/min gas flow and a 20 °C/min heating rate. The oil sample was heated to 900 °C, and the films were heated to 500 °C from room temperature.

The films were visually evaluated on a macroscopic scale to assess the impact of the casting method and vegetable oil content on film quality. Photographs were taken using a 12 MP smartphone camera. The thickness of the film

Table 1. Ecovio®/Vegetable Oil-based film composition and their caption.

Film Composition	Content (phr)*			Caption
	Ecovio®	Natural Oil	Maleinized Oil	
Neat Ecovio®	100	0	0	ECO
Ecovio®/BN	100	5	0	ECO-BN
Ecovio®/BM	100	0	5	ECO-BM
Ecovio®/CAN	100	5	0	ECO-CAN
Ecovio®/CAM	100	0	5	ECO-CAM
Ecovio®/CON	100	5	0	ECO-CON
Ecovio®/COM	100	0	5	ECO-COM

* Incorporation of vegetable oil into the polymer was based on phr (parts per hundred of resin).

samples was measured with a thickness gauge (Model 130.125, DIGIMESS, São Paulo, Brazil) with a 0.01 mm graduation and ±0.02 mm accuracy. Five film samples of each composition (3 × 3 cm) were analyzed, with thickness measured at ten different points on each sample.

The film samples were analyzed for surface morphology using a Leica DM500 binocular optical microscope (Wetzlar, Germany) in transmission mode with a 40x magnification and a 500 µm scale. Fourier transform infrared spectroscopy (FTIR) was conducted using a Shimadzu Prestige 21 spectrophotometer (Kyoto, Japan), covering a range of 4000-500 cm^{-1}. The moisture content was measured by the mass loss method (m_I) (Equation 1), drying five 1.7 × 1.7 cm samples in an oven at 105 °C for 24 h (Solab, Brazil), then cooling them to room temperature and reweighing (m_F).

$$Moisture\,content = \frac{mi - mf}{mi} x100\% \quad (1)$$

where: m_I and m_F are the sample mass (g) before and after drying[19].

Following the ASTM D882 Standard, the tensile strength test was performed using a Universal Testing Machine (Model DL 30000, EMIC, Brazil). The test used a 500 N load cell and a crosshead speed of 50 mm/min at room temperature, measuring tensile strength (MPa) and elongation (%). Results were averaged from six specimens, each 10 mm long and 1 mm wide, for each formulation.

The data were analyzed using One-Way ANOVA and compared between pairs of means with the Tukey Test at a 5% significance level ($p < 0.05$) using OriginPro software.

3. Results and Discussions

3.1 Thermogravimetric analysis (TGA) of vegetable oils

The thermal stability of vegetable oils (both natural and maleinized) is essential for their use as additives in Ecovio®, as they must endure high processing temperatures. TGA analysis was conducted to evaluate this, and the results are shown in Figure 1 and Table 2.

Natural vegetable oils remained stable up to 150 °C when water evaporation and loss of low molar mass compounds occurred[20]. Maleinized babassu (BM) and cotton (COM) oils showed mass losses at 76 and 84 °C, respectively, with BM losing 5.26% and COM losing 3.29%. Natural oils maintained their thermal stability up to 218 °C. BN experienced a significant mass loss of 47.83% between 242 and 398 °C, indicating decomposition and carbonization. Similar findings were reported by Alarcon et al.[21]. CAN had a T_{onset} at 219 °C with a mass loss of 58.68%, linked to chain scission, and a T_{max} of 383 °C[22]. CON had a T_{onset} of 311 °C and a mass loss of 76.98%, likely due to its higher fatty acid content.

For BM and COM, thermal event II happened between 213 and 218 °C, with a notable mass loss. CAM decomposed between 177 and 360 °C, showing a 35.78% mass loss. In the literature, polymers synthesized from maleinized vegetable oils had their thermal stability evaluated. The authors observed that the thermal decomposition of maleic anhydride occurred close to 182 °C[21]. The thermal stability of natural vegetable oils was ranked as CON > BN > CAN. The maleinization process did not enhance the stability of vegetable oils, which vary in fatty acid types and contents based on origin, cultivation, and extraction methods.

3.2 Visual evaluation, thickness, and Optical Microscopy (OM)

Table 3 presents three results: a macroscopic image of each film produced, the average thickness, and the surface morphology analyzed by optical microscopy.

All the films produced were flexible and exhibited few surface defects like cracks and bubbles, indicating that the casting method was effective and provided a degree of standardization. The ECO film, which lacked vegetable oil, was the most transparent. Adding various natural oils to the Ecovio® matrix altered the film's transparency, making it more translucent or opaque, and also affected its gloss. These changes benefit packaging, especially for photosensitive foods that need more opaque materials to reduce light exposure, thereby preserving food quality and nutritional value. The decreased transparency was due to

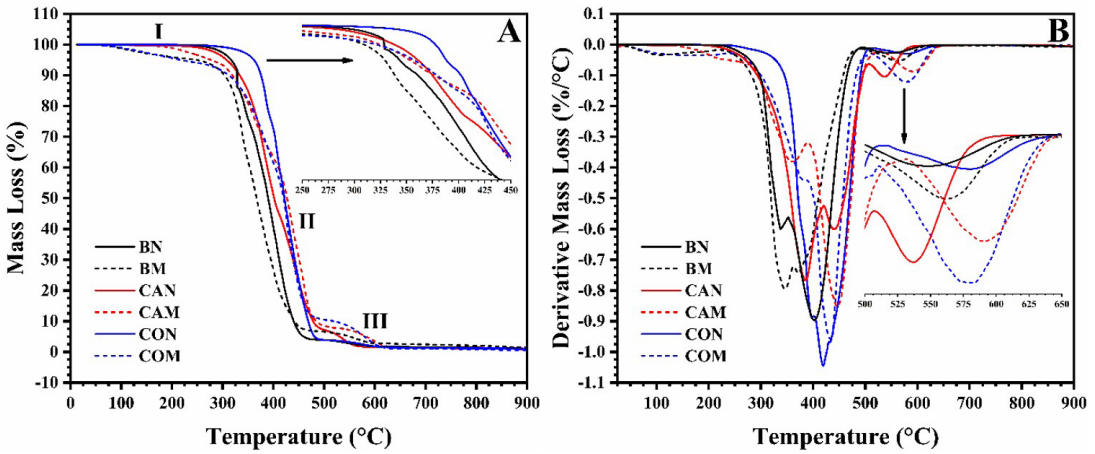


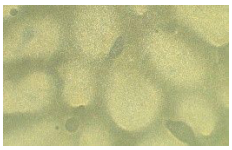
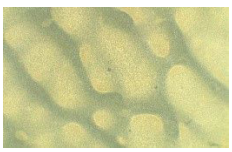
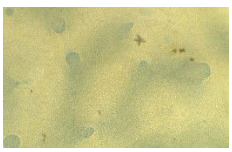
Figure 1. Graphs showing the (A) TGA and (B) DTG curves of vegetable oils.

Table 2. Thermal parameters extracted from the TGA and DTG curves.

Thermal parameters	Vegetable Oils					
	BN	BM	CAN	CAM	CON	COM
Thermal event I						
T_{onset} (°C)	242.52	76.57	219.75	177.62	311.30	84.30
T_{max} (°C)	322.03	92.37	383.55	357.40	382.70	134.20
T_{endset} (°C)	398.59	155.84	417.55	360.68	417.86	163.80
ML (%)	47.83	5.26	58.68	35.78	76.98	3.29
Thermal event II						
T_{onset} (°C)	396.59	213.72	424.27	368.68	487.81	218.80
T_{max} (°C)	402.07	338.00	441.13	446.08	413.20	430.90
T_{endset} (°C)	490.80	488.28	508.54	522.24	517.78	484.14
ML (%)	48.54	89.08	34.77	58.18	16.81	83.59
Thermal event III						
T_{onset} (°C)	495.07	531.20	521.54	537.24	520.94	495.82
T_{max} (°C)	510.35	557.21	440.35	592.12	570.00	576.50
T_{endset} (°C)	588.37	595.78	562.67	609.37	606.28	603.34
ML (%)	2.04	3.55	5.27	5.92	1.99	7.64
Residue (%)	0.37	0.34	1.61	0.33	0.33	0.17

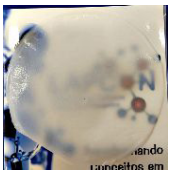
Caption: T_{onset} = Initial thermal decomposition temperature; T_{max} = Maximum thermal decomposition temperature; T_{endset} = Final thermal decomposition temperature; ML = Mass Loss; Residue at 900 °C.

Table 3. Physical and superficial characteristics of the films produced.

Film Composition	Properties		
	Visual Evaluation	Thickness (mm)	OM (500 µm/40x)
ECO		0.049 ± 0.007[a]	
ECO-BN		0.047 ± 0.006[a]	
ECO-BM		0.049 ± 0.006[a]	
ECO-CAN		0.054 ± 0.007[bc]	
ECO-CAM		0.049 ± 0.008[a]	

Means with different letters indicate a statistically significant difference ($p < 0.05$).

Table 3. Continued...

Film Composition	Properties		
	Visual Evaluation	Thickness (mm)	OM (500 µm/40x)
ECO-CON		0.057 ± 0.008^{c}	
ECO-COM		0.065 ± 0.010^{d}	

Means with different letters indicate a statistically significant difference ($p < 0.05$).

the varying refractive indices of the vegetable oil and the polymer matrix, which caused greater light dispersion and increased translucency or opacity.

Regarding the incorporation of maleinized vegetable oils, similar results were observed about the incorporation of natural vegetable oils. It was clear that in the presence of vegetable oil, the film surface became rougher; this was due to only partial compatibility with the polymer matrix, which led to phase separation. Consequently, it was possible to visualize the oil droplets on the film surface on a microscopic scale, which can cause an increase in surface roughness. As the oil droplets are not thoroughly mixed with the polymer, the film edges become more irregular, especially in ECO-COM film. Despite the yellowish color of most vegetable oils, the films maintained the milky appearance resulting from the Ecovio®.

According to Table 3, the average thickness of the films produced varied between 0.047-0.065 mm, within the thickness range mentioned by Barlow and Morgan[23]. According to the authors, the film thickness used in food packaging can vary from 10 to 250 µm (0.01-0.25 mm). Ensuring that the film thickness is determined ensures that the film meets the specifications necessary for its application, such as strength, durability, and flexibility. Films ECO, ECO-BN, ECO-BM, and ECO-CAM did not show a statistically significant difference ($p > 0.05$); that is, the thickness was very similar, which implies reasonable quality control of the film produced and uniformity in production. Balancing thickness and production cost is essential, as thicker films imply higher production costs. However, a considerable thickness was not obtained in the films produced in this research.

The optical micrographs revealed that the ECO film had a smooth macroscopic appearance but was microscopically heterogeneous due to phase segregation. PBAT and PLA, though similar in their structural groups, showed that PBAT polarizable groups led to coalesced clusters and uneven distribution within the PLA phase[24]. Films with natural vegetable oils (ECO-BN and ECO-CAN) displayed larger oil droplets as distinct phases, as vegetable oil does not thoroughly mix with Ecovio®, resulting in droplet formation. Surface tension between the oil and polymer can also lead to droplet formation. Despite partial miscibility, using vegetable oil as an additive benefits flexibility and has ecological and economic advantages. Films with maleinized vegetable oil, such as ECO-CAM and ECO-COM, exhibited greater homogeneity due to maleic anhydride[17]. Maleic anhydride may have facilitated the oil's dispersion in the polymer matrix and reduced phase separation, which improved homogeneity. At the same time, ECO-CON showed good homogeneity even without it, indicating effective interactions with polymer chains.

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectrum of all films produced was obtained to investigate possible interactions between Ecovio® and vegetable oils. The spectrum referring to the neat polymer matrix was also obtained (Figure 2).

The spectrum corresponding to the ECO film exhibited the absorption bands characteristic of its components. For PBAT, the following bands were observed: $-CH_2-$ stretching at 2950 and 1413 cm^{-1}, −C−H stretching at 2929 cm^{-1}, C=O stretching at 1714 cm^{-1}, −C−H stretching at 1502 and 872 cm^{-1}, and −C−H bending at 725 cm^{-1}[25]. For PLA, some absorption bands appeared to overlap with the PBAT bands, as both polymers have a spectrum similar due to their classification as polyesters. Bands located at 1360 ($-CH_3$ deformation), 1276 (−C−O− stretching), and 1180 cm^{-1} (−C−O−C− stretching) were attributed to the PLA[26]. With the incorporation of vegetable oil, it was observed that the bands located between 3000 and 2800 cm^{-1} were more defined for the ECO-BM film and the ECO-CON film. Such bands were attributed to the vibration of symmetric/asymmetric aliphatic hydrocarbons and lipid compounds. The band at 1710 cm^{-1} indicated the ester group in the triglycerides[27].

In the region around 1700-1690 cm^{-1}, C=C bonds were observed, indicating the presence of unsaturated fatty acids from the Diels-Alder reaction with maleic anhydride. A shoulder was observed around 1710 and 1720 cm^{-1}, especially in the ECO-CAM and ECO-COM films, due to the carbonyl stretching associated with the ester group in

maleic anhydride[17,28]. Limited interactions between polymer chains and vegetable oils may be due to the low oil content, which might not have caused measurable changes. However, changes in band intensity, particularly in the ester group, were noted. Future research with varying oil content could enhance the environmental friendliness of these products.

3.4 Thermogravimetric Analysis (TGA)

Figure 3 presents the TGA and DTG curves of the films produced with natural and maleinized vegetable oils, and Table 4 presents the parameters of each thermal event extracted from the curves.

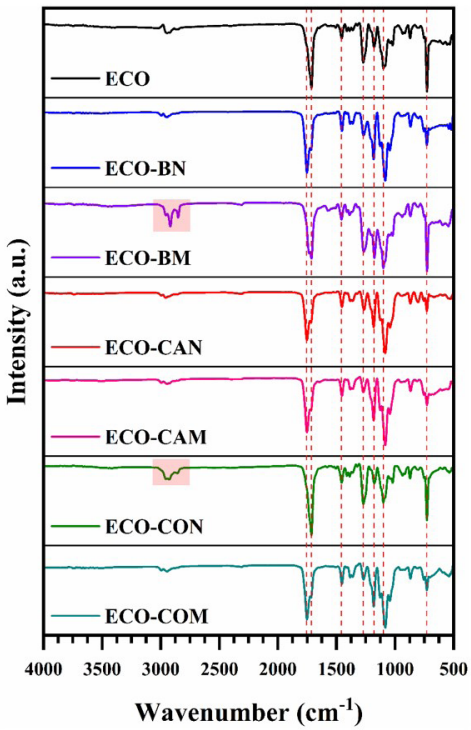


Figure 2. FTIR spectrum related to ECO-based films incorporated with different vegetable oils in the 4000-500 cm^{-1} range.

As shown in Figure 3, the TGA curves showed a similar trend for mass loss; that is, two thermal events were observed. Usually, the beginning of the TGA curve for many materials refers to the loss of water molecules (residual moisture) or low molecular weight compounds; however, this mass loss was minimal for the films produced here, as no thermal event was observed (< 100 °C). The temperature range for mass loss was between 300-450 °C (significant mass loss). The DTG curves corroborated this result due to the two well-defined and relatively symmetrical peaks (inflection point) around 340 and 400 °C, respectively. The thermal events observed are related to the thermal decomposition of the polymer matrix due to the increase in the kinetic energy of the molecules with increasing temperature, which led to the scission of the polymer chains in smaller volatile molecules. The two different thermal events can be explained by the lack of thermodynamic compatibility between the two polymers[29]. Dhakal et al. [30] and Nekhamanurak[31] obtained a similar TGA curve for the Ecovio®.

The thermal curves of films with vegetable oils are similar to ECO film. However, physical or chemical interactions with the polymer matrix can affect the matrix's molecular chain organization and thermal stability (e.g., can inhibit thermal decomposition reactions and/or eliminate free radicals). The ECO-CAN film had the highest T_{onset} value (321 °C), while ECO-BN and ECO-CON also showed higher T_{onset} than ECO film. Incorporating maleinized vegetable oils reduced T_{onset} due to unreacted maleic anhydride in the polymer matrix, creating reactive sites susceptible to thermal decomposition at lower temperatures. Even though the maleinization process can improve the suitability of vegetable oils in polymer matrices, adding new reactive sites and structural changes can make the modified oils more susceptible to thermal degradation, reducing their stability when incorporated into polymers. The residue from initial thermal decomposition was less than 8%, attributed to thermally resistant formulation components requiring higher temperatures for decomposition.

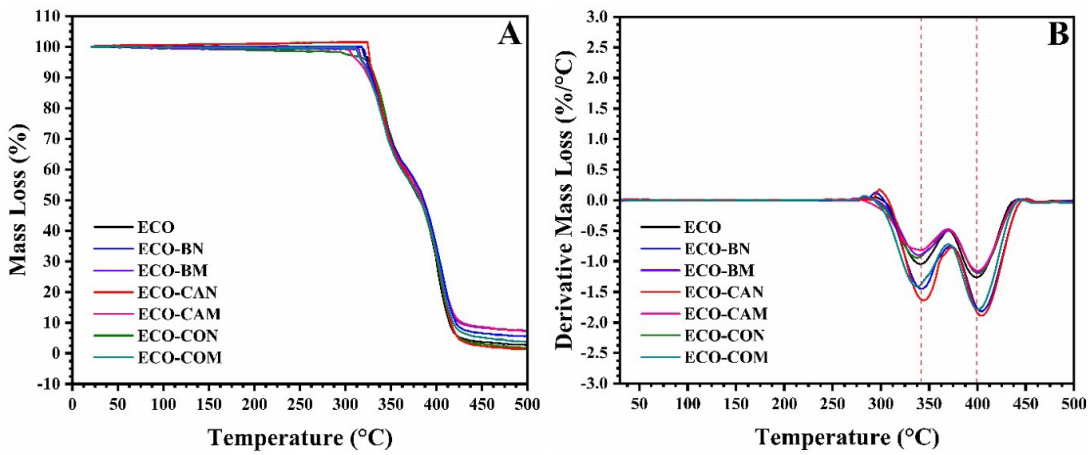


Figure 3. Graphs showing the (A) TGA and (B) DTG curves of the films produced.

Table 4. Thermal parameters extracted from the TGA and DTG curves.

Thermal parameters	Film Composition						
	ECO	ECO-BN	ECO-BM	ECO-CAN	ECO-CAM	ECO-CON	ECO-COM
				Thermal event I			
T_{onset} (°C)	317.14	320.18	314.82	321.22	301.53	319.57	311.20
T_{max} (°C)	337.14	336.97	338.57	344.46	339.34	338.18	337.36
T_{endset} (°C)	342.74	350.26	354.26	348.85	339.73	347.93	350.46
ML (%)	35.26	30.20	32.92	26.48	28.86	33.20	34.35
				Thermal event II			
T_{onset} (°C)	343.01	351.95	394.02	390.09	395.15	390.60	389.88
T_{max} (°C)	402.84	403.20	400.30	404.20	402.30	401.20	402.56
T_{endset} (°C)	412.92	419.77	418.27	418.92	417.69	417.56	418.38
ML (%)	60.80	63.06	61.68	70.35	62.52	68.31	63.42
Residue (%)	2.07	5.66	7.27	1.21	7.5	1.78	3.68

Caption: Residue at 500 °C. ML = Mass Loss.

3.5 Moisture content

Evaluating the moisture content in polymer films applied to food packaging is crucial, as moisture plays a fundamental role in packaged food safety, quality, and durability (shelf-life). In this way, the moisture content was determined, and the result is shown in Table 5.

The ECO film exhibited a moisture content value of less than 2%. The moisture content depends on storage conditions, such as temperature and relative humidity. This value obtained for Ecovio® is due to the moisture absorption from the environment by the polymers that make it up. Furthermore, the polymer's chemical structure allows it to attract and retain water molecules; therefore, biodegradable polymers must be dried before processing due to their moisture sensitivity[32]. Ecovio® has polar hydroxyl and carboxyl groups, which can form hydrogen bonds with water molecules. Incorporating natural vegetable oils (BN and CAN) into the polymer did not significantly change the moisture content value ($p > 0.05$) about the value obtained for the ECO film. The lower value associated with ECO-CAN film may be due to the high concentration of ricinoleic acid in the polymer matrix, the main constituent of castor vegetable oil[22].

The highest value among natural vegetable oils was obtained for the film incorporated with cotton oil, possibly due to more effective plasticizing action, increasing the mobility of the polymer chains and making the polymer more susceptible to moisture absorption. Incorporating maleinized vegetable oils caused significant changes in the moisture content value ($p < 0.05$), mainly for castor (ECO-CAM) and cotton (ECO-COM) vegetable oils. For the vegetable oils mentioned, the moisture content of the films produced was greater than 2%. Maleinization enhances the moisture absorption capacity of nonpolar fatty acid chains by adding polar maleic anhydride groups. Groups that form hydrogen bonds with water can increase moisture content. Films with high moisture content are better for packing aqueous foods, while those with low moisture content are better for pacing fatty foods[14,33].

Table 5. Moisture content determined for the films produced.

Film Composition	Moisture Content (%)
ECO	1.016 ± 0.068^{a}
ECO-BN	1.657 ± 0.726^{ac}
ECO-BM	1.772 ± 0.403^{acd}
ECO-CAN	0.805 ± 0.241^{a}
ECO-CAM	2.894 ± 0.649^{bcd}
ECO-CON	2.648 ± 0.440^{cd}
ECO-COM	2.765 ± 0.702^{d}

Means with different letters indicate a statistically significant difference ($p < 0.05$).

3.6 Tensile strength test

Evaluating tensile strength is crucial to ensure that polymer films used in food packaging meet safety, reliability, and durability standards. Figure 4 presents the tensile strength and elongation properties of films produced with vegetable oils before and after the maleinization.

According to Figure 4, the ECO film presented the highest tensile strength and elongation value, corresponding to 11.05 MPa and 103.87%, respectively. In the literature, similar results were observed in the manuscript by Chen et al.[34] and Mohammadi et al.[35]. The results also showed that incorporating vegetable oils into the polymer matrix reduced tensile strength and elongation. Based on the results obtained, it can be deduced that the polymer chains are more cohesive in the ECO film, allowing for better structural integrity and greater tensile strength. Incorporating babassu, castor, and cotton vegetable oils in Ecovio® may have caused an uneven distribution of stresses, reducing the mechanical properties. The lower values of the mechanical properties may also have occurred due to structural interruptions of the polymer matrix caused by vegetable oils. It is worth mentioning that optical micrographs showed the formation of separate phases in the polymer, which can act as weak points under tensile load. Consequently, with weak points and a less cohesive structure, the matrix may not withstand the applied tension, leading to the observed results.

The film-incorporated maleinized castor oil (ECO-CAM) had the lowest tensile strength at 3.67 MPa, while the film with maleinized cotton oil (ECO-COM) showed the lowest elongation at 3.96%. Higher elongation generally indicates better flexibility in polymer films. Maleinization can sometimes lead to cross-linking between the polymer

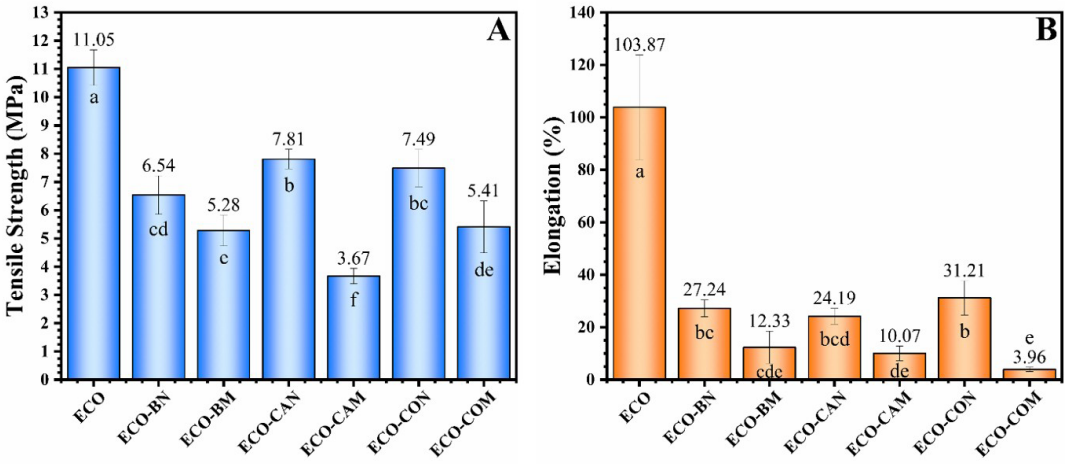


Figure 4. Mechanical properties of Ecovio®-based films: (A) tensile strength and (B) elongation. Means with different letters indicate a statistically significant difference ($p < 0.05$).

chains and the modified oil[36], reducing chain mobility and elongation. This research found that maleinization reduced tensile strength and elongation compared to natural oils. Differences in mechanical properties among the films were attributed to each oil's unique chemical compositions and properties, which affected their interaction with the polymer. These variations influenced the mechanical outcomes despite a consistent 5% oil content. Carbonell-Verdu et al. [37] also observed that adding maleinized cottonseed oil to PLA-based films decreased mechanical properties above 5-7.5 wt%. Although maleinized oils were influential in achieving lower mechanical properties, further research is needed to optimize film properties.

4. Conclusions

This manuscript explored incorporating natural and maleinized vegetable oils into the Ecovio® polymer matrix to create flexible films using the casting method. Natural vegetable oils' thermal stability ranked as CON > BN > CAN, and maleinization did not enhance this stability. The films had minimal surface defects, indicating the casting method's effectiveness and a certain standardization level, with thicknesses ranging from 0.047 to 0.065 mm. Larger oil drops were visible in films with natural vegetable oils, while FTIR confirmed the effective incorporation of oils into the polymer matrix. Maleinized oils reduced the initial thermal decomposition temperature and significantly altered moisture content, particularly for castor and cotton oils. Maleinization also lowered tensile strength and elongation compared to natural oils. The films produced are a promising and sustainable alternative for reducing global plastic waste and producing food packaging.

5. Author's Contribution

- **Conceptualization –** Raquel do Nascimento Silva; Maria Eloisa Sousa Santos; Renata Barbosa.
- **Data curation –** Raquel do Nascimento Silva.
- **Formal analysis –** Raquel do Nascimento Silva; Lucas Rafael Carneiro da Silva.
- **Funding acquisition –** NA.
- **Investigation –** Raquel do Nascimento Silva; Maria Eloisa Sousa Santos.
- **Methodology –** Raquel do Nascimento Silva; Maria Eloisa Sousa Santos; Renata Barbosa.
- **Project administration –** Renata Barbosa.
- **Resources –** Renata Barbosa; Tatianny Soares Alves; Ruth Marlene Campomanes Santana; Amanda Dantas de Oliveira, Laura Hecker de Carvalho.
- **Software –** NA.
- **Supervision –** Renata Barbosa; Tatianny Soares Alves.
- **Validation –** Raquel do Nascimento Silva; Renata Barbosa.
- **Visualization –** Raquel do Nascimento Silva.
- **Writing – original draft –** Raquel do Nascimento Silva.
- **Writing – review & editing –** Renata Barbosa; Lucas Rafael Carneiro da Silva.

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